ELECTRO-MEMBRANE REACTORS FOR DESALINATION AND DISINFECTION OF AQUEOUS SOLUTIONS

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WRC Report No. 964/1/02

Water Research Commission

Electro-membrane Reactors for Desalination and Disinfection of Aqueous Solutions

Final Report

to the Water Research Commission

by

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WRC Report No 964/1/02
ISBN No 1 86845 877 6

August 2002

EXECUTIVE SUMMARY

Introduction

Clean water has become a scarce commodity in many parts of the world. To supply the demand for potable water for the community and clean water for industry, the available sources of water often need to be treated. Fresh water found in lakes, rivers or shallow aquifers are often of reasonable quality and relatively simple purification methods such as sand bed filtration are usually sufficient. However, due to uneven distribution of fresh water supplies in the world, the locally available sources of water are often of relatively low quality (for example high salt content). Besides the conventional desalination processes (like ion exchange and distillation) more advanced technology (like reverse osmosis and electro dialysis) is currently used to remove undesired ionic quantities and species. The costs of such water treatment processes are usually driven by the cost of water pre-treatment (additional equipment to ensure reasonable lifetime of the main unit) and the high cost of the high-tech membranes needed for these processes. In this article a water purification unit will be presented where the technology of electrochemically activated sorption is combined with the micro-filtration properties of ceramic membranes. The novel electro sorption unit developed showed desalination and micro-filtration properties.

Electrochemically activated sorption

Desalination by means of electrochemically-activated sorption can be described as illustrated in Figure 1. The system comprises of an electrochemical cell with two electrodes of which at least one contains incorporated ion exchange resin and is permeable to water. The water to be purified acts as an electrolyte. When a DC voltage is applied between the two electrodes, protons and hydroxyl ions are generated by electrolysis at the surface of the anode and cathode respectively. As a result of the local change in pH, active sites are produced in the ion exchange material and may adsorb cations at the cathode (see Figure 1). Subsequent reversal of the voltage enables the absorbed cations to be desorbed. Hence, no additional chemicals are required to regenerate the ion exchange sites at the electrode. Anions can be adsorbed and desorbed in a similar way at the opposite electrode. Electrochemically activated sorption will be referred to as electro sorption.

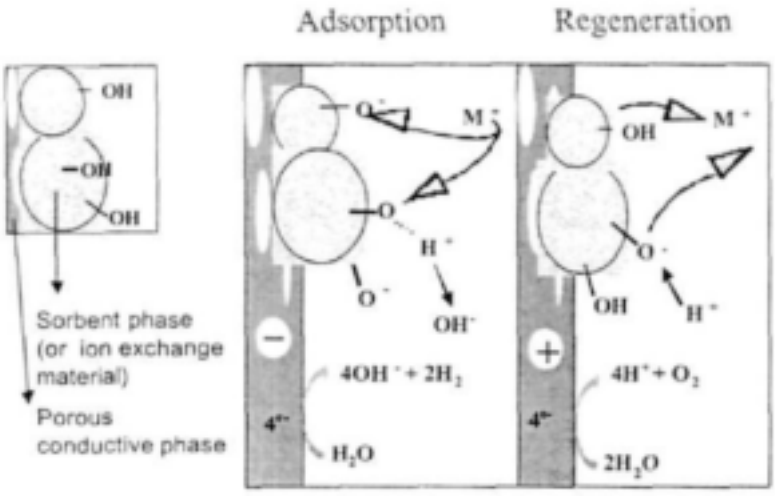

Figure 1. Schematic representation of the electrochemically-activated sorption process

New technology of electro sorption filter

The objective of this study was to develop a new type of purification unit in which ionic species and micro particles can be removed simultaneously based upon electro sorption and micro filtration respectively. The unit should be simple and non-chemical regeneration possible. To avoid high capital cost, relatively cheap base materials should be used and the system should work at low pressures.

Membrane modification for ion sorption

Modified supports consisting of inorganic Al_2O_3 micro filtration membranes were used as precursors. The first modification included the deposition of pyrolytic carbon on the surface of the membrane (at 900°C using liquid petroleum gas) carried out to obtain electro conductive properties. A gold coating ($1g \cdot m^{-2}$) was applied to increase the conductivity. Subsequently, highly dispersed particles of zirconia (ZrO_2) and zirconia phosphate (ZrP) functioning as anion and cation exchange material respectively, were incorporated into the porous structure of the carbonised Al_2O_3 support.

One of the challenges during the development of the sorption electrode was to achieve simultaneous removal of anions and cations. Anions and cations are adsorbed onto the oppositely charged electrodes using conventional electro sorption. With this new technology it was desired to pump the solution through one electro sorption electrode to utilize its filtration property. When initially a randomly mixed ion exchange bed (with cation and anion exchange resin) was used in an electro sorption experiment, non-simultaneous adsorption of ions was observed. The anions were adsorbed

when the sorption electrode acted as anode. After changing the polarity of the electrode, anions desorbed and cations adsorbed. In other words, the permeate was either an acidic solution with an excess of anions or an alkaline solution with an excess of cations.

Simultaneous adsorption of cations and anions became possible after a phosphate gradient was created over the radial cross-section of the sorption electrode. The gradient was realised by exposing the ZrO_2 impregnated on the outer surface of the electrode support material to phosphoric acid and preventing phosphoric acid contact with ZrO_2 impregnated on the inside lumen. This resulted in an electrode with mainly cation exchange material (phosphorized ZrO_2) at the outside and mainly anion exchange material (unreacted ZrO_2) at the lumen side. The results obtained with such an electro sorption electrode are shown in Figure 2.

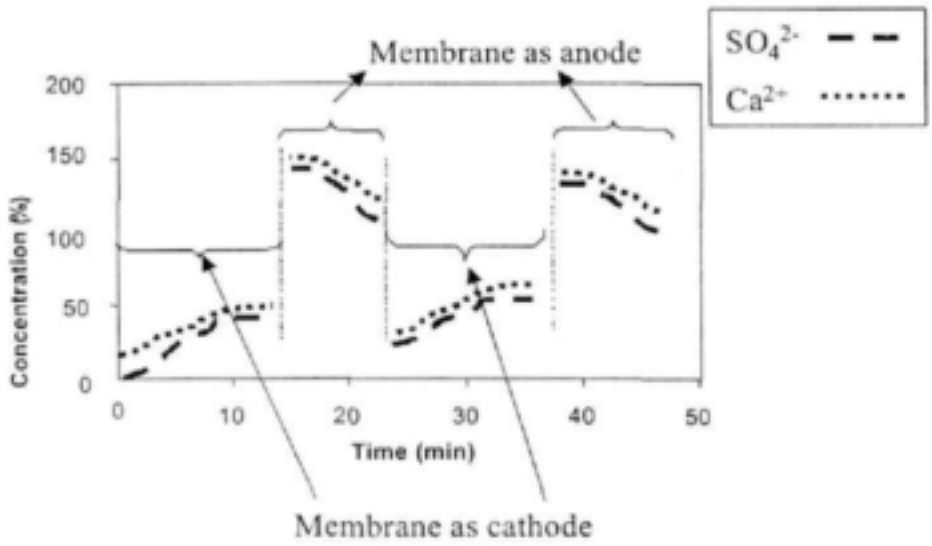

Figure 2. Concentration of SO_4^{2-} and Ca^{2+} in the permeate normalized to the concentration of the feed as function of time. Flow rate 30 ($l \cdot h^{-1} \cdot m^{-2}$), feed solution 1400mg$\cdot l^{-1}$ $CaSO_4$, potential difference 5V

Simultaneous adsorption of cations and anions was observed when the sorption electrode was charged negatively. Simultaneous desorption of cations and anions was observed when the sorption electrode was charged positively. The results obtained without and with a phosphate gradient can be explained based upon the interaction of the pH gradient with the fraction of phosphorized ZrO_2. A schematic representation of electro sorption without and with a phosphate gradient is given in Figure 3.

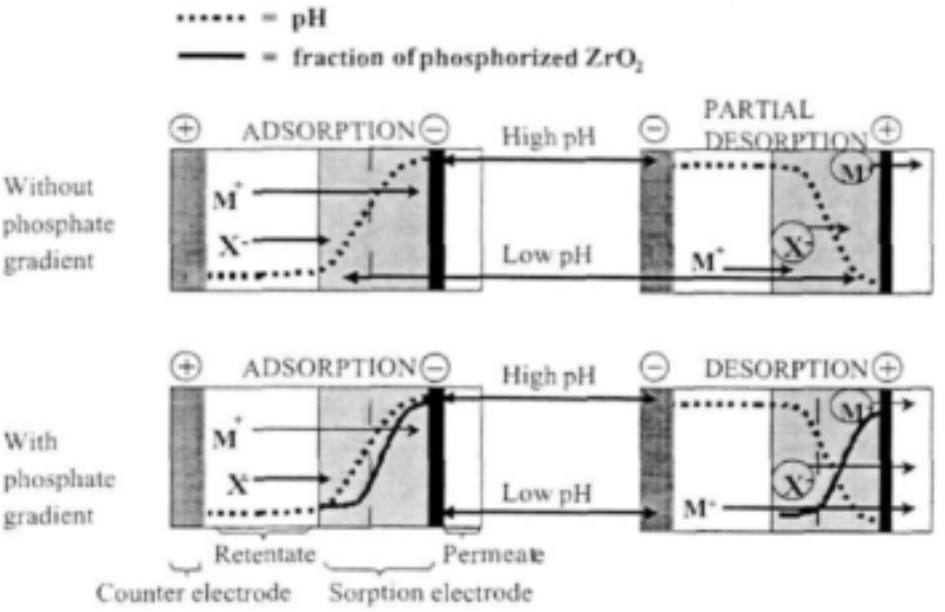

Figure 3. Schematic representation of electro sorption with and without phosphate gradient based on the pH gradient over a sorption electrode in a flow through system

The pH gradient necessary to bridge the pH difference between the anode and the cathode divided the membrane into two regions; one region with high pH (alkaline) and one region with low pH (acidic). In the alkaline region, cations adsorbed onto the activated cation exchange sites (negatively charged ZrP groups). In the acidic region of the sorption electrode, anions adsorbed at the positively charged ZrO^+ groups. When the potential of the electrodes was reversed, the pH gradient was also reversed (H^+ and OH^- production start at opposite electrode). The adsorbed anions then started to desorb and permeated further through the membrane towards the region that just became acidic. If this region of the electrode contains unreacted ZrO_2, the anions will adsorb again (see electrode without phosphate gradient, Figure 3). If this region of the electrode contains only ZrP, the anions will not adsorb but leave the electrode (see electrode with phosphate gradient, Figure 3). The cations in the alkaline part of the electrode can only adsorb at activated ZrP sites. These sites are not present in the electrode with the phosphate gradient. Cations in the acidic part of the membrane will desorb and leave the electrode in the direction of the permeating flow.

Micro filtration properties

The filtration property of the electro sorption electrode was tested by measuring its retention efficiency. The electro sorption electrode rejected 98% of microorganisms in a test solution whereas

a 0.45μm filter (0.45 polypropylene Cameo) rejected only 94% of microorganisms. The electrode's permeability was 0.02 ($m^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) but could be regulated based on the amount of incorporated ion exchange material. The permeability decrease of the electrode due to the presence of particles in the feed solution remained 25% over the duration of an experiment of 24 hours.

Reactors and experimental set-up

The reactor that was used to perform the electro sorption experiments is given in Figure 4.

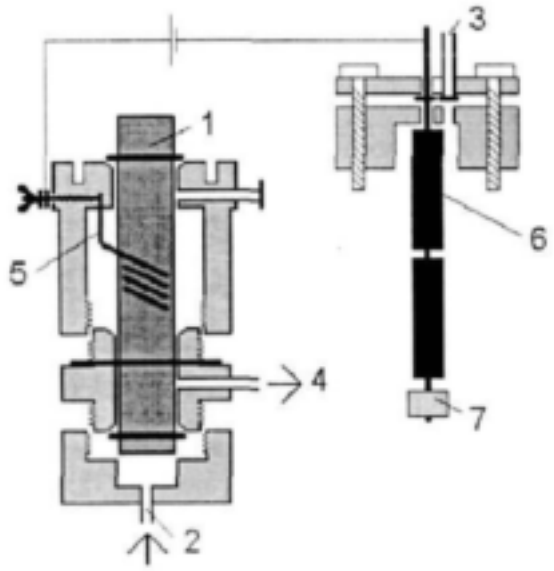

Figure 4. Schematic representation of the second electro sorption reactor design. (1: Sorption electrode, 2: Feed, 3: Reject, 4: Permeate, 5: Stainless steel coil, 6: Carbon rods, 7: PVC shortcut prevention)

For industrial application of the electro sorption filter system, an upscale able and easy to assemble reactor was designed as shown in Figure 5. The stainless steel coil from Figure 4 was changed for conductive, Ni-loaded O-rings (5)

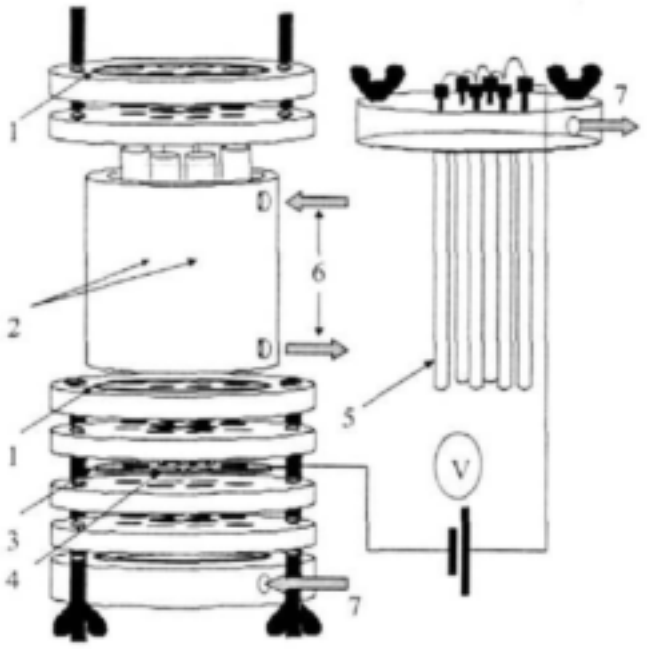

Figure 5. Schematic drawing of the multiple sorption electrode reactor. 1: O-ring, 2: Sorption electrodes, 3: Conductive plate, 4: Conductive O-ring, 5: Counter electrode. 6: In- and outlet of permeate. 7: In- and outlet of reject

Desalination results

Several solutions were treated with the electro sorption filter using the reactor in Figure 4. The ionic composition (in mg l^{-1}) of three solutions treated with the electro sorption unit is given in Table 1.

Table 1 Ionic composition of three solutions treated with the electro sorption unit

Solution	Na^+ (mg l^{-1})	Cl^- (mg l^{-1})	Mg^{2+} (mg l^{-1})	SO_4^{2-} (mg l^{-1})	Ca^{2+} (mg l^{-1})	HCO_3^- (mg l^{-1})
$CaSO_4$				1000	400	
Klipfontein	220	699	74	172	155	-
IEC norm 734	91.6	158.1	18.7	73.9	89.4	244

The percentage ion removal obtained during electro sorption experiments is listed in Table 2. The percentage ion removal was regulated by among other variables, the potential difference between the electro sorption filter and the counter electrode. Ion exchange with Cl^- ions was preferred over ion exchange with SO_4^{-2} ions.

Table 2 Average ion adsorption /desorption obtained by electro sorption.

Solution	Potential (V)	Average % adsorption/desorption				
		Na^+ (%)	Cl^- (%)	Mg^{2+} (%)	SO_4^{2-} (%)	Ca^{2+} (%)
$CaSO_4$	5				60/65	75/35
Klipfontein	5	-6/-4	30/25	36/2	8/12	55/75
Klipfontein	4	-5/-9	15/20	28/0	5/5	30/20
IEC norm 734	5.5	-	70/40	20/10	0/0	75/75

A hybrid system for desalination of Acid Mine Drainage (AMD)

Water recovered by purification of acid mine drainage (AMD) may become a significant source of water in the future. The pH of AMD is usually between 2-5, which makes it difficult to realize the required pH gradient for adsorption and desorption of ions. Moreover, the increase of local pH during the electro sorption process causes ions such as Fe to form precipitation products at such a fast rate that blockage of the electrode might occur before the electrode potential is reversed. Normally precipitates may be dissolved when the potential is reversed but this may be more difficult when the electrode is already blocked. To treat AMD with the electro sorption filter successfully, an additional reactor (see Figure 6) was placed in series with the electro sorption filter. This reactor comprised of a ceramic membrane that was used to separate an electrolysis cell into two compartments, namely an anolyte and a catholyte.

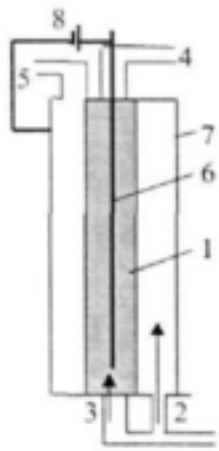

Figure 6. Schematic representation of the electrolysis cell design (1: Ceramic membrane, 2: Feed anolyte, 3: Feed catholyte, 4: Anolyte exit, 5: Catholyte exit, 6: Pt wire (anode), 7: Stainless steel tube (cathode), 8: Power source)

The electrolysis cell in Figure 6 was used to neutralise the AMD (Brugspruit, South Africa) and caused Fe to precipitate before it was fed to the electro sorption filter. The experimental results indicate that the pH of the catholyte can be regulated with the applied current and flow rate through the system. After the precipitate had been removed, a neutral catholyte, practically free of Fe ions was obtained and used for further treatment with an electro sorption filter to remove other ions.

Using the hybrid system (the combination of the reactors from Figure 4 and 6), more than 99% of Fe ionic species and 25% of Ca^{2+} was removed from Brugspruit AMD without decreasing the permeability of the electro sorption filter.

Flat electro sorption materials

One of the main goals of the current project was the development of methods for preparation of electro sorption membranes in the form of plates. These electro sorption membranes are especially promising for large-scale application of electro sorption technology for removal of ions from aqueous solutions. The membranes may be arranged in the form of plate and frame modules, which offer significantly higher volume to flow ratio than tubular membrane modules. In addition it should be significantly easier to supply evenly distributed electric current to the plate surface than to the tube surface.

Non-woven ceramic fiber based materials manufactured by "Thermal Ceramics", USA, from oxides of multivalent metals were used as supports for flat electro sorption membranes. In order to confer electro conductivity onto porous ceramic materials these materials were coated with a layer of electro conductive compound such as pyrolytic carbon. The deposition of carbon was carried out in the gas phase by pyrolysis of natural gas. Zirconium phosphate was selected as additional sorption active component to be introduced into porous matrices of sorption electrodes.

The procedure for the electro sorption membrane preparation from the Kaowool 700 support consisted of two consecutive stages: Deposition of carbon on the ceramic paper by methane pyrolysis at 900 °C for 30 min. This was followed by three consecutive impregnations with zirconium phosphate by a sol gel method followed by phosphoric acid treatment. The molar ratio of phosphorus to zirconium in the impregnated material was 1 to 1.

Plate-and-frame modules

After the membranes with required properties were developed, the process was up scaled to the level at which accurate prediction of membrane performance under full-scale conditions was possible. The principal schematic of the up scaled electro sorption module is shown in Figure 7.

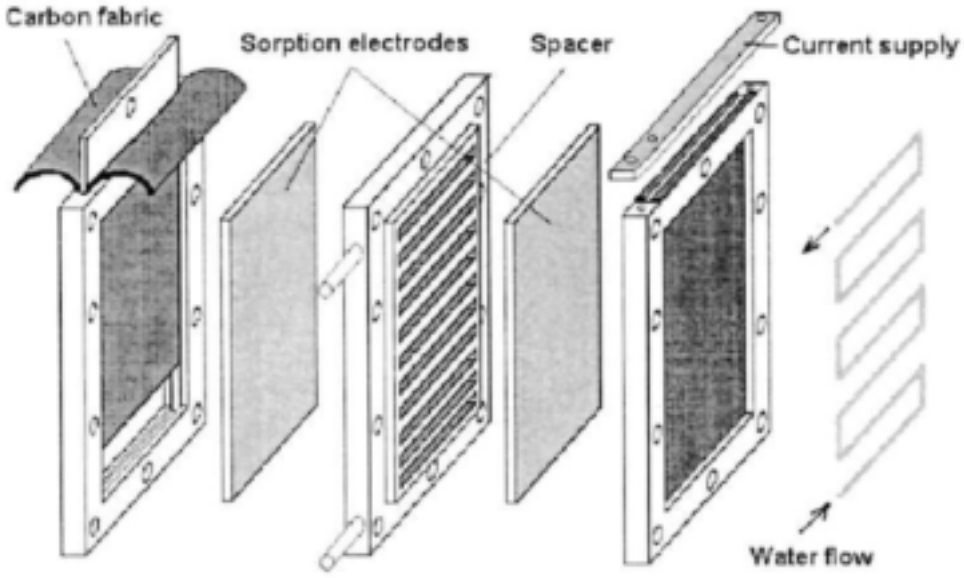

Figure 7. Schematic of plate-and-frame electro sorption module.

The electro sorption module consists of two electro sorption membranes with dimensions 150 x 210 mm and 2 mm thickness. The spacer, that also plays a role in the water flow field, is positioned between the membranes. The design of the spacer / flow field allows for the ratio of turbulent to laminar flows of water inside the module to be as high as possible.

The module design described above allows the assembly of electro sorption units of the plate and frame type from the abovementioned modules. The number of modules in the units will depend on the required productivity and ion content of waters to be treated. It should be noted that the proposed design of the electro sorption unit would allow the use of electro sorption electrodes not just as de-ionization media but also as micro- or ultra filtration media. Another significant technological feature of the proposed electro sorption modular structure is that the modules always work in the form of parallel electric circuits. This allows for the following operational advantages in comparison with the series of desalination cells, which are used for example in electro dialysis. The performance of each individual module can be monitored using its current / voltage characteristics.

The maintenance and membrane refitting in each module can be carried out without shutting down the complete desalination unit. Operation potentials of the units will be equal to operation potentials of each individual module.

Desalination with plate-and-frame modules

Electro sorption experiments were performed using several model solutions closely resembling various kinds of waters and effluents and at least one industrial effluent with significant potential for membrane fouling.

Low salinity solutions with TDS 510 mg· l^{-1} containing Ca^{+2}, Mg^{2+}, Na^{+}, Cl^{-} and SO_4^{2-} ions were tested initially. Desalination as high as 97% was obtained. The study of electro sorption purification of containing sulphate solutions with a content of salts up to 3500 mg l^{-1} was the next investigation phase. The following composition was chosen as a model solution: sodium – 1150; sulphate – 1920; chloride – 230; TDS – 3425 mg l^{-1}. The composition of this solution was close to sulphate containing mine waters. Depending on the solution flow rates purification degrees from 50 to 83% were obtained. The power consumption was between 4 and 5 kW per kg salt removed.

Testing of electro sorption method for the purification of nickel containing wastes was carried out first utilizing model solution of the following composition:

Ni_2SO_4 – 0.011M;

NaCl – 0.008M;

H_2SO_4 – 0.007M.

The removal degrees were from 74 to 96% for sodium and from 46 to 80% for nickel ions

And finally, the desalination of actual electroplating effluent was attempted. The concentrations of the main ions and their removal degrees are shown in Table 3. In this table the content of the brine resulting from the treatment is also given.

Energy consumption was 6.4 kW· kg^{-1} at dU=5V and 11 kW· kg^{-1} at dU=10V. No membrane fouling was observed.

Table 3. Chemical composition of real electroplating effluent, purified and brine solutions in mg· l^{-1}

	Purified solution			Brine
Constituent	Initial	dU = 5V	dU = 10V	
Sodium	183	103	18	1490
Sulphate	1739	998	65	17200
Chloride	210	98	5	220
Nickel	635	424	< 1	6430
TDS	4196	1623	89	25340

Electrochemical methods for the generation of disinfecting agents

Disinfection of water supplies is essential to the health of the world's population. The most often-used disinfection technology has been that of chlorination via the addition of chlorine or chlorine compounds to water supplied to domestic users. However, in rural areas of developing countries a major problem still remains.

Current electrochemical methods for the generation of disinfecting agents are dominated by the chlor-alkali industry, based on the electrolysis of brine to produce chlorine, sodium hydroxide and hydrogen. Alternative technologies such as the use of electro membranes could be employed as they may reduce the energy consumption and thus the cost of chlorine production, allowing the production of cheaper chlorine products for all communities and a disinfection technology that is reliable, appropriate and effective for small and rural communities not served by urban infra-structure.

This project focused on hypochlorite generation via the electrolysis of brine and its specific objectives were:

- The development of dimensionally stable anodes with electro catalytic coatings for optimisation of chlorine evolution as opposed to oxygen evolution
- Development of a cell design that allows minimal toxic chlorate generation
- Design cells with good current efficiency for chlorine generation (better than that of existing technologies)
- Low power consumption, less than that in conventional cells
- Facility to control the pH of the hypochlorite solution produced.

Design of cells for electrochemical generation of disinfecting agents

The cell designs separated the anodic and cathodic compartments to prevent mixing of the cathodic and anodic products. A diaphragm, porous to aqueous inorganic ions, was employed to divide the cell. To minimize diffusion of hydroxide ions through the diaphragm back into the anolyte (brine), the catholyte (water) movement was designed as a separate flow stream. Hence brine flowed through the anode chamber and was converted to low pH hypochlorite whereas water flowed through the cathode chamber and was converted to high pH sodium hydroxide solution. For practical reasons of availability the diaphragm chosen was a porous inorganic tubular membrane (aluminium – zirconium oxide based). The tubular shape allowed a cell to be readily designed and constructed consisting of tubes of different diameters. Two different membrane coatings were utilised in this project, RuO_2, which has a rutile structure and is electrically conducting, and Co_3O_4, a conducting spinel oxide. The RuO_2 coating proved to be unstable and is not further discussed here. The Co_3O_4 coating was applied thus: CoO was deposited on a titanium rod 5 mm in diameter. The starting material was Co_3O_4 which, when vaporised in a vacuum above 900°C, loses oxygen and is converted to CoO. The vaporisation was achieved by plasma deposition. However, CoO is non-conducting. It was converted to a conducting form of Co_3O_4 by electrochemical activation (oxidation). Activation was achieved by using the anode in the cell under hypochlorite generation operational conditions with a current density of 6 $mA \cdot cm^{-2}$ for 15 hours. During this period the colour of the coating changed from dark blue to black and a comparison of the galvanostatic polarization curves and hypochlorite current efficiencies were used as indicators of the termination of the oxidation process in the anode coatings. Later experiments found it preferable to pre-coat the titanium substrate with a layer of platinum prior to coating with CoO. This prevented oxidation of the titanium at the CoO/Ti interface during electrochemical activation.

Generation of hypochlorite using the electrolysers

Flows of anolyte and catholyte were controlled by gravity feeds of brine (sodium chloride in water as anolyte) and distilled water (catholyte). Hypochlorite and dissolved chlorine were analysed by back titration of liberated iodine with thiosulphate following addition of excess acidified potassium iodide. Hypochlorite concentrations were converted to *available chlorine* concentrations for comparison purposes. The presence of chlorate was tested by the manganese oxidation test.

Chemical considerations

In the cell, hydrogen is evolved at the steel rod or wire cathodes and OH^- ions accumulate. In the anolyte Cl_2 is evolved at the anode. Overall, two moles of added sodium chloride were converted to one mole of NaOCl. Under conditions of low pH in the anolyte, the hypochlorite existed almost entirely as HOCl, disproportionation to chlorate was suppressed and decomposition to oxygen was slow. Thus the anolyte should consist of dissolved chlorine, HOCl and HCl in water along with any unconverted NaCl. The catholyte should consist of dilute sodium hydroxide solution.

Generation of hypochlorite using the cobalt oxide electrolyser

The best results were obtained at 0.4 A using a low concentration of NaCl (25 $g \cdot l^{-1}$) with flow rates of 50 $ml \cdot h^{-1}$ for the anolyte and 140 $ml \cdot h^{-1}$ for the catholyte. The *figures of merit* for the electrolyser were comparable to those achieved in chlor-alkali cells. Current efficiencies for Cl_2 were almost the same as those for NaOCl, there was no decrease in conductivity over long periods, the anodes were stable and chlorate was not detected. Duplicate experiments on the Co_3O_4 electrolyser at UWC provided broadly similar results. These results correspond to a production of about 11 g of chlorine per day. Some diffusion of hydroxide ions into the anolyte probably did occur and would have caused a reduction in current efficiency.

Process efficiency, energy consumption and cost estimates for removal of salt by the electro sorption process.

By comparing salt removal results obtained in all the electro sorption experiments for all treated solutions it was shown that ions are adsorbed and desorbed to a different extent at different intervals of the experiments. As an example, Table 4 summarizes the process efficiency and energy consumption for different experiments performed using tubular membranes.

Table 4. Summary of results of electro sorption experiments with energy consumption

Exp.	Average adsorption/desorption during experiment (%)					E consumption
No	Na^{+}	Cl^{-1}	Mg^{2+}	SO_4^{-2}	Ca^{+2}	(kWh· kg^{-1})
A				65/30	25/10	8
B				25/15	65/20	15
C1				55/31	55/42	10
C2				45/43	40/42	15
C3				51/33	45/39	13
D				35/40	40/35	13
F				35/30	40/25	13
G				40/30	45/35	9
H				20/30	30/35	13
J				30/35	25/30	9
K				10/10	5/10	21
Q	-6/-4	40/31	36/2	8/12	55/75	25
R	-5/-9	15/20	28/0	5/5	30/20	19
S	-	70/40	20/10	-/-	75/75	55

Under the most efficient conditions the energy consumption was 9 kWh· kg^{-1} removed salt. Moreover, when treatment of model solutions of real effluents was done, the energy costs presented in Table 5 were calculated from the experiments performed.

Table 5. Pilot plant requirements for treating a model solution of Klipfontein and mine water.

Plant Capacity	Water source	
	Model A	Model B
Feed flow rate (m^3· h^{-1})	3	3
The transmembrane pressure (kPa)	150	50
Degree of purification	40% $Ca^{+2}$and 30%Cl^-	50% TDS
Energy cost (kWh· kg^{-1})	19	4

Model A: Klipfontein (TDS 1458mg· l^{-1}, see table 6.1)

Model B: Mine water (TDS 3425mg· l^{-1}, see section 5.2

A comparison of performance between electro sorption and electro dialysis was made and is presented in Table 6.

Table 6. A comparison between electro sorption and electro dialysis

Process parameter	Electro sorption reactor		Electro dialysis
	Flat sheet	Tubular	
DC power supply to reactor	0.7 – 1 kWh· kg^{-1} - ground water 500 TDS 2 –3 kWh· kg^{-1} - mine water 3500 TDS 3-6 kWh· kg^{-1} - electroplating effluent 3000 TDS	25 kWh· kg^{-1} – ground water 500 TDS 15 kWh· kg^{-1} – 1500TDS	0.5 kWh· kg^{-1} - ground water 400 TDS 1.2 kWh· kg^{-1} – mine water 3500 TDS
Pumping energy Total energy consumption	Requires less than 1 bar pressure 0.1 – 0.3 kWh· kg^{-1} Estimated 3 + kWh· kg^{-1} – 3500 TDS	Requires 1-2 bar Pressure 0.2-0.4 kWh· kg^{-1} Estimated 15 kWh· kg^{-1} - 3500 TDS	Requires 4 bar pressure 0.5 – 1 kWh· kg^{-1} for brackish water of 1000 TDS 1.5 kWh· kg^{-1} – 500 TDS 4 kWh· kg^{-1} – 3500 TDS
Membrane fouling	Ions - can be controlled Gasses – possibly H_2S Silica Colloids Large ions - ? Ions - can be controlled		Ions – heavy metals Gasses – O_2, CO_2, H_2S Silica Colloids Dissolved organics Large ions
Pre-treatment	Suspended solids filters	Precipitation of insoluble species	Suspended solids – filters Precipitation – ion exchange softening
Concentration diluting streams	Limited by ion exchange capacity and regeneration ability		Limited by back diffusion
Concentration of electrode stream	No		Additional operation parameter
Temperature	No effect on membrane life		Negative effect on membrane life
Membrane cost	Support R 120 – R 200 m^{-2}, total cost up to R 300 – R 500 m^{-2}	R 6000 m^{-2} cost directly related to ceramic support	R 400 – R 2000 m^{-2}
Stack design	No high voltages – low current leakage through supply ducts		High overall voltages. Requires high resistances of supply ducts
Hydraulic staging	Up to 90% removal possible in one stage		40 – 50% removal in one stage. Requires several stages
$CaSO_4$ saturation	Controlled electrochemically		Maximum 175%

OVERALL CONCLUSIONS INCLUDING RECOMMENDATIONS

Overall conclusions part A

A new type of purification unit was developed that is capable of removing ionic species AND micro particles from aqueous solutions. The unit exhibited non-chemical regeneration ability and required low pressure and only electrical energy for the purification of a solution. The developed purification unit is novel since conventional purification systems can only be used for desalination or microfiltration and require chemicals or high pressures during operation.

In the electrosorption system where microfiltration and desalination are combined, energy losses are difficult to avoid. The minimal energy consumption observed was 8 $kWh \cdot kg^{-1}$. It was calculated that roughly 25% of the protons and hydroxyl ions generated were effectively involved in the activation of sorption material.

The purification was based on microfiltration and electrochemically activated sorption. The purification units were prepared by modification of ceramic-based microfiltration units. The main achievements during the modifications were:

- The preparation of electroconductive and permeable coatings of, nickel, gold and carbon on ceramic substrates were optimized to control both permeability and conductivity
- The preparation of electrocatalytic coatings containing Pt-Si-Mo with high catalytic activity for water electrolysis and methanol oxidation
- Preparation, impregnation and optimization of zirconia and zirconium phosphate as sorption material. Maximal reversible sorption capacity of zirconia was $1.8meq \cdot g^{-1}$, maximal sorption capacity of zirconium phosphate was $1meq \cdot g^{-1}$
- A gradient of phosphorized ZrO_2 over the cross sectional diameter of the tube was essential.

Several reactors were manufactured to support the electrosorption unit. The main achievements in this area were:

- Watertight sealings were prepared by partial impregnation of microfiltration substrates with Na-silicate
- Conductive O-rings could be used to establish electrical contact between the sorption electrode and the potentiostat
- A upscalable and easy to assemble multiple tubular electrode reactor was developed

- A fully automated pilot plant was designed, manufactured and tested. The quality of permeating water was determined by measurements of conductivity and pH. The combination of these parameters was used to start or stop the regeneration and adsorption cycles.

During the optimization of the electrosorption process and preparation procedure the following conclusions were drawn:

- The optimal phosphorization time was found to be 4 hours
- Electrodes prepared from Al_2O_3 supports with 0.9µm pores showed better removal efficiencies than electrodes prepared from Al_2O_3 support with 3µm pores
- The electrical connection between a power source and a sorption electrode could be established using an electro conductive O-ring
- Deposition of Pt decreased the potential difference for water electrolysis. The energy consumption per kg salt removed did however not show any improvements
- The optimal potential difference between the sorption electrode and the counter electrode was found to be 4V. Although 5V potential difference resulted in similar energy efficiency, relatively poorer desorption characteristics were obtained
- The permeation flow should be close to 2ml· min^{-1} (flux: 0.5 m^3· h^{-1}· m^{-2}) when a potential difference of 5V is applied. Lower permeation flows resulted in lower desorption percentage and higher permeation flows resulted in lower removal efficiencies
- Removal efficiencies of both cations and anions >50% were obtained at a permeate/reject ratio of 0.5. Higher ratios led to lower removal efficiencies. Lower ratios may lead to higher removal efficiencies but will lead to low water recovery
- Using the current density as a control parameter during the electro sorption process instead of the potential difference may increase electrode lifetime. Calculation of the minimal required current density may give an indication of the efficiency of the electro sorption process.

Specific properties of the purification unit for different waters sources:

- The simultaneous adsorption of Ca^{2+} and SO_4^{2-} (93 and 69%, respectively) from a 1.4 g· l^{-1} $CaSO_4$ solution. The simultaneous desorption of Ca^{2+} and SO_4^{2-} was observed after switching the sorption electrode to an anode. Adsorption and desorption efficiencies remained unchanged for several cycles

- The filter efficiency of the electro sorption electrode was higher than a standard 0.45 micrometer filter. The permeate of a standard filter contained 6% of the microbes whereas the concentration in the permeate using the electrosorption filter was as low as 2%
- Ca^{2+} and Cl^- were most efficiently removed. Effluents containing large amounts of Fe, Ni or other elements that can easily be reduced may not be candidate ions for electrosorptive removal. All reactions besides water oxidation and reduction, such as reduction of metal ions and oxidation of Cl^- disturb the development of a pH profile necessary for controlled adsorption and desorption of ions
- With the hybrid system where an electrolysis reactor was placed in series with the electro sorption reactor, it was possible to treat Brugspruit water, an acid mine drainage effluent. Over 99% of Fe was removed by neutralizing the Brugspruit water electrochemically and 30% of Ca^{+2} was removed by a single pass through the electrosorption unit

Besides the preparation and extensive testing and optimization of the electrosorption process the following was done:

- Two mathematical models were developed. Model I showed that ionic diffusion could not be neglected. The predictions made with model II are in excellent agreement with the experimental findings for currents up to 100mA
- An alternative desalination system was described in which 72% of Na^+ and 50% of SO_4^{-2} was removed from 0.01M (1.4g· l^{-1}) Na_2SO_4. The total energy consumption for desalination and regeneration was 23.8kWh/kg. The water recovery was 38%. Simultaneously 0.4 liter of H_2 and 0.2 liter O_2 were produced from every 2 liter solution treated

Since the properties of both microfiltration and desalination could be combined in one unit using an electrochemically activated ion exchange mechanism, the project aims were reached.

Overall conclusions part b

Conclusions on generation of disinfecting agents using a hypochlorite generator

The Co_3O_4 electrolyser hypochlorite generator is suitable as a disinfection technology for small and rural communities but is not a viable industrial chlorine generator. The major advantages over existing brine electrolysers include; no generation of toxic chlorate; pH control without the requirement of additional chemicals; and lower power requirements than other systems (suitable for electrical supply from solar panels). At 0.4 A, the electrolyser requires only 32 g of added salt per day to produce 11 g of chlorine, sufficient to disinfect 7200 litres of water at a dose of 1.5 mg· l^{-1}

Cl_2. Hence the electrolyser can produce 50 litres of water per person per day for a community of 144 people at a low cost in terms of added chemicals and energy. A cost comparison based on a small community indicated that annual combined costs for a Co_3O_4 electrolyser water treatment plant were considerably less than for other systems currently in use (i.e. 26% cheaper than Moggod and 18% cheaper than on site hypochlorite).

Overall the generation of hypochlorite by electrochemical means was a success. A research product was constructed that met the objectives of the project, i.e. the *cobalt oxide electrolyser*. In addition, the electrolyser has great potential for practical application as an appropriate reactor for generation of disinfecting agents for rural water supplies.

Recommendation for future work

Simultaneously with the development of the flow through electrosorption system, a non flow-through system using carbonized supports with impregnated ZrP was developed by V.M. Belyakov [1], a research partner in the Ukraine. The non flow-through showed desalination properties with an energy consumption as low as 4kWh· kg^{-1}. The higher energy efficiency for the non flow-through electrosorption system was in line with the assumption that neutralization of hydroxyl ions and protons (resulting in energy loss) is less likely to happen in non flow-through system. In appendix G the economic evaluation of the tubular and flat sheet (non flow-through) electrosorption units is shown. The economic evaluation showed clearly that the production cost of the non flow-through electrosorption system ($4300 per $100m^2$) was much lower than the tubular flow-through system ($69110 per $100m^2$). Besides, the non flow-through flat sheet electrosorption reactor showed no fouling problems, higher removal efficiency and higher water recovery [1]. Future research in flat sheet non flow-through systems is therefore recommended for large scale purification systems.

Simultaneously with the development of the flow through electrosorption system the electro oxidation of organic pollutants on similar ceramic based electrodes has been investigated in this laboratory. The results look promising with high removal efficiencies at low costs. It is recommended to test the properties for decomposition of organic matter on the existing electrosorption membrane. Based on the preliminary work it is likely that organic compounds will be oxidized to a certain extent.

Future prospective

Currently, the Stanford Research Institute (SRI, the world leading organization in new technologies) showed their interest in the electrosorption technology. The following questionnaire was send to the SRI as contribution to their year report. It summarizes the future possibilities of electrosorption and ceramic membranes in general.

1. *When do you expect this technology to be commercialized? Are you looking for a licensor?*

Due to the current problems with clogging of the membrane pores during long term experiments, it is a bit too early to look for commercializing of the flow through technology. The non flow-through ceramic electrosorption system is being commercialized already.

2. *Where will this technology see industrial application?*

The nature of the flow through electrosorption technology allows the treatment of especially water with low salt content. Immediate application can be seen in a) low salinity waters and b) Removal of hard ions in potable water to reduce scaling. After further improvement on the sorption efficiency the flow through electrosorption technology may be suitable for the production of ultra pure water.
At high salt content scaling and fouling become important drawbacks. The non flow-through electrosorption system however can tread effluents with high salinity. Recently the technology is used for nickel recovery from electroplating effluents and being considered as alternative technology for ED brine treatment.

3. *How much will the technology cost (if you can give me a rough estimate)?*

A full cost analysis was done based on 100m^2 electrosorption material.
As a result of the significant cost of ceramic membranes that are used as substrates for our electrosorption material the cost of the flow-through electrosorption material was \$691· m^{-2}.
The non flow-through electrosorption material with even higher sorption capacity per m^2 cost as low as \$43· m^{-2} since much cheaper substrates could be used.

4. *Are you aware of similar technologies either commercialized or under development at this time?*

The idea behind the new technology was to develop a desalination unit working at low pressure, without the need for additional chemical for regeneration and having micro filtration properties. As far as we know there is no other technology that is capable of doing all these in one step. We know

that electrosorption with carbon aerogels is under development in the US. We are also aware that a similar technology, e.g. "electro ion exchange" has already been commercialized. In this technology products of water electrolysis are used to regenerate and activate ion exchange materials as well. In the technology of electro ion exchange additional filters need to be installed to filter the feed water.
These additional filters will also be necessary for electro dialysis systems. Technology of Nano or ultra filtration perhaps with the assistance of electrical charged surfaces may show similar desalination properties. However the working pressure of these units may be considerably higher.

5. *What is the general trend in the ceramic membranes area? Do you think demand is on the increase? Where will ceramic membranes see significant application in the near future?*

Membrane processes are in general very efficient. The demand for membranes in general will keep growing whether it will be polymeric or ceramic. Because of the specific properties of ceramic versus polymeric membranes, ceramic membranes will always be favorable in several areas. The technology to synthesis ceramic membranes can be considered as relatively new. Therefore a lot of new discoveries are still ahead which can boost the possibilities and use in new applications. Significant application of ceramic membranes in the near future can be expected in units for gas separation and in solid electrolytes for fuel cells

6. *Is there a trend towards SMART ceramic membranes (ie a mixture of polymeric and ceramic membranes)?*

There is a trend toward SMART ceramic membranes especially in areas were both membrane types have their limiting properties. Using a mixture of polymeric and ceramic materials in an attempt to prepare membranes with combined properties is an important way of research that can quickly result in membranes with better properties than 100% ceramic or 100% polymeric membranes.

7. *What technical and commercial barriers need to be overcome before ceramic membranes are directly competitive with polymeric membranes?*

Technical problems of ceramic membranes are usually brittleness and density besides the difficulties with up scaling and machining. However nowadays flexible and upscalable ceramic materials are entering the market. Commercial barriers are the relative low amount of suppliers of high quality ceramic materials. Moreover, organic membranes already conquered large part of the market and investors are more likely to choose for the more advanced but known materials over advanced new materials.

A significant increase in the demand for ceramic membranes can be expected when there is an increasing need for membranes with specific properties that ceramic membranes offer. There are reasons to believe that the need for hydrogen in the future will increase. Since several types of ceramic membranes are suitable for hydrogen separation, ceramic membranes will automatically get more attention.

8. *Can you see a decrease in price of ceramic membranes in the near future?*

A decrease of ceramic membranes can be expected mainly if ceramic membranes get more attention from industry and the production rates will increase.

PRODUCTS

Methods for electro sorptive membrane preparation with:

- Conductive layers
- Electro sorptive layers
- Catalytic layers
- Phosphate gradients

Multiple electro sorption membrane reactors

A desalination procedure

Pilot scale electro sorption desalination plant

Hypochlorite Electrolyser

Process and reactor design for simultaneous water filtration and desalination

Developed electro sorptive membranes

Methods for non-chemical regeneration of desalination membranes

Method for electrochemical treatment of AMD

Method for electrochemical treatment of plating solutions containing Ni

Degrees

PhD:

Ceramic based electrosorption electrodes for desalination of aqueous solutions. B.J. Bladergroen. Unpublished Thesis. University of the Western Cape

Honours Projects:

A. Maluleke, Preparation of electro conductive layers on ceramic membranes

S. Maoela, Pt and Pd electroless plating on functionalised ceramic membranes

N.Hendriks Preparation and characterization of dense ZrP based membranes

Publications and conference proceedings

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ACKNOWLEDGEMENT

The research in this report emanated from a project funded by the Water Research Commission and entitled:

Electro membrane Reactors for Desalination and Disinfection of Aqueous Solutions (File No. K5/964)

The financing of the project by the Water Research Committee and the contributions of the members are gratefully acknowledged. This project was only possible with the co-operation of the following individuals and institutions:

Mr. B.J. Bladergroen University of the Western Cape

Ms. L.F.Petrik University of the Western Cape

Members of the Water Research Commission Steering Committee:

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to whom the author wishes to convey his sincere thanks.

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PART A

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LIST OF ABBREVIATIONS

$A_{a/c}$	the flow through surface area of the anolyte/catholyte volume (m^2)
a_{ox}	Activity of the oxidized component
a_{red}	Activity of the reduced component
c	concentration ($mol \cdot l^{-1}$)
D_i	Diffusion coefficient for ion i ($m^2 \cdot s^{-1}$)
$D_{anode\ /\ cathode}$	diameter anode / cathode
$D_{ceramic}$	diameter ceramic
dE/dx	gradient of the potential (=potential difference over a distance dx)
dt	differential unit of time
E^0	standard electrode potential
e	charge of an ion (Coulomb)
E_{anode}	Half cell potential for the oxidation of water
$E_{cathode}$	Half cell potential for the reduction of water
F	Faraday constant ($C\ mol^{-1}$)
$[H^+]_{anolyte}$	proton concentration in anolyte ($mol \cdot l^{-1}$)
$[H^+]_{catholyte}$	proton concentration at cathode
I	current (A)
$I_{Manolyte}$	fraction of the current through the anolyte carried by ion M^+ ($C\ s^{-1}$)
J_{H+}	flux van proton of anolyte to catholyte ($mol \cdot m^{-2} \cdot s^{-1}$)
K	Kohlrausch constant
k	total numbers of samples taken from permeate
$[M^+]$	cation concentration ($mol \cdot l^{-1}$)
n	Number of electrons participating in the reaction
N_A	Avogadro constant
n_{H_2O}	water produced (mol)
R	gas constant ($J\ K^{-1}\ mol^{-1}$)
R	Resistance (Ω)
R_n	removed amount of ions (mmol) in sample n
sJ	number of cationic and anionic species respectively
S	weight of impregnated ZrO_2 (g)
t	time

T	Temperature (K)
U	potential
$v_{a/c}$	the velocity of the solution in anolyte ($m \cdot s^{-1}$)
V_a	volume anolyte (l)
V_c	volume catholyte (l)
V_n	volume of sample n (ml)
W_n	weight of sample n (g)
$[X]_{feed}$	concentration of the X in feed solution ($mmol \cdot ml^{-1}$)
$[X]_n$	concentration of the X in sample n ($mmol \cdot ml^{-1}$)
z	number of ionic charges
z	sign of charge (cation positive, anion negative)
z	number of mols to form on mol of the corresponding salt
ze	charge of one mol of ions, (z is negative for anions and positive for cations

Greek symbols

Λ_m	molar conductivity ($mS \cdot cm^{-1}$)
Λ^0_m	molar conductivity at infinite dilution
$\phi_{a/c}$	flow rate of anolyte / catholte ($m^3 \cdot s^{-1}$)
$\eta_{anode/\ cathode}$	Overpotential at the anode / cathode
$\lambda^0_{an/cat}$	average anion conductivity at infinite dilution
$\tilde{e}_i$	ionic conductivity of ion i ($Ohm^{-1}\ cm^2\ mol^{-1}$)
μ	ion mobility in aqueous solutions ($m^2\ s^{-1}\ V^{-1}$)
ρ	density of samples ($g \cdot ml^{-1}$)
v_i	drift velocity of ion i ($m\ s^{-1}$)

GLOSSARY OF TERMS

Absorption

The process in which one substance penetrates into the body of another substance, termed the absorbent. An example is the absorption of water into soil.

Activated Carbon

A water treatment medium, found in block, granulated, or powdered form, which is produced by heating carbonaceous materials, such as coal, wood, or coconut shells, in the absence of air, creating a highly porous adsorbent material. Activated carbon is commonly used for dechlorination

Adsorbate

Any substance that is or can be adsorbed. The liquid, gas or solid substance, which is adsorbed as molecules, atoms, or ions.

Adsorbent

A water treatment medium, usually solid, capable of the adsorption of liquids, gases, and/or suspended matter. Activated alumina and activated carbon are common adsorbents used in water processing.

Adsorption

The physical process occurring when liquids, gases, or suspended matters adhere to the surfaces of, or in the pores of, an adsorbent media such as activated carbon. Adsorption is a physical process, which occurs without chemical reaction.

Aggressive Water

A term usually applied to waters containing acid or oxygen that hasten corrosion (rusting).

Alkali

A substance that creates a bitter taste and a slippery feel when dissolved in water and will turn red litmus paper blue. An alkali has a pH greater than seven and is the opposite of an acid. Highly alkaline waters tend to cause drying of the skin.

Alkalis may include the soluble hydroxide, carbonate, and bicarbonate salts of calcium, magnesium, potassium, and sodium. A hydroxide alkali may also be called a base.

Anion

A negatively charged ion in solution, such as bicarbonate, chloride, or sulphate. An anion [such as chloride (Cl^-)] may result from the dissociation of a salt, acid, or alkali.

Anion Exchange

An ion exchange process in which anions in solution are exchanged for other anions from an ion exchanger. In demineralisation, for example, bicarbonate, chloride and sulphate anions are removed from solution in exchange for a chemically equivalent number of hydroxide anions from the anion exchange resin.

Anode

The positive pole of an electrolytic system. The metal that goes into solution in a galvanic cell. Anodes of metals such as magnesium and zinc are sometimes installed in water heaters or other tanks to deliberately establish galvanic cells to control corrosion of the tank through the sacrifice of the anode.

Aqueous

Containing water; watery.

Backwash

The up flow or counter-current flow of water through a filter or ion exchange medium, lifting the mineral bed and flushing away to the drain the particles of foreign matter that have been filtered from the water supply during the service cycle.

Bar

A unit of pressure. One bar equals 14.5 pounds per square inch (psi) or about 0.987 standard atmospheres.

Base

An alkali that releases hydroxyl ions when dissolved in water. Bases react with acids to form a neutral salt and water. In general they taste bitter rather than sour, and feel slippery and reverse the colour changes produced by acids in indicators. For example, they turn litmus paper blue.

Batch Operation

The utilization of ion exchange resins to treat a solution in a container wherein agitation of the solution and subsequent decanting of the treated liquid accomplish the removal of ions.

Brackish Water

Water containing between 1.000 and 15,000 mg· l^{-1} of dissolved solids.

Breakthrough

The first appearance in the solution flowing from an ion exchange unit of unabsorbed ions similar to those that are depleting the activity of the resin bed. Breakthrough is an indication that regeneration of the resin is necessary.

Brine

A strong solution of salt(s), such as the sodium chloride or potassium brine used in the regeneration of ion exchange water softeners, but also applied to the mixed sodium, calcium and magnesium chloride waste solution from regeneration.

Capacity

In a softener or de-ionizer it is the adsorption activity possessed in varying degree by ion exchange materials. This quality may be expressed as kilograins per cubic foot, gram-milli-equivalents per gram, pound-equivalents per pound, gram-milli-equivalents per milli-litre, etc., where these ratios represent the weight of the ions adsorbed and the denominators, the weight or volume of the adsorbent. It can also refer to the ability of any media to take up a specific contaminant and is rated by time over gallons. As to flow rates, it is the maximum or minimum flow obtainable under given conditions of media, temperature, pressure, velocity, etc.

Cation

A positively charged particle or ion.

Chemical Oxygen Demand (C.O.D.)

The amount of matter, both organic and inorganic, in a water or wastewater which can be oxidized by boiling with a strong oxidizing acid, and expressed as the equivalent amount of oxygen. Often used as a measure of the strength of sewage.

Chemical Stability

Resistance to chemical change which ion exchange resins must posses despite contact with aggressive solutions.

Chlorinator

A mechanical device specifically designed to feed chlorine gas or pellets, or solutions such as hypochlorides, into a water supply in proportion to the flow of water.

Chlorine Demand

A measure of the amount of chlorine that will be consumed by organic matter in water before chlorine residual will be found.

Conductivity

The quality or power to carry electrical current; in water, the conductivity is related to the concentration of ions capable of carrying electrical current. The unit of measure is the mho, which is the reciprocal of resistivity that is the microhm.

Contamination

The addition of any physical, chemical, biological or radiological substance to water that reduces the value of the water, or interferes with its intended use.

Corrosion

The destructive disintegration of metals by electromechanical means. Corrosion of iron and steel is commonly called rusting.

Cycle

A complete course of ion exchange operation. For instance, a complete cycle of cation exchange would involve: regeneration of the resin, rinse to remove excess regenerant, exhaustion, backwash, and finally regeneration again.

Dechlorination

The removal of excess or free chlorine from a water supply by adsorption with activated carbon or by catalytic type filter media.

De-ionization

The removal of the ionized minerals and salts (both organic and inorganic) from a solution by a two-phase ion exchange procedure. First, positively charged ions are removed by a cation exchange resin in exchange for a chemicaly equivalent amount of hydrogen ions. Second, negatively charged ions are removed by an anion exchange resin for a chemically equivalent amount of hydroxide ions. The hydrogen and hydroxide ions introduced in this process unite to form water molecules. The term is often used interchangeably with demineralisation. The cation resin is regenerated with an acid and the anion resin is regenerated with sodium hydroxide (caustic soda).

Delta P

The difference in pressure between the feed side and the permeate side of a membrane (usually in bar or Pa)

Desalination

The removal of dissolved inorganic solids (salts) from a solution such as water to make it free of dissolved salts. Typically accomplished by reverse osmosis, distillation, or electro dialysis.

Detergent

Usually refers to synthetic detergent, but can be any material with cleansing powers such as soap, alkaline materials, synthetic detergents, solvents, and abrasives. Synthetic detergents are known as surfactants that foam and act like soap but are not made from fatty acids and lye.

Dialysis

The separation of components of a solution by diffusion through a semi-permeable membrane, which is capable of passing certain ions or molecules while rejecting others.

Efficiency

The effectiveness of the operational performance of an ion exchanger. Efficiency in the adsorption of ions is expressed as the quantity of regenerant required to effect the removal of a specified unit weight of adsorbed material, e.g., pounds of acid per kilogram of salt removed.

Effluent

The outflow of a water treatment device. Sometimes used to mean the product water of a given water conditioning device or system.

Electro dialysis

A dialysis process using semi-permeable membranes.

Electrolyte

A chemical compound, which dissociates or ionizes in water to produce a solution that will conduct an electric current. Could be an acid, base, or salt.

Elution

The process of washing out adsorbed material, especially by use of a solvent.

Exchange Sites

Locations on ion exchange resin beads, which hold mobile ions that are available for exchange with other ions in a solution passing through the bed. These sites are also called functional groups.

Ferric Iron

Small solid iron particles containing trivalent iron, usually as gelatinous ferric hydroxide or ferric oxide (Fe2O3), which are suspended in water and visible as "rusty" water. Ferrous (iron in solution) is readily converted to ferric iron by exposure to oxygen found both in water and air. Ferric iron can be removed by filtration, but not by ion exchange.

Ferrous Iron

Usually ferrous hydroxide when dissolved in water, produces a clear solution. Often called clear water iron, it can be removed by ion exchange.

Filter

A device used to clean water by removing iron, silt, taste, odour, colour, etc., before it is fed into the softener or supply lines of the consumer. Includes mechanical, adsorptive, oxidizing and neutralizing filters. Available as media beds in tanks or as cartridge type devices.

Filtration

The process of passing water through a porous substance to remove solids in suspension.

Flash Distillation

A distillation process in which hot water is introduced into a low pressure chamber causing some of the water to flash or quickly turn to steam.

Flocculants

Materials added to water that could cause gelatinous clouds of precipitate to enclose fine particles of foreign material in order to settle or filter them from the water.

Flux

In cross flow filtration, it is the product flow rate through a reverse osmosis, electro dialysis or ultra filtration membrane. It is usually given in terms of volume unit per time per membrane area.

Groundwater

The term describing all subsurface water and the source of well water. It can be found in aquifers as deep as several miles.

Gypsum

A moderately insoluble calcium sulphate containing 20.9 percent water. It is often used to build soil structure and permeability.

Halogens

A family of elements that includes bromine, chlorine, fluorine, astatine, and iodine. They are very active chemically. They are commonly found as the ionic component in compounds with various other elements.

Hardness

A characteristic of natural water due to the presence of dissolved calcium and magnesium; water hardness is responsible for most scale formation in pipes and water heaters, and forms insoluble "curd" when it reacts with soaps. Hardness is usually expressed in grains per gallon, parts per million, or milligrams per litre, all as calcium carbonate equivalent. Temporary hardness, caused by the presence of magnesium of calcium bicarbonate, is so called because it may be removed by boiling the water to convert the bicarbonates to the insoluble carbonates. Calcium sulphate, magnesium sulphate, and the chlorides of these two metals cause permanent hardness.

Hydrogen Cycle

A complete course of cation exchange operation in which the cation medium is regenerated with acid and them all cations in the water are removed by exchange with hydrogen ions.

Hydro Static Pressure

A measurement of structural strength and ability to hold water pressure. Hydrostatic pressure is more challenging to a system than air pressure because air will compress and absorb impact, whereas water will not.

Hydroxyl

The term used to describe the anionic hydroxide radical (OH-) that is responsible for the alkalinity of a solution.

Inorganic Matter

Matter that is not derived from living organisms and contains no organic product

Ion

An atom, or group of atoms in a solution which function as a unit, and has a positive or negative electrical charge, due to the gain or loss of one or more electrons. It is smaller than a colloid.

Ion Exchange

A reversible process in which ions are released from an insoluble permanent material in exchange for other ions in a surrounding solution; the direction of the exchange depends upon the affinities of the ion exchanger for the ions present and the concentration of the ions in the solution. The ion exchanger media is an insoluble permanent solid medium.

Kinetics

The study of the relationships between temperature, motion, and the velocity of very small particles. It is used to describe the rate of ion exchange reactions.

Mechanical Filter

A filter primarily designed for the removal of suspended solid particles, as opposed to filters that remove contaminants by chemical means.

Microgram per Litre

Also known as parts per billion (ppb). The common symbol for microgram per litre is

$\mu g \cdot l^{-1}$

Microhm

One millionth of an ohm. A unit of measurement used to test the electrical resistance of water to determine its purity. The purer the water, the greater its resistance to conducting an electrical current. Water of absolute purity has a resistance of eighteen million ohms across one centimetre at a temperature of twenty-five degrees Celsius.

Micron

A linear measure equal to one millionth of a meter, or .00003937 inch. The symbol for the micron is the Greek letter "μ". The smallest particle visible to the human eye is 40 microns. Most types of bacteria range from 0.05 to 10.0 microns in size.

Milligram per Litre

($mg \cdot l^{-1}$). A unit concentration of matter used in reporting the results of water and wastewater analyses. In dilute water solutions, it is practically equal to the part per million, but varies from the $mg \cdot l^{-1}$ in concentrated solutions such as brine. As most analyses are performed on measured volumes of water, the $mg \cdot l^{-1}$ is a more accurate expression of the concentration, and is the preferred unit of measure.

Mineral

A term applied to inorganic substances, such as rocks and similar matter found in the earth's strata, as opposed to organic substances such as plant and animal matter. Minerals normally have definite

chemical composition and crystal structure. The term is also applied to matter derived from minerals, such as the inorganic ions found in water. The term has been incorrectly applied to ion exchangers, even though most of the modern materials are organic ion exchange resins.

Molecule

The simplest combination of atoms that will form a specific chemical compound; the smallest particle of a substance which will still retain the essential composition and properties of that substance, and which can be broken down only into atoms and simpler substances.

Nanofiltration

A membrane process that treats water between reverse osmosis and ultra filtration in the filtration/separation spectrum. It can remove particles in the 300 to 1,000 molecular weight range such as humic acid and organic colour found in water. Nanofiltration may be used for selective removal of hardness ions.

Osmosis

A process of diffusion of a solvent such as water through a semi-permeable membrane that will transmit the solvent but impede most dissolved substances. The normal flow of solvent is from the dilute solution to the concentrated solution. Osmosis causes the stronger solution to become more diluted and tends to equalize the opposing solutions.

Osmotic Pressure

The pressure and potential energy difference that exists between solutions on either side of a semi-permeable membrane. This pressure is caused by the tendency of water to flow in osmosis. Every 100 $mg \cdot l^{-1}$ of TDS produces about one pound per square inch of osmotic pressure. Osmotic pressure must first be overcome by water pressure in the reverse osmosis process.

Oxidation

A chemical process in which electrons are removed from an atom, ion or compound. The addition of oxygen is a specific form of oxidation. Combustion is an extremely rapid form of oxidation, while the rusting of iron is a slow form. Oxidation never occurs alone but always as a part of the oxidation-reduction (redox) reaction.

Oxidizing Agent

A chemical substance that brings about the oxidation of other substances in chemical oxidation and reduction reactions. Examples of oxidizing agents include oxygen, ozone, chlorine and peroxide.

Particulate

A term used to describe visible sediment particles, used as both singular and plural.

Parts Per Billion (ppb)

A basis for reporting the results of water and wastewater analysis, indicating the number of parts by weight of a dissolved or suspended constituent, per billion parts by weight of water or other solvent. One part per billion is equal to one microgram per litre, the preferred unit.

Parts Per Million (ppm)

A common basis for reporting the results of water and wastewater analysis, indicating the number of parts by weight of water or other solvent. In dilute water solutions, one part per million is practically equal to one milligram per litre, which is the preferred unit. 17.1 $mg \cdot l^{-1}$ equals one grain per US gallon. One $mg \cdot l^{-1}$ equals one pound per million pounds of water.

Permeability

The permeating flux as function of pressure. Usually given in terms of volume unit per time per membrane area per unit of pressure ($m^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)

pH (potential of Hydrogen)

An expression of the acidity of a solution; the negative logarithm of the hydrogen ion concentration (pH 1 very acidic; pH 14, very basic; pH 7, neutral). e.g., pH 5 is 10 times the acidity of 6 and 100 times the acidity of 7. pH is a measure of intensity and not capacity. It is the logarithm of the reciprocal of the hydrogen ion concentration of a solution. The neutral point of 7 indicates the presence of equal concentrations of free hydrogen and free hydroxide ions.

Physical Adsorption (Van der Waals Adsorption)

Binding of adsorbate to the surface of a solid by forces whose energy levels approximate those of condensation.

Physical Stability

The quality which an ion exchange resin must possess to resist changes that might be caused by attrition, high temperatures, and other physical conditions.

Pores

The complex network of channels in the interior of a particle of a sorbent.

Potable Water

Water which is considered safe and fit for human consumption, culinary and domestic purposes and meets the requirements of the health authority having jurisdiction.

PPB

The abbreviation for "parts per billion".

PPM

The abbreviation for "parts per million".

Precipitate

To cause a dissolved substance to form a solid particle that can be removed by settling or filtering. The term also refers to the solid thus formed.

Preferential Adsorption

Adsorption in which a certain component or certain components are adsorbed to a much greater extent than others.

Pressure Drop

A decrease in water pressure during its flow due to internal friction between molecules of water, and external friction due to irregularities or roughness in surfaces past, which the water flows.

Purification

The removal of undesirable matter from water or wastewater. It is the disinfection of water by the killing of microbial contaminants, such as coliform bacteria. A strict definition means the removal from water of all contaminants.

Regenerant

The solution used to restore the activity of an ion exchanger. Acids are employed to restore a cation exchanger to its sodium form. The anion exchanger may be rejuvenated by treatment with an alkaline solution. Potassium permanganate is used to regenerate a manganese greensand iron and manganese iron and manganese removal filter.

Regeneration

The process of returning the sodium ions to the mineral after it has exchanged all its sodium ions for calcium and magnesium from hard water. This is accomplished by first back washing the mineral bed to free it of all foreign matter, and then passing salt brine through the mineral. The sodium ions attach themselves to the mineral, and the calcium and magnesium combine with the chloride from the brine to form calcium and magnesium chlorides, which are rinsed down the drain. All water softeners using the ion-exchange process are regenerated with these basic steps. In similar fashion cation and anion components of a demineralizer as well as manganese greensand are recharged with comparable sequences.

Rejection

In cross flow membrane filtration and de-ionization, it is the ability of the membrane to reject the passage of dissolved solids and other contaminants into the product water.

Residual

The amount of a specific material remaining in the water following a water treatment process. It may refer to material remaining as the result of incomplete removal such as hardness leakage, or to a substance meant to remain in the treated water such as residual chlorine.

Resin

Synthetic organic ion exchange material, such as the high capacity cation exchange resin widely used in water softeners. Technical name- sulfonated co-polymer of styrene and divinyl benzene.

Reverse Osmosis

A process for the removal of dissolved ions from water, in which pressure is used to force the water through a semi-permeable membrane, which will transmit the water but reject most other suspended and dissolved materials. It is called reverse osmosis because mechanical pressure is used to force the water to flow in the direction that is the reverse of natural osmosis, namely from the dilute to the concentrated solution.

R.O.

The abbreviation for "reverse osmosis".

Sand Filter

A treatment device or structure for removing solid or colloidal material of a type that cannot be removed by sedimentation. Such filters can be gravity rapid-rate or enclosed pressure type.

Salt

The common name for the specific chemical compound sodium chloride (NaCl), used in the regeneration of ion exchange water softeners. In chemistry, the term is applied to a class of chemical compounds, which can be formed by the neutralization of an acid with a base.

Saturated Solution

A solution containing the maximum amount of the dissolved substance that such a solution can hold at this temperature.

Selective Ion Exchange

The use of a selective ion exchange medium with the property of removing specific ions from a solution.

Softened Water

Any water that is treated to reduce hardness minerals to 1.0 GPG (17.1 mg· l^{-1}) or less, expressed as calcium carbonate.

Solvent

The liquid, such as water, in which other materials (solutes) are dissolved.

TDS

The abbreviation for "total dissolved solids".

Total Dissolved Solids

The weight of solids in true solution per unit volume of water, usually determined by the evaporation of a measured volume of filtered water, and determination of the residue weight. TDS

is expressed as mg· l^{-1} per unit volume of water. An electrical conductivity test provides only an estimate of the TDS since non-conductive substances cannot be measured by electrical means.

Total Organic Carbon

The measurement of carbon dioxide produced from organics when a water sample is atomised into a combustion chamber. The amount of carbon covalently bound in organic compounds in a water sample.

Total Solids

The weight of all solids, dissolved and suspended, organic and inorganic, per unit volume of water; usually determined by the evaporation of a measured volume of water at 105 degrees Celsius in a pre-weighed dish.

Turbidity

A measure of the amount of finely divided suspended matter in water, which causes the scattering and adsorption of light rays. Turbidity is usually reported in arbitrary nephalometric turbidity units (NTU) determined by measurements of light scattering. NTU should not exceed 0.5 in potable water. Turbidity can protect bacteria from sterilization.

Ultra filtration

A membrane type system that removes small colloids and large molecules from solutions. Ultra filtration removes particles in size range between 0.002 to 0.1 micron range. The process falls between reverse osmosis and micro filtration as far as the size of particles removed is concerned.

Ultra pure Water

No standards exist describing ultra pure water though it is not considered to be sterile. It is water that has been de-ionized and provides high resistivity and contains no organics.

Water Softening

The reduction or removal of calcium and magnesium ions that are the principle cause of hardness in water.

Zeolite

Naturally occurring or synthetic hydrated sodium alumino-silicate with ion exchange properties. Zeolites have been largely replaced with synthetic organic cation ion exchange resins.

Modified Zeolites can be selectively charged with exchange minerals such as potassium and used to remove undesirable elements such as iron, hydrogen, sulphide, and manganese.

1. INTRODUCTION

Abstract

The drawbacks of excisting desalination unit are high cost of investment, high working pressures, extensive energy consumption, use of chemicals for regeneration, fouling and the complexcity of complete purification systems. These drawbackes, besides the contineous need for purified water, form the base of the current studies. The objectives of the study are to develop a purification unit that overcomes most of these costly drawbacks providing an economical alternative for water desalination. It was decided that the realisation of the objectives could be possible by the combination and modification of electro sorption and microfiltration technology.

1.1 Water purification

1.1.1 The need for good quality water

Access to water has an enormous impact on the quality of life. In many parts of the world, the locally available source of water is not of an acceptable quality to fulfil industrial and domestic needs. It is a responsibility of the government and industry to guarantee the supply of sufficient water for the community and specific industrial processes. The quality of water will be determined by the needs of the end-user. Water for consumption must be of good quality, free of contamination such as bacteria, parasites and viruses, with acceptable low concentrations of ions to avoid acute or chronic illnesses. Taste, smell, colour and turbidity will further determine its quality. The extent to which pollutants influence the economics of a specific process (e.g. product quality and maintenance cost of process units due to abrasion, damage, fouling etc.) determines the quality of water required in industry.

1.1.2 Supply of good quality water

With growing world population, industrialization, lack of planning, change of climate, and irresponsible and unsustainable practice of humans, clean water has become a scarce commodity in many parts of the world. To supply the demand for potable water for the community and clean water for industry, the available sources of water often need to be treated. [1,2]. Fresh water, found in lakes, rivers or shallow aquifers, is often of reasonable quality and relatively simple purification methods such as sand bed filtration are usually sufficient. However, with increasing pollution and

unevenly distributed fresh water supplies in the world, the locally available water is often of relatively low quality (such as seawater with high salt content) and needs more advanced treatment to produce high quality water. Over the last few decades many purification techniques have been developed to serve two purposes simultaneously; A) The purification of low quality water, which is in many instances more economically feasible compared to the alternative of reticulation of fresh water over long distances. B) Concentrating the pollutants, which reduces the cost of treatment of secondary wastes and may increase the recovery of valuable resources. Both purposes are of growing importance since the availability of clean water is decreasing and the regulations regarding the release of secondary wastes are becoming more strict and costly. These regulations are implemented by governments in order to secure a future supply of water and maintain the quality of life. Water purification units for industry may be installed where they are expected to be economically feasible. Water purification units that produce potable water will be applied if financial resources are made available.

1.1.3 The area of research

Impurities found in aqueous solutions can be divided into three different groups, namely solids, organics and ions of inorganic salts. Since the developed water purification techniques are usually suitable for the removal of only one or two group of impurities most water purification plants will consist of a succession of purification units. The complexity of the water purification process normally depends upon the quality of the feed water and also on the specific techniques that are used (see section 1.1.4).

In principle any kind of pollutant can be removed from any kind of aqueous solutions using existing purification technology, but in practice, the source of the water that will be used for the production of desalinated water will be carefully chosen based on an economic evaluation. The location, composition and the amount of purified water required gives an indication of the purification method that can best be employed and what the costs of purification will be. Even though the water source finally chosen for purification may contain relatively low concentrations of pollutants, the concentrations of Na^{+}, Ca^{+2}, Mg^{2+}, CT, SO_4^{-2} and CO_3^{-2} are usually significant due to the abundance of the corresponding natural salts in the earth crust (in addition, CO_3^{-2} becomes available when CO_2 from the air dissolves in water). These ions may be considered as a welcome ingredient in potable water (within certain concentration limits). They provide a source for the daily requirement of

minerals in the human body but can cause serious problems in industrial applications (section 1.1.4). Removing these ions from water is a necessity to prevent extremely costly damage to process units or low quality products. Unfortunately the problem is not solved but merely shifted when water purification is used to remove ions, especially when Ca^{+2} combined with CO_3^{-2} and SO_4^{-2} ions, has the potential to form solid deposits such as $CaSO_4$ and $CaCO_3$. Scale formation and fouling of purification units by these deposits has been widely acknowledged [1]. Depending on the purification method and the ion concentrations, these deposits together with the currently used methods to prevent scaling, are responsible for a large part of the total operational cost of water purification. The development of desalination units with good anti-fouling characteristics that remove ions (with Ca^{+2} and SO_4^{-2} in particular) is of great economic interest and an attractive field of research.

This report will mainly focus on the removal of inorganic salts from ground water sources and industrial effluents. The specific removal of microorganisms will be discussed in chapter 6. In the next section of this chapter, more examples will be given to show the importance of water desalination and several desalination techniques will be discussed.

1.1.4 Water desalination

Besides the necessity of water purification for the production of domestic water, de-ionized or desalinated water is of great economic importance in many industrial production processes. The quality of the products and the reduction of secondary wastes in semiconductor chips production, plating and the petrochemical industry are dependent upon the quality of feed water and the required de-ionization processes. Boiler water for nuclear and fossil-fuelled power plants is treated to remove ionic contaminants such as Mg^{2+}, Ca^{2+}, Cu^{2+}, and Cl^-, and is essential for the prevention of pitting, stress corrosion cracking, and scaling of heat transfer surfaces. For the same reason de-ionization is particularly important on nuclear powered ships and submarines [3]. Other industrial applications could include the removal of toxic ions, especially those containing selenium, from waters produced by agricultural irrigation.

For the removal of sulphate alone, which is a common ingredient in commercial salt, is present in many sources of water and is a potential problem ion with regard to scale formation, many installations have been developed [4-5] but no universal method has yet been found. The main techniques for desalination of aqueous solutions and their associated drawbacks will be discussed

below. The techniques include; distillation, flocculation and coagulation, reverse osmosis, electro dialysis, nanofiltration, ion exchange and lesser known methodologies of capacitive de-ionization, electro de-ionization and electro ion exchange. The newly developed purification technique described in this report will be compared with electro dialysis via an economic evaluation report included in chapter 14.

1.1.4.1 Distillation

In 1996, distillation accounted for approximately 60 percent of the world's desalting capacity. However, distillation is very energy intensive due to the high vaporizing energy of water and therefore less energy efficient than most other techniques. Moreover, distillation units have a high investment/capacity ratio. The total desalting capacity for distillation is decreasing every year [1]. Distillation includes processes such as pervaporation and multistage flash evaporation.

1.1.4.2 Flocculation and coagulation

Flocculation and coagulation are the most conventional techniques for the removal of divalent and trivalent cations. These techniques make use of the low solubility of most metal hydroxides. Addition of acid and base are used for pH adjustment to precipitate the respective metal hydroxide in the form of a flock. The freshly formed flock is often an effective absorber for other pollutants (e.g. dissolved silica [6]) Flocculation and coagulation is usually one of the first steps in a series of purification units. The need for large amounts of chemicals, large settler tanks and additional purification units are drawbacks of this form of purification.

1.1.4.3 Reverse osmosis

Reverse osmosis (RO) is a pressure driven membrane operation in which the solvent of the solution is transferred through a semi-permeable membrane barrier tailored to retain salts and low molecular weight solutes. High operating pressures are required to overcome the osmotic pressure difference between the pure permeate and the saline reject solution. For certain applications RO may be an economically feasible desalination process. However the high cost of investment to deal with extreme pressures (15-80bar) and the sensitivity of the relatively expensive membranes to fouling and scaling are the most important drawbacks.

1.1.4.4 Nanofiltration

Nanofiltration and RO are considered as one process since the basic principles are the same. The main difference is that the network structure of the nanofiltration membrane is much more open

than the RO membrane [6, p. 297]. This implies that the retention of monovalent salts such as Na^+ and Cl become much lower than the retention of bivalent ions such as Ca^{2+} and CO_3^{2-}. The capital cost of nanofiltration processes is usually much lower than reverse osmosis since the permeability of the membranes is much higher [7]. As in RO processes, scaling and fouling of the membranes contribute significantly to the total cost of operation (fouling prevention and membrane replacement).

1.1.4.5 Ion exchange

Ion exchange is a well-known and relatively old desalination method. Typically, columns with ion exchange resins are saturated and subsequently regenerated with acids, bases or salt solutions. These routine maintenance measures produce relatively high amounts of secondary wastes compared with other desalination processes. Secondary wastes typically include acids, bases and/or salt solutions contaminated with anion, cation and ion exchange resins. Given the increasingly high cost of disposal of secondary wastes, ion exchange is becoming less attractive [8-10]. Economic feasibility is mainly possible when this method is used for materials recovery (e.g. from plating effluent) or for the production of high purity water from already relatively clean water sources (thus secondary wastes are minimized). Other points to consider are that ion exchange resins can be expensive [11] and in some situations growth of bacteria on the resins could cause problems [12]. Ion exchange resins used as water softeners are often regenerated with sodium chloride, which add significant amounts of sodium chloride to the purified stream. An additional purification step is often required (like reverse osmosis) to deliver the desired water quality.

1.1.4.6 Electro dialysis

Electro dialysis (ED) is an electrochemical separation process in which an electrical potential difference and ion selective membranes are used to separate ionic species from an aqueous solution and other uncharged components.

The ED system usually consists of a large number of compartments between two electrodes. The compartments are separated by alternative anion and cation exchange membranes and filled with polluted water. A potential difference accompanied by electrochemical reactions (usually reduction of water at the cathode and oxidation of water or chloride at the anode) drives cations through the cation exchange membranes into the adjacent compartment in the direction of the cathode. Anions migrate through the anion exchange membrane into the compartment towards the anode. Concentrated and diluted water will thus be generated in each adjacent compartment. The current

requirement of ED will scale linearly with the salt concentration of the feed, making it less economic than for example RO for feed waters with high salt concentration [10].

The use of ED/EDR for the removal of contaminants from water and wastewaters is generally restricted to small ions such as sodium, calcium, chloride, sulphate, etc. When large organic anions are present in solution, the electrical conductivity and perm selectivity of the membrane decreases with adverse effect on desalination performance.

To maintain performance, the ED membrane stack needs to be cleaned periodically to remove scale and other surface foulants. Special cleaning solutions (dilute acids or bases and anti-scaling agents) are circulated through the membrane stack for in-place cleaning but the membrane stack needs periodic disassembly and mechanical cleansing to remove scale and other surface foulants. Water pre-treatment to prevent scaling combined with cleaning or replacing the membranes form up to 80% of the cost of water purification especially when the feed water contains a significant amount of organic pollutants [13]. Regular stack disassembly is a time-consuming operation and is a disadvantage of the ED process [1].

During the past two and a half decades, the polarity reversal process that is known as *electro dialysis reversal* (EDR) has been developed. In this process the polarity is reversed on a regular basis. Hereby, a large part of the scale is broken up and can be flushed out. This makes EDR less sensitive to scaling than ED. However, the complexity of EDR systems leads to relatively high capital and process costs.

Major ED/EDR applications include desalination of brackish water, recovery of metals and water from electroplating rinse waters and demineralisation of whey, wine and sugar [1]. Since the chief function of the ED/EDR process is the removal of inorganic ions, bacteria, viruses, and neutral organics will be left behind in the dilute stream.

1.1.4.7 Electro ion exchange, electro de-ionization or capacitive de-ionization

The purification system proposed in this report is a modification of a technique named electro ion exchange (EIX). EIX is also known as electro de-ionization (EDI) or capacitive de-ionization (CDI) and operates upon the same principle. An electro ion exchange process can be viewed as an ion exchange bed process in which the resin is electrically regenerated. The technique of electro ion exchange was already described in 1957. The system consists of an electrochemical cell with two

electrodes of which at least one contains incorporated ion exchange resin and is permeable to water. The water to be purified acts as an electrolyte. A schematic representation of electrochemically-activated sorption is illustrated in Figure 1.

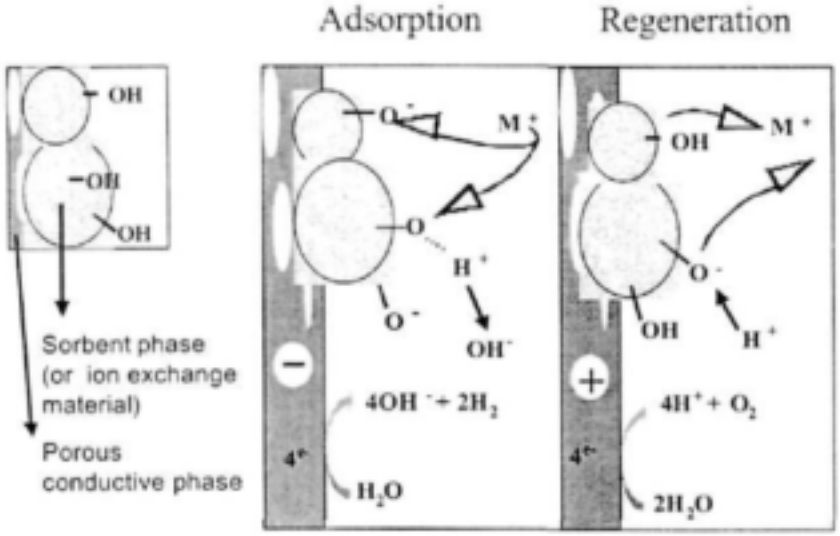

Figure 1.1. Schematic representation of the electrochemically-activated sorption process

When a DC voltage is applied between the two electrodes, protons and hydroxyl ions are generated by electrolysis at the surface of the anode and cathode respectively. Since the purification system proposed in this report is a modification of a technique named electro ion exchange (EIX), this and related techniques will be discussed in more detail. EIX is also known as electro de-ionization (EDI) or capacitive de-ionization (CDI) and operates upon the same principle. An electro ion exchange process can be viewed as an ion exchange bed process in which the resin is electrically regenerated.

The system is comprised of an electrochemical cell that consists of two electrodes preferably both containing incorporated ion exchange resin and being permeable to water. The water to be purified acts as an electrolyte. When a DC voltage is applied between the two electrodes, protons and hydroxyl ions are generated by electrolysis at the surface of the anode and cathode respectively. As a result of the local change in pH, active sites in the ion exchange material are produced and may adsorb cations at the cathode and anions at the anode [15-17]. An alternative view of the mechanism is that hydrogen and hydroxyl ions are displaced from the ion exchange material by cations and anions from the aqueous solution respectively, and migrate through the ion exchange

material to the vicinity of the electrode where they are discharged. Subsequent reversal of the voltage enables the absorbed ions to be eluted so that the working electrode can be regenerated.

Carbon electrodes have mostly been used for the electrolytic de-ionization of water. This is firstly because of the natural cation responsive behaviour of carbon, which is related to the functional groups on the partially oxidized surface of carbon:

$$C{=}O + H_2O \rightarrow C\text{-}OH^+ + OH^-$$

$$\uparrow\downarrow Na^+$$

$$C\text{-}O^-Na^+ + H_2O$$

Secondly, carbon can easily be modified to obtain anion responsive behaviour. In order to achieve this, carbon could be either treated with cation polyelectrolytes or mixed with weakly basic anion exchange material. Since 1957, different configurations of carbon electrodes have been investigated. Carbon packed bed electrodes were developed to create high sorption surface area but the system suffered from high pressure differentials over the carbon bed and poor electrical contact between particles, resulting in inhomogeneous charge distribution [18]. Most of the problems remained with the introduction of carbon fibres as electrodes. The electrical connection of the fibres was difficult to establish and the fibres were mechanically weak [19,20]. Besides carbon, metal plates or meshes (e.g. platinized titanium) have also been used as the current lead. Ion exchange resins are coated onto these feeders using elastomeric binders mixed with graphite for better conductive properties. Thin films of high surface area adsorption material (HSAAM) such as carbon aero-gels attached to these plates showed good electrical uniformity but the devices could be relatively costly [21]. Gradual disintegration of the electrode, release of sorption particles and additional electrical potential drop caused by the non- or low-conductive binder material are the main drawbacks.

Although more stable and improved electro de-ionization systems had the potential to be quite effective in removing ions from liquid [11], such systems have never been developed to the degree that they have become competitive either structurally or operationally compared to the better known separation techniques mentioned before. The scaling and fouling problems are a well know problem in electro purification units as well. The purification efficiency drops when scale is formed.

Generally, these scales form in the presence of polyvalent metal cations such as Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Fe^{3+} and Al^{3+} that can precipitate under local high pH conditions as hydroxides, oxides, sulphates, phosphates, carbonates, mixed oxides, mixed carbonates and fluorides depending on the composition of the solution. Due to the low solubility products of these compounds combined with high local pH, even trace amounts of these metal cations and counter anions in the concentrate streams will be sufficient to cause undesirable precipitation.

To prevent scale of polyvalent cations on the electro de-ionization system, these cations can be removed from the feed stream by adding water softeners or acid injection [22]. This addition of chemicals to the system is in most cases not desirable, considering the initial purpose of purification.

1.1.4.8 Conclusions

If the performance of the desalination techniques (described in section 1.1.1) has to be compared with actual and future requirements of such systems, the following may be concluded:

There is a significant and growing need for an improved desalination method in certain application that

- *significantly reduces or eliminates secondary waste*
- *is cost efficient, with a minimal energy requirement, no additional expensive desalination devices, and minimal costs of investment for the total purification system*
- *exhibits good regeneration properties to avoid frequent replacement of membranes or other parts of the purification unit*

In order to develop an improved desalination system that should meet/satisfy these requirements the following points had to be considered:

1. Conventional desalination systems such as ion exchange and flocculation/coagulation should be avoided if possible. These techniques require a large amount of additional chemicals that will directly contribute to the amount of secondary wastes. Indirectly, downstream the process would require other additional desalination systems.

2. When low energy usage is required, distillation is not favoured as the desalination technique of the future. Using electrostatics to remove ions from water may be much more efficient than using

large pressures to remove water from ions (seeing that the number of ions is always much smaller than the number of water molecules and each water molecule contributes to the total resistance of flow). Moreover, when compared to reverse osmosis, nanofiltration and electro dialysis, electro de-ionization does not require exotic (expensive) membranes, which easily rupture if over pressurized. Furthermore, capital investments for pressurized units are high and energy intensive.

3. Avoiding water pre-treatment and addition of chemicals are likely the most difficult requirement to overcome for a new desalination system. All desalination techniques suffer from scaling and fouling when the feed is not properly treated. These treatments are usually softening treatments by use of ion exchange or flocculation/coagulation, which were not desired for the reasons mentioned in point 1. Without pre-treatment of the feed solution, the formation of solid deposits is hard to avoid. A simple mass balance can show that the concentration in the reject has to increase when the concentration in the product stream decreases. The low saturation limits of several di- and tri-valent salts in the reject are easily exceeded. The desired water recovery and the composition of the feed will determine how many solid deposits will be formed. In the most convenient system these solid deposits would be formed in the bulk of the reject solution where they can easily be removed from the reactor. Deposits formed at the surface or within the matrix of the membranes / sorption phases will be difficult to remove and potentially cause blockage, pressure drop and decrease of flux. Deposits will decrease the ion removal efficiency for electro dialysis and electro de-ionization systems. The most severe problems are to be expected in processes where anions and cations are both removed at the same location. This may happen in ion exchange processes in mixed bed form or capacitive de-ionization where double layers can be formed. During regeneration anions and cations are released in high concentrations in each other's presence. Saturation limits are easily exceeded and pH-independent deposits such as $CaSO_4$ can be formed deep inside the sorption medium. In case of pure ion exchange where either cations or anions are formed, fewer problems are expected. Regeneration of the separated anion and cation exchange phase does not cause immediate deposition and possibly then only in the bulk of the reject. Scale formation during reverse osmosis and nanofiltration, can partially be prevented by applying high reject flows.

1.2 Objectives

The objective of this study was to develop a new type of purification unit in which ionic species and micro particles can be removed simultaneously based on electrochemically activated sorption and micro filtration respectively. The unit should be simple with non-chemical regeneration ability. The

combination of the above will make the system completely novel The expected advantages of the system are:

- Unlike the conventional ion exchange processes, no additional chemicals, whether acids, bases, or salt solutions, are required for the regeneration of the system; instead, electricity is used.
- Unlike conventional membrane processes for desalination such as nanofiltration and reverse osmosis, no high pressures are required for water desalination. Pressurized units are normally expensive and should be avoided.
- Unlike conventional electro de-ionization and electro dialysis processes, no additional filtration process is required since micro-filtration happens simultaneously with ion removal.
- Unlike conventional electro dialysis and reverse osmosis, osmotic pressures between reject and product stream can be avoided since the ions are fixed at the ion exchange sites. Energy losses may be lower.
- The well known fouling characteristics can be avoided by modification of process parameter of conventional electro de-ionization

The process described in this report will further be referred to as an electro sorption filter or electro sorption unit.

1.2.1 Realizing the objectives

Based on the conclusions that were drawn in section 1.1.4.8, the following decisions were made to meet the objectives mentioned above:

The new purification unit should be based on the electro de-ionization process. The process does not require high pressures or exotic membranes, which avoids expensive investments. Secondly this process is energy efficient (see conclusion 2, section 1.1.4.8). However, some modifications should be implemented to avoid the drawbacks of the conventional method. These drawbacks (mainly fouling related) are mentioned in section 1.1.4.8, conclusion 3. Double layers and simultaneous adsorption of ions (locally) should be avoided and pure ion exchange should occur instead to avoid formation of precipitates in the porous ion exchange medium. It was decided to operate the sorption electrode at high potentials to allow excessive water electrolysis at the sorption electrode surface. The advantages hereof are that double layer formation may be disturbed and ion exchange material may be more effectively activated or regenerated. Moreover, electro oxidation of organic pollutants

may increase the quality of the purified water, simultaneously reducing another important source of fouling. Unfortunately the energy consumption may be higher than in a pure electro de-ionization system but the prevention of fouling without using chemicals ensures a simple purification system, which is of higher priority.

Another main decision was that inorganic micro- or ultra filtration membranes should be used as a base for the electro de-ionization electrode. This would provide the system with the unique property of ion removal and micro filtration simultaneously. Moreover, forcing a flow of ions through a porous microstructure filled with ion exchange material will enhance the kinetics of ion exchange since diffusion distances are small compared to non-flow through ion exchange media.

The sorption unit should be assembled as follows:

An inorganic micro or ultra filtration membrane should be coated with an electro conductive and stable electrode material. The product should be sufficiently electro conductive, permeable and porous to allow impregnation of suitable cation and anion exchange material (which will be referred to as the sorption phase). After immobilization of the ion exchange material, the sorption unit should be tested for ion removal efficiency, capacity and filtration performance on different polluted solutions. Catalysts may be imbedded in the sorption electrode matrix to enhance the electro catalytic performance towards water electrolysis and improve the energy efficiency of the sorption unit.

1.3 The scope of the project

The sorption electrodes with the above-mentioned properties were prepared from two different types of ceramic substrates. Chapter 2 describes how electro conductive and electro catalytic coatings of different electrode materials were applied on the external/internal surface of the tubular ceramic substrates and what the properties of the different coatings were. Chapter 3 describes the development of synthesis methods and optimisation of properties of electro sorption materials based on fibrous ceramics. The design of the electro sorption modules for tubular and flat sheet membrane elements is described in chapter 4 including a controlling system on pilot plant scale. Results on ion removal using a model solution of $CaSO_4$ and the importance of the zirconium phosphate gradient inside the sorption electrode are discussed in chapter 5. Optimisation of the electro sorption process is described in chapter 6. In chapter 7 the desalination performance of the flat sheet and tubular sorption electrodes is tested for different modulated and real water sources. The filtration properties of the tubular sorption electrode are also demonstrated. In chapter 8 an economic evaluation

compares the flat sheet and tubular sorption elements with electro dialysis. Chapter 9 describes the electro membrane reactors for desinfection of aqueous solutions.

1.4 References

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2 DEVELOPMENT OF THE SYNTHESIS METHODS AND OPTIMIZATION OF PROPERTIES OF ELECTRO SORPTION MATERIALS BASED ON POROUS CERAMICS

Abstract

The porous ceramic substrate that was chosen as support for the sorption electrodes had to be modified to obtain the essential conductivity, electrocatalytic and ion exchange properties. The prepared conductive coatings on porous ceramic supports consist either of carbon, gold or nickel or a combination of carbon and gold. Carbon coatings were obtained by pyrolytic decomposition of LPG gas, gold was sputter coated and nickel coatings were formed by electroless plating. The permeability for water and electrical resistance of each coated support were measured and compared. Pyrolytic carbon was deposited throughout the support whereas the nickel and gold coatings were formed on the outer surface of the support. The resistance of a carbon coating could be regulated between 0.5 and 2 $\Omega \cdot cm^{-1}$ of support while the permeability decreased to levels as low as 25% of the permeability of the unmodified support. The nickel and gold coatings had no significant effect on the permeability and could be prepared with a resistance of respectively 0.25 and 1 $\Omega \cdot cm^{-1}$ of support.

The deposition of Si-Mo and Pt to increase the catalaytic activity of the sorption electrode were described as well. The current-voltage characteristisc of carbonized ceramic supports and carbonized supports with Si-Mo-Pt were compared. The supports with Si-Mo-Pt showed a significant reduction of the electrolysis potential compared to the support which was only carbonized (0.8V at $25mA \cdot cm^{-2}$ as anode and 1V at $25mA \cdot cm^{-2}$ as cathode).

The incorporation of zirconia and zirconium phosphate from different sources was carried out under different conditions. The ion exchange capacity was then measured in order to find the optimal sorptin material. A ZrO_2 sol was used to incorporate ZrO_2 particles inside a ceramic substrate. 300°C was sufficient to immobilized the particles. A maximum reversable anion exchang capacity of 1.8 $meq \cdot g^{-1}$ was found for ZrO_2 obtained from commercial available source. By phosphorizing the ZrO_2 particles a cation exchange capacity of 1 $meq \cdot g^{-1}$ was obtained.

This chapter is divided into three parts. The first part (section 2.1) describes how the support material obtained its conductive properties. In the second part (section 2.2) it will be shown how

highly dispersed Pt can reduce the energy requirement for water electrolysis and the third part describes how to incorporate the optimal sorption phase into the porous structure.

2.1 Electro conductive coatings on porous ceramic supports

2.1.1 Introduction

The preparation of porous electrodes is of interest for a variety of applications that include systems where a high electrochemically active surface area is desired, such as in fuel cells, electro-synthesis, anodic decomposition of organic pollutants or electro sorption materials. For all these applications the production of an electrode at minimal cost, with optimal hydrodynamic properties, mechanical and chemical stability and sufficient electrochemical activity is essential. Noble metals are known to be chemically stable and exhibit good electro conductive and electro catalytic properties [1,2] but are very expensive. Instead of manufacturing a porous electrode from these expensive materials, the production cost of a porous electrode may be minimized by coating a suitable, cheaper matrix with a porous coating of electro conductive material. In this report, a porous ceramic support is chosen as a suitable matrix because of its relatively low cost, high surface area, high chemical and mechanical stability and its filtration properties. The prepared porous electrodes were specifically developed as sorption electrodes and had to meet the following requirements:

- The conductive coating should have low electrical resistance to minimize the potential drop over the axial length of the substrate during the electrolytic process
- The coated substrate must be permeable and the pores of the substrate must remain accessible for the sorption phase that will subsequently be incorporated. (The incorporation of sorption material will be discussed in the section 2.3.)
- The conductive coating should have high chemical stability under anodic and cathodic conditions.
- The porous electrode must exhibit high catalytic activity towards water electrolysis

Thin coatings of noble metal may suit the requirements mentioned above very well. Instead of preparing a continuous layer of the noble metal (to obtain electro conductivity) a more economical approach would be to use a fraction of this expensive material in highly dispersed form on top of a cheaper conductive coating to obtain high electro- catalytic activity. Deposition of highly dispersed carbon in the form of an electro-conductive coating has been described before [3,4] and showed promising stability and conductive properties. Carbon was therefore selected as one of the materials

for electro conductive coatings. Besides carbon, nickel and gold were also tested as potential electrode materials. The preparation of both nickel [5,6,7,8] and copper [9] coatings on non-conductive substrates is well described. Nickel was chosen for its high resistant to corrosion in concentrated alkaline solutions and its low overpotential for the oxygen and hydrogen evolution reaction [10] (lowest among the non-noble metal materials). Gold is an excellent electro-conductive material and coatings of gold are extensively used as conductive layers [11]. Gold is relatively stable and cheaper than platinum or palladium.

The potential usefulness of the various coating materials for electro sorption supports may be determined by a combination of factors such as electrical resistance, electrochemical stability and the effect on the permeability of the initial substrate.

2.1.2 Experimental

The preparation of electro conductive coatings using carbon, gold or nickel will be discussed separately. Two different types of supports were used as a matrix for the coatings. Details of the unmodified supports are given in Table 2.1.

Table 2.1 Main characteristics of the tubular porous aluminium oxide element before coating procedure

Support type	I	II
Outer diameter (mm)	10	10
Inner diameter (mm)	7	7
Average pore size (µm)	0.9	3
Porosity (vol %)	40-45	40
Permeability ($m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$)	2.5-2.6	4.2-4.3
Length (mm)	105	105

The permeability of the substrates was measured before and after coating, using the dead end method [11]. The electrical resistance was measured over a distance of 5cm in the axial direction of the support using a Fluke 73 multi-meter. Morphology was studied using scanning electron microscopy (SEM). Elemental analysis was done using energy dispersive X-ray spectroscopy (EDX). The electrochemical stability of the electro conductive coatings was tested with cyclometric

voltammetry, using an AUTO PGST-30 potentiostat/galvanostat instrument (ECO Chemie BV, The Netherlands). By changing the electrode from anode to cathode for several hundreds of cycles in 0.5M Na_2SO_4, the test method simulated the conditions of the sorption electrode in real life operation. A platinum wire and a saturated calomel electrode were used as counter and reference electrodes respectively. The current density is given in amperes per geometric cm^2.

2.1.2.1 Preparation methods

Carbon coating

Ceramic substrates were coated with carbon by pyrolytic decomposition of methane (analytical grade, Afrox) or LPG gas (Afrox). The coatings procedure was as follows: A support was placed in the middle of a quartz tube (∅ 5cm) and centred with a mild steel wire to prevent the support from touching the tube. Subsequently, the quartz tube was put in a tube furnace. The pyrolytic gas was fed from one side into the tube at a flow rate of 50 $ml \cdot min^{-1}$. To optimise the coating conditions, carbonisation was done at temperatures between 700 and 900°C while the duration of the experiment varied from 30 to 300 minutes.

Nickel coating

Ceramic substrates were coated with nickel by electroless plating [5]. Prior to plating, the substrates were activated using an $SnCl_2$ and a $PdCl_2$ solution (Pd^{2+} was reduced by Sn^{2+} to metallic Pd particles which initiated the auto catalytic process of nickel plating). The compositions of the solutions are tabulated in Table 2.2. All solutions were prepared with ultra pure water (Modulab water systems, U.S. Filter) unless otherwise stated.

Table 2.2 Compositions of the activation solutions

Solution	$SnCl_2.2H_2O$ (Saarchem)	$PdCl_2$ (Aldrich)	HCl (32%) (Saarchem)
Tin chloride	$1g \cdot l^{-1}$	-	$1ml \cdot l^{-1}$
Palladium chloride	-	$1g \cdot l^{-1}$	$1ml \cdot l^{-1}$

The supports were initially submerged in the $SnCl_2$ solution for 5 minutes and then rinsed with de-ionized water. Subsequently the supports were submerged in the $PdCl_2$ solution for 5 minutes and rinsed with de-ionized water. These steps were repeated five times before the support was dried in

a furnace at 120°C for 12 hours. After activation, the supports were connected to an overhead stirrer using connection A or B as illustrated in Figure 2.

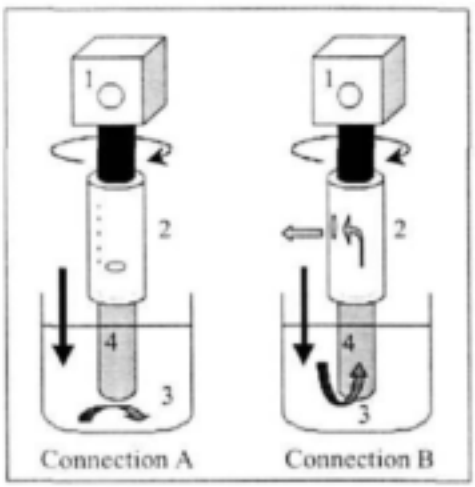


Figure 2.1. The reaction set-up with connection A and B for electroless nickel plating. 1: Overhead stirrer, 2: Silicon tubing, 3: Plating solution, 4: Porous ceramic support

Whilst rotating slowly, the support was submerged in 10ml nickel-plating solution at various temperatures (between 60 and 95°C) for various times (5 to 15 minutes). The composition of the plating bath is shown in Table 2.3.

Table 2.3 Composition of the nickel-plating bath

Compound	Concentration ($g \cdot l^{-1}$)
$NiSO_4 \cdot 6H_2O$ (Aldrich 99%)	31
$NaH_2PO_2 \cdot xH_2O$ (Aldrich 99%)	54
$(CH_3COO)_2Pb \cdot 3H_2O$ (Merck 99.5%)	0.005
Lactic acid (Alfa Aesar, 60%)	50
Acetic acid (Saarchem, 99.8%)	38
pH	4.5

When connection A was used, trapped air inside the support prevented the plating solution from entering the lumen side of the support. When connection B was used, the plating solution could

enter the lumen side as the air inside the support could escape via the hole in the silicon tube that connected the support to the stirrer (Figure 2).

Gold coating

Ceramic substrates were coated with gold using an Edwards S 150B sputter coater. The Argon pressure in the sputter chamber and the potential difference between the cathode and the anodic gold plate were set to 0.04 kPa Argon and 1kV. The deposition time was varied from 3 to 10 minutes. After this first period of gold deposition, the substrates were turned around and sputtered for the same period of time in order to ensure that an even coating was obtained.

2.1.3 Results and discussion

The properties of the carbon, nickel and gold-coated supports were determined by characterizing their permeability, resistance, the uniformity of the deposited electro conductive phase and the electrochemical stability. The characteristics of the different coatings will be discussed separately.

2.1.3.1 Carbon coating

Over 95% of the carbon-coated supports had a homogeneous dark grey appearance. No colour difference existed between lumen, outer surface or cross section of the tube. The SEM images of the supports before and after carbonisation look very similar (compare Figure 2.2 A/C with 2.2B/D respectively). The only difference was small particles (1µm in size) on the lumen and outside of the carbonised membrane. These micron-sized particles were most probably carbon particles. However, these particles possibly do not play a significant role in the total electro conductivity of the membrane since the distance between the particles is too large. The actual conductive layer is too thin and smooth to be detected with SEM.

Some supports showed areas where no carbon was deposited even after a relatively long pyrolysis time (5 hours). The shape and size of these uncarbonised areas were irregular. The cause of the formation of such uncoated areas was possibly due to minor intrinsic differences in composition of the untreated support as the irregularities were only seen on lengths of supports that had been cut from the same tube.

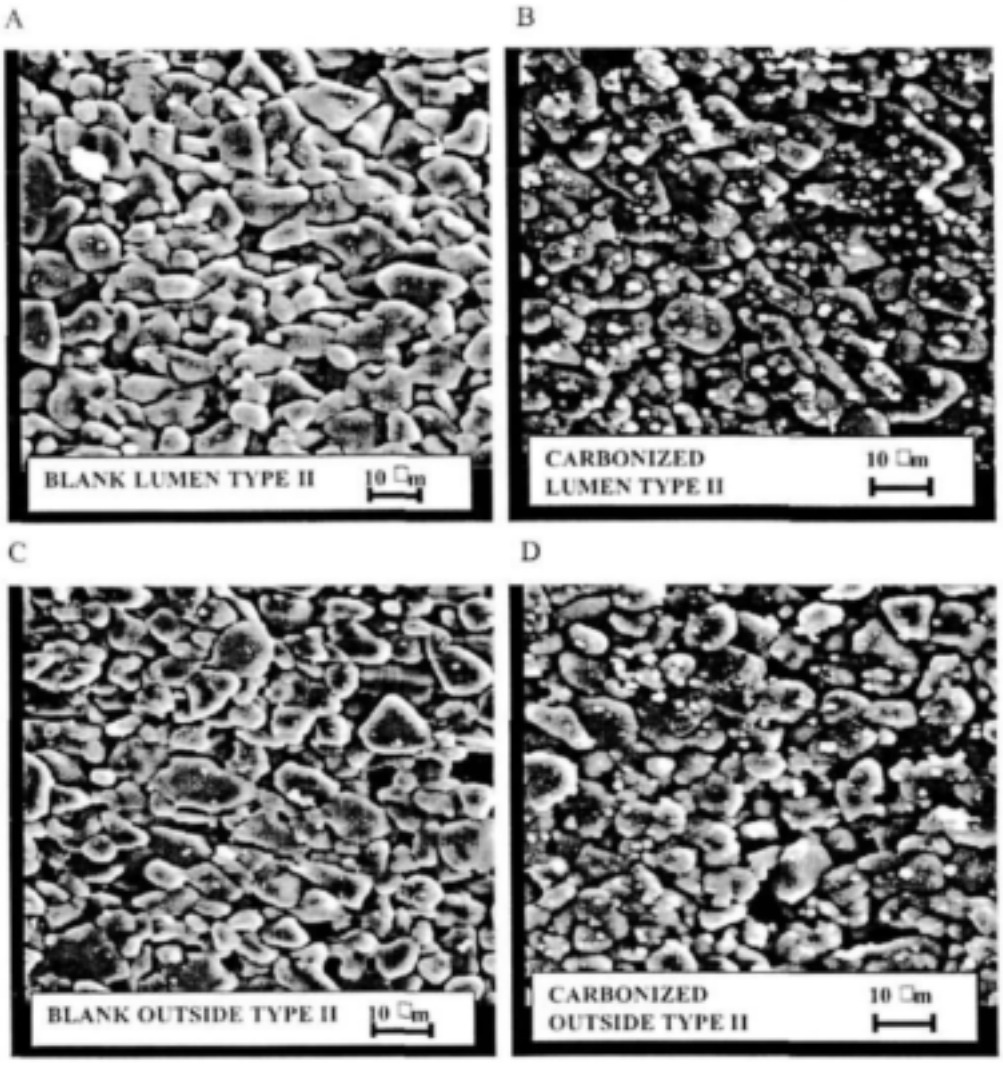


Figure 2.2. SEM images of blank support (left side) and carbon coated supports (right side). A) Outer side, B) carbonised outer side, C) lumen side, D) carbonised lumen side.

The effects of carbon deposition on the permeability and the conductivity of a ceramic support are shown in Table 2.4. Conditions used for supports 3, 4 and 5 were replicated once, whereas conditions for supports 6, 7, 8, 9 and 10 were replicated three or more times. The average values obtained in the replicated studies are given. The results show that the conductive coating with lowest resistance was formed when LPG was used as a pyrolysis gas at 900°C (support 7 and 10). When methane was used as pyrolysis gas no significant carbon deposition could be seen and the resistance of the support remained over 500 $\Omega \cdot cm^{-1}$ at both pyrolysis temperatures (support 3 and

4). Temperatures higher than 900 °C were not investigated as Belyakov et al [3] indicated that structural changes of the ceramic surfaces (probably the formation of carbites or reduction of the oxides) were observed at higher temperatures.

Table 2.4 The effects of carbon deposition on the permeability and the conductivity of ceramic support

Support No.	Type	Treatment	Pyrolytic Gas	T (°C)	Time (min)	Permeability (**)	(%)	Resistance ($\Omega \cdot cm^{-1}$)
1	I	None	-	-	-	2.5	100	>1000
2	II	None	-	-	-	4.2	100	>1000
3	II	Carbonised	Methane	800	150	3.9	93	>1000
4	II	Carbonised	Methane	900	150	3.7	88	>500
5	II	Carbonised	LPG	800	150	3.0	71	95
6	II	Carbonised	LPG	900	150	0.21	5	0.6
7	II	Carbonised*	LPG	900	150	1.1	26	0.5
8	II	Carbonised*	LPG	900	30	3.2	75	2.0
9	I	Carbonised*	LPG	850	150	1.5	60	3
10	I	Carbonised*	LPG	900	150	0.55	23	0.5
11	I	Carbonised*	LPG	900	30	1.7	67	2.3

*Supports rapidly removed from the hot furnace after pyrolysis

** permeability in $m^3m^{-2}bar^{-1}h^{-1}$

Table 2.4 also shows that the permeability can decrease drastically (only 5% remains) with decreasing resistance (see support number 6). However when the supports were removed from the furnace and cooled down outside the furnace after pyrolysis, significantly less permeability was lost (compare support 6 and 7). High molecular weight products that were formed during pyrolysis at temperatures below 700°C and adsorbed onto the support during the cooling period may have been the cause for the significantly higher loss of permeability. The influence of pyrolysis time on loss of permeability and resistance is shown in Figure 2.3. It was shown that resistance decreased at the expense of permeability.

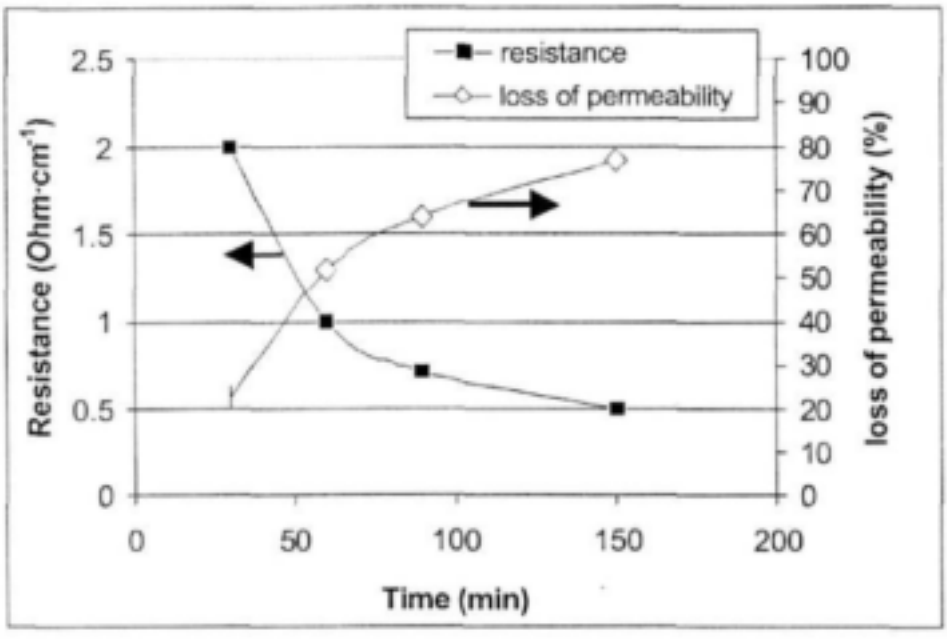


Figure 2.3. The effect of pyrolysis time on permeability and resistance (pyrolysis at 900°C using LPG)

Cyclic voltammetry (CV) was used to show the stability of the carbon coating. Figure 2.4 shows scan 6, 20, 80 and 260 of the CV test where the current density versus the potential indicated the electro 7catalytic activity for water electrolysis. Within the first few scans (1-6) the current density as a function of the potential decreased slightly (15% at −2V and 20% at 2V versus a saturated calomel electrode). Very little difference in current density as a function of the potential was observed between the 80th and the 260th scan.

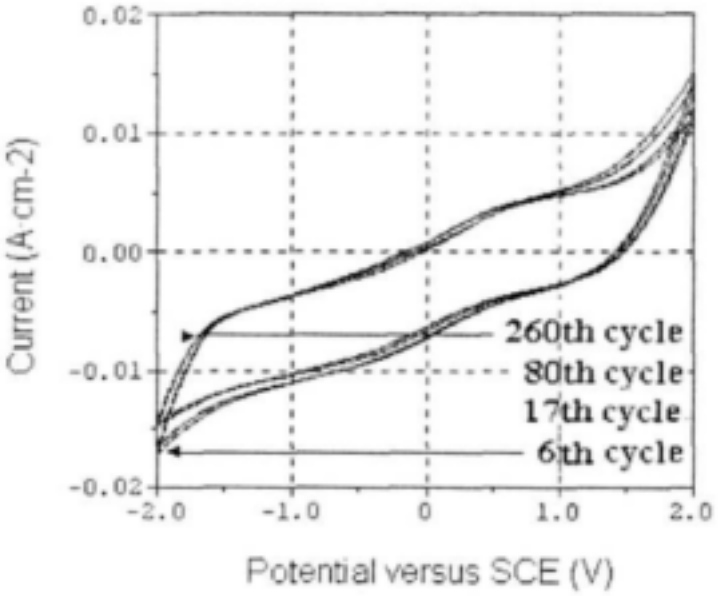


Figure 2.4. The stability of carbon coating

2.1.3.2 Nickel coating

Porous nickel coatings with resistance of $1\Omega \cdot cm^{-1}$ were prepared on the surface of ceramic supports. Bath temperatures below 90°C resulted in slow growth of the nickel layer. Acceptable nickel coatings were prepared at a bath temperature of 92°C. For support 12 where connection A was used (Figure 2.1), a nickel layer was formed on the outside of the ceramic tubular support only. When connection B was used (support 13), a nickel coating was also formed on the lumen side of the support. In order to diminish the effect of depletion of nickel at the lumen side of the support, the support was lifted out of the solution (under N_2 gas) every 2 minutes. This allowed the small volume of plating solution inside the support (with relatively low nickel content) to mix with the bulk of the plating solution containing a higher amount of nickel. Hence, more nickel could grow on the lumen side of support number 14, as is shown by the EDX results tabulated in Table 2.5. No nickel was found inside the pores of the support.

Table2.5 EDX result on electroless nickel plated ceramic supports

Support No	Type	Connection used	Ni content (%) outside	cross section	lumen
12	I	A	60	0	0
13	II	B	55	0	15
14	II	B*	54	0	40

* During the electroless plating the support was lifted out of the plating solution every 2 minutes

Table 2.6 shows the resistance and permeability characteristics of nickel-coated supports. Electro conductive coatings were prepared with a resistance of about 1 $\Omega \cdot cm^{-1}$ support with very low resistance to flow. Lifting the support out of the solution every 2 minutes during the nickel plating experiment could reduce the resistance of the coating at the lumen side. This is attributed to the increased Ni content as described at the beginning of this section.

Table 2.6 Permeability and conductivity characteristics before and after electroless nickel plating

Support No.:	Type	Treatment	Connection	Permeability ($m^3m^{-2}bar^{-1}h^{-1}$)	Resistance ($\Omega \cdot cm^{-1}$) Outside	Lumen
1	I	None		2.7	>1000	>1000
2	II	None		4.2	>1000	>1000
12	I	Ni plated	A	2.7	1	>1000
13	II	Ni plated	B	4.1	0.9	1000
14	II	Ni plated	B*	4.0	1.2	1.6

* During the electroless plating the support was lifted out of the plating solution every 2 minutes

The SEM results (Figure 2.5A/C before nickel coating and 2.5B/D after nickel coating) displayed a significant change in the appearance of the support surface. Large nickel flakes covered part of the support. In these flakes fine pores were observed. Particles on the lumen side appeared significantly smaller than those observed on the outer surface of the support. A micrograph of the edge of the support (see Figure 2.5E) showed that nickel only deposited close to the outer surface of the support (see marked areas) and no nickel inside the support.

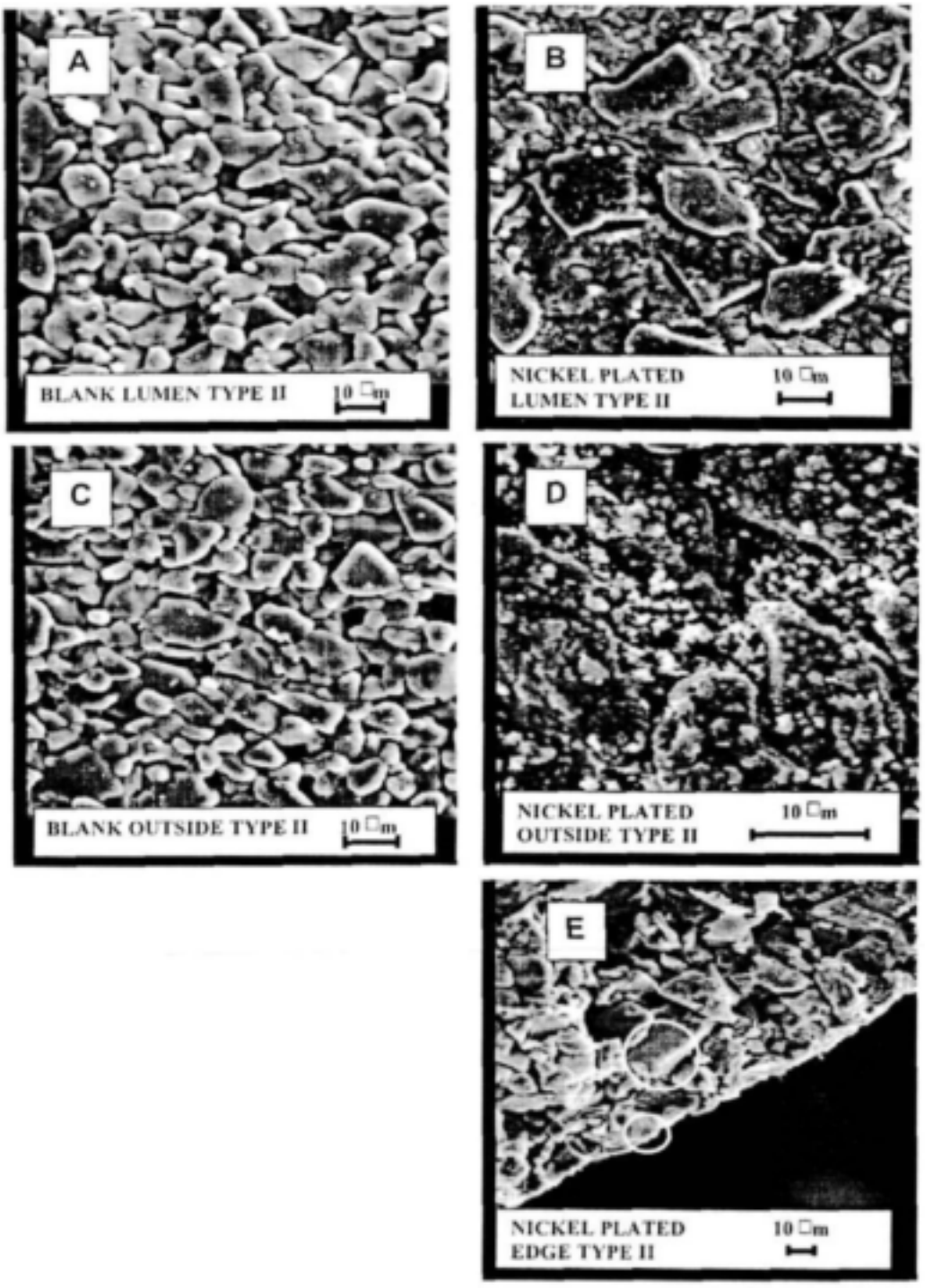


Figure 2.5. SEM images of blank support (left) and nickel coated supports (right).

A) Outer side, B) Ni plated outer side C) lumen, D) Ni plated lumen, E) Ni plated edge

Cyclic voltammetry scans were performed to obtain an impression of the stability of the nickel coating. The cycles started at −2V, the potential was increased at a rate of 0.05V· s^{-1} and returned at 2V. The electrolyte was 0.5M Na_2SO_4. Figure 2.6 shows scan 2, 4, 6 and 10. The rapid decrease of the current density of each subsequent cycle as function of the nickel potential indicated the instability of the nickel coating under the chosen conditions.

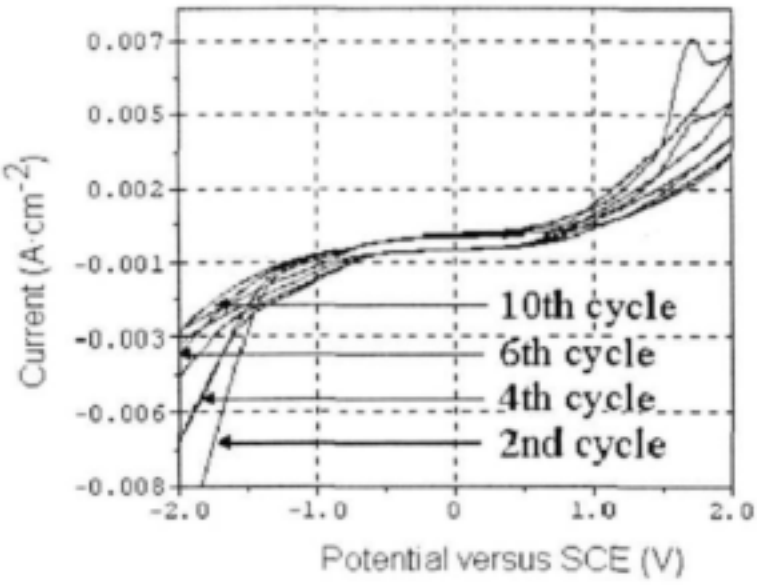


Figure 2.6. The stability of nickel coating

2.1.3.3 Gold coating

Gold coatings were formed on ceramic supports by ion beam sputtering. In general the gold coatings had a homogeneous appearance but slightly more gold deposited upon the side of the support that was facing the golden target. The resistance of the support coated for 3 minutes increased rapidly when currents over 100mA were applied on the coating. The coatings prepared by sputtering for 10 minutes per side were stable when currents over 500mA were applied. Table 2.7 shows the resistance and permeability characteristics of gold-coated supports. Gold coatings were obtained with an electrical resistance as low as 0.25 Ω· cm^{-1} with virtually no loss of permeability. In fact an increase in permeability was observed repeatedly in several experiments.

Table 2.7 Permeability and conductivity characteristics before and after gold sputtering

Support No.:	Type	Treatment	Permeability ($m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$)	Resistance ($\Omega \cdot cm^{-1}$) Outside support
1	I	None	2.6	>1000
2	II	None	4.2	>1000
15	I	Gold sputtering	2.7	0.22
16	II	Gold sputtering	4.2	0.24

An increase of hydrophylicity of the support surface due to gold deposition could be the cause of the increased permeability. The first 210 scans obtained with cyclic voltammetry for gold-coated supports are shown in Figure 2.7. No decrease of current density as a function of the gold potential was observed during those cycles. The gold coating appeared to be very stable under the chosen conditions.

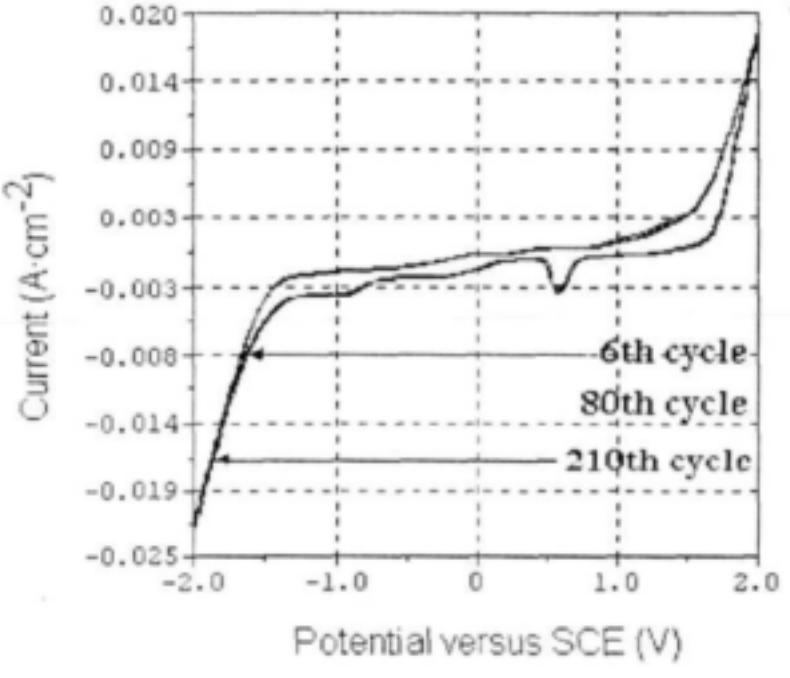


Figure 2.7. The stability of gold coating

2.1.4 Conclusions for electro conductive coatings on porous supports

- The resistance of a carbon coating could be regulated between 0.5 and 2 $\Omega \cdot cm^{-1}$ support, maintaining permeability as high as 75%. The carbon coating was dispersed throughout the support with good electrochemical stability properties.
- The resistance of gold sputtered coatings was about 0.25Ω per centimetre of support. The permeability of the substrate increased between 0-5%. The stability of the gold coating was excellent when used as an anode or cathode in 0.5M Na_2SO_4 electrolyte solutions.
- The resistance of the electroless plated nickel coatings was about 1Ω per centimetre of support. The permeability of the substrate decreased between 0-5%. Depending on the experimental conditions the nickel coating could be formed on the outer and/or lumen side of the substrate. The nickel coating was unstable under testing conditions of cyclic voltammetry in 0.5M Na_2SO_4 electrolyte

2.2 Electro catalytic coatings for water electrolysis

2.2.1 Introduction

In chapter 1, describing the electro sorption process, it was shown that the adsorption and desorption of ions depended upon the local pH near the ion exchange sites of the sorption material. The local pH can be controlled by the polarity of the electrodes, which will determine whether water is oxidized or reduced. The system current will determine how many protons and hydroxyl groups are generated. The electrolysis of water is essential for the electro sorption process and demands the greater part of the total energy consumption. This chapter will discuss how the energy requirement for water electrolysis can be reduced without decreasing the amount of proton/hydroxyl ions generated. Besides an increase in energy efficiency, the effectiveness of the sorption process may also improve since side reactions are less likely to occur at a reduced potential difference.

2.2.1.1 Energy consumption for water electrolysis

The amount of energy required for water electrolysis can be calculated from the product of cell potential (U), current (I) and time (t) [12]:

$$U \cdot I \cdot t = Energy$$
$$\left[\frac{J}{C}\right]\left[\frac{C}{s}\right][s] = [J] \qquad (2.1)$$

The current through the electrolysis system and the time are directly coupled to the amount of water electrolysed by Faradays law [12]:

$$\frac{I \cdot t}{nF} = n_{H_2O} \qquad (2.2)$$

where n number of electrons participating in the electrolysis of water (-)

n_{H_2O} water produced (mol)

F faradays constant ($C \cdot mol^{-1}$)

The adsorption efficiency of the electro sorption cell will therefore also be directly related to current and time. In contrast, the potential used for the electrolysis of water ($E_{electrolysis}$) is not directly related to the rate of electrolysis and can be subdivided into different contributing parts [1, p7, 145]:

$$E_{electrolysis} = (E_{anode} - E_{cathode}) - RI - \eta_{anode} - \eta_{cathode} \qquad (2.3)$$

Where E_{anode} Half cell potential for the oxidation of water

$E_{cathode}$ Half cell potential for the reduction of water

η_{anode} Overpotential at the anode

$\eta_{cathode}$ Overpotential at the cathode

RI part of the potential drop due to ohmic resistance and system current

The two half reactions for the electrolysis of water

$E_{cathode}$ $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ E^0=-0.828 V (2.4)

E_{anode} $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$ E^0=-1.229 V (2.5)

The value of the half-cell potential (E) can be calculated using the Nernst Equation [12]:

$$E = E^0 + \left(\frac{RT}{nF}\right)\ln\left(\frac{a_{ox}}{a_{red}}\right) \qquad (2.6)$$

where: R Gas constant

T Temperature

n Number of electrons participating in the reaction

a_{ox} Activity of the oxidized component

a_{red} Activity of the reduced component

2.2.1.2 Reducing the energy requirement

Reduction of the current or time would reduce the energy consumption. However, the current is directly coupled to the amount of protons and hydroxyl ions produced that activate the ion exchange material. A reduction of current and time may lead to reduced performance of the sorption process. The most obvious way to reduce the energy requirement without reducing the capacity of the electro sorption process is probably to minimize the electrolysis potential. This can be achieved by lowering one or more of the individual parameters mentioned in formula (3.6). An attempt to minimize the IR drop was made by preparing conductive coatings with minimal resistance, as described in chapter 2. The half-cell potentials are more or less fixed since the concentration of the oxidized and reduced components (among others H^+ and OH^-) should comply with the conditions for electro sorption. The most suitable factors to optimise the electrolysis potential that are not likely to affect the efficiency of the electro sorption electrodes are the overpotentials at the cathode and anode. This will be verified in chapter 9.

The overpotential or charge transfer resistance depends upon the electro catalytic properties of the electrode material and the number of electro catalytic active sites available. The most active non-noble metal for water electrolysis is nickel, which is therefore used in many industrial applications for water electrolysis [2-9]. However, the pH in an electro sorption system is changed from acidic to alkaline after every subsequent cycle of the electro sorption process. In chapter 2 it was shown that Ni was very unstable under such conditions. Taking the harsh environmental changes into consideration, the choice of a suitable material with both exceptionally low charge transfer resistance for water electrolysis and stability under cathodic and anodic conditions is limited. Pt is the most suitable material but its high price a drawback. Only very low loadings and high dispersion of Pt may be economically feasible.

Pt deposition techniques such as electro or electroless plating on carbonised ceramic supports that were studied extensively in our laboratory, showed how the activity of Pt towards the catalytic oxidation of methanol could be optimised. It was decided to test such catalytic layers for their catalytic activity towards water electrolysis.

2.2.2 Experimental

ZrO_2/metal composite supports (Degussa) were used as base material for the preparation of two electrodes. One electrode was prepared by carbonising the support for 30 min at 900°C with a flow of 50ml· min^{-1} of LPG. The other electrode was doped with silico-molybdic acid after carbonisation and electroless plating with Pt. The exact preparation procedure is described in Appendix A. The electro catalytic activity of both electrodes was tested and compared to the activity of plain Pt foil for water electrolysis. The testing procedure was identical to that described in Appendix A.

2.2.3 Results and discussion

The weight increases obtained during the preparation of the electrodes are listed in Table 2.8.

Table 2.8 Weight measurements of the electrodes after several preparation steps

No	Support weight (mg)	Weight increase after subsequent treatment (mg· cm^{-1})		
		Carbon	Si-Mo (after 2 depositions)	Pt-plating
1	158.0	1.3	-	-
2	159.5	1.2	0.3	1.2

The current-voltage characteristics shown in Figure 2.8 represent the catalytic activities of three different electrodes. The higher the catalytic activity of an electrode, the lower the electrode potential needs to be in order to reach a certain current density. Therefore, the most active electrode could be selected by comparing the electrode potential at equal current densities. Figure 2.7 showed that the carbonized electrode with Pt/Mo-Si was more active than the pure Pt electrode and much more active than the carbonized electrode without Pt and the Mo-Si compound.

The energy requirements of the electro sorption process may be decreased, by coating electro sorption electrodes with Pt. This will be tested in Chapter 5.

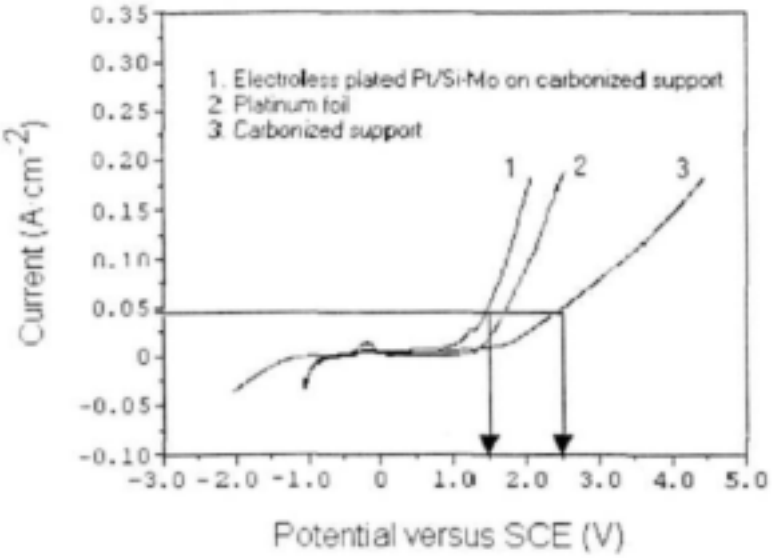


Figure 2.8. Linear sweep scan for differently coated surfaces in 0.05M Na_2SO_4, 50mV· s^{-1}, 22°C

2.2.4 Conclusion for electro catalytic coatings for water electrolysis

The energy requirements for electrolysis at electrodes of carbonised ceramic/metal composite materials can be significantly reduced by electroless plating of Pt onto the surface of the carbonised ceramic/metal composite materials modified with silicomolybdic acid (Aldrich).

2.3 The sorption phase

2.3.1 Introduction

The function of the sorption electrode is discussed previously (chapter 1). A sorption electrode is prepared by combination of an electro conductive and a sorption phase. The most important property of the sorption phase is its ion exchange behaviour. The number of ion exchange groups per m^2, the accessibility of the ion exchange groups and their affinity towards different ions in solution will greatly influence the final removal efficiency and capacity of the sorption phase [22]. In order to optimise the sorption characteristics of a sorption electrode, the sorption material type and its morphology must be carefully chosen.

2.3.1.1 Choice of sorption material

The majority of organic ion exchangers are composed of a matrix of irregular three-dimensional macromolecular networks of hydrocarbon chains. These hydrocarbon chains possess functional groups (e.g. sulfonic acid ($-SO_3^-H^+$), carboxylic acid ($-CO_2H$), quaternary ammonium ($N^+R_3OH^-$) and amino groups (NR_2 [23]) which mainly determine their ion exchange properties. The ion exchange capacity of most commercially available organic ion exchange resins ranges between 1-6 meq· g^{-1} and many resins are stable in a pH range from 0-14 [23, pp 212-253]. These properties seem superior to many materials, especially natural occurring inorganic ion exchange materials, which were used before organic ion exchangers were synthesized (e.g. mineral clays). However, for potential application as sorption electrodes, the success of organic ion exchangers is questionable. The material becomes chemically unstable when it is utilized in an oxidative environment. Degradation of the ion exchanger may occur when the electrode acts as an anode and oxygen evolves. Another disadvantage of organic ion exchange material is its low mechanical stability at elevated temperatures. These elevated temperatures are often desirable in order to lower the electrical resistance and hence, to increase the efficiency of electrolysis [24]. Most commercially available anion exchange resins (OH based) become mechanically unstable above 60°C [23, pp 212-253].

Among the available inorganic ion exchange materials, there is one group of elements that exhibits high ion exchange capacity and shows excellent chemical and mechanical stability. The phosphates of elements such as Ti, Hf, Sn, Th and Zr show cation exchange capacities between 4-8 meq· g^{-1} [23, p 77]. The oxides of such elements have the ability to adsorb cations and anions in alkaline and acidic environment respectively and show ion exchange capacities of 1-2 meq· g^{-1}. These properties make the oxides and phosphates of elements in groups IVA and IVB of the periodic table suitable to be used as sorption phases in a sorption electrode [23,26,26]. ZrO_2 and TiO_2 show the most promising ion exchange properties when they are partially phosphorized [26]. Partially phosphorized TiO_2 shows slightly higher adsorption capacity when pH neutral salt solutions are added to this material whereas partially phosphorized ZrO_2 shows significant higher sorption capacities when the sorbent is polarized [26]. Since the sorbent material in a sorption electrode will be polarized continuously, ZrO_2 is apparently the sorption material with the most suitable properties.

2.3.1.2 Morphology of the sorption material

It is reported that crystalline zirconium phosphate (further referred to as ZrP) has a higher adsorption capacity towards Na^+ but a lower adsorption capacity towards Ce ions compared to amorphous ZrP [28,30]. At present, amorphous ZrP is used in commercially available electrochemical cation-exchangers. However, ion exchange with these materials is accompanied by a small degree of phosphate elution [31]. Phosphate elution from crystalline ZrP has not been observed. For this reason crystalline ZrO_2 and ZrP were prepared and tested for their adsorption capacities for the specific ions of interest.

2.3.1.3 ZrO_2 sol

Once ZrO_2 and ZrP had been selected as the optimum sorption materials, it was necessary to prepare them in the most suitable form. The sorption material had to be incorporated into the matrix of a ceramic support with maximum dispersion. This would ensure quick access of ions to a large number of ion exchange groups. Hence, the sorption material was preferably prepared in the form of a sol. Generally ZrO_2 is obtained by adding an excess of base to a solution of zirconium salt. When a zirconium salt is dissolved in water, the cationic species that arise are proposed at present to be polynuclear cations such as $Zr_4(OH)_8^{8+}$ which are thought to be cyclic [25, p 164]. Polymerisation occurs between tetrameric units in the aqueous species when alkali is added to the solution. Rapidly formed precipitates are normally randomly arranged tetramers and therefore amorphous. Transformation of the amorphous phase into a crystalline form may be possible by means of boiling under reflux.

Two objectives of this study are presented in this chapter. The first objective was to find the best source of ZrO_2 particles, which would provide the highest sorption capacity in milli equivalents per gram material (meq· g^{-1}). The second objective was to incorporate these particles onto the porous matrix of a ceramic support in such a way as to optimise the trade off between high ion exchange capacity and the permeability of the support (the complete blockage of pores needs to be avoided). The preparation of different sols will be described, where after all steps involved in optimising the incorporation of particles onto a porous support are discussed. These steps include amongst others; the optimum temperature needed to immobilize the zirconia particles onto the support, the best source of ZrO_2 particles, the required concentration of the ZrO_2 sol and the drying time of the support required after submersion into the ZrO_2 sol prior to heat treatment. Finally, the effect of the phosphorization of the ZrO_2 particles will be described. All conclusions arrived at are based upon

the differences in ion exchange capacity of the impregnated supports for Na^+, K^+, Cl^- and SO_4^{2-}. The ion exchange capacities are obtained from the results of sorption experiments.

2.3.2 Experimental

The experimental work was divided into four sections namely; the preparation of a ZrO_2 sol, the selection of the optimum heat treatment after incorporation of the ZrO_2 particles, further optimisation of the impregnation procedure necessary for incorporating the ZrO_2 particles into the matrix of a porous support and the actual sorption experiments. A detailed description of the experimental work of each section is given in the subsequent paragraphs. Two types of supports were used upon which to support the sorption material particles. Details of these supports are given in Table 2.9.

Table 2.9. Main characteristics of the tubular porous ceramic support before incorporation of the sorption phase

Membrane	Type I	Type II	Type III
Composition	100% α-Al_2O_3	100% α-Al_2O_3	70% α-Al_2O_3 30% ZrO_2
Outer diameter (mm)	10	10	12
Inner diameter (mm)	7	7	10.5
Average pore size (µm)	0.9	3	0.2
Porosity (%)	39	39	40
Permeability ($m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$)	2.8-3.0	4.6-4.8	0.10-0.12
Length (mm)	105	105	105

Prof. Belyakov from the Institute of General and Inorganic Materials in Kiev, Ukraine supplied support type III. The support was classified as an ultra filtration membrane. Porous supports, type I and II, were manufacture by Inoceramic in Germany. The average pore size of this support indicated potential micro filtration properties. A schematic overview of all experimental work that was done to optimise the sorption properties of the impregnated porous support is given in Figure 2.9 and is described as follows:

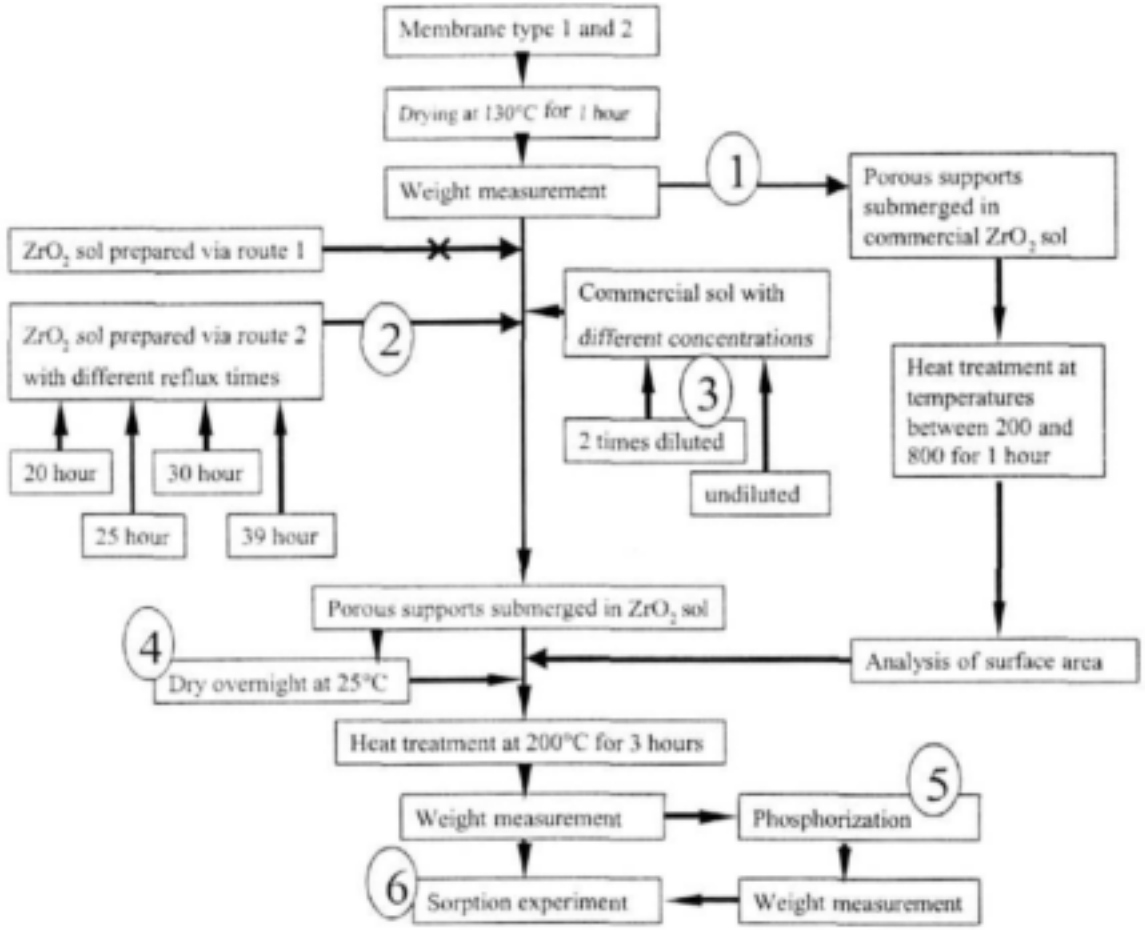


Figure 2.9. Schematic overview of all experiments that were done to optimise the sorption properties of porous supports that were impregnated with ion exchange material

Prior to impregnating the membrane with different ZrO_2 sols, the supports were dried in a furnace at 130 °C for 1 hour and weighed. The supports were initially completely submerged in 15 ml commercially available ZrO_2 sol (Alfa Aesar), (Figure 2.9, no.1). This first batch of submerged supports was used to determine the optimum heat treatment required after submersion. Thereafter the supports were submerged into different ZrO_2 sols prepared in the lab using preparation route 2 (Figure 2.9, no.2) using different reflux times. For further optimisation of the impregnation procedure the following parameters were varied; the sol concentration (Figure 2.9, no.3), the drying process (Figure 2.9, no.3) and degree of phosphorization (Figure 2.9, no.5). The effect of all the different parameters upon adsorption capacity was determined by sorption experiments (Figure 2.9, no.6).

2.3.2.1 Preparation of the ZrO_2 sol

The following two approaches were used to prepare a ZrO_2 sol. All pH measurements were taken with an INGOLD HA405 EO 07 glass electrode. $ZrOCl_2 \cdot 8H_2O$ was initially supplied by Alfa Aesar and later from China and the Ukraine. Material obtained from the latter source was recrystallized [32] from a saturated solution of zirconyl chloride in 6M HCl. This solution was prepared by adding 650g $ZrOCl_2 \cdot 8H_2O$ to 0.5 litres 6M HCl at 95°C. The slurry obtained after cooling the solution from 95 to 5°C was filtered and washed with small portions (less than 5% of the total volume) of cold ultra pure (UP) water (1°C). The residue was dried for 5 days in a desiccator containing self-indicating silica gel. The water content was determined using simultaneous thermographic analysis (STA).

Preparation of monoclinic hydrous zirconia via route 1

Ref [32,34]: Ultra pure water was added to 32.2 gram of $ZrOCl_2 \cdot 8H_2O$ up to a total volume of 100ml to make a 1M zirconyl chloride solution. Gelatinous, amorphous hydrous zirconia was precipitated under heavy stirring and drop wise addition of 25% ammonia solution (BDH Ammonia solution AG) to a 1M $ZrOCl_2$ solution. The ammonia solution was added until pH 4 was reached. The precipitate was filtered and thoroughly washed with ultra-pure water. An equal weight of water was added to the filter cake and stirred until a smooth slurry was formed. The slurry was refluxed for 5 days.

Preparation of monoclinic hydrous zirconia by route 2

Ref [32]: Ultra pure water was added to 32.2 gram of $ZrOCl_2 \cdot 8H_2O$ ("Alfa Aesar, Chinese or Ukrainian") up to a total volume of 100ml to make a 1M zirconyl chloride solution. A 25% ammonia solution was added drop wise to the vigorously stirred zirconyl chloride solution to adjust the pH to a value of 2. Precipitates formed were redissolved upon heating. The clear solution obtained by this means was transferred into a round bottom flask. Subsequently the solution was refluxed for 3 days. Samples of the sol were taken after 20, 25, 30,39 and 72 hours of refluxing.

2.3.2.2 Optimal heat treatment after incorporation of the ZrO_2 particles

Supports that were submerged into commercial ZrO_2 sol were exposed to different temperatures ranging from 110 to 800 °C for 1 hour. The surface areas of the different supports were measured using N_2-adsorption porosimetry before and after 15 minutes of ultra sonic treatment. Ultra sonic treatment was carried out by putting the analysed samples in a beaker with ultra pure water, inside

an ultrasonic bath. After 15 minutes of ultrasound treatment, the samples were dried and prepared for a second surface analysis.

2.3.2.3 Further optimisation of the impregnation procedure

The impregnation procedure describes the process of incorporating particles into a porous matrix. The following parameters that might effect the way particles are finally incorporated were investigated: the source of the sol, the influence of the sol concentration, the influence of the drying procedure before the heat treatment and the effect of phosphorizing ZrO_2 particles.

2.3.2.4 Influence of the source of ZrO_2 particles

In order to find the most suitable source of ZrO_2 particles to be impregnated into the matrix of the support, five supports were immersed into 15ml of a ZrO_2 sol, each originating from a different source. The first source was a commercial sol (a 20% (w/w) colloidal dispersion of ZrO_2 in water stabilized with 15% acetic acid supplied by Alfa Aesar. The other four ZrO_2 sols were prepared via route 2 (section 2.3.2.1) with respectively 20, 25, 30 and 39 hours of reflux. After being submerged for 12 hours, the supports were taken out of the sol, wiped off with paper towel and placed in a furnace. The furnace was heated up at $5°C \cdot min^{-1}$ and kept at 200°C for 3 hours. A sorption experiment was performed for each support (as described in 2.3.2.8).

2.3.2.5 Influence of the sol concentration

To investigate the effect of the sol concentration on the sorption capacity and the hydrodynamic properties of a sorption support, three supports were treated with varying concentrations of sol. Support no.1 was submerged in the commercial sol (for details see section 2.3.2.4) and support no.2 and no.3 were submerged in a twice diluted commercial sol (obtained by mixing the undiluted sol with ultra pure water in a 1:1 ratio). After 12 hours of submersion the supports were treated as previously described. The impregnation procedure for support no. 3 was repeated and twice impregnated with twice diluted commercial sol. A sorption experiment was performed for each support as described in 2.3.2.8.

2.3.2.6 Influence of the drying procedure

Two supports were submerged in 15ml of commercial sol (for details see section 0). Thereafter, both supports were dried at room temperature for one day before they were heated to 200°C for 3 hours. A sorption experiment was performed for both supports. The results of the sorption

experiments with these substrates were compared with impregnated supports that were not dried before heat treatment.

2.3.2.7 The effect of phosphorization

Three supports were impregnated as described in section 0, two supports with commercial sol and one support with the ZrO_2 sols prepared using route 2 refluxed for 30 hours (section 2.3.2.1). To phosphorize the incorporated ZrO_2, the supports were submerged in 15% H_3PO_4 (HOLPRO AG) for 24 hours, washed with ultra pure water and treated with 25% NH_3 solution (BDH Ammonia solution AG). Thereafter the supports were air dried overnight and placed in a furnace. The furnace was heated up at 5°C· min^{-1} and kept at 200°C for 3 hours. A sorption experiment was performed for each support as described in section 2.3.2.8

2.3.2.8 Sorption experiments

A schematic of the experimental set up that was used to test the sorption capacity of ZrO_2 impregnated supports is shown in Figure 2.10. The membrane (1) was sealed with two Viton O-rings. The feed solution was pumped in at the reactor inlet (2), permeated through the porous membrane and was collected as permeate at the reactor outlet (3). The tube clamp (4) was completely closed during the experiment. The pressure over the membrane could be monitored with the pressure gauge (5).

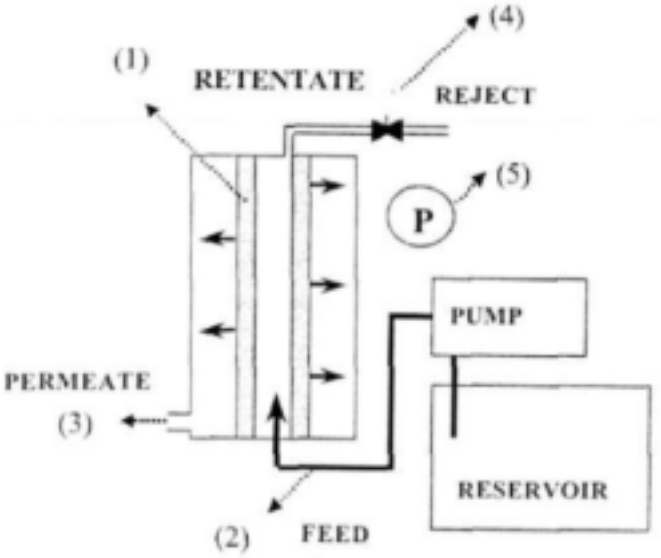


Figure 2.10. Schematic representation of the experimental set up used to measure the sorption characteristics of different supports: 1) Tubular support 2)

One acidic and one alkaline feed solution were used for each experiment. The composition of the acidic feed solution was 0.01M MX + 0.01M HX with X = SO_4^{2-} or Cl^-, and M= Na^+ or K^+. The composition of the alkaline solution was 0.01M MX + 0.01M MOH. The acidic feed solution was replaced by the alkaline feed solution once the concentration and composition of ions in the permeate became equal to the concentration and composition of ions in the feed solution (in other words once the membrane was totally saturated with anions or, in case of regeneration, all cations had desorbed). The experiments were stopped once the composition and concentration of ions in the permeate were equal to the composition and concentration of ions in the alkaline feed solution (in other words once the membrane was totally saturated with cations or all anions had desorbed). To check the reproducibility of the sorption properties some supports were subjected to several cycles in a row, changing the feed from acidic to alkaline, based upon the concentration of ions in the permeate. Samples of permeate were taken after different time intervals. The concentration of anions was measured with ion chromatography and cations were measured with atomic adsorption spectroscopy as detailed in section 1. Besides the ion concentration, the sample weight was measured and the pressure difference between the feed side and permeate side recorded for each specific time interval.

2.3.3 Results and discussion

2.3.3.1 Preparation of the ZrO_2 sol

Preparation of monoclinic hydrous zirconia route 1:

Several attempts were made to prepare a clear ZrO_2 sol by using preparation route 1 (section 1.2.1.1). The amount of ammonia that was needed, to add to the zirconyl chloride was not specified by either Belyakov et al [34] or Clearfield [32]. No details were given regarding the stirring speed. Total blockage of the filter occurred when an attempt was made to filter the suspension with filter no.40 or 1 (Whatman). Therefore the filter cake could not be thoroughly washed and the white suspension obtained after adding an equal weight amount of water never turned into a clear transparent sol. Gelatinous zirconia was formed in the pH range between 3 and 5 as expected but a clear sol was never obtained. Samples of the sol dried at 110°C were examined by Xray diffraction spectroscopy (XRD). A crystalline phase for NH_4Cl and ZrO_2 was observed (see Figure 2.12). The ZrO_2 phase was a mix of monoclinic and cubic crystal habit. The contamination with NH_4Cl that was apparent could be expected since the filter cake could not be properly washed.

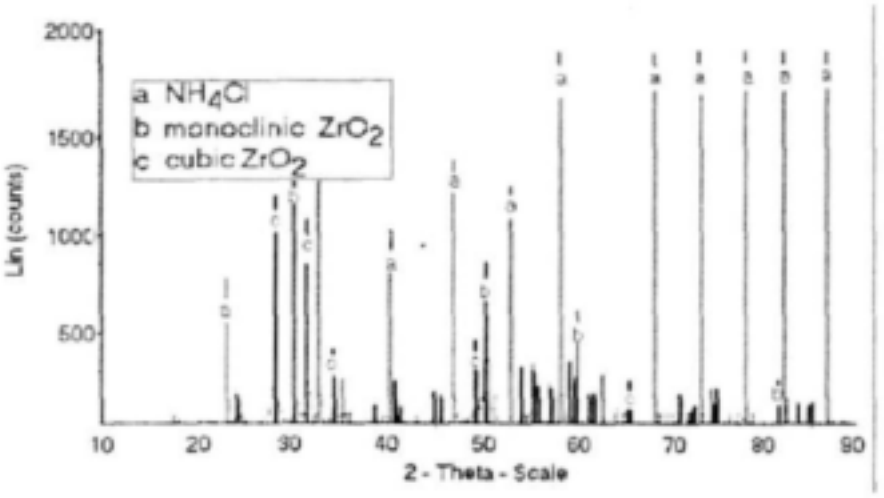


Figure 2.11. XRD results of ZrO_2 prepared via route 1 and dried at 110°C

The XRD results of dried samples of commercial sol (Figure 2.12A) indicate the existence of cubic microcrystallites according to peak broadening visible in the XRD spectrum . Crystal growth during calcination of the dried commercial sol resulted in clear peaks of monoclinic ZrO_2 as shown in Figure 2.12B.

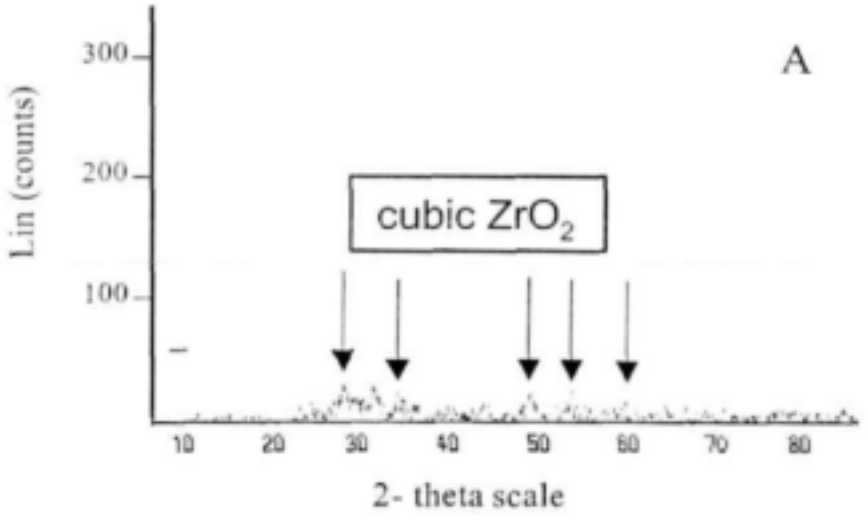


Figure 2.12. XRD results of ZrO_2 obtained from commercial sol. A, sol dried at 110°C.

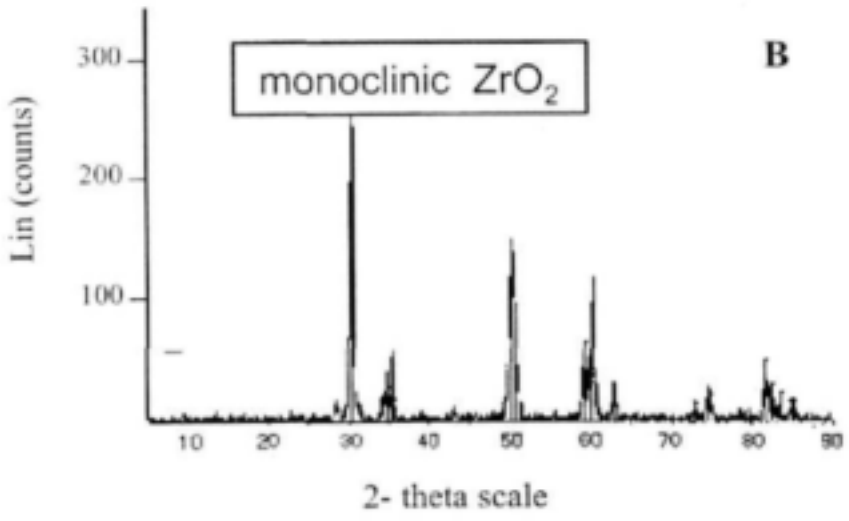


Figure 2.12. XRD results of ZrO_2 obtained from commercial sol. B, sol calcined at 800°C

Since no clear zirconia sol could be prepared using procedure 1 a few attempts were made where the ammonia solution was added till pH 9 was reached. The idea was to stabilize the sol in an alkaline media instead of the usual acidic media. The filter cake was washed with diluted ammonia (pH 9) and mixed with an equal weight of water. The obtained slurry was refluxed for up to 5 days. Again, the suspension never turned into a clear transparent sol.

Preparation of monoclinic hydrous zirconia via route 2:

Ammonia was added drop wise to the 1M $ZrOCl_2$ solution whilst the pH increased from 0.2 to 1.9. After the precipitate thus formed, a clear solution appeared that was re-dissolved by heating (90°C). After the clear solution had been refluxed for 20 hours the solution started to turn white but remained transparent for at least 20 hours more. After 72 hours of refluxing a white suspension was formed. As boiling under reflux continued, the hydrolytic polymerisation of OH groups continued resulting in growth of particles. The product of this polymerisation process can be expressed by $[ZrO_b(OH)_{4-2b} \cdot x \cdot H_2O]_n$ where b lies between 1 and 2 [23, p143]. At a certain point in time the particles became too heavy, which resulted in precipitation of the particles. The sols obtained at 20, 25, and 30 hours are all stable sols, no precipitate could be detected within a period of one month. After a month, a thin layer of white precipitate was found in the sample of the sol that was refluxed for 39 hours.

2.3.3.2 Optimal heat treatment after incorporation of the ZrO_2 particles

The assumption was made that surface area relates directly to sorption capacity, since the amount of hydroxyl groups at the surface relate to the sorption capacity [23, p 145]. Therefore surface area analysis was done on six supports that were all submerged into commercial ZrO_2 and thereafter treated at different temperatures. The results are listed in Table 2.10 and show that the surface area decreased as the temperature of the heat treatment increased.

Table 2.10 The result of heat treatment on surface area

Experiment No	T (after impr.) (C°)	Surface area ($m^2 \cdot g^{-1}$)	Surface area after Ultra sonic treatment
0	-	1.9	1.9
1	110	-	1.9
2	300	8.1	8.4
3	500	6.7	6.5
4	600	4.2	4.4
5	700	3.8	3.8
6	800	3.1	3.1

The support heated at the lowest temperature (300°C) showed the highest surface area and may show the highest sorption capacity and probably the best sorption kinetics [34, p. 160]. The higher the surface area the smaller the average size of the individual ZrO_2 particles and hence the supports with the highest surface area would have the best accessibility to the ion exchange groups. The results in Table 2.10 also show that a heat treatment at 300°C was sufficient to immobilize the ZrO_2 particles upon the porous matrix. This conclusion could be drawn by comparison of the surface areas obtained before and after the ultrasonic treatment. When the ZrO_2 particles were not immobilized by any heat treatment as in experiment 1 (Table 2.14), the surface area after the ultrasonic treatment was equal to the surface area of the unmodified matrix. This indicates that all the ZrO_2 particles had been removed from the matrix by the ultra sonic treatment. Unfortunately no value for the surface area before ultra sonic treatment could be given for experiment 1 since the N_2-adsorption measurement requires a heat treatment of the sample up to 260°C.

2.3.3.3 Further optimisation of the impregnation procedure

The influences of the difference in the impregnation procedure were compared based on calculated ion exchange capacity of impregnated ZrO_2. The ion exchange capacity (IEC) of the ZrO_2 was calculated as the sum of all adsorbed ions divided by the weight of impregnated adsorbent (S). The sum of all ions was derived by measuring the difference in concentration between the feed and the permeate solution. The following equations were used:

$$IEC = \frac{\sum_{n=1}^{k} R_n \cdot z}{S} \tag{2.7}$$

$$R_n = \left([X]_{feed} - [X]_n \right) \cdot V_n \tag{2.8}$$

$$V_n = \frac{W_n}{\rho_n} \tag{2.9}$$

where: k total number of permeate fractions before change of feed solution

R_n removed amount of ions (mmol) in fraction n

S weight of impregnated ZrO_2 (g)

z number of ionic charges

$[X]_{feed}$ concentration of X in feed solution (mmol· ml^{-1})

$[X]_n$ concentration of X in sample n (mmol· ml^{-1})

V_n volume of sample n (ml)

W_n weight of sample n (g)

ρ density of samples (g· ml^{-1})

The density of all samples is taken to be 1.00 g· ml^{-1} since concentration of all ions is below 0.01 g· ml^{-1} at all times.

Table 2.11 summarizes the cation and anion exchange capacities of supports that were all modified with ZrO_2 but with some changes in the preparation procedure (making one change at a time). Variables changed are; the source of ZrO_2 sol, the ZrO_2 sol concentration, the drying time before the heat treatment, the phosphorization of the impregnated ZrO_2 particle, and the support used. The effect of all the variables on the sorption capacity will be discussed separately based on the results in Table 2.11.

2.3.3.4 Influence of the source of ZrO_2 particles:

The commercial available sol showed the highest anion sorption capacity (1.8 meq· g^{-1}). The sorption capacity of the immobilized sol during the first experiment is usually higher than the second or the third experiment (compare the values of SO_4^{2-} adsorption capacity between cycle 1 and cycle 2 of experiment 1, Table 2.11). Partially irreversible ion exchange could be an explanation. Table 2.12 shows the amount of the adsorbed and desorbed ions during different cycles of experiment 1.

The amount of anions adsorbed in the first cycle is higher than the total amount of anions desorbed. From the second cycle of the experiment onwards the amount of adsorbed ions is equal to the amount of ions desorbed (complete regeneration). The amount of ions adsorbed is calculated from the sum of the removed ions of all permeate samples. The ion exchange capacity calculated in subsequent experiments is fairly stable (compare experiment 1, cycles 3, 4 and 5). Comparison of the ion exchange capacities of two differently impregnated supports would not be valid in cases where the irreversibly exchanged ions are included. The sorption capacity value should represent the stabilized properties of the sorption support. Therefore Table 2.11 shows only the values of the ion exchange capacity obtained from a second cycle.

Table 2.11. The effect of different impregnation parameter on ion sorption capacity

Support		Varied impregnation parameter [b]	IEC of ZrO_2 or ZrP (meq· g^{-1}) [c]			
No	Type [a]		SO_4^{-2}	Cl^-	Na^+	K^+
1	1	Commercial sol, 1st cycle	3.7		0.1	
	1	Commercial sol, 2nd cycle	2.6		0.1	
	1	Commercial sol, 3rd cycle		1.7		0.5
	1	Commercial sol, 4th cycle		1.8		0.4
	1	Commercial sol, 5th cycle		1.5		0.5
2	1	P2-sol refluxed for 20 hours	1.6		0.1	
3	1	P2-sol refluxed for 25 hours	1.6		0.1	
4	2	P2-sol refluxed for 25 hours	1.5		0.1	
5	1	P2-sol refluxed for 30 hours	2.6		0.3	
6	1	P2-sol refluxed for 39 hours	1.9		0.2	
7	1	Commercial sol, 2 times diluted	2.4		0.2	
8	1	2* impr. with 2 times diluted commercial sol	2.2		0.2	
9	1	Air dried for 1 day prior to heat treatment	2.4		0.2	
10	1	Commercial sol, phosphorized	-		-	
11	2	Commercial sol, phosphorized	0.2		1.8	
12	2	P2-sol refluxed for 30 hours, phosphorized	0.0		1.0	
13	2	P2-sol refluxed for 30 hours, phosphorized	0.0		1.1	
14	2	P2-sol refluxed for 30 hours, phosphorized		0.0		1.1

a) P2 refers to the preparation route 2 of the crystalline ZrO_2 sol

b) type of membrane, details are shown in Table 2.9

c) ion exchange capacity calculated from the 2nd cycle unless indicated differently

The sol prepared via route 2 and refluxed for 30 hours showed the second highest sorption capacity (compare experiment 2-6, Table 2.11). Even though the zirconium content of the four sols with different reflux times were equal, the sol with the lowest reflux time contained the highest amount of zirconyl ions, which do not contribute to the amount of ion exchange groups.

Table 2.12. Amount of anions adsorbed and desorbed during cycles 1-5 of experiment 1

Cycle of experiment 1 No.	Ion	Adsorbed SO_4^{-2} (mmol)	Desorbed SO_4^{-2} (mmol)
1	SO_4^{-2}	0.76	0.50
2	SO_4^{-2}	0.50	0.51
3	Cl^-	0.63	0.64
4	Cl^-	0.68	0.63
5	Cl^-	0.62	0.62

The sol that was refluxed for 39 hours probably contained the smallest amount of zirconyl ions. However, a significant amount of the hydroxyl groups may have been lost by further oxolation between the hydroxyl groups on the surface of particles [23, p 145]. The oxolation reaction can be written as [36]:

$$Zr - OH + HO - Zr \rightarrow Zr - O - Zr + H_2O \qquad (2.10)$$

An optimum between the quantity of ion exchange groups formed and the amount of monomers in the sol was reached after about 30 hours of refluxing. Typical adsorption and desorption characteristics as a function of time are shown in Figure 2.13 and Figure 2.14 respectively.

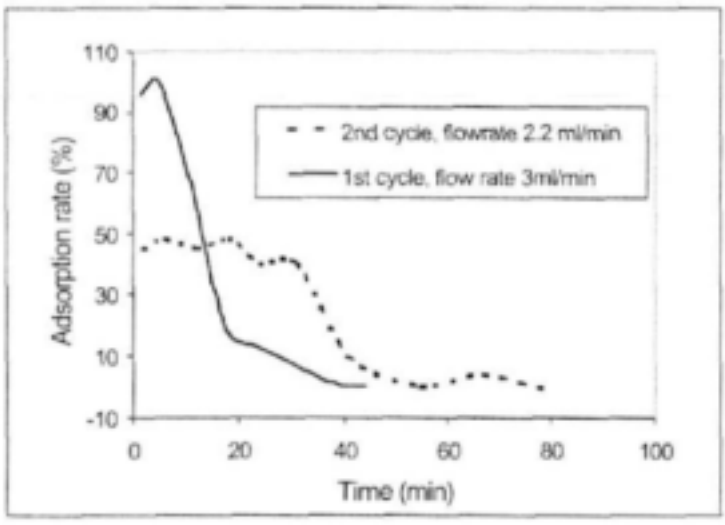
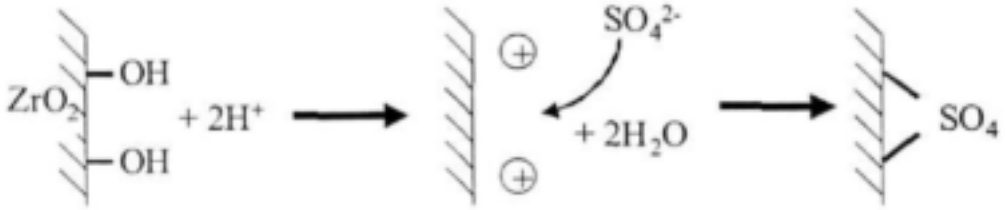


Figure 2.13. Adsorption rate as a function of time. Feed solution: 0.01M Na_2SO_4 + 0.01M H_2SO_4

All impregnated supports that were subjected to their first cycle showed around 100% adsorption of ions in the initial stage of the experiment. When they were subjected to a subsequent cycle, the adsorption rate reached only a maximum of 50% (See Figure 2.13). As discussed in section 2.3.2 8., the acidic feed solution used during the first part of the cycle had the following composition: 0.01M MX + 0.01M HX (with X = SO_4^{2-} or Cl, and M= Na^+ or K^+). The ratio of anion charges versus proton charges in this feed solution is 2:1. This can be clarified by an example where SO_4^{2-} and Na^+ are taken as the ions in solution. The feed solution is thus: 0.01M Na_2SO_4 + 0.01M H_2SO_4 and thus 2 proton charges versus 2x2 anion charges. For complete adsorption of SO_4^{2-}, an equal amount of charges would be required according to the following reaction scheme:



(2.11)

This scheme is valid for ZrO_2 since the isoelectric point (IEP) is 6.05, which means that only a relatively small amount of OH groups would dissociate from the ZrO_2 surface without protons being added.

The amount of protons present in the feed solution can only activate half of the ion exchange sites that are required for 100% adsorption of the anions. Therefore an adsorption rate of 50% is the theoretical maximum. The reason that 100% of the ions could be adsorbed during the first cycle of the experiment was because the ion exchange sites of the sol particles are already protonated because of the low pH of the sol.

The influence of the flow rate through the membrane on the final sorption capacity was not significant but there was a small difference in sorption efficiency. As shown in Figure 2.15, the desorption rate is slightly higher at low flow rates.

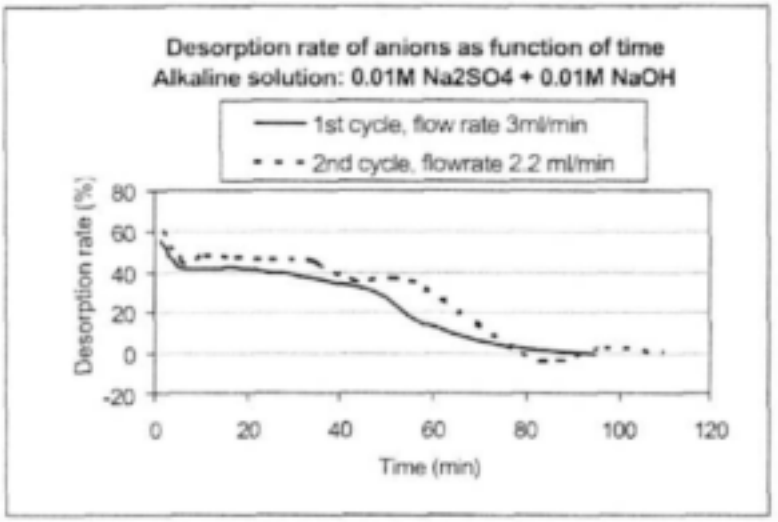


Figure 2.14. Desorption rate as a function of time

Values for the exchange capacity for hydrous zirconia reported elsewhere [23] are between 1 and 2meq· g^{-1}. The possible explanation for the high value of the sorption capacity for SO_4^{2-} (often >2 meq· g^{-1}) compared to that of Cl⁻ (1.6-1.8 meq· g^{-1}) and ref.[23] could be that SO_4^{2-} was partially present in the form of HSO_4^-. As shown in Figure 2.16 a significant part of the SO_4^{2-} is present as HSO_4^- around and below a pH value of 2 [37].

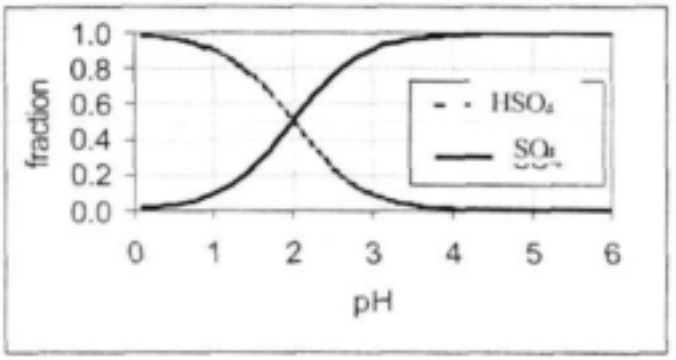


Figure 2.15. Fractions of SO_4^{2-} and HSO_4^- as a function of the pH of H_2SO_4

HSO_4^- can be adsorbed at a single ion exchange site instead of at a double ion exchange site. If adsorption of HSO_4^- took place, the value of the calculated sorption capacity for SO_4^{2-} would have been higher than it actually was. The formulas used to calculate the fractions of HSO_4^- and SO_4^{2-} respectively were:

$$\alpha_{HSO_4^-} = \frac{[H^+]\cdot K_1}{[H^+]\cdot K_1 + K_1\cdot K_2 + [H^+]^2}, \text{ and } \alpha_{SO_4^{2-}} = \frac{K_1\cdot K_2}{[H^+]\cdot K_1 + K_1\cdot K_2 + [H^+]^2} \qquad (2.12)$$

with: $K_1 = \frac{[H^+]\cdot[HSO_4^-]}{H_2SO_4} = 10^4$, and $K_2 = \frac{[H^+]\cdot[SO_4^{2-}]}{HSO_4} = 0.01$

where: $[H^+]$ proton concentration

K_1 and K_2 equilibrium constants for the ionization steps of the first and the second proton of H_2SO_4, respectively

2.3.3.5 Influence of the sol concentration

Impregnation of diluted sol did not result in an improvement in sorption capacity for SO_4^{2-} (Compare experiment number 1 cycle 2 with 7 and 8). From the experimental results obtained, there is no advantage in impregnating the supports with diluted sols. Table 2.13 shows the effect of the sol concentration on the weight of ZrO_2 incorporated and the permeability of the support.

Table 2.13. ZrO_2 loading and the effect on the permeability of the support

Support		Weight increase After impregnation	SO_4 ion exchange Capacity (meq· g^{-1})		Permeability [b]
No. [a]	Type	(mg)	Support	ZrO_2	(l· m^{-2}· bar^{-1}· h^{-1})
1	1	0.38	0.06	2.6	30.0
7	1	0.18	0.03	2.4	39.6
8	1	0.37	0.05	2.2	18.2
9	1	0.55	0.08	2.4	14.4
10	1	0.87	0	0.2	0.4

a) The numbers of the supports used in this table correspond with those in Table 2.15

b) Average permeability during collection of all samples

The permeability was calculated using the following equation [21]:

$$p_n = \frac{V_n}{A_s\cdot\Delta P\cdot t} \qquad (2.13)$$

where: p_n permeability of the support during the collection of sample n (l· m^{-2}· bar^{-1}· h^{-1})

V_n Volume of sample n (l)

A_s flow through surface area of support (m^2)

ΔP_n pressure difference between the feed side and the permeate side of the support during the collection of sample n (bar)

t time taken to collect sample n (h)

The support impregnated with diluted commercial sol (sol mixed with ultra pure water ratio 1:1, support number 7) showed the lowest weight increase and the lowest IEC for the support. The support impregnated twice with the diluted commercial sol (support number 8) showed a similar weight increase and IEC as support 1 which was impregnated once with the undiluted commercial sol. However, although support 1 and 8 showed similar weight and IEC, the permeability of support 1 was almost 40% higher. This difference could be caused by different particle distribution within the matrix of the support. It is possible that particles impregnated during an earlier impregnation adsorb the anions that may be stabilizing the particles in the sol. As a result those particles may aggregate and precipitate causing relative low uniformity. The singly impregnated support may thus have more uniformly deposited particles causing less resistance to flow. Unfortunately, no analysis of infiltration depth or of the homogeneity was carried out to confirm this explanation.

2.3.3.6 Influence of the drying procedure

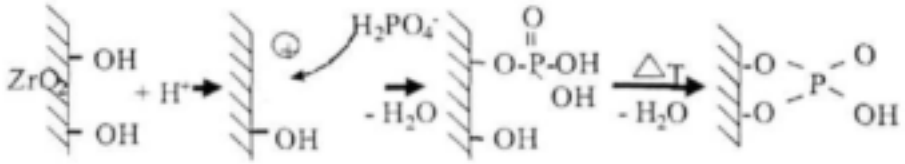
Support number 9 was dried for one day after impregnation and before the heat treatment. The weight increase and permeability after impregnation of this support is also shown in Table 2.18. The weight increase was about 50% more than the weight increase of supports that were not allowed to dry before the heat treatment. A significant amount of ZrO_2 seemed to be blown off the support during the relatively rapid drying process in the furnace. However, although the amount of ZrO_2 blown off the support would not add to the IEC of he support, it seemed to prevent a large reduction in permeability as shown in Table 2.13.

2.3.3.7 Effect of phosphorization

For both the commercial and the prepared sols the ion adsorption characteristics changed from anion exchanger to cation exchanger after phosphorization. A comparison of supports numbered 1-9 (not phosphorized) with supports numbered 10-14 (phosphorized) in Table 2.11 shows that phosphorization of the supports impregnated with commercial sol led to the highest cation sorption capacity (1.8 meq· g^{-1}). The maximum sorption capacity of ZrP would be reached if all phosphate groups could bind two single charged ions, as is described in the following equation [23, p. 14]

$$Zr(HPO_4)_2 + 2Na^+ \rightarrow ZrNa(PO_4)_2 + 2H^+ \qquad (2.14)$$

In this case the maximum capacity in milli equivalent per gram ZrP would be 7.2 (1g $Zr(HPO_4)_2$=3.6 mmol=7.2mmol H^+). The ZrO_2 seemed only to be partially phosphorized since the highest capacity shown in Table 2.15 was only 1.8 meq· g^{-1} for support 11. The sorption capacities for anions before phosphorization were slightly higher than the sorption capacity for cations after phosphorization. It is possible that H_2PO_4 ions are initially adsorbed onto the ion exchange active sites of the ZrO_2 and during the heat treatment ZrP is formed according to the following reaction scheme:



(2.15)

In general phosphorization causes a very significant loss of permeability. Support number 10 (support type 1) became virtually impermeable after phosphorization. Only supports of type 2 could be used to test the cation exchange capacities of phosphorized ZrO_2

2.3.3.8 Influence of support on sorption capacity

The sorption capacity of the impregnated ZrO_2 did not depend upon the type of membrane used for impregnation. This was found by comparing experiment 3 and 4 as shown in Table 2.15. The higher degree of particle dispersion in the matrix of the membrane with the higher surface area (membrane type 1) did not have a significant effect on the final sorption capacity of ZrO_2. This conclusion was strengthened by the results obtained from the IEC measurements as a function of the sol concentration. Support 7, which was impregnated with a diluted sol, was expected to exhibit relative high dispersions of ZrO_2 particles. However support 7 showed a lower IEC than support 1, which was impregnated with the undiluted sol.

No conclusions on kinetic behaviour of ZrO_2 are presented because the differences in permeability and the varying amount of ZrO_2 loaded into the support made it very difficult to do comparative experiments.

2.3.4 Conclusions for the sorption phase

- A proper preparation route was found to prepare a ZrO_2 sol with crystalline particles. A reflux time of 30 hours gave an optimum sorption capacity
- The maximum reversible sorption capacity was 1.8 meq· g^{-1} ZrO_2, which was obtained from use of a commercial sol
- Complete immobilization of ZrO_2 particles occurred by heating the supports up to 300°C after impregnation of the sol
- The concentration of the impregnated sol did not effect the sorption capacity of the ZrO_2
- A maximum cation exchange capacity of 1 meq· g^{-1} was reached by phosphorizing ZrO_2 particles prepared from the commercial sol
- Drying the supports after impregnation, prior to heat treatment, led to a 50% higher ZrO_2 loading onto the support. A similar percentage decrease in permeability was measured.

2.4 Overall conclusions of Chapter 2

- The best electro conductive properties of the sorption electrode may be expected when gold will be used as conductive phase
- Highest sorption efficiency may be expected for supports impregnated with commercial ZrO_2 sol. The impregnated material should be partially phosphorized to obtain cation exchange properties

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3 DEVELOPMENT OF SYNTHESIS METHODS AND OPTIMIZATION OF PROPERTIES OF ELECTRO SORPTION MATERIALS BASED ON FLAT PLATE FIBROUS CERAMICS

Abstract

The preparation of flat electro sorption materials from ZrP and TiP on different ceramic support and the design of a sorption cell are described. Mechanically stable products were obtained after deposition of pyrolytic carbon and impregnation of ZrP. When polarized at a potential difference of 10V, 95% of ions were removed from 510g· l^{-1} salts mixture while the current density did not exceed 6mA· cm^{-2}. The water purification characteristics of the cell did not change significantly over up to 10 sorption - desorption cycle.

3.1 Introduction

One of the main goals of the current project was the development of methods for preparation of electro sorption material in the form of plates. These electro sorption membranes are especially promising for large-scale application of electro sorption technology for removal of ions from aqueous solutions. The membranes can be arranged in the form of plate and frame modules, which offer significantly higher volume to flow ratio than tubular membrane modules. In addition it may be significantly easier to supply evenly distributed electric current to the plate surface than to the tube surface. During the development of composition and synthesis methods of the plate electro sorption membranes it was taken into account that the final product should possess the following properties:

-ability to adsorb ions in ion exchange processes
-electro conductivity
-porosity
-good mechanical properties

It was decided to use rigid flat porous ceramic or ceramic like matrices as supports for the preparation of composite electro sorption materials. It is known that ceramic and ceramic like materials prepared from oxides of polyvalent metals possess adsorption ion exchange properties both for cations and anions. This property allows the use of such materials as electro sorption membranes if electro conductivity is conferred onto them. Potentially one could use electro

conductive ceramic materials for preparation of electro sorption membranes, but these are currently extremely expensive. The problem of making low cost ceramic electro conductive was solved by the method of pyrolytic deposition of carbon on the surfaces of flat ceramic supports.

Another limitation of metal oxide ceramic materials used for electro sorption is their low ion exchange capacity. In order to increase the ion exchange capacity of ceramics used in the study, high sorption capacity compounds were impregnated into the porous matrices of flat supports.

3.2 Experimental

3.2.1 Starting materials

Sorption electrodes in the form of plates were prepared using two types of support materials:

1. Plate elements from porous oxide ceramics prepared using technology developed by the company "INMA" (Ukraine). The characteristics of initial ceramic elements are presented in Table 3.1.

2. Non-woven ceramic fibre based materials, or ceramic papers, prepared from oxides of multivalent metals. Manufacturing company "Thermal Ceramics" (USA). The main characteristics of ceramic paper grades that were used for preparation of electro sorption membrane electrodes are presented in Table 3.2.

Table 3.1 Main characteristics of rigid porous ceramic plate elements for preparation of electro sorption membranes.

Parameter	
Length, mm	100
Width, mm	40
Thickness, mm	1
Composition	70% Al_2O_3 + 30% ZrO_2
Average pore diameter, microns	0.19
Specific surface area, $m^2 \cdot g^{-1}$	4.5 - 5.0

Table 3.2 Main characteristics of flexible paper type porous ceramic elements that were used for preparation of electro sorption membranes.

Trade mark of ceramic paper	Chemical analysis % weight		Nominal density	Fibre index
	Al_2O_3	SiO_2	kg· m^{-3}	%
K-Shield BF Paper	51	49	130-160	75
Kaowool 500 Grade Paper	47	53	190-225	50
Kaowool 700 Grade Paper	47	53	175-210	55

3.2.2 Deposition of carbon on ceramic materials

In order to confer electro conductivity onto porous ceramic materials they were coated with a layer of electro conductive compound such as pyrolytic carbon. The deposition of carbon was carried out in the gas phase by pyrolysis of natural gas. The ceramic materials were placed in the quartz reactor through which natural gas was passed at a predetermined flow rate and then heated to the desired temperature.

3.2.3 Introduction of additional adsorbents into the porous structure of ceramic materials.

Phosphates of titanium and zirconium were selected as additional sorption active components to be introduced into porous matrices of sorption electrodes. This choice was justified by the following reasons:

(a) Phosphates of titanium and zirconium are well known inorganic ion exchangers, which possess relatively high ion exchange capacity.

(b) Phosphorus - unsaturated materials based on phosphates of titanium and zirconium are capable of adsorption of both anions and cations from aqueous solutions.

(c) Phosphates of titanium and zirconium possess high ionic conductivity, which is a very important property for their effective application in the process of electrochemically-activated sorption.

The following laboratory method was used for the introduction of zirconium phosphate into ceramic porous structures. The method is based on impregnation of the porous materials with crystalline sol of zirconium dioxide.

For the preparation of sol, a 25 % solution of NH_3 was added in small portions (2-3 ml) to 1 litre of 1 M solution of $ZrOCl_2$ whilst heating and stirring mechanically. The temperature of the heating did

not exceed 90°Ñ. Each following portion of NH_3 solution was added only after complete dissolution of zirconium hydroxide precipitate. The addition of NH_3 solution was terminated once dissolution of zirconium hydroxide precipitate within 20 minutes. The raw sol obtained was boiled using a reflux condenser for 25 hours to allow the formation of the crystalline structure. There after the sol was cooled to ambient temperature and filtered. Ceramic materials were immersed in 1 M sol of zirconium dioxide that was prepared as described above. The immersion time was 12 h. After removal from the sol, the membranes were wiped with filter paper and placed into a 15% solution of phosphoric acid for 15 h. This operation was aimed at the transformation of zirconium dioxide into zirconium phosphate. After phosphoric acid treatment the membranes were washed with distilled water, air-dried for 24 h at room temperature and then for 2-3 h at 200°C.

The introduction of titanium phosphate was carried out by the following means. Ceramic support materials were immersed into a 1 M solution of $TiCl_4$ for 6 h. There after the solution containing ceramic materials was cooled to 0°C. The membranes were removed from the cold solution, wiped with filter paper and placed into a cold (0°C) 15% solution of phosphoric acid for 15 h in order to transform the titanium salt in the pores of the ceramic into zirconium phosphate. Cooling of the solutions was necessary in order to achieve the deposition of the titanium salt in the form of a mechanically strong and homogeneous gel. The membranes obtained by this method were thoroughly washed using distilled water, air dried for 24 h at room temperature and further dried for 2-3 h at 200°C.

In order to achieve maximum density of zirconium and titanium phosphate deposition inside the membrane porous matrices the impregnation operations described above were repeated up to 3 times.

3.2.4 Testing of sorption properties of newly prepared membrane materials

Preliminary testing of the sorption activity of the newly prepared materials was carried out by ion adsorption using 0.1 M solution of NaCl under static conditions. The membrane plates were ground into particles of several millimetres, placed into glass beakers and the NaCl solution was poured upon the particles. The duration of the adsorption process was 24 h. The solution was separated from the adsorbent and the concentration of Na^+ and Cl^- ions was determined analytically.

Evaluation of sorption activity of the membranes under the condition of electrochemical activation was carried out in the following way. The model solution was constantly stirred in a glass vessel, which contained two flat electrodes with dimensions 50 x 20 mm. The distance between the electrodes was 10 mm. One of the electrodes was a piece of electro sorption membrane and the counter electrode was made of graphite. Electric current was passed through the system for 0.5 h under potentiostatic conditions. After that time the solution was removed from the vessel and analysed.

By this means the optimal composition and density of the electro sorption membranes was determined. The membranes that showed the best performance were selected for testing in the electro sorption cell, which design is shown in Figure 3.1.

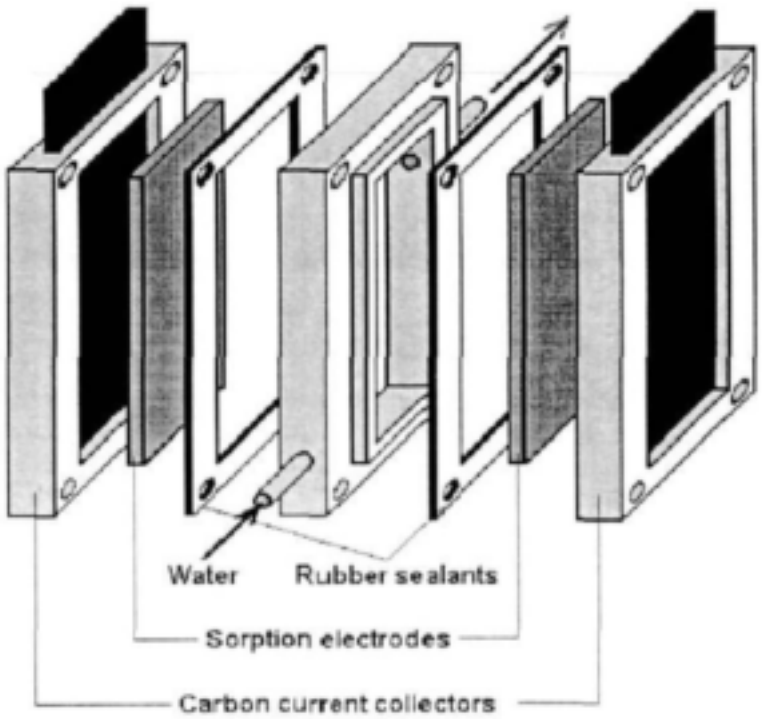

Figure 3.1 Schematic of electrochemical adsorption cell for testing properties of electro sorption membranes prepared in plate form.

The design of the cell allowed plate electro sorption membranes with dimensions 3x8 mm to be strongly pressed against graphite current collectors. Working solutions were pumped through the cell with pre-determined flow rates using peristaltic pumps. The working volume of the working compartment of the cell was 25 cm^3. The cell compartments were pressurized with rubber O-rings.

3.2.5 Methods of analysis

The concentration of sodium ions was determined by flame photometry with the aid of device PAZ (Ukraine). Analysis of nickel calcium and magnesium ions concentration was carried out by an atomic absorption method, with the aid of a spectrophotometer Pye Unicam 8800 (UK).

The concentration of sulphate ions was determined with the help of titration by Barium Chloride (BaC_{12}) solution in the presence of Rhodizonate as indicator. Chloride ions were determined with the help of ion selective electrodes (manufactured by Radelkis, Hungary).

3.3 Electro sorption properties of composite membrane materials based on rigid and flexible flat ceramic supports

The initial electro sorption testing experiments in this part of the project dealt with determination of the influence of carbon deposition onto electro sorption membranes, and their sorption capacity under static conditions without application of an electric field. During the study it was established that the adsorption capacity of the membranes towards cations was very low. At the same time, as shown in Table 3.3 these materials demonstrated significant anion exchange activity in the case of chloride ions. Ceramic paper based samples have anion exchange capacity similar to that of rigid metal oxide ceramic samples. As far as cation exchange properties are concerned, the difference between those two materials can be explained by the difference in their composition. Silica is present in large quantities in ceramic paper based membranes while rigid plate membranes contain zirconia and no silica.

Table 3.3 Influence of temperature of pyrolytic carbon deposition on adsorption capacity of ceramic paper based membranes towards chlorine ions. Ion concentration given in meq g^{-1}

Type of base ceramic paper	Pyrolysis temperature, °C		
	800	900	1000
K-Shield BF Paper	0.096	0.124	0.102
Kaowool 500 Grade Paper	0.063	0.076	0.089
Kaowool 700 Grade Paper	0.112	0.039	0.023
Porous Oxide Ceramics	0.120	0.092	0.090

* Adsorption capacity was determined using analytical data of chlorine ions removal from 0.1 M solution of NaCl at adsorbent to solution volume ratio of 1: 20.

Analysis of data presented in Table 3.3 shows that the temperature of pyrolytic deposition of carbon has very little influence on adsorption capacity of the membranes. This testifies to the fact that pyrolytic carbon does not have any significant adsorption activity. The drop in adsorption capacity observed in the case of the Kaowool 700 paper based sample can be explained by lower thermal stability of that paper.

Due to the fact that cation exchange capacity of ceramic paper based membrane samples coated with pyrolytic carbon was low, the next step of the study was to determine the nature and optimal composition of the cation exchange phase that could be introduced into the porous matrices of the membranes. Although initial experiments were carried out using two inorganic cation exchangers, namely phosphates of zirconium and titanium, it was established that the structure vs. adsorption performance relationship is similar for both materials, but that the former is a more robust adsorbent when working under real electro sorption conditions. All further studies described in this chapter were conducted using only zirconium phosphate as sorption active filling material. The data describing adsorption properties of ceramic paper based membranes impregnated with zirconium phosphate are presented in Table 3.4 and Table 3.5. It should be noted that data presented in Table 3.5 deals with membrane materials containing both zirconium phosphate and pyrolytically deposited carbon. Since it was established in previous experiments that the temperature of deposition of pyrolytic carbon does not have influence on the adsorption capacity of the resulting membrane, all carbon deposition operations were carried out at an optimal temperature of 900 °C.

Table 3.4 Relationship between the number of consecutive impregnations with zirconium phosphate (ZrP) of different ceramic materials (rigid porous plate and papers) on its content in resulting composite materials (C,%) and their adsorption capacity* (A, meqv. g^{-1})

Initial support type	Number of impregnations with ZrP					
	1		2		3	
	C, %	A, meqv. g^{-1}	C, %	A, meqv. g^{-1}	C, %	A, meqv. g^{-1}
Porous Ceramic	5.2	0.11	9.3	0.7	11.8	0.20
K-Shield BF Paper	61.2	1.05	74.9	1.30	79.1	1.40
Kaowool 500 Grade Paper	56.9	1.01	70.2	1.25	77.8	1.35
Kaowool 700 Grade Paper	57.7	1.04	68.5	1.21	75.6	1.35

* Sorption capacity was determined according to uptake of sodium ions from 0.1M solution of NaCl at the volume ratio of adsorbent to solution of 1: 50.

Table 3.5 Relationship between the number of consecutive impregnations with zirconium phosphate (ZrP) of different ceramic materials (rigid porous plate and papers) which were initially coated with pyrolytic carbon at 900 °C, 30 min on Zr on its content in resulting composite materials (C,%) and their adsorption capacity* (A, meqv. g^{-1})

Initial support type	Number of impregnations with ZrP					
	1		2		3	
	C, %	A, meqv. g^{-1}	C, %	A, meqv. g^{-1}	C, %	A, meqv. g^{-1}
Porous Ceramic	5.0	0.12	9.5	0.15	11.2	0.18
K-Shield BF Paper	81.9	1.40	88.7	1.53	90.5	1.58
Kaowool 500 Grade Paper	65.4	1.19	83.9	1.50	88.2	1.58
Kaowool 700 Grade Paper	68.9	1.25	85.5	1.53	89.0	1.60

* Sorption capacity was determined according to uptake of sodium ions from 0.1M solution of NaCl at the volume ratio of adsorbent to solution of 1 : 50.

The analysis of data presented in Table 3.4 and Table 3.5 shows that in all cases the introduction of zirconium phosphate into ceramic materials results in significant increase in the adsorption capacity. A direct relationship between the material structures, quantity of impregnated zirconium phosphate and the adsorption capacity was clearly visible in all experiments. Moreover, the inflexible structure of heavy porous ceramics limits the maximum possible quantity of zirconium

that can be introduced into the rigid ceramic plates, and as a result, the maximum adsorption capacity of electro sorption membranes produced using these plates as supports. The much more flexible porous structure of ceramic papers consisting of silica and alumina fibres allowed the introduction of significantly higher quantities of zirconium phosphate thus obtaining higher values of ion exchange capacity in resultant electro sorption membranes.

It is also apparent from results presented in Table 3.4 and Table 3.5 that for different types of ceramic papers the quantity of zirconium phosphate introduced closely correlates with the density of initial papers as presented in Table 3.2. It is possible to introduce more zirconium phosphate in ceramic papers with lower density.

It can be seen from the experimental curves presented in Figure 3.2 that an increase in the number of consecutive impregnations of zirconium phosphate results in an increase in sorption capacity, which reaches its maximum after three impregnation operations. It should be noted that the sorption capacity of the composite material depends on the quantity of zirconium phosphate introduced into it, but not as much on the structure on the initial ceramic paper. It is also clear from Figure 3.2 that the deposition of carbon carried out before the phosphate impregnation operation does not significantly decrease the sorption capacity.

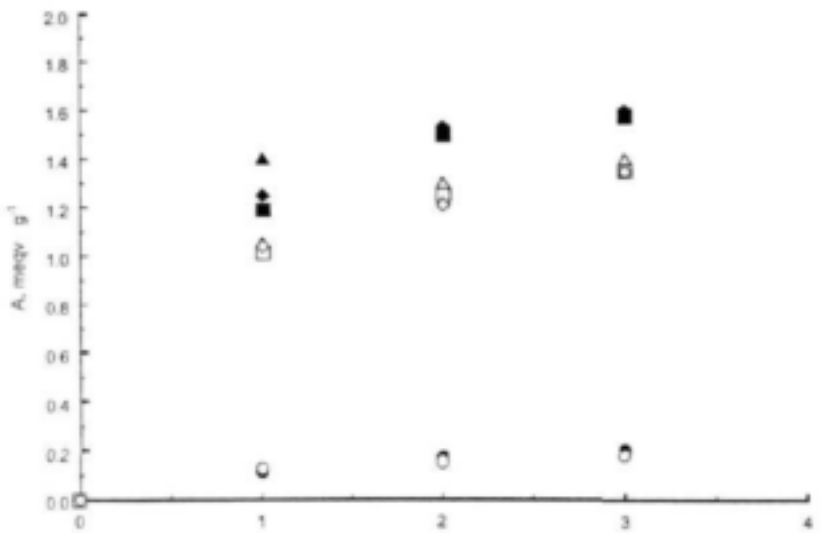

Figure 3.1 Relationship between the numbers of consecutive impregnations, n, of different ceramic materials (rigid porous plate and papers) with zirconium phosphate, on their adsorption capacity A.
○ Ceramic plates without carbon, ● Ceramic plates with carbon, ◇ □ △ ◆ ■ ▲ Ceramic papers

without carbon, Ceramic paper with carbon

Increase in the sorption capacity of carbon-coated materials was observed after zirconium phosphate deposition when compared with non-coated initial ceramic papers. It was found in the current study that deposition of pyrolytic carbon onto ceramic papers significantly improved their mechanical properties and chemical stability against hot solutions of acids and bases. Another important property relationship was found between the quantity of zirconium phosphate introduced into the porous structures of ceramic papers and their mechanical durability. The durability of initial non-treated ceramic papers drops in the following sequence:

Kaowool 500 Grade Paper > Kaowool 700 Grade Paper > K-Shield BF Paper

After the pyrolysis and introduction of the phosphate the durability changes in the opposite manner as shown below:

K-Shield BF Paper > Kaowool 700 Grade Paper > Kaowool 500 Grade Paper

The results obtained in this part of the study allowed the selection of the most promising flat ceramic membrane elements for electro sorption testing. These elements were produced from both rigid porous ceramic plates and ceramic papers as starting materials. In all cases pyrolytic carbon was deposited at 900°C and zirconium phosphate was introduced by three consecutive impregnations. The cathodic polarization of the electro sorption membranes was carried out at a potential difference of 10V. Electro sorption tests were carried using a model solution of the following composition:

Ca^{2+} - 73.3 mg· l^{-1};
Mg^{2+} - 51.5 mg· l^{-1}
Na^{+} - 115 mg· l^{-1}
Cl^{-} 130 mg· l^{-1};
SO_4^{2-} - 140 mg· l^{-1}.

The results of electro sorption experiments are summarized inTable 3.6.

Table 3.6. Removal of metal cations from model solutions by electro sorption

Initial support type	Ion removal degree, %					
	Ca^{2+}		Mg^{2+}		Na^{+}	
	0 V	-10 V	0 V	-10 V	0 V	-10 V
Porous Ceramic	28.2	60.5	39.7	85.3	15.4	40.2
K-Shield BF Paper	70.4	92.8	83.2	94.3	48.2	75.4
Kaowool 500 Grade Paper	65.3	88.2	75.4	90.6	45.4	69.3
Kaowool 700 Grade Paper	68.2	90.1	78.3	91.2	48.0	71.2

The results obtained during the study of the influence of electric field on adsorption properties of membrane materials containing pyrolytic carbon and zirconium phosphate demonstrated that electrochemical activation resulted in a two-fold increase in their ion exchange capacity at least. This effect manifests itself in a higher removal of ions from aqueous solutions. It was also found that adsorption of anions increases during anodic polarization with a potential difference of 10 V in a similar way.

The results of the previous parts of this chapter may be summarized in the following way. The study of manufacturing procedures, structural properties and adsorption capacity of flat electro sorption membranes have demonstrated that fibrous non woven flexible ceramic materials (ceramic papers) are the strongest candidates for use as supports in membrane manufacturing. The addition of an active sorption compounds such as zirconium or titanium phosphates into the porous matrices of ceramic papers resulted in a significant increase in their capacity to adsorb both cations and anions. It was also shown that the introduction of an electro conductive compound such as pyrolytic carbon allowed the use of phosphate impregnated ceramic papers as effective electro sorption electrodes and the control of their adsorption efficiency by direct application of electric current. The highest adsorption capacity, mechanical stability and the ability to remove ions from aqueous solutions was observed in the case of electro sorption membranes prepared using ceramic paper Kaowool 700 as initial support material. These membranes were prepared by deposition of pyrolytic carbon at 900°C and three consecutive impregnations with zirconium phosphate.

3.4 Optimisation of electro sorption properties of composite membranes produced from ceramic papers

The possibility of preparation of sorption electrodes as plate-and-frame or flat sheet membrane elements based on fibrous ceramic materials and zirconium phosphate was shown in the previous part of this report. The next main research task was the determination of optimal conditions for the preparation of flat sheet sorption membranes. This required solution of the following problems:

(a) The choice of optimal composition for sorption active component of sorption membrane elements

(b) The development of an optimal configuration of sorption electrodes

In this part of the study two sorption active components such as zirconium phosphate and titanium phosphate were used. A comparative study of sorption properties of composite inorganic membrane materials based on ceramic paper filled with titanium and zirconium phosphate (three impregnations) was carried out in order to choose the optimum composition of composite sorption materials. Due to the fact that the molar ratio of phosphorus: metal in phosphates of zirconium and titanium determines its adsorption capacity towards cations and anions, electro sorption membranes with different molar ratios in their composition were synthesized and tested. Changing contact time of the material with phosphoric acid during the phosphorization stage of the membrane synthesis procedure controlled the composition of phosphates of zirconium and titanium, which were deposited into ceramic porous matrices. Ceramic paper Kaowool 700 served as starting material for the preparation of electro sorption materials. A 1.0 M NaCl solution was used for evaluation of sorption properties of the membrane without electrical polarization. The results of this study are presented in Table 3.7.

Table 3.7 Sorption capacity of composite membranes prepared by the impregnation (three impregnations) of titanium (TiP) and zirconium (ZrP) phosphates into Kaowool 700 ceramic paper.

	Sorption capacity, mg. g^{-1}			
Molar ratio	TiP		ZrP	
P : Me	Na^+	Cl^-	Na^+	Cl^-
1.5	124	35	115	30
1.0	95	63	92	60
0.5	60	70	55	65

The following conclusions could be drawn from this section:

- sorption capacity of composite membranes prepared using zirconium phosphate and titanium phosphate are practically identical;

- the lower the phosphorous content in the membrane, the lower its sorption capacity towards cations and the higher towards anions;

- membranes with a molar ratio metal: phosphorous = 1 are optimal for simultaneous sorption of cations and anions.

The next step of the study was to prepare sorption electrodes from phosphate materials selected as candidates for the preparation of electro sorption composite membranes and to investigate their sorption properties under electrical polarization. The electrodes of different dimensions (thickness) were prepared by placement of the phosphate - impregnated ceramic paper pieces in contact with current-collecting flat metal sheets. The results are summarized in Table 3.8

Table 3.8. Influence of polarization and dimensions of sorption electrodes on their sorption capacity for Na^+ ions from 0.01N Na_2SO_4 solutions.

Thickness of sorption electrodes, mm	Sorption capacity, $mg.g^{-1}$			
	TiP		ZrP	
	without potential	E= - 0.3 V	without potential	E= - 0.3 V
1	20	35	19	51
2	20	32	19	48
5	20	27	19	41
10	20	22	19	37

The conclusions made after completion of this part of the study were as follows:

- the cathode polarization of the membranes increased their sorption capacity;

- the influence of polarization on sorption capacity is more pronounced for zirconium phosphate based materials (a rise in the sorption capacity up to 150 %);

- the increase of thickness of sorption electrodes results in a lower specific sorption capacity;
- the influence of the type of current-collecting metal of sorption electrodes on the sorption capacity was not specific;
- impregnation with zirconium phosphate (ratio metal : phosphorous = 1) gave an optimum material for the preparation of sorption membranes.

The last stage of optimisation of the content of sorption electrodes was multiple sorption-desorption testing under electro sorption conditions. The electro sorption cell shown in Figure 3.1 was used for the testing. Tests were carried out utilizing a model solution of the following composition:

Ca^{2+} - 73.3 mg· l^{-1}
Mg^{2+} - 51.5 mg· l^{-1}
Na^{+} - 115 mg· l^{-1};
Cl^{-} - 130 mg· l^{-1};
SO_4^{2-} -140 mg· l^{-1}.

The results obtained for sorption electrodes containing titanium and zirconium phosphates (molar ratio P : Me = 1, three impregnations) are presented in Table 3.13.

Table 3.9 Degree of model solution purification by the electro sorption module equipped with titanium and zirconium phosphate containing electro sorption electrodes.

No. of sorption - desorption cycles	Degree of purification, %			
	TiPh		ZrP	
	without potential	dU = 10 V	without potential	dU = 10 V
1	55	82	53	97
2	52	85	56	92
5	56	81	51	95
10	54	83	52	96

The following conclusions can be made from Table 3.9:

- passage of an electrical current through the sorption cell greatly increases degree of purification from ionic impurities;

- influence of polarization on the degree of purification is more pronounced for electro sorption membranes made of zirconium phosphate;

- the water purification characteristics of the cell do not change significantly over up to 10 sorption - desorption cycles.

- the results obtained have shown good performances of the electro sorption method for the purification of solutions with a small content of salts (up to 0.5 g· l^{-1}).

The study described in the present chapter of the report resulted in optimisation of the method for manufacturing composite sorption materials for the process of electro sorptive removal of ions from aqueous solutions. Kaowool 700 grade ceramic paper with the thickness of 1/16 inch was selected as the initial support material for up scaling of the electro sorption technology and for testing of model solutions and industrial effluents.
The procedure for the electro sorption membrane preparation from the Kaowool 700 support consisted of two consecutive stages:

(a) Deposition of carbon on the ceramic paper by methane pyrolysis at 900 °C during 30 min;
(b) Three consecutive impregnations with zirconium phosphate by a sol gel method followed by phosphoric acid treatment. The molar ratio of phosphorus to zirconium in the impregnated material was 1.

4 DESIGN OF THE ELECTRO SORPTION MODULES FOR TUBULAR AND FLAT SHEET MEMBRANES

Abstract

The development of the tubular and flat sheet electro sorption modules is described. It is shown how conductive O-rings were used to establish the electrical connection in multi tubular membrane reactors and how Na-silicate could be used to prevent corrosion of the O-rings. The configuration with the highest potential for application was found to be a carbonised membrane, with a carbon rod inside the carbonised substrate acting as a counter electrode and having a flow directed away from the centre. Automation of the electro sorption process with tubular electro sorption units was controlled by measuring the pH and conductivity of the permeate stream. The reactor for flat sheet electro sorption units was designed in a way that the performance of each individual module could be monitored using its current / voltage characteristics. The maintenance and membrane refitting in each module could be carried out without shutting down the complete desalination unit. In addition, the potential differences over the total unit were equal to the potential difference over each unit.

4.1 Introduction

Besides the choice of the right materials for the sorption and electro conductive phase, the choice of the right reactor configuration and experimental set-up was of great importance. The development of the tubular and flat sheet electro sorption modules is described step by step in section 4.1 and 4.2 respectively. In section 4.3, a pilot plant with automated control over the electro sorption process will be presented.

4.2 Reactor development for tubular sorption electrodes

4.2.1 Reactor design and set-up for electro sorption experiments

The first set of potential driven adsorption experiments was carried out using the set-up shown in Figure 4.1.

A sorption electrode of 5cm in length was connected to a potentiostat (Amel 2063 for max 5V DC and the Kikusiu Pad 35-5L for max 10V DC). A 15cm spiral wound Pt wire (1mm ∅) was used as the counter electrode. A detailed description of the sorption experiment itself is given in chapter 5.

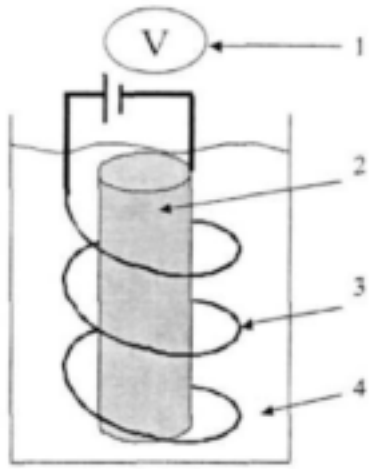

Figure 4.1. Schematic overview of the first set-up for electro sorption experiments [1];
1) Potentiostat, 2) Sorption electrode, 3) Counter electrode, 4) Beaker with salt solution

The ion concentration of the bulk solution and the applied potential difference between the counter and the sorption electrode, for several electrode materials, was measured as a function of time. The sorption capacities of the first sorption electrodes were of such a low value that the changes in ion concentration in the bulk solution (due to ion adsorption or desorption) were often within the experimental error of the ion analysis. More valuable information about the sorption characteristics of the different sorption material (using the set-up shown in Figure 4.1) may have been obtained by impedance spectroscopy measurements. However, the proper equipment for this kind of measurement was not available at that stage of the project.

The experimental set-up needed some adaptations for industrial application of the sorption electrode. Therefore a continuous flow electro sorption reactor was developed. The reactor design allowed the sorption properties of the sorption electrode and its filtering capacity to be combined. A schematic overview of the set-up with the continuous flow reactor used for electro sorption experiments is shown in Figure 4.2. The set-up included a Watson 313S tube pump, the reactor, a reservoir, a pressure gauge, a tube clamp and the same potentiostat as previously described. A model solution of 0.01M $MgSO_4$ was pumped from the reservoir into the reactor.

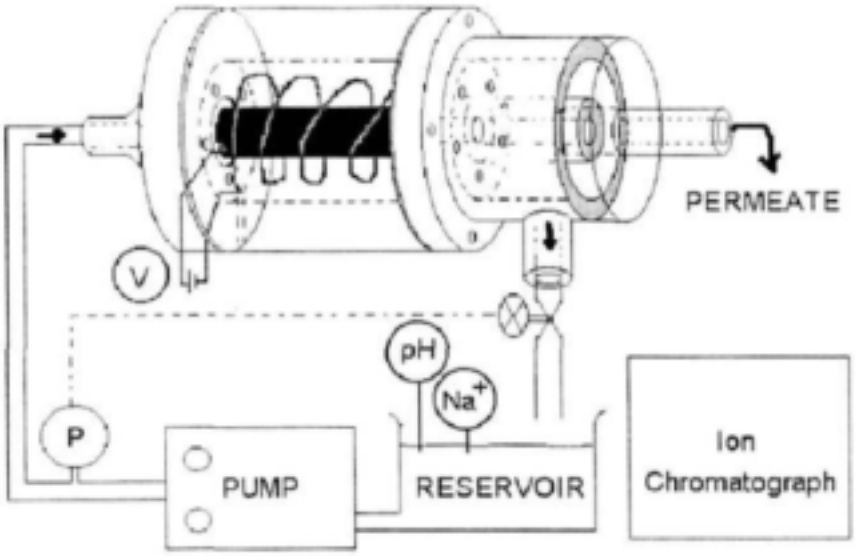

Figure 4.2. Schematic view of the second set-up for electro sorption experiments

The pressure difference between the outer and lumen side of the sorption electrode was regulated by means of a tube clamp and by monitoring the pressure gauge. Using this set-up, the ion sorption characteristics could be coupled with permeability characteristics of the differently prepared sorption electrodes

4.2.2 Reactor development towards an industrially applicable design

A second reactor design was manufactured (see Figure 4.3). The sorption electrode (1) was connected to the power source (8) via a stainless steel coil (5). The feed solution entered the reactor at (2) and exited the reactor as reject (3) and permeate (4). The counter electrode (6) was prevented from touching the sorption electrode via a square shaped piece of insulating material (7).

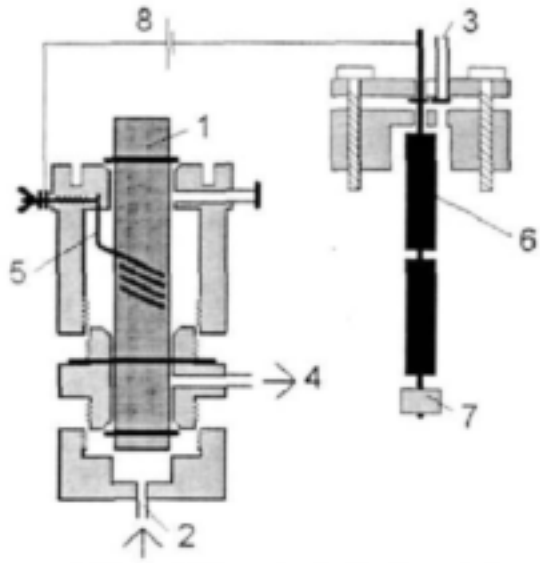

Figure 4.3. Schematic representation of the second electro sorption reactor design. (1: Sorption electrode, 2: Feed, 3: Reject, 4: Permeate, 5: Stainless steel coil, 6: Carbon rods, 7: PVC shortcut prevention, 8: Power source)

The main difference between the set-ups in Figure 4.2 and Figure 4.3 was that the latter had an extra inlet. The feed solution could be introduced at either the inside or the outside of the sorption electrode. This option created the possibility to achieve the most efficient sorption electrode composition and counter electrode position as will be discussed. Another important change between the first and the second reactor design was the choice of a carbon rod as counter electrode. Besides the fact that a carbon rod was much cheaper than a platinum wire, the difference in geometric surface and surface roughness between the carbon rod and the platinum wire resulted in a much higher surface area of the counter electrode. This may result in a higher adsorption capacity of the sorption electrode. Finally, the potential drop was caused by the resistance between counter and sorption electrode (IR drop was lowered by reducing the distance of the two electrodes.

The reactor displayed in Figure 4.3 needed two more changes to become a fully industrially applicable electro sorption reactor.

- The total electro sorption electrode area had to be up scaleable
- The reactor had to be easy to assemble

Figure 4.4 shows the multiple sorption electrode reactor that was designed to meet these requirements. The problems encountered with the difficult to assemble coil connection in the earlier designs were solved by the introduction of conductive O-rings.

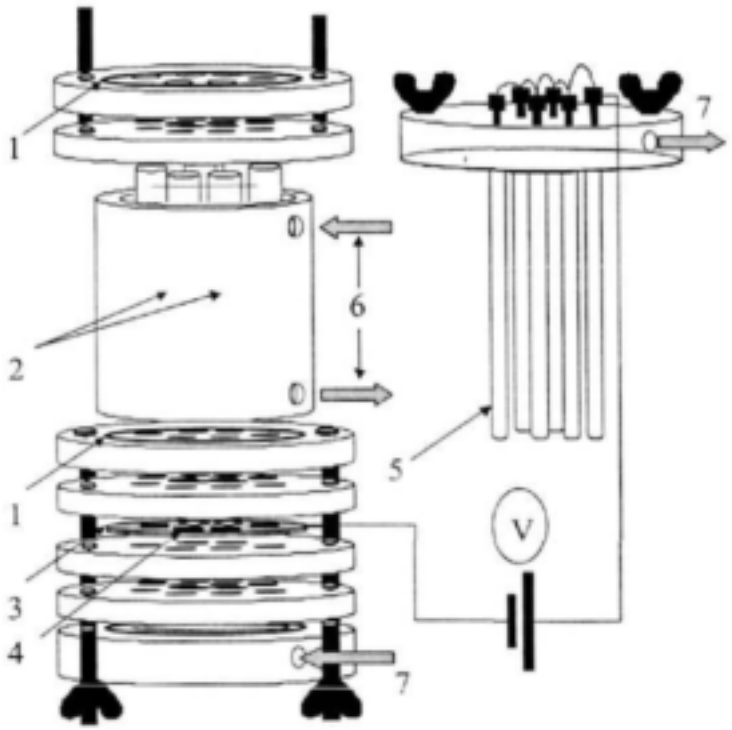

Figure 4.4. Schematic drawing of the multiple sorption electrode reactor. 1: O-ring, 2: Sorption electrodes, 3: Conductive plate, 4: Conductive Oring, 5: Counter electrode. 6: In- and outlet of permeate. 7: In- and outlet of reject

The elasticity of the nickel loaded O-rings (VEPAC, Muizenberg, Cape Town South Africa) allowed easy assembly with sufficient conductive properties to provide an electrical connection between the sorption electrode and the potentiostat without significant potential loss. Clamps with screws were used to keep the reactor together instead of parts that needed to be screwed into each other. Several electro sorption electrodes could be fitted per reactor. The principle of the set-up remained unchanged. The pump was used to generate a pressure difference between the lumen and outside of the sorption electrode that resulted in a flow permeating through the electrode. To avoid rapid degradation of the electro conductive O-ring, contact with water should be avoided. Appendix B describes what was done to keep these O-rings dry.

4.2.3 Reactor optimisation

After the industrially applicable design had been developed, the following three main questions had to be answered in the context of the search for the optimum reactor design:

(a) What is the most effective location for the electro conductive phase of the sorption electrode? The possibilities are that the electro conductive phase should be:

- dispersed throughout the substrate like a carbon coating
- on the outside surface only, like a gold or a nickel plated coating
- on the outside surface (for gold or nickel) and the inside (for nickel). In this case no additional counter electrode is needed. The counter electrode is incorporated into the same sorption electrode

(b) Where should the counter electrode be situated?

- inside the sorption electrode like a carbon rod or carbonised substrate
- outside the sorption electrode like gold sputtered or Pt sputtered Ti foil
- on both sides. This configuration is a special case and has been reported in a preliminary report [2] but not for flow through applications. The better name for this sorption device would be a sorption support since there is no conductive phase required

(c) Should the permeate flow toward or away from the centre of the sorption electrode

The combinations listed above give options with a high variety of possible configurations with regard to sorption electrode composition, counter electrode position and flow direction. All the different combinations are tabulated in Table 4.1. From these combinations, there are only nine options that result in different configurations.

The combinations are listed in such an order that the schematic representations of the "B" combination will look exactly like the "A" combination. As an example, the configuration of combination 3A and 3B are schematically represented in Figure 4.5.

Table 4.1 Combination of sorption electrode compositions, counter electrode position and flow direction.

Combination No	Location of electro-conductive phase	Flow direction of permeate	Counter electrode
1a	Throughout carbon	Away from centre	Carbon rod
1b	Throughout carbon	Towards centre	Gold sputtered Ti Foil
2a	Throughout, carbon	Towards centre	Carbon rod
2b	Throughout, carbon	Away from centre	Gold sputtered Ti Foil
3a	Outside Au	Towards centre	Gold sputtered Ti Foil
3b	Inside Ni	Away from centre	Carbon rod
4a	Outside Au	Away from centre	Carbon rod
4b	Inside Ni	Towards centre	Gold sputtered Ti Foil
5a	Outside Au	Away from centre	Pt sputtered Ti Foil
5b	Inside Ni	Towards centre	Carbon rod
6a	Outside Au	Towards centre	Carbon rod
6b	Inside Ni	Away from centre	Pt sputtered Ti Foil
7a	Outside Ni, inside Ni	Away from centre	-
7b	Outside Ni, inside Ni	Towards centre	-
8a	Outer surface (gold)	To centre	Carbonised support
9a	-	To centre	Carbon rod + Ti foil
9b	-	Towards centre	Carbon rod + Ti foil

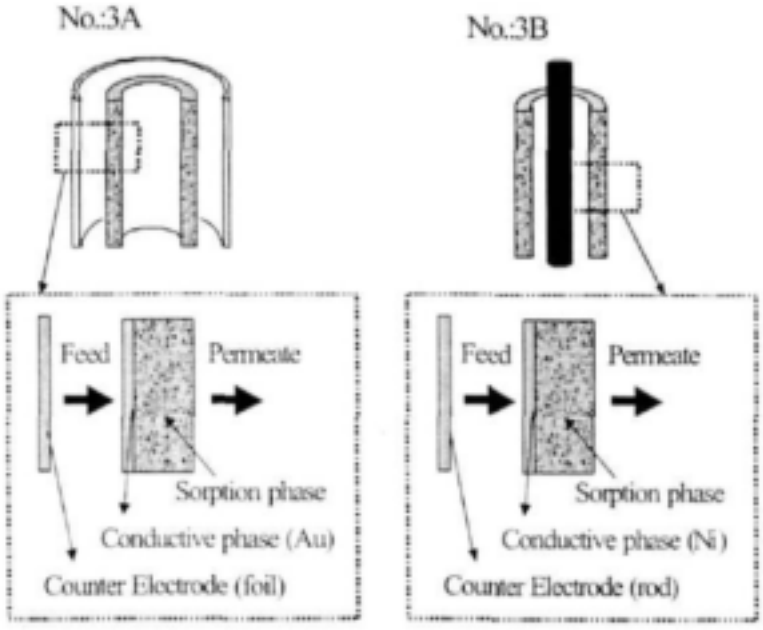

Figure 4.5. Different combination of counter electrode, sorption electrode and permeate direction resulting in similar configurations

No difference in configuration could be found between combination XA and XB. The reason why the combinations "B" were not subjected to an electro sorption experiment is that no difference in sorption behaviour may be expected when compared to combination "A". Eight different configurations were tested. All eight configurations are shown in Figure 4.6. The configurations of these combinations were all different.

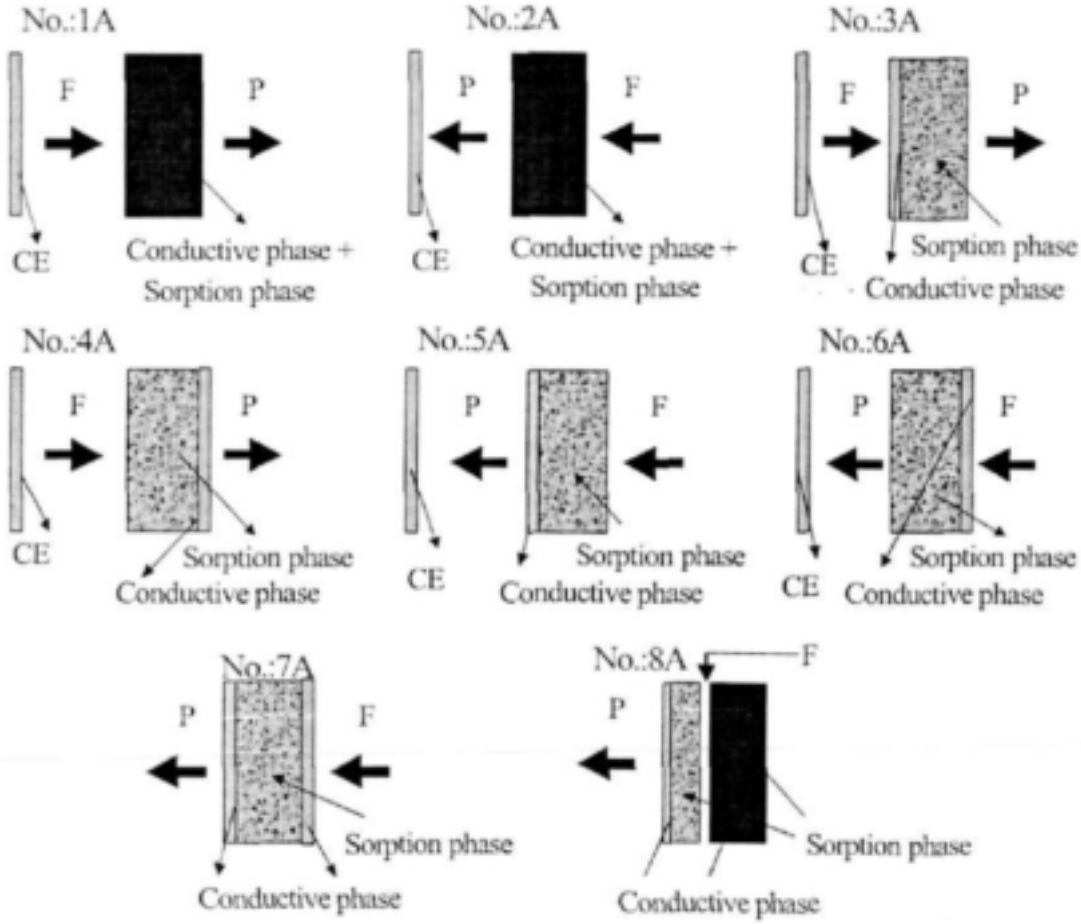

Figure 4.6. Different combinations leading to different configurations, F=Feed, P=permeate, CE=counter electrode

In order to use a carbonised support as counter electrode as described by combination 8A, a double electrode reactor had been developed. The schematic drawing of the double electrode is illustrated in Figure 4.7. The double electrode reactor can readily be up scaled as well. In this design support type II is the counter electrode and slides inside support type I. At the top and bottom side of the

reactor an electro-conductive connection is established using the electro-conductive O-ring to connect the two supports with the power source and to make these either a cathode or anode.

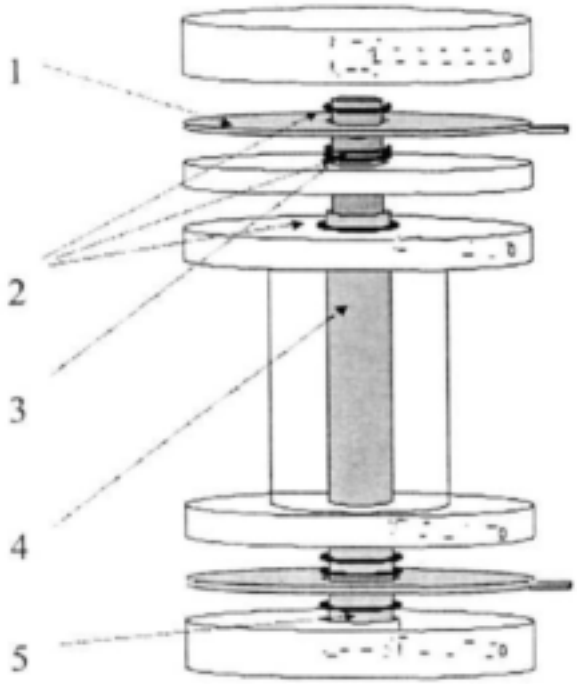

Figure 4.7. Schematic drawing of the double support reactor. 1) Conductive plate, 2)Viton O-rings, 3) Conductive O-ring, 4) Support type II, 5) Support type I

4.2.3.1 Experimental

In order to compare the different configurations, supports of type I and II (see Table 2.1 for details) were subjected to standard electro sorption experiments (described in chapter 5). The experimental set-up used is shown in Figure 4.3. For experiment 1 to 9 (see Table 4.2), the reactor shown in Figure 4.3 was used but slightly modified to adapt to the required configurations. Supports type II were used and all impregnated with the commercial available ZrO_2 sol as described in section 2.3.

4.2.3.2 Results

The results of all the electro sorption experiments conducted for each tested configuration are listed in Table 4.2.

Table 4.2. Results of electro sorption experiments for all tested configurations

Exp	Config.	Max adsorption/desorption (%)		Simultaneous removal*	
No.	No.	SO_4^{2-}	Ca^{2+}	Adsorption	Desorption
1	1A	70/30	60/35	Simultaneous	Simultaneous
2	2A	40/20	30/20	Not simultaneous	Not simultaneous
3	3A	20/50	0/10	Not simultaneous	Not simultaneous
5	4A	80/10	60/80	Simultaneous	Not simultaneous
6	5A	10/05	5/10	Not simultaneous	Not simultaneous
7	6A	30/20	30/20	Not simultaneous	Not simultaneous
8	7A	94/0	30/0	Simultaneous	Not simultaneous
9	8A	90/30	40/15	Not simultaneous	Not simultaneous
10	9A	5/5	5/0	-	

* Simultaneous removal of cations and anions

Most of the configurations (2A, 3A, 5A, 6A and 8A) suffer from the same problem. Cations and anions are not adsorbed simultaneously. Acidification of the sorption phase (caused by the protons generated by electrolysis of water at the anode) results in desorption of cations and adsorption of anions. After switching the polarity of the electrodes the alkalinity of the sorption phase results in the opposite; anions desorb and cations adsorb. Using these configurations will not lead to the production of clean water since the permeate will always contain an increased concentration of either anions or cations. Moreover the permeate will be acidic or alkaline to compensate the excess of anions or cations respectively.

The most promising electro sorption results were obtained using configuration 1A where simultaneous adsorption of cations and anions was observed and reasonably high sorption efficiencies were reached. It is believed that simultaneous adsorption is only possible when a pH gradient within the sorption phase can be established. The use of carbon as electro conductive phase with the direction of flow away from the centre as in configuration 1A resulted in this pH gradient. The working of the pH gradient will be discussed in more detail in chapter 6. With configuration 4A and 7A a pH gradient could be expected as well, but the location at which cation exchange groups became anion exchange groups is probably shifted further from the centre of the sorption phase towards the direction of the flow.

Experiment 4 shows reasonable sorption efficiencies. However, desorption of SO_4^{2-} seems to be a problem. By comparing the results of experiment 1 with 4, better desorption values were obtained when a conductive coating mixed with the sorption phase (carbon coating) is used instead of a surface coating (gold). As discussed above this difference might be caused by the difference in position to establish the pH-gradient. Another possible explanation is that in configuration 1 the release of SO_4^{2-} is facilitated by the charge of the conductive phase deposited under the sorption phase.

While testing configuration 3A in experiment 3 it was found that Ca^{2+} was not adsorbed. Ca^{2+} will only be adsorbed onto ZrO_2 at significantly higher pH [4]. Apparently the necessary pH could not be reached because the configuration allowed quick neutralization of the protons and hydroxyl ions formed. Its seems necessary to have the sorption phase in between the electrode conductive coatings to avoid the neutralization of formed protons or hydroxyl ions before they can activate the ion exchange groups.

Configuration 5A seemed to be one of the least efficient in terms of ion adsorption. Using this configuration, the feed had to permeate through the sorption phase first before it reached an electrode. Because of the pH neutrality of the feed, the ion exchange groups were thus not activated and no adsorption could take place. The sorption phase might have been activated by some of the produced protons or hydroxyl ions only when the feed solution entered the region close to the electro conductive layer. It is thus recommended that the feed solution should be in contact with an electrode before it comes in contact with he sorption phase. This would be the case if the sorption phase were located between the electrodes. Since nickel is not a very stable material under anodic conditions, the nickel coatings in configuration 7A started to dissolve as soon as the experiment started, resulting in a constantly decreasing current. After half an hour the current dropped to about half of the initial value. The numbers given in Table 4.2 are most likely influenced by the changing properties of the conductive coating. Another technique to coat the inside of a tube was not available. Hence, configuration 7A was not investigated further. Since it was believed that carbon coatings should be necessary to enhance sulphate desorption, configuration 7A was no longer considered to be one of the potential possibilities.

The main problem with configuration 9 was the high resistance between the electrodes. The current generated by the applied potential difference was too low to produce sufficient protons and hydroxyl groups to activate all ion exchange groups necessary for the sorption process.

4.2.3.3 Conclusions on reactor optimisation

- Conductive O-rings could be used to facilitate the assembly of a sorption electrode reactor
- An up scalable and easy to assemble electro sorption electrode reactor was designed and manufactured
- Na-silicate could be used to prevent corrosion of the conductive O-rings
- In general simultaneous removal of anions and cations was only found when the sorption phase was placed between the cathode and the anode
- Desorption of SO_4^{2-} usually took place faster when carbonised coatings were used
- The configurations with the highest potential for application was found to be a carbonised membrane, a carbon rod inside the carbonised substrate acting as a counter electrode and with a flow directed away from the centre

4.3 Reactor development for flat sheet sorption electrodes

The small-scale electro sorption module, which is shown in Figure 3.1, was used for testing the composite electro sorption membrane properties during the developmental phase of their manufacturing and optimisation. After the membranes with the required properties were developed, it became necessary to upscale the process to the level at which accurate prediction of membrane performance under full-scale conditions was possible. It was also intended to carry out electro sorption experiments using several model solutions closely resembling various kinds of waters and effluents and at least one industrial effluent with significant potential for membrane fouling. Finally the up scaled electro sorption module was needed for the preliminary cost analysis of the electro sorption process.

The principal schematic of the up scaled electro sorption module is shown in Figure 4.8. In its design, all the prior findings about the behaviour of the flat electro sorption membranes under the influence of electric fields of various intensities were used. The module was produced from materials with the lowest possible cost and its design allowed for easy full scale manufacturing operation to give plate and frame electro sorption installations with high total membrane surface areas. The electro sorption module consisted of two electro sorption membranes with dimensions 150 x 210 mm and 2 mm thickness. The spacer that also played a role in the water flow field was positioned between the membranes. The design of the spacer / flow field allowed for the ratio of turbulent to laminar flows of water inside the module to be as high as possible. The internal free volume, or working volume of the module was 100 cm^3. The supply of electric current to the

membranes was carried out via the current collector made of carbon cloth with high graphite content and copper current leads, which were sandwiched between pieces of the carbon cloth. The current collectors were pressed against the electro sorption membranes and the separator by means of bolts that are not shown in the picture. The module was leak proofed by rubber washers (not shown).

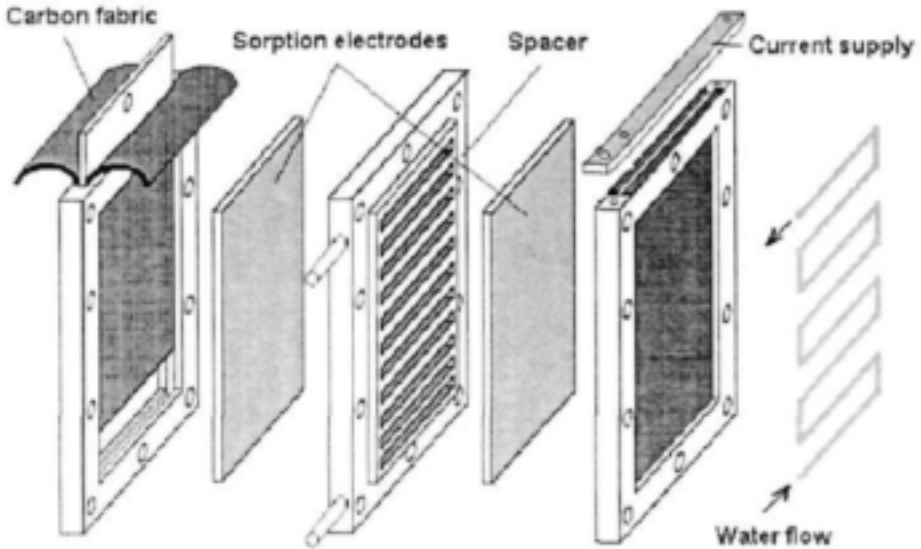

Figure 4.8. Schematic of large-scale electro sorption module.

The module design described above allows the assembly of the electro sorption unit using plate and frame modules. The number of modules in the unit will depend on required productivity and ion content of waters to be treated. A possible layout of the electro sorption unit is shown in Figure 4.9(a). It should be noted that the proposed design of the electro sorption unit would allow the use electro sorption electrodes not just as de-ionization media but also as micro- or ultra filtration media. In this case the unit operation will carried out in the mode presented in Figure 4.9(b). The working solution would enter one of the electro sorption modules, flow through the electro sorption membrane where both de-ionization and filtration would take place and then flow out of the module.

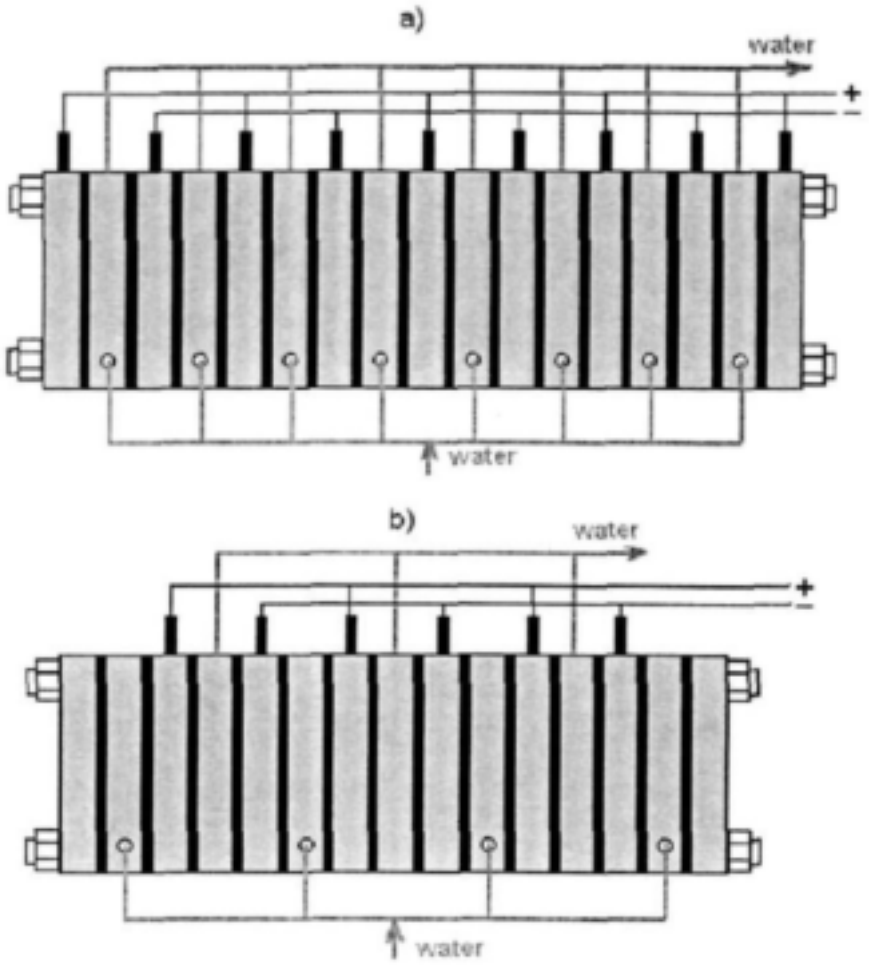

Figure 4.9. Layouts of electro sorption units for water cleaning in sorption mode (a) and combined sorption and filtration modes (b).

Another significant technological feature of the proposed electro sorption modular structure is that the modules always work in the form of a parallel electric circuit. This allows for the following operational advantages in comparison with a series of desalination cells, which are used for example in electro dialysis:

(a) The performance of each individual module can be monitored using its current / voltage characteristics.

(b) The maintenance and membrane refitting in each module can be carried out without shutting down the complete desalination unit.

(c) Operation potentials of the units will be equal to operation potentials of each individual module.

4.4 Automated control for an electro sorption process (pilot plant)

During the course of the project the bench scale set-up described in section 4.2 was upgraded to a fully automated pilot plant. One of the challenges was to design and test a relatively cheap automation system. The pilot plant included the tubular sorption electrode reactor. However, this reactor could be replaced by the flat sheet sorption electrode reactor without further adaptations.

4.4.1 Description of the pilot plant

The pilot plant consisted of a primary and a secondary stage as illustrated in Figure 4.10. The primary stage included a high-pressure water circulation loop that incorporated a 120-litre storage tank (1), a 1 micron depth filter (2), a re-circulation pump (3) and a pressure-regulating valve (4) with indicating gauge (0-4 bar) (5). The secondary stage comprised flow-indicating rotameters (0-200$\ell \cdot h^{-1}$) (6) with flow control valves (7a) before and (7b) after the electro sorption filter reactor (8). Both valves (7a and 7b) were used to regulate the ratio of permeate/reject and the pressure difference over the electro sorption filter. The pH and conductivity of the permeate flow was measured via an in-line pH probe (9) and an in-line conductivity probe (10) respectively. Both probes were connected to a corresponding meter, which were connected to a controlling computer (11). The computer activated a solenoid valve (12) downstream from the permeate line that lead the outflow of the permeate to a storage vessel containing purified or wastewater. Another solenoid valve (13) directed the reject either back into the reservoir or to waste. Simultaneously, the computer regulated the polarity of a potentiostat (0-24V DC, 0-5A) (14) that supplied the current to the electro sorption units.

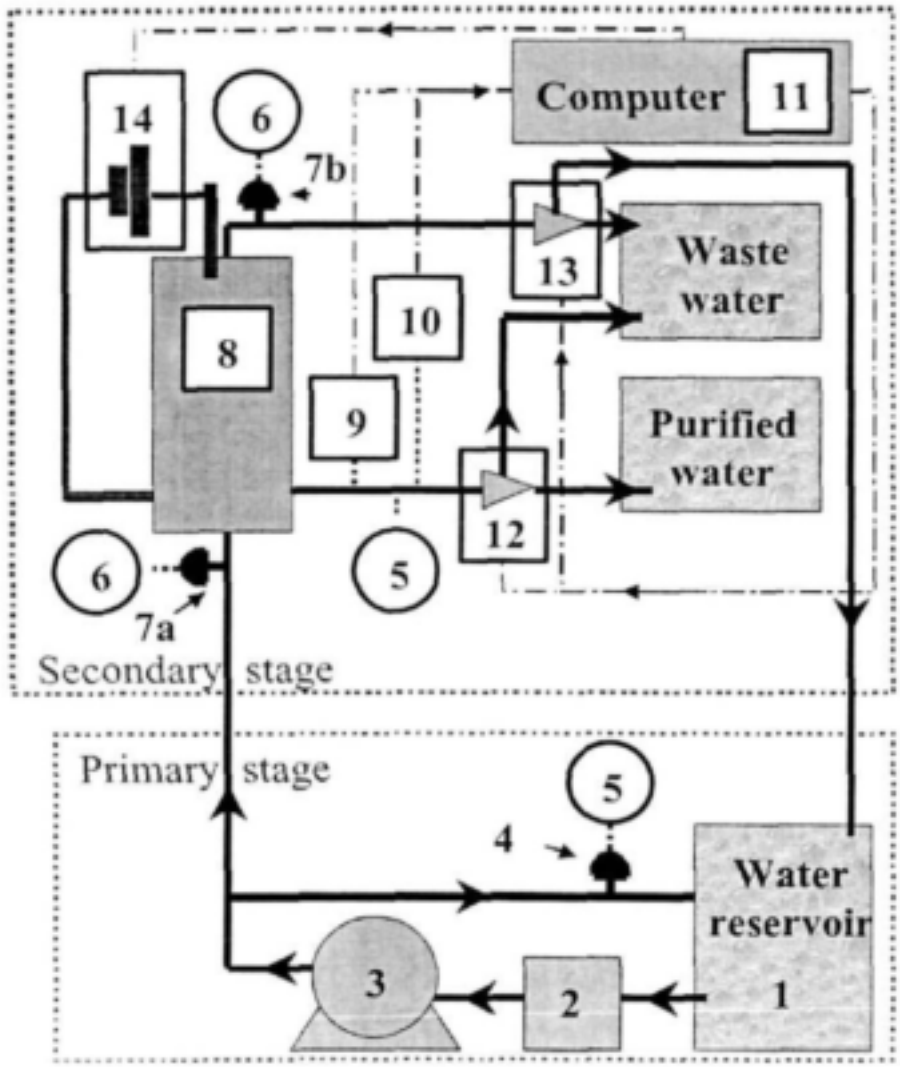

Figure 4.10. Schematic drawing of pilot plant for electro sorption

The design of the high-pressure water circulation loop in the primary stage allowed the supply to the secondary stage of any desired flow rate (between 0 and 200 l· h^{-1}) at an independent pressure, with a maximum of 4 bar. During long term fouling tests constant independent pressure was necessary to obtain accurate permeability results.

4.4.2 Automation

The automated water purification pilot plant could be divided into an analytical and a controlling system. The function of the analytical system was to measure the quality of the water and to detect

abnormalities or unsafe situations. The function of the controlling system was to respond dynamically, based on the information of the analytical system. It was of importance that the analytical system provided sufficient information to the controlling system to realize the desired separation of good and bad quality water.

4.4.2.1 Analytical system

The concentrations of different ions can be measured using a variety of ion-selective electrodes. Unfortunately, such electrodes are relatively expensive and many different electrodes are required to obtain a complete analysis of the water quality. Less expensive analytical tools are required for an economically feasible system. The conductivity of a solution may give an indication of its salt content and measuring devices are relatively cheap. However, it should be investigated how the conductivity of a solution is influenced by the presence of highly mobile ions, such as protons and hydroxyl ions. The concentrations of these ions are likely to vary during a desalination process based on electro sorption.

Figure 4.11 shows the conductivity of a 0.005M Na_2SO_4 solution as a function of the pH. Conductivity was calculated via the law of independent migration of ions [3, p 822], which says that the conductivity can be expressed as the sum of contributions from the individual ions. The following formula was used [3]:

$$\kappa = c \cdot \Lambda_m^0 = \left(c(\nu_{Na^+} \lambda_{Na^+}^0 + \nu_{SO_4^{2-}} \lambda_{SO_4^{2-}}^0) + 10^{-pH}(\lambda_{H^+}^0 + \tfrac{1}{2}\lambda_{SO_4^{2-}}^0) + 10^{(14-pH)}(\lambda_{OH^-}^0 + \lambda_{Na^+}^0) \right) \qquad (4.1)$$

where:

Λ_m	molar conductivity (mS· cm^{-1})
c	concentration of Na_2SO_4 (mol· l^{-1})
δ	moles of ions to form 1 mol of salt
λ_i	ionic conductivity of ion i (see Table 3.3) (Ohm^{-1} cm^2 mol^{-1})
10^{-pH}	concentration of protons (= counter anions) in solution (mol· l^{-1})
$10^{(14-pH)}$	concentration of hydroxyl ions (= counter cations) in solution (mol· l^{-1})

This formula shows that the influence of pH on the conductivity of the Na_2SO_4 solution is only considerable at values lower than 4 or higher than 10. The desired pH of the permeate is between pH 5 and 9, in which range the conductivity change is less than 1%. This means that measurement of the conductivity may give a suitable indication of the salt concentration.

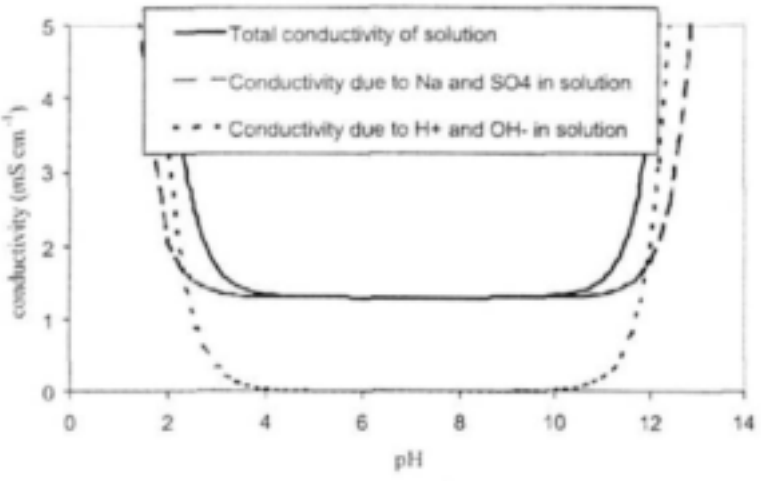

Figure 4.11. Calculated conductivity of 0.005M Na_2SO_4 solutions with additional H_2SO_4 or NaOH to adjust pH

Due to different affinities of each ion in solution towards the sorption material, the rate of ion removal will differ for each ion. To predict the conductivity of the solution when ions are not adsorbed to the same extent the ionic conductivities of some common ions were examined. The values of ionic conductivities for some ionic species are presented in Table 4.3

Table 4.3 Ion conductivities at infinite dilution and 25°C

Ion	Ionic conductivity (Ohm^{-1} cm^2 mol^{-1})	Equivalent conductance (Ohm^{-1} cm^2 $equivalent^{-1}$)
H^+	349.8	349.8
OH^-	197.6	197.6
Na^+	50.11	50.11
Mg^{2+}	106.12	53.06
Ca^{2+}	119.00	59.5
Cl^-	76.34	76.34
SO_4^{-2}	159.6	79.8

Table 4.3 shows that the difference of the equivalent conductance between Na^+, Mg^{2+} and Ca^{2+} (50.1, 53.1 and 59.5) is less than 20%. The difference between Cl^- and SO_4^{2-} is less than 5%. This means that the total decrease of ion conductivity can directly be used to determine the total ion

removal even when the ions are adsorbed at different rates. During desalination, the system could thus be sustained without pH measurements. However, the pH is an important quality parameter of pure water and acceptably pure water should have a pH value of between pH 5.5 and 8. It was therefore decided that both the pH and conductivity of a treated solution was necessary to supply sufficient information to the controlling system.

4.4.2.2 Controlling system

The controlling system comprised a pH meter, a conductivity meter, three relays (220V AC/24V DC), two solenoid valves, a level switch, and a computer. The computer was equipped with a data acquisition package (BORWIN 2.1). The conductivity meter, pH meter and two of the three relays were connected with the BORWIN A/D board in the computer. The BORWIN software could be configured such that the two relays were activated based on individual or combined signal output values. The programming of the Input/Output commands in the BORWIN software will be discussed in the subsequent section. The first relay controlled two solenoid valves. These valves directed the flow of permeate and reject as described in section 0. The second relay controlled the polarity of the power source. The power supply to the re-circulation pump was controlled by a third relay. This relay was energized via the 24V DC output from the potentiostat and switched off via a level switch situated in the storage tank when the water level dropped below a safe level. This safety mechanism was important, as the Pro-Con pump head fitted to the system could not operate without water circulating through it.

4.4.2.3 Programming

The BORWIN software should be programmed in such a way that relays were switched in the correct position at any time to ensure that high and low quality water were separated and that regeneration or desalination started when the electro sorption unit was saturated or regenerated respectively.

First, the quality of water had to be determined as a function of pH and conductivity. In Figure 4.12 an example is given where the quality of purified water met the following requirements as indicated by area I:

- The pH of this water had to be between A and B
- The conductivity had to be less than x% of the feed water conductivity

The water within area 1 answered these requirements. During regeneration the quality of water had to meet different requirements as indicated by area II:

- The pH of this water had to be between C and D
- The conductivity had to be less than (1+y) * feed water conductivity. The extra y% was necessary since a theoretically 100% regeneration may only be reached at infinite time.

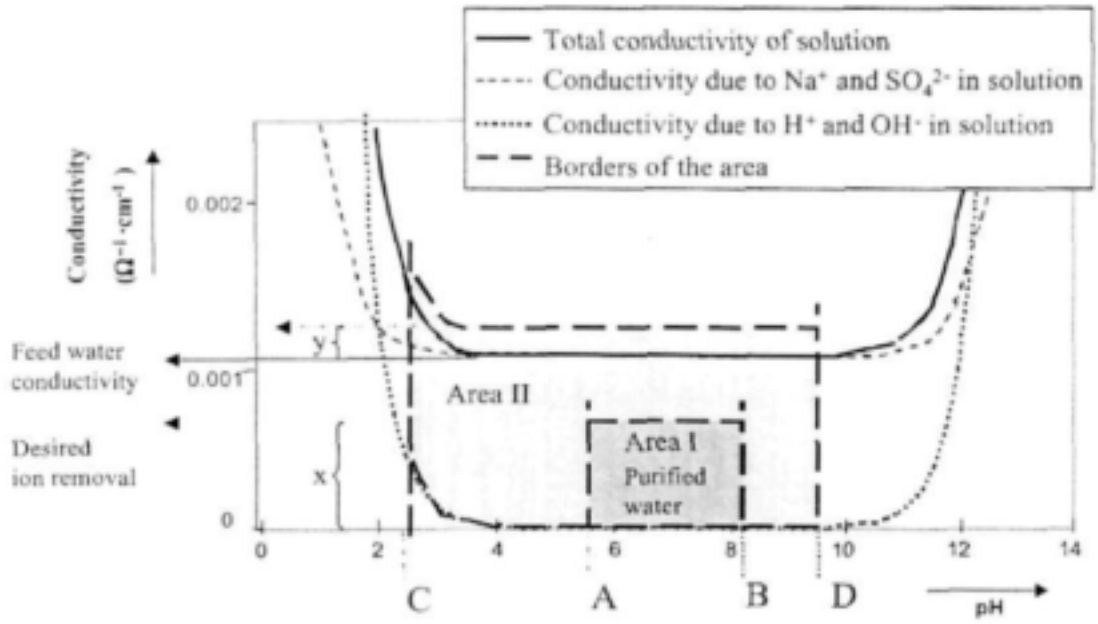

Figure 4.12. pH and conductivity areas for automation of pilot plant control system

For the permeate, the requirements from Figure 4.12 could be translated to the following logic operations:

1. IF pH < 8 AND pH > 5.5 AND CONDUCTIVITY < X* conductivity feed THEN relay 1=ON (permeate would be directed to purified water tank) and relay 2=ON (polarity of sorption electrode stayed or switched to cathode)
2. If relay 2=ON (during desalination) AND (pH > 8 OR pH < 5.5 OR CONDUCTIVITY > X* conductivity feed) THEN relay 1=OFF (permeate would be directed to waste water) and relay 2=off (polarity of sorption electrode switched to anode, regeneration would start)
3. IF relay 2=OFF (during regeneration) AND (CONDUCTIVITY <1.1*conductivity feed OR CONDUCTIVITY < 1.1* (10^{pH} *calculated ionic conductivity of solution)) THEN relay 2=ON_time (20)

Operation 3 allowed the regeneration to stop for 20 seconds (change of polarity) in a situation where the conductivity was dominated by protons. This meant that the electrode could be totally regenerated but the conductivity remained far above the conductivity of the feed because of the low pH value. The pH was likely to be low since the sorption electrode acted as anode during regeneration. Since the feed was a mixture of ions, formula 4.1 needed to be slightly modified to calculate the ion conductivity of the solution:

$$\kappa = \left(\sum_{x=1}^{s} c_x \nu_x \lambda_x^0 + \sum_{y=1}^{r} c_y \nu_y \lambda_y^0 + 10^{-pH} (\lambda_{H^+}^0 + \lambda_{\overline{anion}}^0) \right) \qquad (4.2)$$

where: Λ_m^0 molar conductivity at infinite dilution

Λ anion to form 1 mol of salt

$\lambda_{x \text{ or } y}$ ionic conductivity of cation x or anion y (see Table 3.3)

s,r number of cation and anions respectively

$\lambda_{\overline{anion}}^0$ average anion conductivity at infinite dilution

The relation between the molar conductivity at infinite dilution (Λ_m^0) and the molar conductivity (Λ_m) is given by the Kohlrausch equation:

$$\Lambda_m^0 = \Lambda_m - K\sqrt{c} \qquad (4.3)$$

where c concentration

K Kohlrausch constant

The majority of the ions in the feed solution are strong electrolytes (ionophores). Strong electrolytes show low Kohlrausch constants. However the assumption made in equation 4.1 and 4.2 that $\Lambda_m^0 \approx \Lambda_m$ introduces an error of 10-30% for concentrations of 0.01M NaCl and Na_2SO_4 [4]. Higher accuracy might be expected at lower concentrations.

4.4.3 Experimental

4.4.3.1 Programming

A detailed list of instructions for the operator of the pilot plant is given in Appendix C. The programming of the logic (logic operations described in section 4.3.2.3) was entered in BORWIN's software and is also included in Appendix C.

4.4.3.2 Testing

Three solutions with suitable pH and three solutions with suitable conductivity were used to simulate different "imaginary" permeate solutions and to test the functioning of the logic. The details of the solutions are listed in Table 4.4. The combination of data collected from the pH probes placed in solution 1-3 and conductivity probes placed in solutions 4-6 could be used to simulate different water qualities. The logic of the BORWIN software was confirmed by the response of the solenoid valve and the polarity relay.

Table 4.4. Details of the solutions used for testing the pilot plant programmed logic.

Solution	pH	Conductivity ($mS \cdot cm^{-1}$)	Comment
1	7	-	pH calibration solution
2	4	-	pH calibration solution
3	10	-	pH calibration solution
4	-	0	Ultra pure water
5	-	0.144	Calibration solution 0.001 KCl
6	-	0.714	0.005 KCl

4.4.4 Results and discussion

Table 4.4 displays the observed response of the solenoid valve and polarity relay as a reaction to the measured pH and conductivity. Unfortunately technical problems with BORWIN software prevented the combination of the pH and conductivity data. The problem was that the program could not detect both pH and conductivity simultaneously. However, a meaningful response could still be generated by entering the values of pH after measurement manually before running the program for conductivity detection. The results are shown in Table 4.5. The imaginary feed concentration was set at $0.7 mS \cdot cm^{-1}$, X at 0.5 and Y at 1.1. This simple test shows that the instructions to each relay were correct based upon the measured pH and conductivity. The results indicate that the logic is suitable to automate the pilot plant.

Table 4.5 Response of the solenoid valve and polarity relay as a function of pH and conductivity values.

Combination of solutions	pH	Conductivity (mS cm^{-1})	Quality *	Observed action		Remark
				Solen.1	Polarity	
1+4	7.0	0	I	ON	ON	Correct action
3+4	10	0	III	OFF	OFF	Correct action
1+6	7.1	0.715	II	OFF	ON	Correct action
1+5	7.0	0.140	I	ON	ON	Correct action
2+6	4.0	0.717	III	OFF	OFF	Correct action
2+4	4.0	0	II	ON	OFF	Correct action

* Quality I and II see section 6.2.3, Quality III is outside area II

4.4.5 Conclusions

An automation program was developed that in principle has the potential to automate the electro sorption pilot plant. Based on predetermined conditions of pH and conductivity of permeating water, regeneration, electro sorption and flow direction could be controlled.

4.5 References

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5 STUDY OF DESALINATION OF $CASO_4$ BY MEANS OF TUBULAR ELECTRO SORPTION MODULES

Abstract

In this chapter a 0.01M $CaSO_4$ model solution was used to study the electro sorption process. Sorption experiments with solutions containing only one source of salt (such as $CaSO_4$) were necessary to understand the process of electro sorption before more complex solutions could be treated. An electro sorption process where the electrode was used in *flow through mode* had not been described before, hence was not entirely understood.

By trying to combine the filter properties of a ceramic membrane with the properties of an electro sorption electrode a fundamental difference with the conventional method of electro sorption was introduced. Instead of realizing the adsorption of anion and cations on opposing charged electrodes, adsorption of both ions had to take place on a single electrode. The first objective that had to be met was to realize simultaneous adsorption and desorption of cations and anions. In section 5.2, it is described how simultaneous removal of ions was achieved. In section 5.3, the sorption electrode was further optimised.

5.1 Introduction

In this section the effect of carbon, gold, ZrO_2 and phosphoric acid treatment of the ZrO_2 on the sorption characteristics was investigated. Several differently modified sorption electrodes were prepared and tested via an electro sorption experiment.

5.2 *The development of a ZrP gradient in the sorption electrode for the removal of $CaSO_4$*

5.2.1 Experimental

5.2.1.1 Preparation of the sorption electrodes

Porous Al_2O_3 ceramic tubes type 1 (see chapter 2.3 for support characteristics) were used as support for preparing the sorption electrodes. The differences in the preparation conditions are given in Table 5.1.

Table 5.1 Description of differently modified sorption electrodes

Electrode type	Description of modification
1	Carbonised
2	Carbonised and impregnated with ZrO_2
3	Carbonised and impregnated with ZrO_2. Finally treated with H_3PO_4
4	Gold sputter-coated
5	Gold sputter-coated and impregnation with ZrO_2
6	Gold sputter-coated and impregnation with ZrO_2. Finally treated with H_3PO_4
7	Carbonised, gold sputter-coated and impregnation with ZrO_2. Finally only the outside of the electrode was treated with H_3PO_4

The carbonising process was performed at 900°C for 30 minutes over a flow of 50ml· min^{-1} LPG as described in section 2.1. The gold sputtering was carried out as in section 2.1, impregnated with commercial ZrO_2 sol (20% w/w), heat treated at 200°C for 1 hour (section 2.3), and then phosphorized with 15% H_3PO_4 as described in section 2.3.

Electrode type 7 was prepared by immersing a ZrO_2-impregnated support in phosphoric acid. The support was sealed at both ends to prevent acid entering the lumen side. The ZrO_2 on the outside side of the support was hence exposed to a higher concentration of phosphoric acid for a longer period than the ZrO_2 at the lumen side of the support. This resulted in a sorption electrode that had a higher fraction of phosphorized ZrO_2 on the outside than on the lumen side.

5.2.1.2 Measurement of ion adsorption and desorption properties

After the pyrolytic carbon deposition, the gold coatings and/or the partial phosphorization of the impregnated ZrO_2 sol, the sorption electrode was placed in the single tube reactor (Figure 4.3). The reactor was connected as illustrated in Figure 4.2. A model solution of 0.01M $CaSO_4$ was used to determine the electro sorption efficiency of the electro sorption electrode. Ion concentrations in the reject and permeate were measured as a function of time and a potential difference applied between the sorption and counter electrode. Initially the sorption electrode was used as a cathode, with a 5 V difference between the sorption and the counter electrode. The flow rate of permeate was regulated by the pressure difference over the lumen and inside of the sorption electrode. The flow rate of the

reject was set to be 30-60 l· h^{-1}· m^{-2}. Samples of permeate and reject were collected continuously, in 10-20ml aliquots. After collecting two, three or four samples, the sorption electrode was changed to operate as an anode by switching the polarity of the power source. New sets of samples of permeate and reject were then collected. The potential of the sorption electrode could then be switched back again to operate as a cathode.

5.2.1.3 Characterization methods

The permeability of the sorption electrode was measured before and after carbonisation, impregnation with ZrO_2, and modification with phosphoric acid, using the dead-end method [7]. The value of the *real conductivity* (in cm^{-1}· Ω^{-1}) of the sorption electrode could not be determined since the exact area through which the current applies, was not known. In order to determine to what extent the sorption electrodes conducted electricity, conductivity was calculated as the inverse of the resistance· cm^{-1} (cm· Ω^{-1}). The resistance was measured over a distance of 5cm, using a Fluke 73 multimeter. Sulphate concentrations in the samples were determined using a Bischoff IONCHEM 2000 ion chromatograph with a Hamilton PRP-X100 anion exchange column. The concentration of calcium was determined with a Philips PU9100 atomic adsorption spectrophotometer.

5.2.2 Results and discussion

5.2.2.1 The electro sorption electrode

The effects of carbonisation, gold sputtering, ZrO_2 impregnation and treatment with phosphoric acid on the permeability and the conductivity of the electro sorption electrode are listed in Table 5.2. The values tabulated are the average values of three experiments. A 20% decrease in permeability was observed due to the deposition of carbon inside the pores of the alumina. The conductivity increased to 0.5 cm· Ω^{-1}. Longer carbonisation times led to higher conductivity and a decrease in permeability, as reported in chapter 2.

Table 5.2. The effect of different modifications of ceramic tubes on their permeability and conductivity

Modification	Duration (h)	Permeability ($m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$)	Conductivity ($cm \cdot \Omega^{-1}$)	Weight (g)
None		3	$<10^{-7}$	12.0
Carbonising	0.5	2.2	0.5	12.1
Gold sputtering	2*0.16	2.3	3	12.102
ZrO_2 impregnation	24	0.2	3	12.5
ZrO_2 + Phosphoric acid	4	0.04	3	12.7
ZrO_2 + Phosphoric acid	12	0.01	3	12.7

The conductivity of a sorption electrode of 10 cm should be at least 2 $cm \cdot Ohm^{-1}$ to remain within necessary limits. Assuming that the acceptable limit was 10%, the ceramic substrate should then be carbonised for about 2 hours to reach sufficient conductivity. The permeability decrease was expected to be more than 90% (see chapter 2)].

After gold sputtering, the conductivity increased to 3 $cm \cdot \Omega^{-1}$ while permeability remained unchanged. A slight increase in permeability was frequently seen, possibly because gold covered some part of the hydrophobic organic surfaces (formed by the incomplete pyrolysis of LPG). The small amount of gold deposited on the substrate was determined by the weight increase during sputtering.

After impregnation with ZrO_2 the permeability decreased by about 90%, with no effect on the conductivity. A second impregnation resulted in a similar decrease in permeability. The treatment with phosphoric acid resulted in a decrease in permeability of between 90 and 100%, depending upon the reaction time of the acid with the ZrO_2.

5.2.2.2 Ion adsorption and desorption results

The sorption characteristics (similar to those performed in section 2.3) of all the different types of sorption electrodes were examined and the results summarized in Table 5.3.

Table 5.3. *The effect of different modifications on sorption properties of the ceramic supports*

Type[1]	Flow rate ($l \cdot h^{-1} \cdot m^{-2}$)	C_p/C_f[2] (c) (%)		C_p/C_f[3] (a) (%)		Removal Efficiency (%)		Regeneration ability
		Ca^{2+}	SO_4^{2-}	Ca^{2+}	SO_4^{2-}	Ca^{2+}	SO_4^{2-}	
1	50	110	85	90	121	10 (a)	15 (c)	Yes
2	30	113	36	43	27	57 (a)	73 (a)	No
3	1	-	-	6	53	94 (a)	-	No
4	70	107	88	93	120	7 (a)	12 (c)	Yes
5	50	150	48	97	54	3 (a)	52 (c)	No
6	30	85	88	11	126	89 (a)	12 (c)	No
7	30	7	31	148	191	**93 (c)**	**69 (c)**	**Yes**

1 details of the ceramic support are listed in Table 2.1

2 C_p/C_f (c); the concentration of ions in the permeate of a cathodic sorption electrode as a percentage of the concentration of ions in the feed stream ($1.4 g \cdot l^{-1}$ $CaSO_4$)

3 C_p/C_f (a); the concentration of ions in the permeate of an anodic sorption electrode as a percentage of the concentration of ions in the feed stream ($1.4 g \cdot l^{-1}$ $CaSO_4$)

(a) Sorption electrode is used as anode

(c) Sorption electrode is used as cathode

The concentrations of ions in the permeate (C_p) are presented as percentages of the concentration of those ions in the feed stream (C_f). A distinction is made between the permeate samples collected at an anodic sorption electrode, and samples collected at a cathodic sorption electrode. For all types of sorption electrodes, measurements of the cation and anion concentrations in the reject were usually: C_r/C_f 110-130% for Ca^{2+} and 70-90% for SO_4^{2-} with a cathode as counter electrode and C_r/C_f 70-90% for Ca^{2+} and 110-130% for SO_4^{2-} with an anode as counter electrode. The electrode types with similar results are grouped together for discussion.

Sorption electrode types 2, 3, 5 and 6

A decrease of > 70% SO_4^{2-}concentration in the permeate was obtained after the support was impregnated with ZrO_2. Treatment of the ZrO_2-impregnated electrode with phosphoric acid (sorption electrode types 3 and 6) resulted in a > 90% decrease in Ca^{2+} concentration. Hence, the preferred anion-exchange property of ZrO_2 and the preferred cation exchange property of $Zr(H_2PO_4$

were demonstrated clearly. Since ions adsorbed irrespective of the potential of the sorption electrode, regeneration was not possible.

Sorption electrode types 1 and 4

The result obtained with electrodes 1 and 4, which were not impregnated with ion exchange material, prove the presence of another ion separating mechanism besides adsorption and desorption of ions onto activated ion exchange sites. The concentration increase of cations and decrease of anions in the permeate for the cathodic sorption electrode and visa versa for the anodic sorption electrode may be caused by the electrolysis of water. In order to maintain electro-neutrality of the solution, a nett cation flux towards the cathode and a nett anion flux to the anode were generated [9]. This mechanism will be explained in more detail in chapter 6.

Sorption electrode type 7

The simultaneous adsorption of calcium and sulphate (93 and 69%, respectively) was achieved on a cathodic sorption electrode that was carbonised, sputter-coated with gold and, after impregnation with ZrO_2, treated with phosphoric acid from the outside only. Switching the electrode to the opposite potential allowed desorption of both adsorbed cations and anions, and thus an increase of Cp/Cf over 100% (the concentration of cations and anions in the permeate became higher than the concentration of those ions in the feed, 148% for Ca^{2+} and 191% for SO_4^{2-}). The percentage increase of Ca^{2+} and SO_4^{2-} concentration in the permeate with regard to the feed solution as a function of the electrode potential and time, are shown in Figure 5.1. The flow rate was 30 ($l \cdot h^{-1} \cdot m^{-2}$) and the concentration of the feed solution was 1.4g$\cdot l^{-1}$ $CaSO_4$.

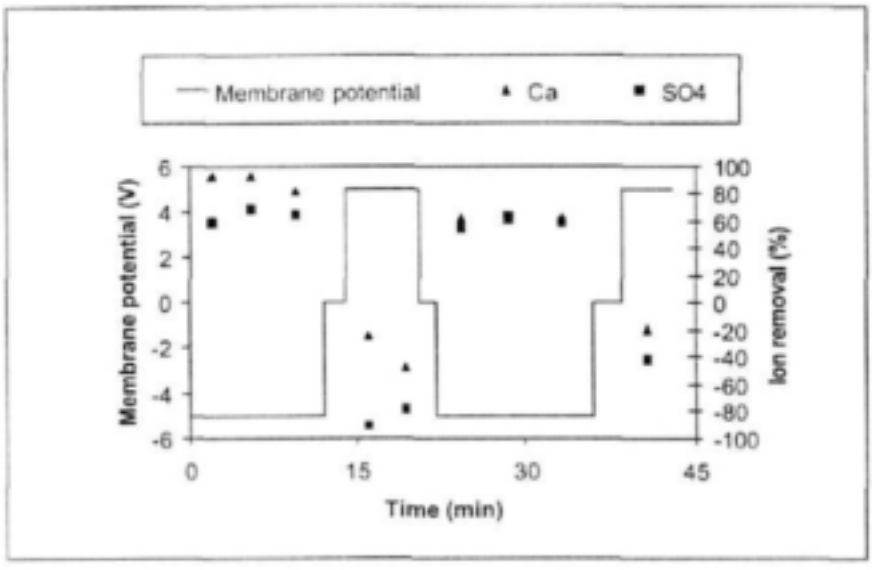

Figure 5.1. Rates of Ca^{2+} and SO_4^{2-} removal in the permeate as a function of sorption electrode potential and time. Flux 30 ($l \cdot h^{-1} \cdot m^{-2}$), Feed solution 1.4g

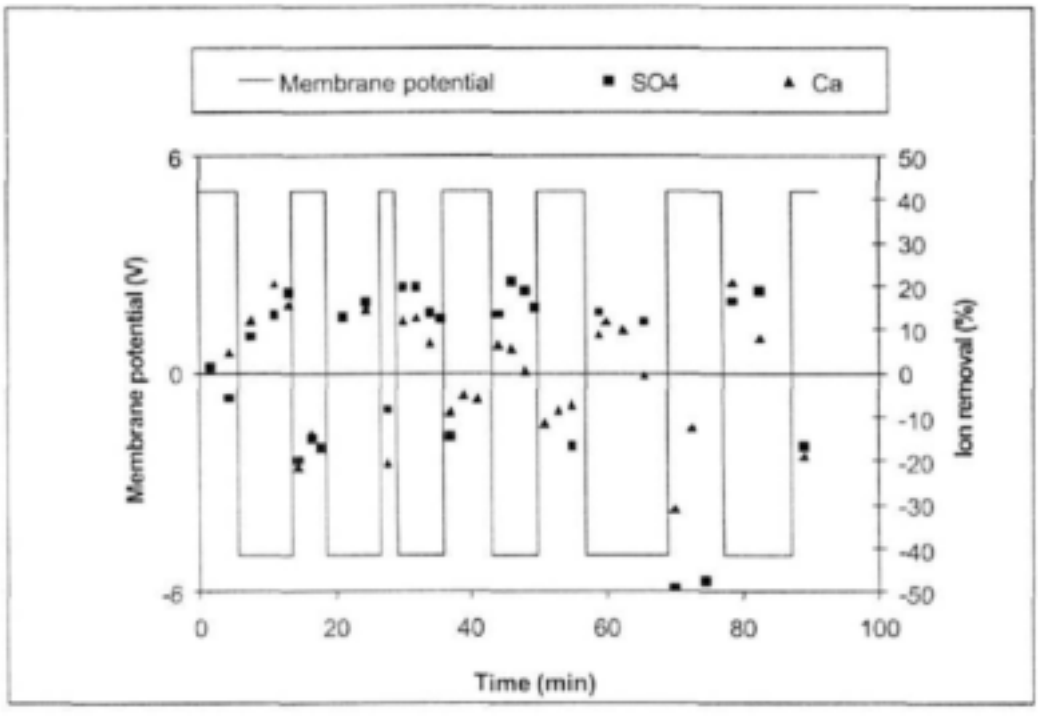

Figure 5.2. Rates of Ca^{2+} and SO_4^{2-} removal in the permeate as a function of sorption electrode potential and time. Flux 150 ($l \cdot h^{-1} \cdot m^{-2}$), Feed solution 1.4g $\cdot l^{-1}$

Figure 5.2 describes a similar electro sorption experiment but operated at a faster flow rate of 150 l· h^{-1}· m^{-2}. The adsorption and desorption efficiencies for Ca^{2+} and SO_4^{2-} were reduced significantly, but the adsorption and desorption characteristics showed the same trend. Moreover, the adsorption and desorption efficiencies remained unchanged for several cycles indicating the potential of the tubular sorption electrode as desalination system.

5.2.2.3 ZrP gradient hypothesis

A schematic representation of electro sorption without and with a phosphate gradient is given in Figure 5.3.

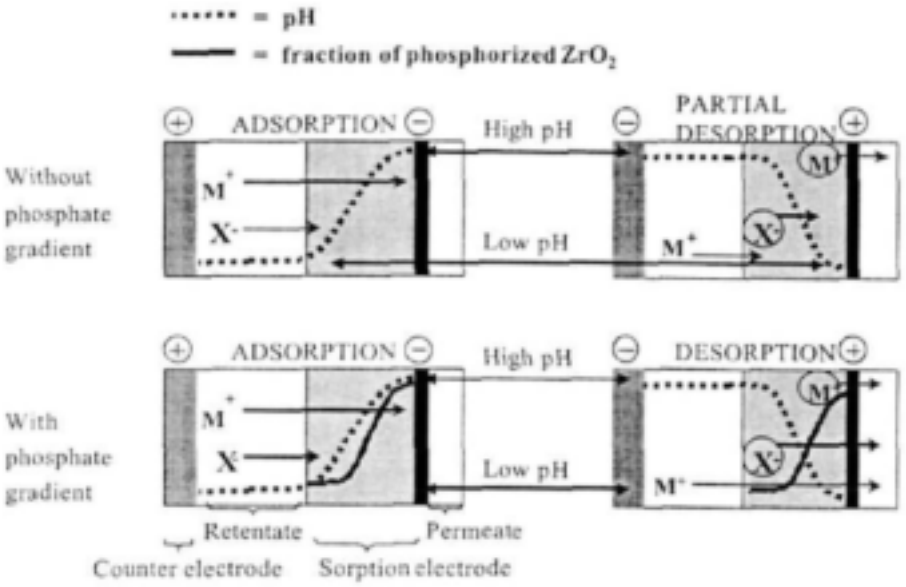

Figure 5.3 Schematic representation of electro sorption with and without phosphate gradient based on the pH gradient over a sorption electrode in a flow through system.

The results obtained without and with a phosphate gradient can be explained based upon the interaction of the pH gradient with the fraction of phosphorized ZrO_2. The pH gradient necessary to bridge the pH difference between the anode and the cathode divided the membrane into two regions; one region with high pH (alkaline) and one region with low pH (acidic). In the alkaline region, cations adsorb onto the activated cation exchange sites (negatively charged ZrP groups). In the acidic region of the sorption electrode, anions adsorb at the positively charged ZrO^+ groups. When the potential of the electrodes was reversed, the pH gradient was also reversed (H^+ and OH^- production start at opposite electrodes). The adsorbed anions then start to desorb and permeate further through the membrane towards the region that just became acidic. If this region of the

electrode does contain unreacted ZrO_2, the anions will adsorb again (see electrode without phosphate gradient, Figure 5.3). If this region of the electrode contains only ZrP, the anions will not adsorb but leave the electrode (see electrode with phosphate gradient, Figure 5.3). The cations in the alkaline part of the electrode can only adsorb at activated ZrP sites. These sites are not present in the electrode with the phosphate gradient. Cations in the acidic part of the membrane will desorb and leave the electrode in the direction of the permeating flow.

The results recorded for the electro sorption electrode were in agreement with the theory described above. The simultaneous adsorption of Ca^{2+} and SO_4^{2-}, up to 60%, was found when the sorption electrode was used as a cathode. Simultaneous desorption was achieved when the sorption electrode was changed to an anode by changing the polarity. Figure 5.2 shows the electro sorption results of a similar electrode at a higher flow rate than the experiment described in Figure 5.1. The adsorption efficiencies for Ca^{2+} and SO_4^{2-} did not exceed 30%, but the adsorption and desorption characteristics showed the same pattern. Figure 5.2 also shows that adsorption and desorption efficiencies remained unchanged for several cycles.

5.3 Conclusions

Electrochemically-activated ceramic-based electro sorption electrodes were prepared and tested, and the following conclusions made:

- 70% of 960 mg·l^{-1} sulphate ions could be adsorbed via electrochemical-activated electro sorption onto carbonised porous ceramic substrates that were impregnated with ZrO_2.
- 90% of 400 mg·l^{-1} calcium ions could be adsorbed via electrochemical-activated electro sorption onto carbonised porous ceramic substrates that were impregnated with ZrO_2 and treated with phosphoric acid.
- The simultaneous adsorption of Ca^{2+} and SO_4^{2-} (93 and 69%, respectively) from a 1.4 g·l^{-1} $CaSO_4$ solution was achieved using tubular sorption electrodes. The simultaneous desorption of Ca^{2+} and SO_4^{2-} was detected after switching the sorption electrode to an anode. A gradient of phosphorized ZrO_2 over the cross sectional diameter of the tube appeared to be essential.
- Adsorption and desorption efficiencies remained unchanged for several cycles.

6 OPTIMIZATION OF THE ELECTRO SORPTION PROCESS AND THE ELECTRODE PRODUCTION PROCEDURE FOR TUBULAR MEMBRANES

Abstract

Optimisation of the electrode preparation and the process conditions for electro sorption are described. ZrO_2 impregnated alumina supports, phosphorized for 4 hours produced electrodes that showed similar cation and anion removal. The optimised flux and potential to obtain minimal energy consumption and good regeneration characteristics was 0.5 $m^3 \cdot h^{-1} \cdot m^2$ and 4V respectively. The optimised energy consumption for desalination was 8kWh $\cdot kg^{-1}$. It was calculated that roughly 25% of the protons and hydroxyl ions generated were effectively involved in the activation of sorption material which indicate significant loss of energy. In an electro sorption system operated in flow through mode combining filtration and desalination, significant energy losses are difficult to avoid. The deposition of platinum on the electro sorption membrane did not lower the energy consumption.

6.1 Introduction

It was shown in section 5.2 that a radial phosphate gradient in the tubular sorption electrode enabled simultaneous removal of cations and anions and that simultaneous release of those ions was observed when reversed polarity was applied. Hereby the desired functionality of the electro sorption system was achieved. Subsequently the electro sorption process had to be optimised. The main goal here was to increase the cost efficiency of the process and minimize fouling during operation. By investigating the effect of variables such as permeation rate, permeate / reject ratio, electrode potential and current density on the electro sorption behaviour, the process could be better understood. At the end of this chapter a standardized preparation method is given which aims for the production of consistent electro sorption electrodes with optimal energy efficiencies and fouling resistance.

6.2 Experimental

In order to optimise process parameters, different electrodes were prepared and tested under a variety of conditions. One parameter was changed at a time in order to investigate its effect on the total process. During all the experiments a standard solution of 0.01M $CaSO_4$ was used as the feed solution.

6.2.1 Electrode preparation

The electro sorption electrodes used during the optimisation experiments were prepared in four sequential steps unless specified differently. The individual steps were executed as described in the corresponding chapters. Step 1 and 2 in chapter 2, step 3 in chapter 4 and step 4 in chapter 7.

In step 1, Al_2O_3 supports type I and II (see chapter 2.3 for support characteristics) were carbon coated via pyrolytic decomposition of liquid petroleum gas (LPG) at 900°C. The LPG flow was set to 50ml· min^{-1} and was flowed over the support for 30 and 60 minutes. The carbonised supports were gold sputtered in step 2. In step 3, the carbonised and gold-coated supports were impregnated with commercial available ZrO_2 sol (20% w/w particles) and heat-treated at 200°C for 1 hour. The impregnated supports were then plugged from both sides and submerged several times into a 15% H_3PO_4 solution to ensure adequate exposure, then rinsed with ultra pure water and heat treated at 200°C for 1 hour. The Pt deposition is described in Appendix D. In between each individual step the weight of the support was measured. Thereafter, the prepared sorption electrode was used to treat a 0.01M $CaSO_4$ model solution. Table 6.1 gives an overview of all electrodes that were prepared and tested to obtain the necessary optimisation.

Table 6.1 Differences in preparation procedures of the sorption electrode

Electrode		Preparation step and procedure parameter				Comment
No	Type	1[a] (min)	2[b]	3[c] (%w/w)	4[d] (hours)	
1	I	30	Std	1%	2	-
2	I	30	Std	1%	8	-
3	I	30	Std	1	4	-
4	II	30	Std	1%	4	-
5	II	30	Std	2%	4	-
6	I	30	Std	1%	4	Sealed membrane tip before step 1 (chapter 4.3)
7	I	30	Std	1%	4	Pt coated membrane (chapter 2.2)
8	I	60	Std	-	-	-

[a] Duration of carbonising process, [b] Std stands for standard gold sputtering procedure, [c] Number of impregnation, [d] Phosphorization time

6.2.2 Electro sorption process

The majority of the experiments were performed with the second reactor design (Figure 5.3) in set-up 2 (see chapter 5). A modified version of the third and more advanced reactor system (as detailed in Figure 5.4, but with just one electrode instead of six) was used to investigate the functionality of the conductive O-ring. The tip of the electrode used in this reactor was modified with Na-Silicate as described in chapter 4.3 before carbonisation was performed. Table 6.2 shows all the different parameters that were varied during a series of sorption experiments. Either the potential difference or the current density could be independently varied.

Table 6.2 Different sets of experimental parameters chosen during the optimisation of sorption experiments

Experimental Set Number	Potential difference (V)	Flow rate Permeate ($ml \cdot min^{-1}$)	Ratio Permeate/reject (%)	Current Density ($mA \cdot cm^{-2}$)
1	5	2	10	-
2	5	2	0.5	-
3	4	2	0.5	-
4	3	2	0.5	-
5	5	0.5	0.5	-
6	5	4	0.5	-
7	-	2	0.5	100

6.3 Results and discussion

The complete details of analytical data obtained using the experimental parameters described in this chapter are presented in Appendix E. Unfortunately, the obtained data for many experiments did not show a predictably stable pattern. Figure 6.1 shows the results of three identically performed preparations and electro sorption tests. The fluctuations observed were significant.

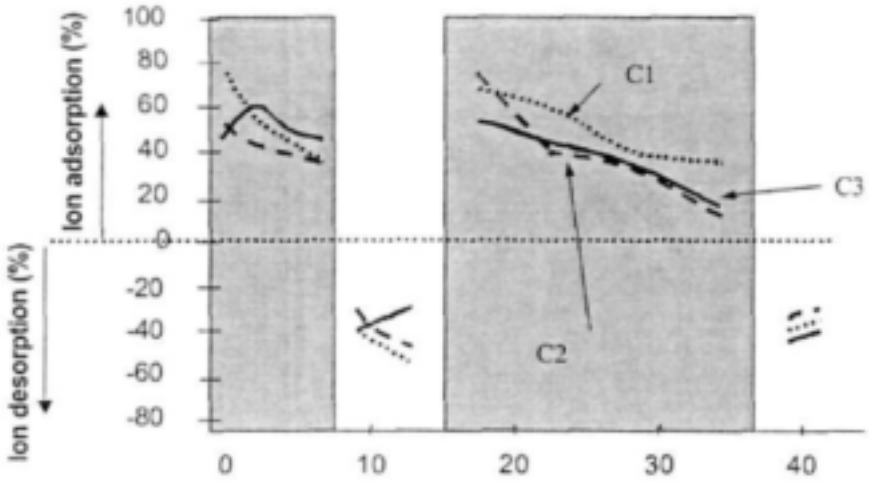

Figure 6.1. Adsorption/desorption characteristics for Ca^{+2} as function of time for three similarly prepared electro sorption electrodes under replicated conditions C1, C2, and C3

In order to make well-founded conclusions each optimisation experiments should be reproduced several times. Considering the amount of work each experiment required, this was not found to be practical. It was decided to concentrate on the general trends observed during the experiments, since those were similar as can be seen in Table 6.3. The tabulated results (Table 6.4 - Table 6.8) discussed in this chapter summarize these trends.

Table 6.3 Replication studies of electro sorption experiments

Exp. No	Electrode No	Set [a] No	Average adsorption/desorption (%) SO_4^{-2}	Ca^{+2}	E [b] (kWh· kg^{-1})
C1	3	2	55/31	55/42	10
C2	3	2	45/43	40/42	15
C3	3	2	51/33	45/39	13

[a] Experimental parameter set listed in Table 6.2

[b] Energy consumption during adsorption cycle

Upon consideration there appeared to be two main reasons for the electro sorption experiments to be rather unpredictable, as:

A) The preparation of the electrode was not completely reproducible. During a replicated carbonisation process of two different Al_2O_3 supports, the deviation in the weight increase of the two carbonised supports was usually between 0 and 20%, sometimes even more. Fluctuations in the amount of carbon deposited resulted in fluctuations in the amount of ZrO_2 impregnated and thus also in different permeability. An explanation for the differences in the amount of carbon deposition is difficult to offer without further studies. The intrinsic differences between the different supports have been mentioned in chapter 2 as a possible reason. Fluctuations in the gas flow were observed. Use of a mass flow controller instead of a flow indicator may add to the reproducibility of the carbonisation process. The amount of ZrO_2 that could be impregnated in the following step is dependent upon the amount of carbon that was deposited. Differences in permeability observed after impregnation with ZrO_2 most likely had an important effect upon the penetration depth of phosphoric acid resulting in a variable degree of phosphorization and hence, a fluctuation in the phosphate gradient. This will directly influence the adsorption/desorption characteristics of the electrode. The lack of reproducibility in membrane preparation was the main reason why the performance of the multiple tube membrane reactor was not tested. Such a reactor may only work efficiently if the properties of the membranes were more or less similar, especially the permeability.

Table 6.4 Weight and weight increase during the preparation of sorption electrodes

Support	Weight (g)	Weight increase (g)		
	Initially	Carbonised	Impregnated with ZrO_2	Phosphorized
1	11,90	0,1012	0,3687	0,166
2	11,89	0,0882	0,4187	0,193
3	11.47	0,1042	0,3586	0,190
4	11,69	0,1479	0,2379	0,121
5	11,45	0,0916	0,3635	0,167
6	11,55	0,1151	0,3428	0,161
7	11,80	0,1135	0,3573	0,175

B) During experiments gas bubbles formed at the electrodes due to water electrolysis that caused blockage and obstruction to flow and resulted in fluctuation of the reject flow rate. This constantly changed the residence time of the water between the sorption and the counter

electrodes, causing pH fluctuation. This may have influenced the ion exchange process and the final concentration of ions in the reject and permeate. The use of low reject flows (necessary to obtain simultaneous removal of ions see section 6.2.3) and narrow tubing (ID 0.15cm used to reduce dead volumes) increased the problems with discontinuous flow. Redesigning the reactor may reduce a part of the problem.

The tabulated results discussed in this chapter also include a value for the energy consumption (E_c). This is the energy consumption per kilogram of removed salt. The values are calculated with the following formula:

$$E_c = \frac{\sum_{s=1}^{k} (\Delta V \cdot I_s \cdot t_s)}{\sum_{s=1}^{k} \left(\left(\left(c^f_{cation} - (c_{cation})_s \right) \cdot M_{cation} + \left(c^f_{anion} - (c_{anion})_s \right) \cdot M_{anion} \right) \cdot V_s \right)} \qquad (6.1)$$

where

s	permeate sample
k	number of samples collected during sorption cycles
ΔV_s	Potential difference between sorption- and counter electrode for sample (V)
I_s	Average current withdrawn during the collection of sample (A)
t_s	total time to collect sample (seconds)
c^f	Feed concentration (mol· l^{-1})
c^f_s	Concentration of ions in sample (mol· l^{-1})
M	Molar mass (kg· mol^{-1})
V_s	Volume of sample (l)

6.3.1 Electrode preparation

The effect of the four variables that were changed during the preparation of the electro sorption electrode will be discussed separately.

6.3.1.1 The effect of phosphorization time

The summarized results in Table 6.5 show that the optimum phosphorization time of the electrode is 4 hours. A longer or a shorter phosphorization time led to undesired large differences between the amounts of cations versus anions adsorbed. Moreover, desorption rates were low which would lead to long regeneration cycles.

Table 6.5 The effect of phosphorization time upon electro sorption

Exp. No	Electrode No	Set [a] No	Step 4 [b] (hours)	Adsorption/desorption (%) SO_4^{-2}	Ca^{+2}	E [d] (kWh· kg^{-1})
A	1	2	1	65/30	25/10	8
B	2	2	12	25/15	65/20	15
C	3	2	4	55/31	55/42	10

[a] Experimental parameter set listed in Table 6.2

[b] Phosphorization time

[c] Average ion adsorption and desorption %

[d] Energy consumption during adsorption cycle

6.3.1.2 The effect of the amount of ZrO_2 impregnated onto several Al_2O_3 supports

The permeability and changes in mass before and after the different steps of the preparation procedure are shown in Table 6.6. It was observed that electrode 3 had much lower permeability than electrode 4. Electrode 5 was practically impermeable. The main difference between Al_2O_3 supports type I and II is the average pore diameter, 0.9 and 3 micrometer respectively, and their porosity. This difference may explain why support type I shows a much lower permeability after one impregnation with 20% (w/w) ZrO_2 than support type II.

Table 6.6 Permeability and change during the preparation of the electrode

Electrode No	Type	Permeability ($m^3 \cdot m^{-2} \cdot bar^{-1} \cdot h^{-1}$) / Weight increase (g) Initially	Carbonised	Impregnated. ZrO_2	Phosphorized
3	I	2.6 / 11.69	2.0 / 0.094	0.7 / 0.352	0.05 / 0.171
4	II	4.2 / 11.47	3.2 / 0.1042	1.5 / 0.3586	0.2 / 0.190

The summarized results of the sorption experiments are listed in Table 6.7 detailing the amount of ZrO_2 impregnated onto different Al_2O_3 supports. The electrodes 3 and 4 showed significant differences. The experimental results indicate that supports with larger pores may be much less efficient (at least under the set conditions). This may be ascribed to the differences in the phosphorization profile or less favourable adsorption kinetics due to the larger pores and resultant lower active surface area. Another reason could be that supports with small pores are more likely to exhibit cation exchange properties. Ceramic supports filled with ZrP previously had shown cation selective properties [1]. Moreover, the relatively high concentration of SO_4^{-2} ions in the reject (up to

38%) during electro sorption experiment 3 supports this argument. Hence, it would be harder to achieve equivalent ion selective properties of the sorption electrode when support type II is used.

Table 6.7. Effect of support type upon electro sorption

Exp.	Electrode		Set [a]	Step 3 [b]	Adsorption/desorption (%) [c]		E [d]
No	No	Type	No.	#	SO_4^{-2}	Ca^{+2}	(kWh· kg^{-1})
C	3	I	2	1	55/31	57/42	10
D	4	II	2	1	35/40	40/35	13
E	6	II	2	2	Impermeable		

[a] Experimental parameter set listed in Table 6.2

[b] Number of impregnation of commercial ZrO_2 sol (w/w 20%)

[c] Average ion adsorption and desorption rates

[d] Energy consumption during adsorption cycle

6.3.1.3 The effect of the electro conductive O-ring

As described in chapter 5, a titanium wire was used to establish the electrical contact between the power source and the sorption unit. However to upscale the reactor, an electro-conductive O-ring should be used. The summarized results in Table 6.8 proved that the electrical connection between a power source and a sorption electrode could be established via an electro conductive O-ring. The adsorption/desorption characteristics were similar to those obtained with the standard wire connection (chapter 5.1). After these results were obtained the decision was taken to continue the optimisation experiments using the reactor with the wire connection (Figure 5.3) in order to avoid the time consuming process of sealing the membrane tip.

Table 6.8. Comparison of electro conductive O-rings and standard wire connection

Exp.	Electrode	Set [a]	ΔV	Tip	Adsorption/desorption (%) [b]		E [c]
No	No	No		Sealing	SO_4^{-2}	Ca^{+2}	(kWh· kg^{-1})
F	6	8	5.0	Yes	35/30	40/25	13
G	3	8	4.2	No	40/30	45/35	9

[a] Experimental parameter set listed in Table 6.2

[b] Average ion adsorption and desorption rates

[c] Energy consumption during adsorption cycle

The results of experiments G and F are comparable. The deviations are similar to the deviations between replicated experiments C1, C2 and C3 discussed previously. As explained at the beginning of section 6.3, the deviation could be caused by several variables. However the energy consumption using conductive O-rings was expected to be slightly higher. The connection via the conductive O-ring introduced between 5 and 8 Ohm of additional resistance. When electro sorption is running at 100 mA, Ohm's law indicates a potential drop of about 0.5-0.8V, indirectly causing lower adsorption performance and thus higher energy consumption values.

6.3.1.4 The effect of dispersed Pt particles on energy consumption

In chapter 3 it was shown that the potential for water electrolysis could be greatly decreased by the addition of highly dispersed Pt particles. The results listed in Table 6.9 showed the performance of two electro sorption electrodes one with and one without Pt.

Table 6.9. The effect of dispersed Pt on the energy consumption during an electro sorption experiment

Exp. No:	Electrode No:	Set [a] No:	ΔV	Pt mg· cm^{-1}	Adsorption/desorption (%) [b] SO_4^{-2}	Ca^{+2}	E[c] (kWh· k^{g-1})
G	3	7	4.2	0	40/30	45/35	9
H	7	7	3.9	3.1	20/30	30/35	12

[a] Experimental parameter set listed in Table 6.2

[b] Average percentage of adsorption / desorption of anions and cations

[c] Energy consumption during adsorption cycle

As predicted in chapter 3, the potential difference between the sorption and the counter electrode did decrease from 4.2 to 3.9. However, the adsorption rate of ions was significantly lower, leading eventually to higher energy consumption per kg removed salt than for the electrode without Pt particles. Moreover, the decrease of 0.3V between electrodes 3 and 7 was much lower than expected based on the results obtained in chapter 3 where the electrolysis potential decreased more than one volt. These unexpected results gave rise to a new hypothesis of how the electro sorption process could differ from the theory that was formulated in chapter 2. It could be presumed that electrolysis of water took place at the inside surface of the sorption electrode. A sufficiently conductive carbon coating would facilitate this since the inside lumen of the sorption electrode was closest to the counter electrode. Since the Pt particles were mostly formed on the outside of the

electrode they could not play any significant role. This could explain the relatively high potential difference of 3.9V required for the generation of only 100mA of electrical current compared to the 4.2V required to generate the same current with a standard electrode without Pt. Alkaline water (generated at the inside of the electrode by reduction of water) enters the permeable electrode and causes Ca^{2+} to adsorb in the phosphorized region. SO_4^{-2} ions were already excluded as a result of the cation exchange properties of the electrode. As mentioned earlier, the reject contained up to 38% more SO_4^{-2} ions than the feed solution. Considering the reject/permeate flow ratio of 2, this could mean over 75% removal in the permeate. This mechanism however does not include an explanation for the high percentage of SO_4^{2-} desorption observed during the regeneration cycles in several experiments. The final mechanism of electro sorption is perhaps a combination of both proposed mechanisms. Many more systematically performed sorption experiments would be necessary to reveal the true mechanism and decide whether additional Pt could be used to increase the energy efficiency. It may only become clear after more carefully designed experiments. It may be possible that if Pt^{+4} is occupying ion exchange sites, deposition before impregnation might be a solution.

6.3.2 Electro sorption process

The effect of the potential difference, permeate flow, permeate reject ratio and current density on the electro sorption characteristic will be discussed separately. The effect of the variables will also be related to the energy consumption of the electro sorption process.

6.3.2.1 The effect of the potential difference on the electro sorption process

The summarized results of three electro sorption experiments where potential differences between the counter and the sorption electrode varied from 3 to 5, are shown in Table 6.10.

Table 6.10. The effect of electrode potentials upon electro sorption

Exp. No	Electrode No	Set [a] No	ΔV^b	I	Adsorption/desorption (%)		E^c (kWh· kg^{-1})
					SO_4^{-2}	Ca^{+2}	
C	3	2	5	130	55/31	57/42	10
J	3	3	4	80	30/35	25/30	9
K	3	4	3	30	10/10	5/10	21

[a] Experimental parameter set listed in Table 6.2

[b] Potential difference between sorption electrode and counter electrode

[c] Average current measured during adsorption cycle

[d] Average percentage of adsorption / desorption of anions and cations

[e] Energy consumption during adsorption cycle

Even though the pure electricity consumption (I*V*t) is going down with decreasing potential difference and current, experiment K in Table 6.10 shows a dramatic increase of energy consumption per kg removed salt. Apparently the protons and hydroxyl generated did not activate sufficient ion exchange groups and the average removal efficiencies decreased more rapidly than the energy consumption. Comparing experiment C and J, the decrease in removal efficiency as a result of lower potential was more or less balanced with the decrease of energy consumption. However, when a potential difference of 4 volts was applied (experiment J) a better adsorption/desorption ratio was observed than in experiment C where 5 volt was applied. It was shown previously that moderate adsorption rates, and regeneration of the electrode before the electrode becomes saturated, resulted in better desorption characteristics. These better characteristics may be obtained by avoiding the precipitation or deposition of solid matter such as sulphate salts inside the pores of the sorption electrode. Potential differences higher than 5V are not applied since rapid degradation of the electrodes and possible side reactions should be avoided.

6.3.2.2 The effect of the permeate flow on the electro sorption process

The summarized results of three electro sorption experiments C, L and M are shown in Table 6.11, where the permeate flow through the electrode was varied.

Table 6.11. The effect of the permeate flow on the electro sorption process

Exp. No	Electrode No	Set [a] No	Permeate ($ml \cdot min^{-1}$)	Adsorption/desorption (%)[b] SO_4^{-2}	Ca^{+2}	E[c] ($kWh \cdot kg^{-1}$)
C	3	2	2	55/31	57/42	10
L	3	5	0.5	60/65	75/30	31
M	3	6	4	27/23	25/20	8

[a] Experimental parameter set listed in Table 6.2

[b] Average percentage of adsorption / desorption of anions and cations

[c] Energy consumption during adsorption cycle

The ion content of the permeate decreased (i.e higher ion removal was achieved) with decreasing permeate flow. The longer residence time for the ions inside the electrode and the more extreme local pH's may explain these results. However, the decrease in the volume of collected sample had a larger effect on the energy consumption than the increase of adsorption efficiency (see formula 5.1), especially at permeation rates below 2ml· min^{-1}. The high permeation rate seems to be more energy effective, however the pumping cost will increase with the permeation rate and should be considered in a more complete set of optimisation experiments.

6.3.2.3 The effect of the permeate/reject ratio on the electro sorption process

The summarized results of the electro sorption experiments C and N with two different permeate/ reject ratios, are shown in Table 6.12. These results show that the adsorption efficiencies are significantly influenced by permeate / reject ratios.

Table 6.12. Results of electro sorption experiments for different permeate / reject ratios

Exp. No	Electrode No	Set [a] No	P / R ratio [b] (ml· min^{-1})	Adsorption/desorption (%) [c] SO_4^{-2}	Ca^{+2}	E [d] (kWh· kg^{-1})
C	3	2	2	55/31	57/42	10
N	3	1	10	25/20	30/15	15

[a] Experimental parameter set listed in Table 6.2

[b] Permeate / reject ratio

[c] Average percentage of adsorption / desorption of anions and cations

[d] Energy consumption during adsorption cycle

Permeate/ reject ratios lower than 0.5 were not measured. Besides the negative impact on the total water recovery that lower ratios would bring, it was believed that the concentration of hydroxyl ions necessary to activate the cation exchange material would be too greatly diluted by the high reject flow. Poor adsorption/desorption characteristics were obtained in experiment M where high permeate flow rates were tested.

To obtain high water recovery, all the feed solution should be pumped through the electrode. In that case an equal amount of anion exchange and cation exchange groups would be activated. However, the results of experiment N do not support this theory. One reason is a serious flow problem that was observed during the experiment. The produced gas at the reject side accumulated in the volume

between the electrode causing discontinuous flow rates and irregular current patterns. With formula 6.2 it could be confirmed that the gas flow (J_g) during the experiment was even larger than the reject flow (J_r). In this formula Faradays law (I=nF) was used to calculate the O_2 produced (mol· s^{-1}) and the ideal gas law (PV=nRT) was used to convert this number into m^3· s^{-1}:

$$J_g = \frac{I}{n_e F} \cdot \frac{RT}{P} > J_r \quad \rightarrow \quad \frac{0.10}{2 \cdot 96485} \cdot \frac{8.314 \cdot 300}{3.0 \cdot 10^5} = 4.3 \cdot 10^{-9} > 3.3 \cdot 10^{-9} \qquad (6.2)$$

$$\left[\frac{m^3}{s}\right] = \frac{\left[\frac{C}{s}\right]}{[-]\left[\frac{C}{mol}\right]} \cdot \frac{\left[\frac{Jmol}{K}\right][K]}{\left[\frac{J}{m^3}\right]} > \left[\frac{m^3}{s}\right]$$

where:

I	Current through membrane (C· s^{-1})
n_e	Number of electrons involved in oxidation of water (=2, see reaction 2, chapter 2)
F	Faraday constant (96485 C· mol^{-1})
R	Gas constant (8.314 J· K^{-1}· mol^{-1})
P	Pressure at reject side (=3.0 10^5 N· m^{-2})
T	Reactor temperature (=300K)
J_r	Reject flux (permeate flux / permeate/reject ratio)

6.3.2.4 Control of current density or potential difference

All experiments A till W were either performed under potentiostatic or galvanostatic conditions. During experiments under galvanostatic conditions no current peaks were generated. These current peaks occur during potentiostatic conditions at the start of the experiment and at the moment the polarity is switched. These current peaks (up to 500 mA) may damage the electro conductive layer.

Using constant current may possibly have another advantage. Since the current represents the amount of hydroxyl and protons generated it should be possible to calculate the minimal current (I_m) required for a specific desired removal rate. This can be done using the following formula:

$$\frac{I_m}{F} = \frac{I_m}{N_A \cdot e} = \frac{I_d}{N_A \cdot e \cdot A} = \left(c^I - c_s^{II}\right) \cdot z \cdot J_p \qquad (6.3)$$

where:

F	Faradays constant ($C \cdot mol^{-1}$)
N_A	Avrogado constant
c^f	Concentration of ions in the feed ($mol \cdot l^{-1}$)
c_i^p	Desired concentration of ions in the permeate ($mol \cdot l^{-1}$)
J	Permeate flux ($m^3 s^{-1}$)
I_d	Current density ($C \cdot s^{-1} \cdot m^{-2}$)
A	Permeate surface area (m^2)
z	Valence of the ion
e	Electron

This minimal electrode current would be sufficient to reach the desired removal if the following conditions are met:

A) no reaction besides water hydrolysis takes place at the electrode surfaces. In this case the production of protons is exactly equal to the production of hydroxyl groups.

B) cation exchange groups are present from the lumen surface through the matrix to the middle of the sorption electrode and an equal amount of anion exchange groups are located throughout the other half of the sorption electrode.

C) the reaction of protons and hydroxyl ions with the ion exchange material is sufficiently fast that these ions do not have time to react together and neutralize to form water.

In practice these assumptions will possibly lead to significant deviation from this calculated minimal current. However, this deviation expresses the efficiency of the electro sorption process to a certain degree. For example: the minimum current required to obtain the results of experiment G (40% removal of Ca^{2+} and SO_4^{2-} from a 0.01M $CaSO_4$ feed solution, with a flow rate of $2ml \cdot min^{-1}$) can be calculated as follows:

$$I_{min} = (0.01 - 0.01 * 0.4) * 2 * \frac{0.002}{60} * 96485 = 0.026A$$

$$\frac{C}{s} = \left(\left[\frac{mol}{l}\right] - \left[\frac{mol}{l}\right]\right) * [-] * \frac{\left[\frac{l}{min}\right]}{\left[\frac{s}{min}\right]} * \left[\frac{C}{mol}\right] = [A]$$

As the results of experiment G were obtained at 0.1A. Only 26% (0.26/0.100*100%) of the generated H^+ and OH^- is effectively involved in activation of the sorption material. It is believed

that a significant amount of H^+ neutralizes with OH^- when the solution near the anode is pumped through the sorption electrode towards the cathode. This neutralisation reaction is pure loss of energy but seems difficult to avoid for a electro sorption reactor operating in flow through mode.

6.3.3 Conclusions on sorption experiment using tubular electrodes

The series of optimisation experiments performed in this section led to the following findings with regard to preparation of the sorption electrode:

- The optimal phosphorization time was found to be 4 hours.
- Electrodes prepared from Al_2O_3 supports with small pores showed better removal efficiencies than electrodes prepared from Al_2O_3 support with larger pores.
- The electrical connection between a power source and a sorption electrode could be established using an electro conductive O-ring.
- Deposition of Pt decreased the potential difference for water electrolysis. The energy consumption per kg salt removed did however not show any improvements.

The series of optimisation experiments performed led to the following findings with regard to the optimum conditions for the sorption experiment:

- The optimal potential difference between the sorption electrode and the counter electrode was found to be 4V. Although 5V potential difference resulted in similar energy efficiency, relatively poorer desorption characteristics were obtained.
- The permeation flow should be close to $2ml \cdot min^{-1}$ (flux: 0.5 $m^3 \cdot h^{-1} \cdot m^{-2}$) when a potential difference of 5V is applied. Lower permeation flows resulted in lower desorption percentage and higher permeation flows resulted in lower removal efficiencies.
- Removal efficiencies of both cations and anions >50% were obtained at a permeate/reject ratio of 0.5. Higher ratios led to lower removal efficiencies. Lower ratios may lead to higher removal efficiencies but will lead to low water recovery.
- Using the current density as a control parameter during the electro sorption process instead of the potential difference may increase electrode lifetime. Calculation of the minimal required current density may give an indication of the efficiency of the electro sorption process.

6.4 References

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7 DEVELOPMENT OF ELECTRO SORPTION DESALINATION METHODS FOR DIFFERENT TYPES OF EFFLUENTS

Abstract

The flat sheet electro sorption electrodes were found very efficient for an inductrial nickel effluent. Up to 80% of nickel could be removed and the energy consumption was as low as 6kW · kg^{-1}. No fouling was observed after several cycles eventhough the nickel solution showed a significant amount of organic matter (COD 802). The flat sheet electro sorption electrodes were also found very efficient for the treatment of mine water solution with high SO_4^{-2} content (2700mg· l^{-1}) with removal efficiency and energy consumption of 90% and 4kW· kg^{-1}.

For tubular electro sorption electrodes, it was found that the sorption electrode was most successful for waters with mainly Ca^{2+} as problematic ion. A significant removal of SO_4^{2-} ions could only be demonstrated when the quantities of other anions such as Cl^- were relatively low. Severe fouling of the sorption electrodes was observed during treatment of waters containing large amounts of ions like nickel and iron. For iron containing acid mine drainage this problem was solved after a hydrid system was developed that removed >99% of Fe ions by electrochemical neutralization of the feed before it entered the electro sorption unit. During the filter efficiency tests is was found that the electro sorption unit rejected up to 3 times more microbes than a standard 0.45 micrometer filter. The permeability decrease caused by rejected microbes was about 30% of the initial permeability.

7.1 Introduction

This chapter describes the performance of the tubular and flat sheet electro sorption modules in the treatment of an acid mine drainage sample and 6 model solutions representing real effluents or ground water. Tubular and flat sheet sorption electrodes are discussed separately in section 7.2 and 7.3 respectively.

7.2 Study of desalinations of aqueous solution by means of tubular electro sorption modules

Besides treatment of $CaSO_4$ discussed in chapter 6, four model solutions, prepared to simulate different types of water sources, were treated with the tubular developed electro sorption system. The ionic composition of the model solutions used is listed in Table 7.1.

Table 7.1 Ionic composition of four different model solutions treated with the electro sorption unit

Solution → Ion ↓	1 Klipfontein Model / Real	2 IEC norm 734 Model	3 Nickel effluent Model / Real	4 Grootvlei Model / Real
Ca^{2+}	155 / 155	89.4	- / 24	438 / 438
Mg^{2+}	74 / 74	18.7	- / 16	196 / 196
Na^{+}	220 / 272	91.6	- / 183	320 / 320
Ni^{2+}			635 / 635	
SO_4^{-2}	172 / 172	73.9	1080 / 1739	2742 / 2741
CT	699 / 699	158.1	0 / 210	198.1 / 228
HCO_3^{-}		244		
Fe^{2+}				297 / 296.7
F^{-}	- / 3.5			
Si	- / 17.5			
K^{+}	- / 12.9		- / 3	- / 76

The ion concentration of wastewater chosen for testing ranged from several hundreds of mg· l^{-1} (IEC norm 734) to several thousands of mg· l^{-1} (Grootvlei water). This range of concentrations in the feed water was chosen to determine which working range of ionic impurities the electro sorption system could be applied to. Unlike solutions number 1, 2 and 4 that originated from ground or surface water, solution 3 was a nicked effluent. It was investigated to discover whether electro sorption could find application to remove and/or recover nickel from this effluent stream.

7.2.1 Experimental

7.2.1.1 Preparation of the sorption electrode

The electro sorption units used to treat the different solutions were prepared according to the standard preparation procedure as described in Appendix D. Tubular Al_2O_3 type I supports were used as support to prepare the electro sorption electrodes. Step 2 was left out since the reactor with the coil connection was used and did not require impermeable electrode edges. Step 7 was also not performed since the results obtained with Pt plated electrodes were not very promising (see section 5.3.2.4). Moreover the stability of the Pt deposits in the presence of several pollutants had not been tested. For the treatment of the nickel effluent an additional electrode was prepared that did not contain any ion exchange material.

7.2.1.2 The electro sorption experiment

Table 7.2 shows the quantities of different salts that were mixed to obtain the different model solutions simulating the chosen waters and effluent. For non of the solutions acid of base was added to adjust the pH. Grootvlei water was the only solution with fine particles.

Table 7.2 Quantities of different salts mixed to obtain model solutions

Salt	Klipfontein		IEC norm 734		Nickel effluent		Grootvlei	
	Mmol· l^{-1}	mg· l^{-1}	mol· l^{-1}	mg· l^{-1}	mmol· l^{-1}	mg· l^{-1}	mmol· l^{-1}	mg· l^{-1}
NaCl	5.9	346.1						
$MgCl_2 \cdot 2H_2O$	3.0	289.9						
$NaHCO_3$			4	340				
$MgSO_4$			0.77	93			8.1	970.3
$CaCl_2$	3.9	568.1	2.23	249			2.7	303.1
Na_2SO_4	1.8	254.5					7.0	990.7
$CaSO_4$							8.2	1409.8
$FeSO_4$							5.3	1476.3
$NiSO_4$					0.011	1700		
TDS		1458.6		682		1700		5150.2

For the electro sorption experiment, a sorption electrode was placed in a reactor designed as described in Figure (4.3) in set-up 2 (see chapter 4). The experimental conditions used during the treatment of the different solutions are shown in Table 7.3.

Table 7.3 Control parameters for the sorption experiments on model solutions of real waters at constant voltage.

Experiment No.	Solution No.	Power source mode [a]	Flow rate Permeate (ml· min^{-1})	Ratio Permeate/Retentate (%)
Q	1	P 5V	1	1
R	1	P 4-5V	1	1
S	2	G 0.1A	1	1
T	3	P 4V	2	1
U	3	P 4V	2	1
V	4	P 4V	2	1
W	4	G 0.1A	2	1

a) Power source either in Galvanostat (G) or Potentiostat (P) mode.

Tube clamps in the reject line were used to regulate the permeate/reject ratio. The pressure difference over the sorption filter was controlled by the peristaltic pumping rate. During each experiment, samples were taken at different sampling intervals and opposing electrical fields. A complete overview of experimental conditions is given in appendix E.

7.2.2 Results and discussion

7.2.2.1 The electrode preparation

The weight measurements of the electro sorption electrodes after different steps of the preparation procedure are listed in Table 7.4. The electrodes were identified by the experiment in which they were used. Significant differences were observed in the amount of carbon deposited during carbonisation. Possible causes were discussed in chapter 5.

Table 7.4 Changes observed during the preparation of sorption electrodes

Support	Weight (g)	Weight increase (g)		
	Initially	Carbonised	Impregnated with ZrO_2	Phosphorized
Q	11.78	0.1023	0.3564	0.1641
R	11.94	0.0886	0.4159	0.1912
S	12.01	0.0945	0.3680	0.1690
T	11.81	0.0779	0.4314	0.1972
U	12.12	0.1013	Not impregnated	Not phosphorized
V	12.05	0.0955	0.3680	0.1637
W	11.89	0.1105	0.3473	0.1601

7.2.2.2 The electro sorption experiment

Detailed information for each experiment is presented in Appendix D. The experiments could be divided into a set of cycles. Each cycle contained an adsorption and desorption step in which the sorption electrode was charged negatively and positively respectively. The adsorption / desorption characteristics of each electro sorption experiment, carried out as indicated by Table 7.3, will be discussed separately for each solution treated. The characteristics of the reject will then be discussed. This section will end with a general overview of the sorption experiment and its effect on different ions. The energy consumption of all experiment will be shown and discussed in Chapter 8.

7.2.2.3 Electrosorptive treatment of Klipfontein

Two experiments Q and R were performed in which simulated Klipfontein water was tested. The experimental details of experiment Q and R can be found in Appendix E. The adsorption / desorption results of various ions in permeate generated during experiment Q, are shown in Figure

7.1. The lower figure presents the current and potential used as function of time. The ion adsorption and desorption results are given as percentage of the concentration of ion in the feed solution.

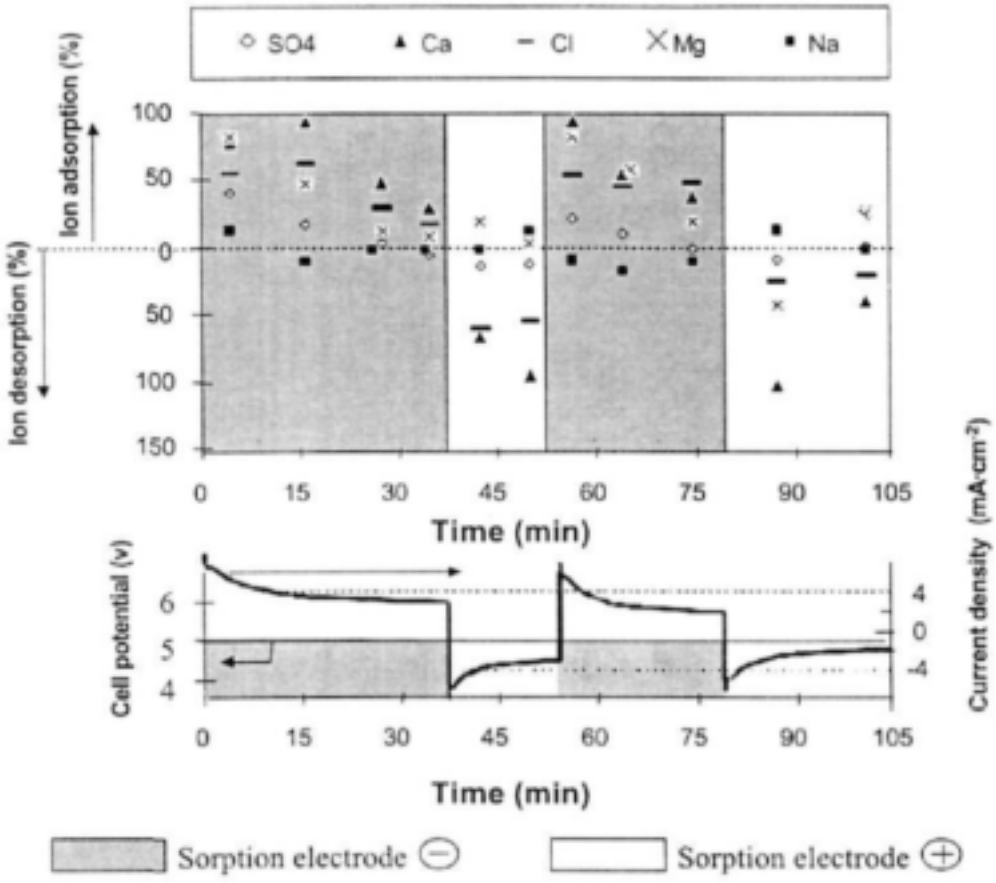

Figure 7.1 Adsorption/desorption characteristics during first two cycles of electro sorption experiment Q

During the first 10 minutes of the adsorption step relatively high ion adsorption (40-80%) was observed for all ions except Na^+. During the second 10 minutes of the experiment the adsorption for Ca^{2+} and Cl^- ions showed a further increase whereas Mg^{2+} and SO_4^{2-} adsorption gradually started to decrease. This trend was observed for several experiments and will be discussed in section 6.1.4. It was also observed that the removal efficiency (=percentage of ion adsorption) decreased from cycle to cycle. The decrease in removal efficiency could be due to a gradual decrease of the average current observed between each subsequent cycle. Two different types of current decrease could be distinguished. A periodic current decrease occurred in each potential step, as well as a decrease of the average current between each subsequent cycle. The current decrease observed during each

sorption step may be ascribed to the increasing hydrolysis potential during the time that the local pH at the electrode was reaching equilibrium. The value of the local pH will influence the hydrolysis potential as can be determined via the Nernst equation (chapter 3, equation 3.6). It can be calculated that at the moment that the potential is reversed, the potential for water hydrolysis is minimal which results in a current maximum. As the pH equilibrated, the current reached a stable value. The decrease of the average current between cycles may be explained by the small degradation of the carbon coating as described in chapter 2

Figure 7.2 shows the results of experiment R. In contrast to experiment Q, the applied voltage was increased manually during experiment R to maintain a constant current.

The use of a constant current resulted in more constant adsorption/desorption characteristics between the subsequent cycles of an experiment. Table 7.5 shows the summarized results of the experiments in which simulated Klipfontein water was treated. Despite the lower average ion removal of experiment R, the energy consumption was lower than for experiment Q. Experiment R showed better desorption characteristics as well. These results were in accordance with the results presented in chapter 5 where better desorption characteristics was found for electro sorption performed with relatively low currents.

Table 7.5 Results of electro sorption experiments using Klipfontein feed water

Exp.	Average adsorption/desorption during experiment					E^a
No	Na^+	Cl^-	Mg^{2+}	SO_4^{-2}	Ca^{+2}	(kWhr kg^{-1})
Q	-6/-4	40/31	36/2	8/12	55/75	25
R	-5/-9	15/20	28/0	5/5	30/20	19

[a] Average energy consumption during adsorption cycle

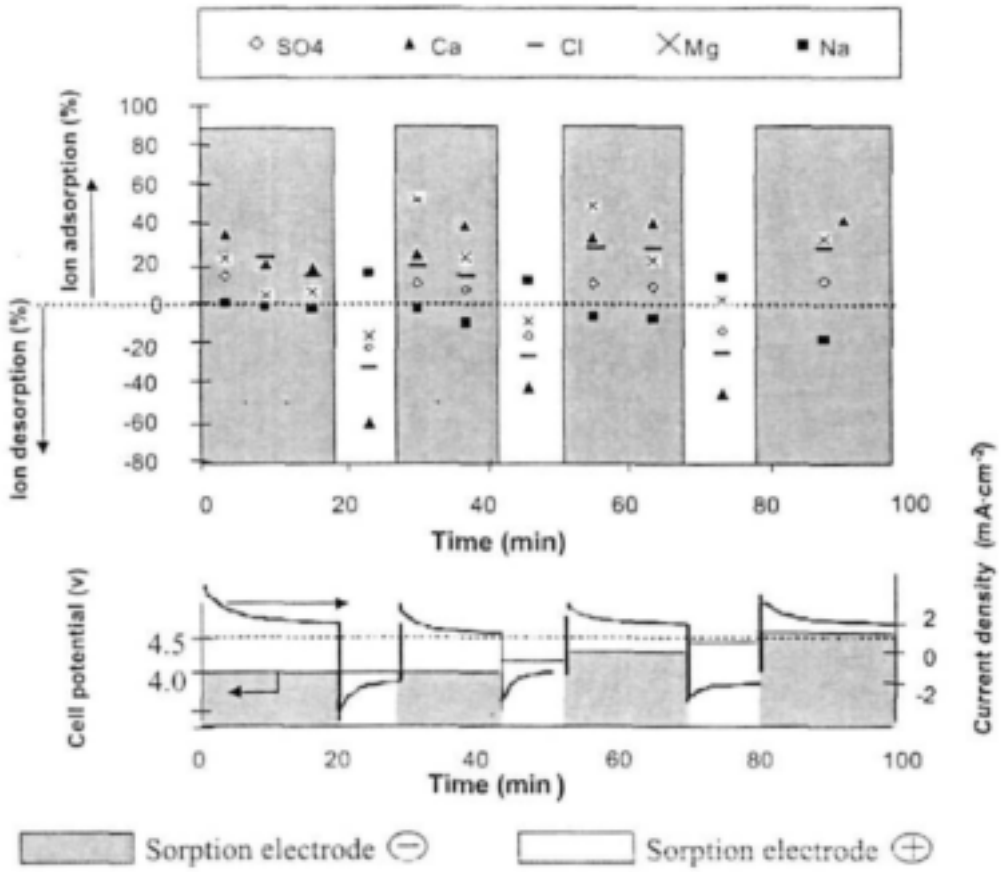

Figure 7.2 Adsorption/desorption characteristics during first three and a half cycles of electro sorption experiment R

7.2.2.4 Electrosorptive treatment of IEC norm 734

One electro sorption experiment S was performed in which simulated IEC norm 734 water was tested. The experimental details of experiment S can be found in Appendix E. The adsorption / desorption results for various ions in the permeate generated during experiment S, are shown in Figure 7.3. The ion adsorption and desorption results are given as percentage of the concentration of the ion in the feed solution.

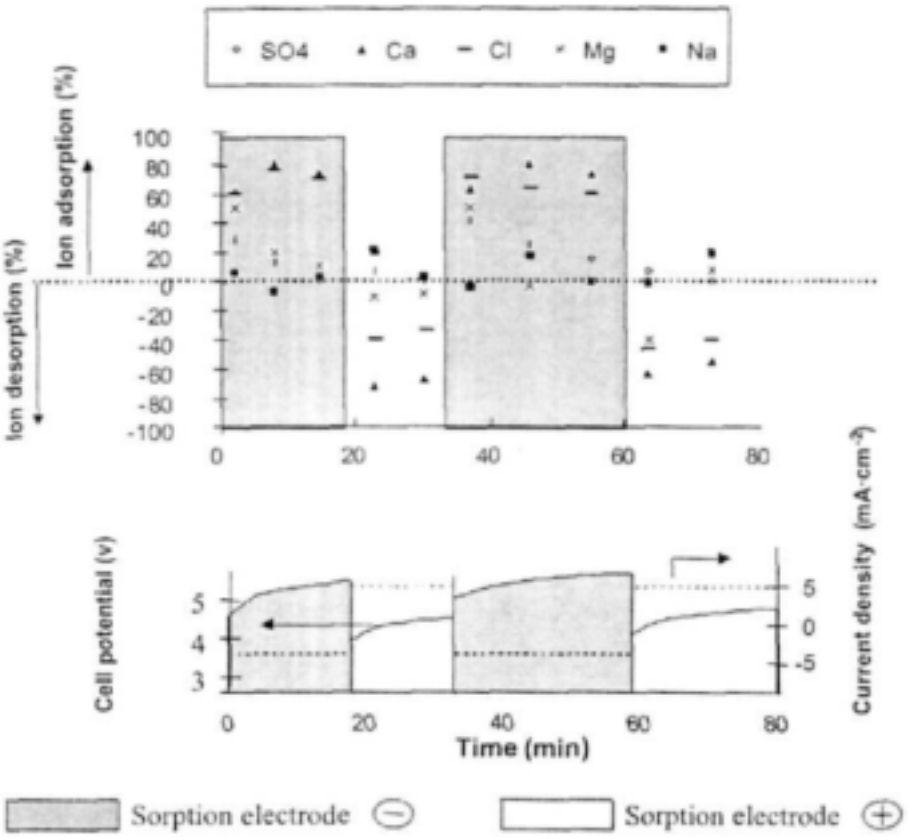

Figure 7.3 Adsorption/desorption characteristics during first two cycles of electro sorption experiment S

The Ca^{+2} and Cl ions were most successfully removed from the permeate during the cathodic cycle, similar to the adsorption results obtained for the treatment of Klipfontein water. Table 7.6 shows the summarized results of the experiments treating simulated IEC norm 734 water.

Table 7.6 Results of electro sorption experiments using IEC norm 734 feed water

Exp.	Average adsorption/desorption during experiment					E[a]
No	Na^{+}	Cl^{-}	Mg^{2+}	SO_4^{-2}	Ca^{+2}	(kWh· kg^{-1})
S	-	70/40	20/10	-/-	75/75	55

[a] Average energy consumption during adsorption cycle

7.2.2.5 Nickel effluent

Two adsorption experiments T and U were performed in which a model solution simulating nickel effluent was treated. The experimental details of experiment T and U can be found in Appendix E. The adsorption / desorption results for various ions in the permeate generated during experiment T are shown in Figure 7.4. The ion adsorption and desorption results are given as a percentage of the concentration of the ion in the feed solution.

Nickel removal was significant during all the adsorption steps when the electrode was used as a cathode. Significant removal of SO_4^{2-} was only observed during the first adsorption cycle of the experiment. Neither Ni nor SO_4^{2-} desorption could be measured after switching the sorption electrode to anodic mode. After disassembly of the reactor a grey deposit, most likely metallic nickel, was found on both the sorption and the counter electrode. The deposition of metallic nickel could be expected based on the low half-cell potential of Ni (-0.23V) [1]. The electro-deposition of nickel on the sorption electrode could explain why nickel removal was observed. After switching the polarity deposition of nickel took place at the counter electrode. The metallic nickel on the anodic sorption electrode may have started to dissolve (oxidized), but at a slower rate than that of the deposition process since the nickel concentration in the permeate did not increase during the desorption cycles.

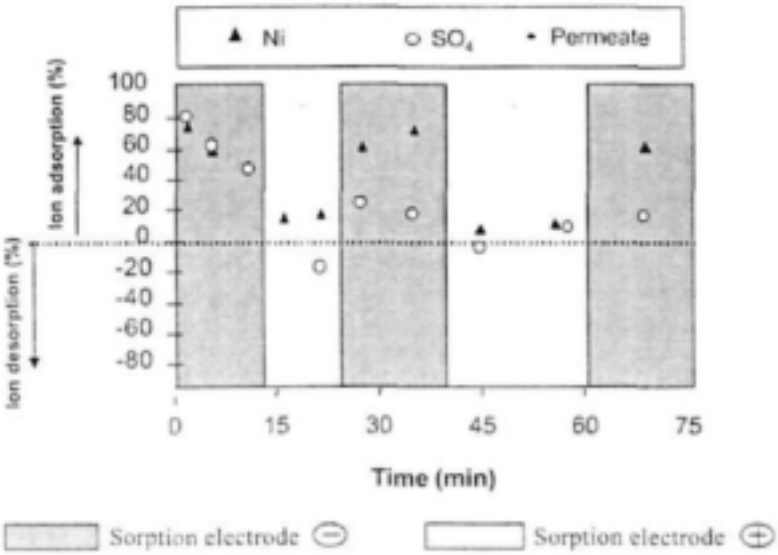

Figure 7.4 Adsorption/desorption characteristics during first two cycles of electro sorption experiment T

The electrochemical reduction of nickel may have replaced the electrochemical reduction of water and thus the generation of OH^- ions. Hence regeneration of the anion exchange sites and thus the desorption of SO_4^{-2} could not occur through absence of OH^- ions.

To confirm that the electro sorption results on the nickel effluent were mainly controlled by electro deposition of Ni instead of irreversible ion exchange, experiment U was carried out using an electrode without ion exchange material, as described in Table 10.4. The adsorption / desorption results of this experiment are illustrated in Figure 7.5 and showed a similar pattern for Ni removal throughout the experiment. Significant SO_4^{2-} removal was not observed as could be expected from an electrode without the ion exchange component ZrO_2.

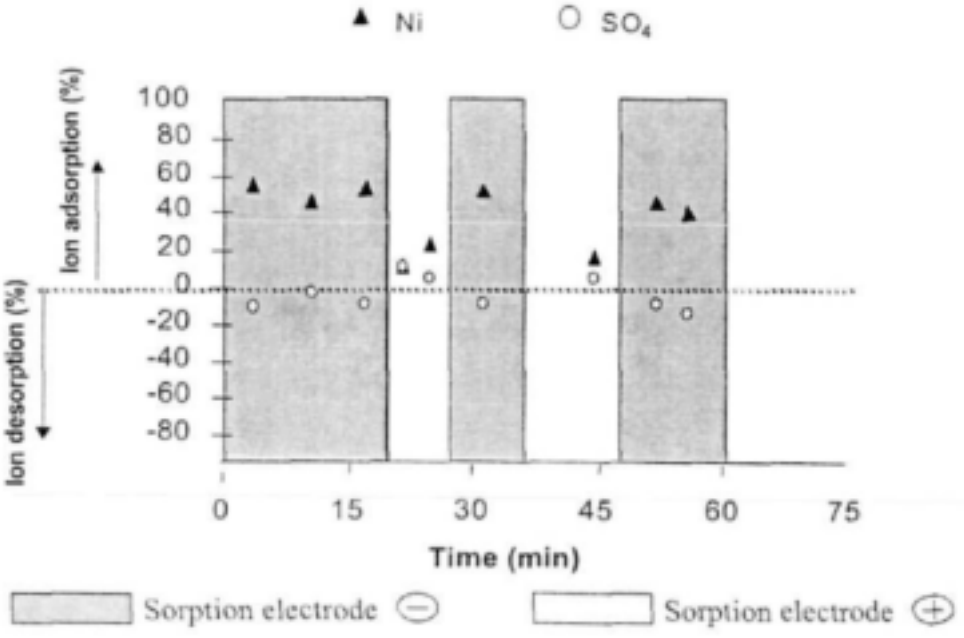

Figure 7.5 Adsorption/desorption characteristics during first two cycles of electro sorption experiment U

7.2.2.6 Electrosorptive treatment of simulated Grootvlei water

Experiment V was performed in which the model solution of Grootvlei water was treated with tubular sorptionelectrodes. The experimental details of experiment V can be found in Appendix E. The adsorption / desorption results for various ions in the permeate generated during experiment V are shown in Figure 7.6. The ion adsorption and desorption results are given as a percentage of the

concentration of the ion in the feed solution. In the lower figure the permeation flux is given as a function of time.

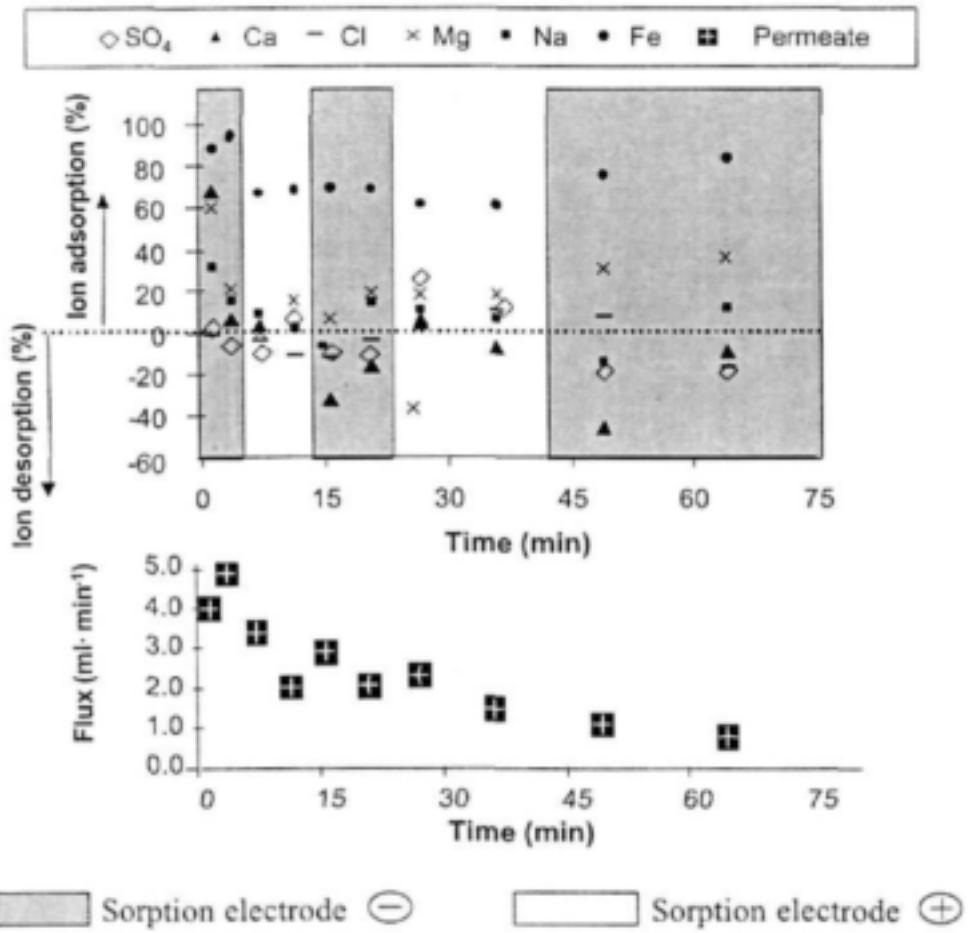

Figure 7.6 Adsorption/desorption characteristics and permeate flux during first two cycles of electro sorption experiment V

The adsorption / desorption characteristics of this experiment show poor adsorption and desorption results for all ions except Fe. Fe removal was probably effected as a result of mechanisms including adsorption, deposition of iron hydroxides or metallic iron upon the cathode (with E^0_{Fe} =-0.409V [1, page 85]). The ion content in the permeate was at all times 60% of the feed concentration. Desorption of Fe could not be observed. During the experiment green and brown precipitates settled out in the storage vials for permeate and reject liquors. The precipitates may be formed as a reaction product of ionic species in the Grootvlei water with species formed at the electrode surface. At the anode where O_2 may evolve as a result of water oxidation (see reaction 3.2) insoluble oxides may

be formed. At the cathode where pH may increase as a result of water reduction (see reaction 3.1), insoluble hydroxides may be formed. Part of the insoluble species may have precipitated inside the sorption electrode causing the decreasing flux. The pressure difference over the membrane was managed at 2 bars during the experiment (see Figure 7.6).

7.2.2.7 Ionic composition of the reject flow

Analysis of the ionic components in the reject stream showed similar trends for all treated solutions. The adsorption/desorption results and pH of such a typical reject flow at different sampling intervals and electrode potentials are given in Figure 7.7.

When the sorption electrode is negative the concentration of anions in the reject is usually higher than the concentration in the feed stream. For cations the opposite is observed. This change in ion concentrations can be explained based upon the electrode reactions. When sorption electrode was negatively charged, the pH of the reject often decreased to a value near pH 2, as can be seen in Figure 7.7. The low pH was caused by the generation of protons (see reaction 3.2) at the counter electrode, which was the anode at this point in the cycle. To compensate the charges of the protons generated in the reject, anions were attracted towards the reject and cations were repelled. Thus, the anion concentration in the reject increased and the cation concentration in the reject decreased. The concentration increase and decrease of anions and cation respectively was often more pronounced for the divalent ions. This may be related to the specific ion mobility and will be explained in more detail in the next chapter.

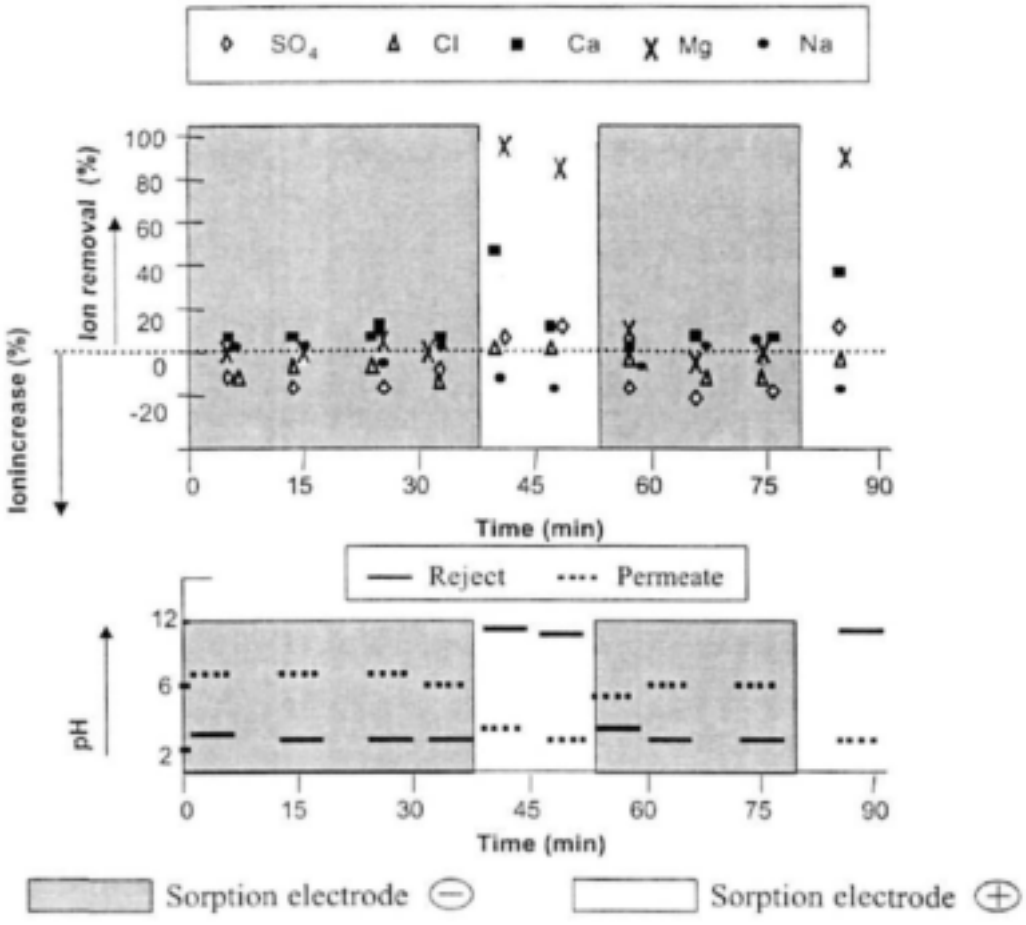

Figure 7.7 Typical characteristics of the reject solution during two cycles of an electro sorption experiment

When the sorption electrode was positively charged, the pH of the reject increased to a value near 12 and a decrease in anion concentration was observed (see Figure 7.7). The pH increased to a value near 12. The high pH was caused by the generation of hydroxyl ions (see reaction 3.2) at the counter electrode, which was the cathode at this point in the cycle. To compensate the charges of the generated hydroxyl ions in the reject, anions were repelled from the reject and cations were attracted. Thus, the anion concentration in the reject decreased and the cation concentration in the reject increased. Conversely, a strong decrease of the Mg^{2+} and the Ca^{+2} ion concentration in the reject was measured. However, white precipitation products, observed in the reject samples, did settle out but were not included in the samples for cation concentration analysis. Even though the precipitated were not analysed, the high pH of the reject and the low solubility products of $Mg(OH)_2$ and $Ca(OH)_2$ strongly indicate the origin of the white precipitate.

The acidic and alkaline reject flows are part of the secondary waste. Unfortunately the volumes of these wastes are significant since a minimal reject flow is required (see section 5.3). However, acidic reject can be utilized to dissolve pH dependent deposits inside the electro sorption electrode. This possible application of the acidic reject still has to be investigated.

7.2.3 Overview of electro sorption for different ions

By comparing all the experimental results of all treated solutions it was shown that ions are adsorbed and desorbed to a different extent at different intervals of the experiments. The adsorption and desorption characteristics for each ion will be discussed separately.

7.2.3.1 Cation

Na^+

Na^+ ions are least affected by the electro sorption experiment. In many cases the Na^+ concentration slightly increased during the adsorption cycle when the sorption electrode was negatively charged. The electro sorption process proved unfeasible for the removal of Na^+ from aqueous solutions.

Mg^{2+}

At certain stages in the sorption experiment (usually just after switching the sorption electrode to cathodic mode) Mg^{2+} was removed to a reasonable extent. However the desorption characteristics of Mg^{2+} was poor, likely due to the low solubility of $Mg(OH)_2$ as a possible reason. This may be illustrated in Figure 7.8. During the desorption cycle of an experiment when the sorption electrode was positively charged, $Mg(OH)_2$ may precipitate inside the sorption electrode as a result with high local pH (situation I). During the adsorption cycle when the sorption electrode was negatively charged, the solid $Mg(OH)_2$ may redissolve since the local pH changed from alkaline to acid. The redissolved ion could subsequently be transported towards an alkaline environment where it again could precipitate (situation II). Mg^{2+} ions may then only be released from the sorption electrode in the next desorption cycle (situation III).

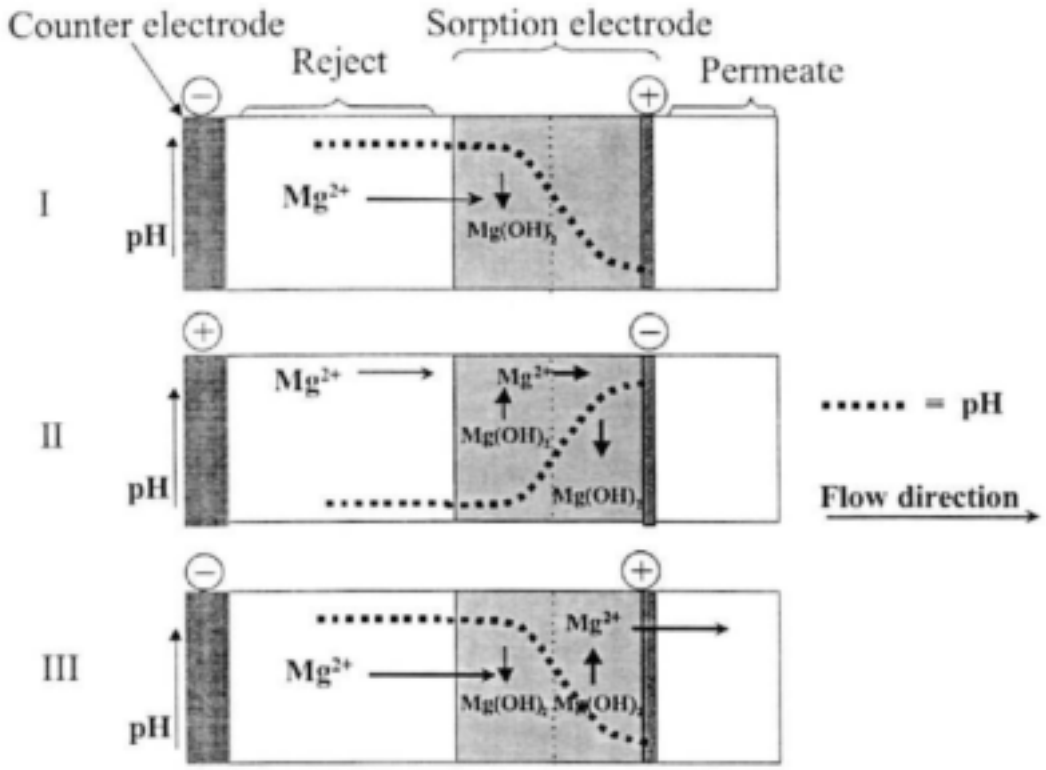

Figure 7.8. Schematic overview of proposed Mg^{2+} transport mechanism

Based on the proposed mechanism, the concentration of Mg^{2+} in the permeate after the first cycle would not significantly differ from the Mg^{2+} concentration in the feed solution. This is in agreement with the experimental findings.

Ca^{2+}

Calcium ions are most effectively removed by the method of electro sorption. The higher solubility of $Ca(OH)_2$ compared to $Mg(OH)_2$ may be the reason that Ca^{2+} shows relative high removal efficiency when the electrode was negatively charged and good desorption characteristics when the sorption electrode was positively charged. These results were obtained for more than one cycle.

7.2.3.2 Anions

Cl^- and SO_4^{2-}

In the experiments Q, R, and S where both Cl^- and SO_4^{2-} ions were present, Cl^- was more effectively removed than SO_4^{2-}. At the initial stage of the adsorption cycle of the experiment when relatively

many unsaturated anion exchange sites were available, a significant removal of SO_4^{2-} ions could be observed besides CT. After the sorption electrode became saturated, desorption of SO_4^{2-} could be detected while adsorption of CT ions continued. Apparently the SO_4^{2-} ions were replaced by CT ions. The lower affinity of SO_4^{2-} ions to ZrO_2 compared to CT ions was reported before [3]. The removal of CT ions due to oxidatio n and Cl_2 gas production may be a point of further study.

7.2.4 Conclusions for tubular sorption electrodes

- The sorption electrode will be most successful for waters with mainly Ca^{2+} as problematic ion. A significant removal of CT, and Ca^{2+} was demonstrated using the electro sorption system developed.

- A significant removal of SO_4^{2-} ions could only be demonstrated when the quantities of other anions such as CT were relatively low.

- Effluents containing large amounts of Fe, Ni or other elements that can easily be reduced may not be candidate ions for electrosorptive removal. All reactions besides water oxidation and reduction, such as reduction of metal ions and oxidation of CT disturb the development of a pH profile necessary for controlled adsorption and desorption of ions.

7.3 Study of desalination of aqueous solutions by means of flat sheet electro sorption modules

The flat sheet electro sorption modules were tested with a industrial nickel effluent and a mine water source. The electro sorption results are discussed in section 7.3.1 and 7.3.2:

7.3.1 Nickel effluent with flat sheet sorption electrodes

Electro sorption tests with flat sheet electrodes were carried out utilizing model solution of the following composition:

Ni_2SO_4 – 0.011M;

NaCl – 0.008M;

H_2SO_4 – 0.007M.

Taking into consideration, that nickel and sodium ions can have different soeption and electrochemical behaviour, the kinetics of sorption of these ions from separate salts was investigated. The results obtained with the electro sorption module equipped with zirconium phosphate containing electro sorption membranes at dU = 5 V are presented in Table 7.7.

Table 7.7. Removal degree (%) for sodium and nickel cations.

Cation	Time, min			
	5	10	20	30
Sodium	74	87	93	96
Nickel	46	59	73	80

The rate of sorption of nickel ions was lower than the sorption rate of sodium ions. Therefore in the study of desalination using actual electroplating effluent the feed flow of solution in the electro sorption module was reduced to 100 ml· h^{-1}. The results of treatment of nickel containing industrial effluent are listed in Table 7.8.

Table 7.8 Chemical composition of real electroplating effluent, purified and regenerated solutions (in mg· l^{-1})

	Initial	Purified		Regenerated
Constituent		dU = 5V	dU = 10V	
Sodium	183	103	18	1490
Potassium	3			
Calcium	24			
Magnesium	16			
Ammonia	10.6			
Nitrate + Nitrite	1.6			
Sulphate	1739	998	65	17200
Chloride	210	98	5	220
COD	802			
Nickel	635	424	< 1	6430
Iron	1.67			
TDS	4196	1623	89	25340

Energy consumption was 6.4 kW· kg^{-1} at dU=5V and 11 kW· kg^{-1} at dU=10V. No membrane fouling was observed.

7.3.2 Mine water effluent

The experimental results described in part 3.3 of the report demonstrated the effectiveness of the application of an electro sorption unit equipped with flat composite electro sorption membranes for the removal of salts from solutions with low salt content up to 500 mg· l^{-1} The study of electro sorption purification of sulphate solutions with a content of salts up to 3500 mg· l^{-1} was the next investigation phase. The following composition was chosen as a model solution:

Na_2SO_4 – 0.02M;

NaCl – 0.01M;

(sodium – 1150; sulphate – 1920; chloride – 230; TDS – 3425 mg· l^{-1}

The composition of this solution is close to sulphate containing mine waters. The removal of salts from such solutions has industrial value. The obtained results for mine water model solution purification using the electro sorption module equipped with zirconium phosphate containing sorption electrodes at U=5 V and I = 0.15 Aare listed in Table 7.9.

Table 7.9 Mine water model solution purification.

Flow rate, ml· h^{-1}	Passed volume, Ml	Purification degree, %	Energy consumption, kW · kg^{-1}
200	100	83	5.16
400	150	72	4.06
800	200	50	4.38

7.3.3 Conclusions for flat sheet electro sorption system

- The flat sheet electro sorption system was highly effective for the removal of nickel (up to 80% removal). In contrast with the tubular electro sorption system, no fouling of the electro sorption unit was observed although the nickel solution showed significant amount of organic matter (COD 802). The energy consumption is as low as 6kW · kg^{-1}.
- The flat sheet electro sorption system was highly effective for the treatment of mine water. In contrast with the tubular electro sorption system, no fouling of the electro sorption unit was observed The energy consumption is as low as 4kW · kg^{-1}.

7.4 Hybrid system

7.4.1 Introduction

Results presented in chapter 6 that precipitates formed during the electro sorption process caused substantial decrease of electrode permeability. Ions that easily form insoluble precipitates such as Fe should therefore not be present in the solution entering the electro sorption unit. These solutions should furthermore be pH neutral. For acidic or alkaline solutions it would be hard to realize the desired pH gradient. The abovementioned restrictions would make electro sorption a poor water purification system for treatment of acidic mine drainage water (ADM) containing high ion content, which effluent is a huge source of contaminated water in South Africa.

A simple electrolysis system could be used to neutralize a part of the AMD flow (ϕ_c) as illustrated by Figure 7.9.

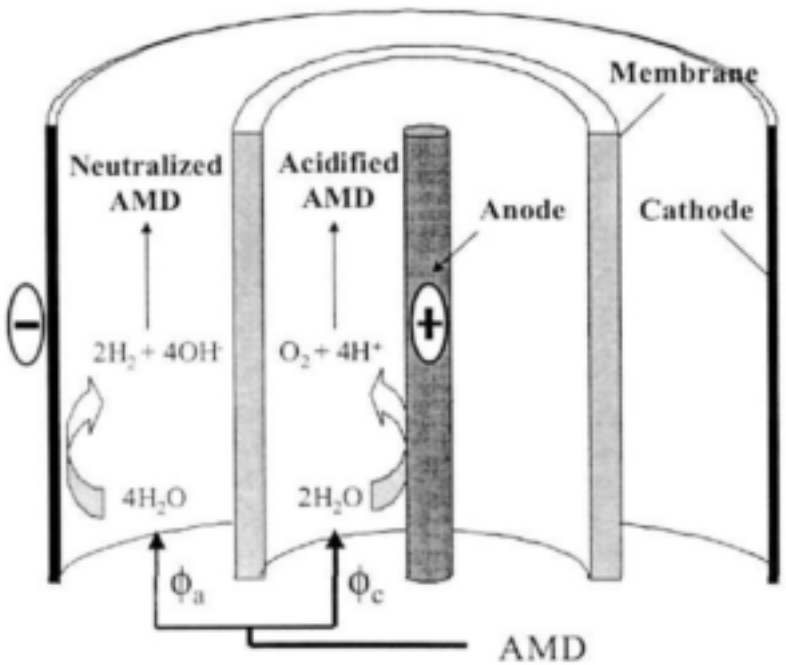

Figure 7.9. Neutralization and acidification of AMD by water electrolysis

Precipitation of insoluble species formed in neutralized AMD has been reported previously [2] and may reduce the concentration of certain ions such as Fe considerably. Neutralizing AMD water and precipitation of readily insoluble species combined with further desalination using electro sorption offers opportunities for water purification. In this chapter a hybrid system will be presented.

7.4.2 Experimental

The acid mine drainage known as Brugspruit water was drawn on 12-04-2001 from the abandoned T and DB mining operation near Witbank in Gauteng, South Africa. The hybrid system that was used to treat this water consists of an electrolysis reactor upstream from an electro sorption reactor as shown in Figure 7.10. This electrolysis reactor (1) was build by placing a coil (∅ 5mm) of platinum wire (1m length, ∅ 1mm) inside a ceramic membrane (type III see table 2.1). The ceramic membrane was placed inside a stainless steel tube (8cm length, ∅ 16mm). The platinum wire was used as anode, the stainless steel tube as cathode and the membrane as a diaphragm. To build the electrolysis reactor (1) a stainless steel tube was used as a cathode. After the insoluble species in the catholyte are precipitated and removed, the solution is led to the inlet of the electro sorption reactor.

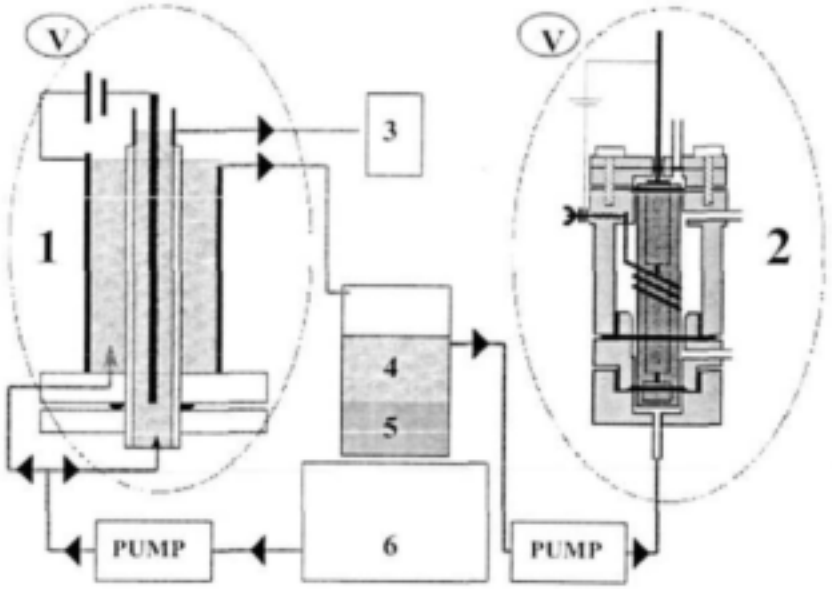

Figure 7.10. Schematic overview of the hybrid system: 1) Electrolysis system as shown in Figure 7.9. 2) Electro sorption reactor as shown in Figure 3.2. 3) Reservoir for waste water
4) Neutralized AMD 5) Precipitate 6) AMD reservoir

7.4.2.1 Neutralization of real Acid Mine Drainage

The electrochemical cell (number 1, Figure 7.10) was used to neutralise part of AMD. The current and potentials used during the neutralization step are tabulated in Table 7.7.

Table 7.10 Experimental conditions for the treatment of AMD

Experiment	A	B
Flow rate anolyte (ml· min^{-1})	8	8
Flow rate catholyte (ml· min^{-1})	11	9
Current	100	150

The catholyte was collected and transferred into a separation funnel. The orange brown precipitate started to settle within minutes at the bottom of the funnel and was separated from the supernatant liquid (clear catholyte) after 24 hours. The pH of the catholyte, feed and anolyte was recorded and the ion concentrations of Na^{+}, Ca^{+2}, and Fe were measured using AA. The total dissolved solid content (TDS) was determined by measuring the weight of solids left behind after evaporating 10ml of sample over 1 day at 60° C, then slowly heating up to 120° C for 1 hour.

7.4.2.2 Electro sorption of pre-treated Acid Mine Drainage

The preparation of the electrode, the reactor and the reactor set-up used were similar to the experiments described in chapter 5. The electro sorption was performed using the power source as a galvanostat at 100mA, the flow rate was regulated at 2ml· min^{-1} and 1.3ml· min^{-1} for permeate and reject respectively.

7.4.3 Results and discussion

7.4.3.1 Neutralization of Acid Mine Drainage

The Fe concentration and pH of the anolyte, the catholyte and the feed solution, for the experiments A and B are listed in Table 7.8. The first experimental results indicate that the pH of the catholyte can be regulated electrolytically with the current through the system. It should be possible to find the right combination of experimental conditions for any feed solution to obtain a catholyte that is pH neutral. Moreover, the Fe content in the catholyte after the precipitates had been removed was below the detection limit of the Atomic adsorption instrumentation (0.5 mg· l^{-1} for Fe). This result indicated that more than 99% of Fe ions precipitated when the pH of the AMD solution was electrolytically increased to 7.9. Fe ions precipitated for 90% when the pH of AMD was electrochemically increased to 4.7. While the Fe ions precipitates settled to the lower part of the separation funnel, the volume of the transparent catholyte increased with time. The longer the sedimentation time, the higher the volume of clear and Fe free catholyte. After 1 day the

precipitates were concentrated in 10% of the catholyte volume. The rest of the catholyte was fed to the electro sorption unit to remove other ions like Ca^{+2} and Cl^-.

Table 7.11. Fe content and pH of electrochemically treated Brugspruit water

Experiment	Catholyte		Feed		Anolyte	
	pH	Fe (mg· l^{-1})	pH	Fe (mg· l^{-1})	pH	Fe(mg· l^{-1})
A	4.8	5	2.9	50	2.2	55
B	7.9	0	2.9	50	2.1	56

The total dissolved solids (TDS) results of the feed solution, the anolyte and the catholyte were 8.9, 9.27 and 8.2 g· l^{-1} respectively. The difference in TDS between the catholyte and the anolyte is 700mg· l^{-1} while only 50 mg· l^{-1} of Fe was removed from the catholyte. It was possible that besides Fe other ions present in the orange-brown sediment were removed. The ion transport during electrolysis as discussed in the previous chapter might be another cause for the large difference in TDS between anolyte and catholyte. Anions like Cl^- and SO_4^{-2} ions have higher mobility than cations like Na^+. During electrolysis more Cl^- and SO_4^{2-} will be transported from the anolyte to the catholyte than Na^+ from the catholyte to the anolyte resulting in higher TDS in the anolyte.

7.4.3.2 Electro sorption of pre-treated AMD

The summarized results of the electro sorption experiments with neutralized Brugspruit water are shown in Table 7.9. The conductivity of the permeate is slightly lower than the conductivity of the feed solution but a proper indication of the ion removal could not be given in contrast with the suggestions in chapter 6. The relatively high concentration of Na^+ ions (1400mg· l^{-1}) compared to other cations in the feed was probably the reason for this result.

Table 7.12. The summarized results of the permeate of the electro sorption experiment with neutralized AMD

Cycle	Conductivity (mS· cm^{-1})		pH		Ca^{+2} (mg· l^{-1})	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Adsorption	8.7	8.2	7.9	8.2	163	114
Regeneration	8.7	9.3	7.9	3	163	201

As was shown in chapter 5, Na^+ ions are not adsorbed. Even at significant removal efficiency of Ca^{2+}, the decrease in conductivity of the permeate during the adsorption cycle was not significant. Besides a pH and a conductivity meter, a Na^+ indicator would be necessary to control experiments with relative high amounts of Na^+ in the feed solution.

The decrease of permeability during the experiment was about 15% in 90 minutes. This was much lower than the permeability decrease observed for the AMD water that was directly treated with the electro sorption system (see section 7.1).

7.4.4 Conclusions

- With the hybrid system where an electrolysis reactor was placed in series with the electro sorption reactor, it was possible to treat Brugspruit water, an acid mine drainage effluent.
- Acid solutions could be separated into a neutral and a more acidic solution using the electrolysis cell.
- Over 99% of Fe could be removed by neutralizing the Brugspruit water. During electro sorption 30% removal efficiency was obtained for Ca^{+2}.

7.5 Filtration properties of the electro sorption electrodes

7.5.1 Introduction

The ion adsorption properties of the electro sorption electrode were extensively explored in previous chapters. It was claimed in chapter 1 that the sorption electrode would be able to remove ions from aqueous solutions and act as a micro- or ultra filtration unit simultaneously. In this chapter the results of experiments to determine the filtration properties of the sorption electrode are presented.

7.5.2 Experimental

Two electrodes (W and X) were prepared according to the standard preparation procedure described in Appendix E. Al_2O_3 type II substrates were used as support for the electro sorption electrode with an initial pore diameter of 3 micron. Step 2 and 7 were not performed. During the preparation, the

mass increases were measured. Electrode X was placed in ultra pure water for 7 days before the filtration experiment was performed.

For the filtration experiments, the electrode was placed in the second electrode reactor (Figure 5.3). The reactor was subsequently connected to the pilot plant. The reservoir of the pilot plant was initially filled with Ultra Pure water. The reject flow bypassed the solenoid valves as well as the pH and conductivity probes and led straight into the reservoir. The BORWIN programme did not need to be activated since the experiments were only carried out to investigate the filtration properties of the sorption electrode. Permeate samples were collected several times at which point the collection time, sample volume, reject flow rate, pressure difference and electrode potential were recorded. When the permeability seemed reasonably stable with time, the reservoir was filled with an industrial related effluent solution. The solution consisted of a mixture of ionic species and microbes. It was specifically requested not to give further details about the solution. The solution will further be referred to as the microbe solution. Permeate and reject samples were collected for analysis over a period of 12 hours and permeability of the electrode was calculated. The samples collected during the experiments using the microbe solution were analysed with a spectrophotometer (Spectronic Genesys 5, Milton Roy)) at 480nm. The measured absorbance was used as a measure of the microbe content. One sample was obtained by filtering the microbe solution using a 0.45µm polyethylene filter (Cyclone). This sample could be used as a reference point for the filter property of the sorption electrode.

7.5.3 Results and discussion

The results of mass increase measurements of the electrodes W and X are tabulated in Table 7.10. Electrode X contained 10% more ZrO_2. Both electrodes showed no significant difference with regard to mass increase. The aim of the filtration experiment was to see to what extend the microbes could be separated from the aqueous phase using the electro sorption unit. Simultaneously the permeability of the sorption electrode was measured as a function of time to get an idea of the fouling characteristics. First the permeability of ultra pure water was measured as a function of time before testing the fouling effect of the microbe solution.

Table 7.13 Increase in mass during the preparation of sorption electrodes

Support	Weight (g)	Weight increase (g)/Permeability ($m^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)		
	Initially	Carbonised	Impregnated with ZrO_2	Phosphorized
W	12.1837	0.0882	0.4187	0.2113
X	12.2433	0.0742	0.4535	0.2280

7.5.3.1 Permeability and fouling of the sorption electrode

Figure 7.11 shows the permeability as a function of time. An enormous decrease in permeability in time even when filtering ultra pure water was observed for both electrodes, especially during the first 20 hours. The electrode soaked in water for 7 days showed the highest decrease in permeability. After about 20 hours the loss of permeability seemed to become stable but a gradual decrease could still be observed after 80 hours.

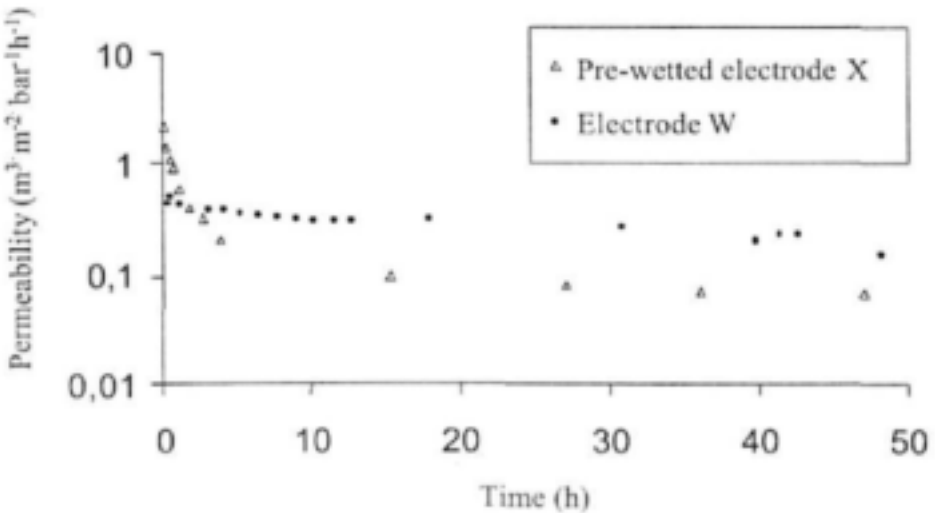

Figure 7.11. Permeability of sorption electrode W and X as function of time

The results obtained were quite surprising. The initial explanation offered was that water adsorption between the layered structure of ZrO_2 and ZrP [4] caused the decrease of permeability in time. However, the electrode that was soaked in water for 7 days (assuming that water adsorption equilibrium had been reached) showed an even more drastic decrease of permeability in time. Apart from loose ZrO_2 or ZrP particles inside the electrode, blockage could possibly be caused by traces of oil or impurities brought into the system via the pump or tubing of the "new" pilot plant.

Backflush (or backwash) is often used in micro- and ultra filtration systems to clean membrane surfaces [6]. The effect of backflush with air (1.4 bar, 1 minute) and water (3 bar, 1 minute) on the permeability of the sorption electrodes is shown in Figure 7.12. The permeability after the backflush did increase slightly but dropped down relatively quickly. The particles that appeared to be blocking the electrode were probably entrained inside the electrode and thus difficult to remove.

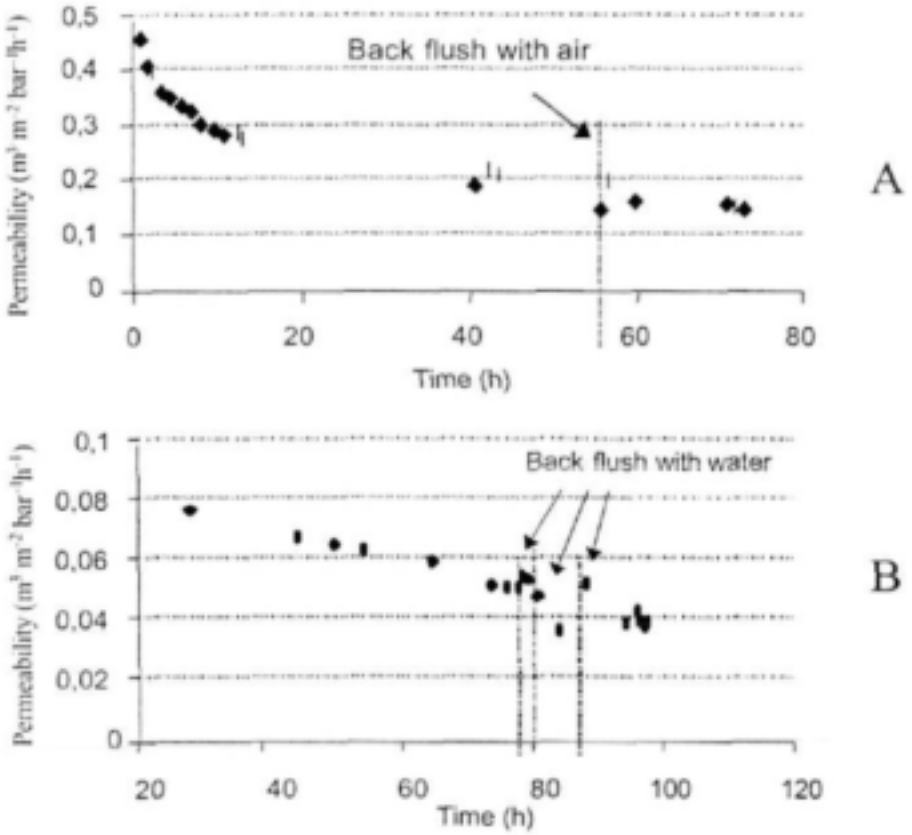

Figure 7.12. The effect of backflush on the permeability of a sorption electrode using A) air and B) water

Table 7.11 shows further permeability results. These results were obtained from measurements taken after 50 hours when the permeability had become more or less stable. The calculated permeability under different conditions showed insignificant differences. In other words, the permeability seemed to be independent of electrode potential, reject flow rate or pressure difference (between 0.9 and 1.7 bar).

Table 7.14 Permeability as a function of ΔP, flow rate reject and electrode potential

ΔP (bar)	Flow rate reject ($l \cdot h^{-1}$)	Potential [a] (V)	Permeability ($m^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)
1.7	50	0	0.142
1.4	50	0	0.137
1.1	50	0	0.138
0.9	50	0	0.136
0.9	15	0	0.135
0.9	15	5	0.134

a) Potential difference between sorption and counter electrode

b) Transmembrane pressure difference

Figure 7.13 shows the change in flux during permeation of ultra pure water compared to microbe solution.

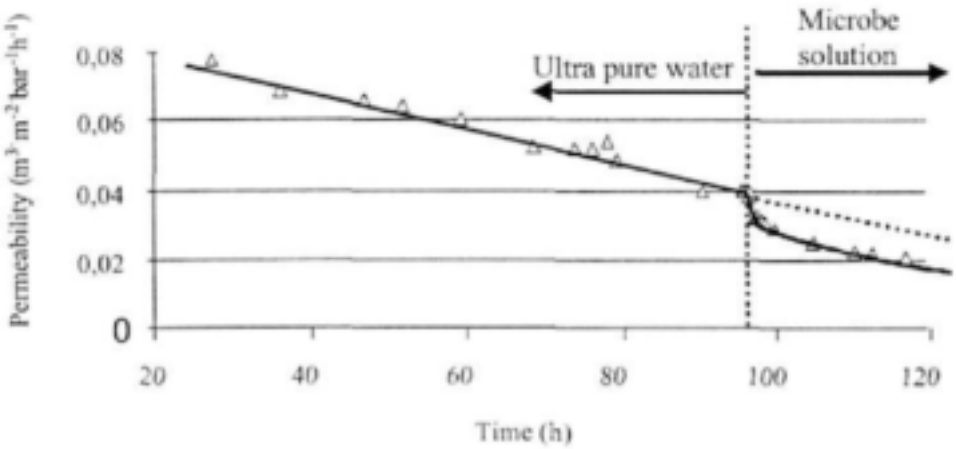

Figure 7.13. Change in permeability during permeation of ultra pure water and microbe solution. ΔP is 0.9, T=35°C

A strong decrease of permeability as a function of time could be seen just after the microbe solution was pumped through the sorption electrode. A few hours thereafter the permeability decrease showed a similar trend as the extrapolated permeability results with ultra pure water. The permeability drop caused by the microbes seem to be more or less 30% and fairly stable over time. Treatment of raw water with ultrafiltration membranes [7] showed similar results as shown in Figure 7.14. The visual difference between the reject and the permeate were clear as is shown in Figure 7.15

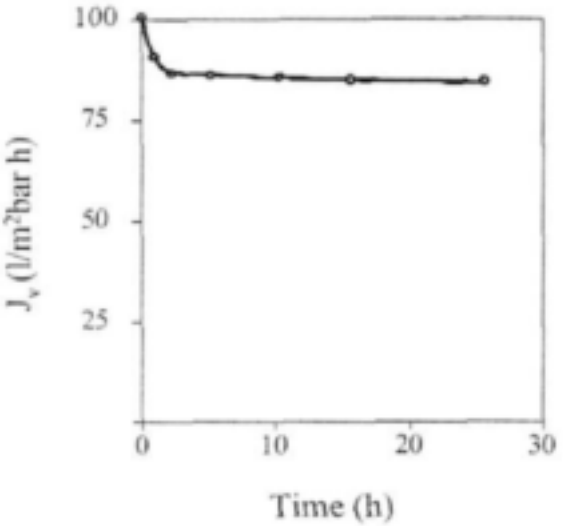

Figure 7.14. Changes in permeability during treatment of raw water [7]

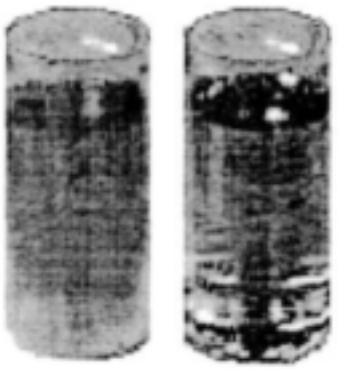

Figure 7.15. Reject (left) and permeate (right) of microbe solution

7.5.3.2 Separation properties of the sorption electrode

The permeate was collected as a clear solution while the feed solution and the reject looked cloudy as shown in Figure 7.15. Table 7.12 shows that the electro sorption electrode rejected at least 96% of the microbes. The efficiency of the electro sorption electrode was found to be higher than the efficiency of the 0.45µm filter. The retention coefficient (R_{OD}) for the electro sorption unit and the polypropylene filter 0.45µm was calculated using the following equation [7].

$$R_{OD} = (1 - \frac{abs_p}{abs_r}) * 100 \qquad (7.1)$$

where abs_p absorbance permeate sample

abs_r absorbance reject sample

Table 7.15 Retention coefficients for electro sorption electrode and 0.45µm sample filter

Sample Set [a]	Time (h)	Absorbance Permeate	Reject	R_{OO} (%)	Filter [b]
1	-	0.024	0.382	94	0.45 µm filter
2	0.39	0.015	0.454	97	Sorption electrode X
3	0.78	0.017	0.389	96	Sorption electrode X
4	1.18	0.017	0.399	96	Sorption electrode X
5	1.86	0.008	0.412	98	Sorption electrode X
6	3.01	0.007	0.398	98	Sorption electrode X
7	7.93	0.008	0.36	98	Sorption electrode X
8	13.28	0.009	0.389	98	Sorption electrode X
9	15.57	0.006	0.389	98	Sorption electrode X
10	19.92	0.007	0.408	98	Sorption electrode X
11	23.65	0.01	0.444	98	Sorption electrode X

a) Sample set consisting of permeate and reject

b) Sorption electrode X after 95 hours with ultra pure water

The separation efficiency was possibly even higher since an ultra pure water sample was taken as a reference solution with 0% microbes. A possible error may have been introduced because the absorbance of the ionic species in the microbe solution was neglected. During the calibration of the spectrophotometer it became clear that the concentration of microbes in solution was proportional to the absorbance Figure 7.16.

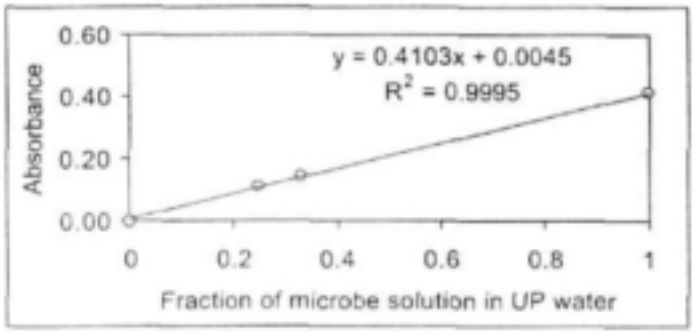

Figure 7.16. Calibration of the spectrophotometer. Absorbance as a function of the fraction of microbe solution in ultra pure water

7.5.4 Conclusions on micro filtration properties of electro sorption membranes.

- The electro sorption electrode could be used to separate microbes from the microbe solution with an efficiency of at least 96%.

- The filter efficiency of the electro sorption electrode was higher than a standard 0.45 micrometer filter. The permeate of a standard filter contained 6% of the microbes whereas the concentration in the permeate using the electro sorption filter was as low as 2%.

- The permeability decrease caused by rejected microbe solution was about 30% of the initial permeability.

7.6 References

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8 ECONOMIC EVALUATION AND COMPARISON OF ELECTRO SORPTION PROCESSES WITH OTHER WATER TREATMENT MEMBRANE PROCESSES

Abstract

The economic evaluation of the tubular and flat sheet electro sorption membrane based on cost and capacity of the sorption material showed that flat sheet electro sorption membrane are $45 per m^2. The cost of the tuibular electrosoprtion membranes were much higher ($690 per m^2) but may still be interesting if microfiltration of the feed stream is required. The cost of water purification using the developed electro sorption modules is compared with the cost of water purification using electro dialysis.

8.1 Cost of sorption material for tubular and flat sheet electro sorption systems

The operational calculations for production of 100 m^2 sorption composite for the flat sheet electro sorption process and 100 m^2 tubular sorption electrodes are described. The calculations were based on the following statements:

- Material production by Ltd. Facilities
- The equipment which is used for the production is rented at the production base of Ukrainian National Academy of Sciences
- The prices for the raw materials, electrical energy are actual on July 2001. The dollar rate at that moment: 5.35 hrivna per 1 USA dollar
- Provision for taxation corresponding to the effective law.

The analysis of filter production pattern demonstrates that the main expenses are connected with the value of used raw materials, and also fuel and electrical energy up to 38%. The labour cost equals approximately 8% from the total expenses. Therefore 46% of the expense was composed of the labour cost, raw material and energy cost. So to decrease the cost of sorption composite material it is necessary to decrease the cost of raw materials, electrical energy, increase the equipment productivity and decrease labour expenses. The taxes for the production, including 30% tax on income, are equal to 27,5%. The income, left at the venture, is equal to 11,7%.

8.1.1 Cost Analysis for Metal Filter Manufacturing

Material type

Table 8.1 shows the complete breakdown of costs for sorption composite material based on fibrous ceramic paper and zirconium phosphate. The costs are calculated per 100m^2, which is the the maximum possible scale for meaningfull predictions.

Table 8.1 Quantity of material: 100 m^2

N	Cost factors	Percentage of cost	Cost in USD	
		Tubular/Flat sheet	Tubular	Flat sheet
1.	Raw materials (Table 8.2)		45270	1400
2.	Fuel and electricity		200	200
3.	Main salaries (Table 8.3)		220	340
4.	Additional salaries		50	152
5.	Pension and trade union funds	30 / 36	60	170
6.	Equipment maintenance	100	372	372
7.	Unemployment fund	1.5	0	5.6
8.	Chernobyl fund	10	0	37.2
9.	Plant-related cost		46172	2676.8
10.	Non-manufacturing cost	1% p.9	461.72	26.8
11.	Projected cost		46633.72	2703.6
12.	Transport	3-5% p.11	1865.35	108.1
13.	Complete cost with transport		48499.07	2811.7
14.	Road maintenance fund	1% .19	484.99	26.8
15.	Complete cost with all fund payments		48984.06	28.38.5
16.	Profit	25%	12246.02	709.6
17.	Wholesale price		61230.08	3548.1
18.	VAT	20	8572.21	709.6
19.	Customer price		69802.29	4257.7

Table 8.2 and Table 8.3 show how the raw materials cost and main salaries were calculated. The suggested customer price for 100 m^2 of sorption composite material based on fibrous ceramic paper with zirconium phosphate was $4257.70. The customer price for 100m^2 of tubular sorption electrode was estimated on $62970.73. The largest part of the cost was due to the relatively high price of tubular ceramic supports. The lower cost of other zirconyl chloride and phosphoric acid

supports are due to the lower impregnation volume. 1 tube of 1m length had a surface area of $0.022m^2$ thus to get $100m^2$, 4500 tubes are needed.

Table 8.2 Raw materials expenditure

Raw materials	Quantity		Price		Total
	Tubular	Flat sheet		Tubular	Flat sheet
Ceramic tubes (#)	4500	-	10	45000	
Ceramic Paper (m^2)	-	100	5.0		500
Zirconyl Chloride (kg)	25	200	5.0	125	500
Phosphoric acid (kg)	15	100	3.0	45	300
Other				100	100
Total				45270	1400

Table 8.3 Labour costs

Unit operation	Measuring unit	Quantity	Qualification level	Total ($)	
				Tubular	Flat sheet
Chemical treatment	worker	2	IV	120	240
Pyrolysis and drying	-"-	1	III	100	100
Total				220	340

8.2 Cost of electro sorption for tubular and flat sheet electro sorption systems

In this section an estimation is given for the total cost to construct two electro sorption plants with electro sorption electrodes with surface area of $100m^2$, one based on tubular sorption electrodes and one based on flat sheet sorption electrodes. Hereafter, the capacity of the plants will be compared based on experimental results obtained on small scale.

8.2.1 Cost of pilot plant

Table 8.4 shows the estimated cost of a tubular and a flat sheet electrode reactor. In Table 8.5 the total costs are calculated for the realisation of the electro sorption capacity of the sorption electrode.

Table 8.4 Estimated cost of a tubular and a flat sheet electrode reactor with $1m^2$ sorption electrode

Description	Quantity		Cost ($)	
	Tubular	flat sheet	tubular	flat sheet
Flat sheet electrodes ($1m^2$)		1		14.00
Tubular sorption electrodes (1 m^2)	45		453.00	
Carbon electrodes (0.6cm OD, length 100cm)	45	1	135.00	10.00
Base materials			10.00	10.00
Labour, instruments, machinery (20$\cdot$ h^{-1})	4	2	80.00	40.00
Subtotal			140.00	80.00
Total including accessories 20% [1] (connections, wires, O-rings)			818.00	140.00

Table 8.5 Total cost for the realisation of the electro sorption system

Description	Cost ($)	Cost ($)
	Tubular	flat sheet
Pilot plant	10,000.00	10,000.00
100 Reactors (100x value in Table 8.4))	81,800.00	14,000.00
Installation equipment (10%)	9,180.00	2,400.00
Transportation of the main materials (3%)	2,754.00	800.00
Auxiliary equipment	3,000.00	3,000.00
Civil infrastructure and engineering	1,000.00	1,000.00
Subtotal	107,734.00	31,200.00
Total including engineering studies and all other costs (+10%)	118,507.40	34,320.00

8.2.2 Capacity of the pilot plant

Costs associated with the sorption experiment treating the Klipfontein model solution with tubular sorption electrodes (see section 6.1) and the sorption experiment treating a mine water model solution were calculated. The calculated plant capacity is shown in Table 8.6. The pilot plant with flat sheet sorption electrodes was more effective and energy efficient than the tubular electrodes for the removal of salts. With a similar electrode surface it was possible to obtain a higher degree of purification even when a feed solution with higher TDS was used. Moreover, the total cost of the

purification system with $100m^2$ flat sheet sorption electrodes was much lower than that of a pilot plant with $100m^2$ of tubular electrodes. The filtration properties using the tubular electro sorption system were not demonstrated with these experiments.

Table 8.6 Pilot plant requirements for treating a Klipfontein model solution and a mine water model solution.

Plant Capacity	Water source	
	Model A	Model B
Feed flow rate ($m^3 \cdot h^{-1}$)	3	3
The trans membrane pressure (kPa)	150	50
Degree of purification	40%Ca^{+2} and 30%Cl	50% TDS
Energy cost ($kWh \cdot kg^{-1}$)	19	4

Model A: Klipfontein (TDS 1458$mg \cdot l^{-1}$, see Table 7.1)

Model B: Mine water (TDS 3425$mg \cdot l^{-1}$, see section 5.2)

The costs of simultaneous removal of suspended solids and ionic species from aqueous solution using tubular electro sorption filtration are high. Flat sheet electrodes are easy to upscale and relative large loading of sorption phase can be realized resulting in higher sorption capacity per unit of area. The energy consumption of the tubular electrode systems is also relatively high. This may be partially a result of the fact that the sorption electrode is used in flow through electro sorption electrode.

8.3 Running cost

8.3.1 Running cost of the tubular electro sorption module

The running cost of the electro sorption system and the energy requirement are already shown in chapter 6. In Table 8.7 the results are presented in summary.

Table 8.7 Results of electro sorption experiments

Exp. No	Average adsorption/desorption during experiment Na^+	Cl^-	Mg^{2+}	SO_4^{-2}	Ca^{+2}	E consumption (kWh· kg^{-1})
A				65/30	25/10	8
B				25/15	65/20	15
C1				55/31	55/42	10
C2				45/43	40/42	15
C3				51/33	45/39	13
D				35/40	40/35	13
F				35/30	40/25	13
G				40/30	45/35	9
H				20/30	30/35	13
J				30/35	25/30	9
K				10/10	5/10	21
Q	-6/-4	40/31	36/2	8/12	55/75	25
R	-5/-9	15/20	28/0	5/5	30/20	19
S	-	70/40	20/10	-/-	75/75	55

Under the most efficient conditions the energy consumption was 9 kWh· kg^{-1} removed salt. A comparison of performance between electro sorption and electro dialysis was made and is presented in the next section. The negative adsorption/desorption values for Na^+ means that the concentration of ionic species in the permeate increased during the adsorption step. This unusual result was observed with Na^+ ions only. It is believed that Na^+ ions, which have lower affinity towards the ion exchange sites than doubly charged ions, are pulled through the membrane to compensate for the charges of the adsorbed Ca^{2+} and Mg^{2+} ions.

8.4 Possible economic application for the electro sorption

The damage caused by scale on heating elements in household apparatus such as boilers, kettles, Irons and washing machines is well known. The scale mainly consists of $CaCO_3$ that is formed on hot surfaces in the presence of Ca^{+2} and CO_3^{-2} ions. The electro sorption unit could prevent formation of $CaCO_3$ by adsorbing the ions when the element is hot. After heating the ions may be desorbed back into the water since the ions are not harmful for the user but only for the heating element. Scale will thus not be accumulated on the surface of the element. It is important to note that the sorption unit would not be expensive. The flat sheet sorption electrode could be a potential candidate.

A comparison of performance between electro sorption and electro dialysis was made and is presented in Table 8.8.

Table 8.8 Comparison of performance between electro sorption and electro dialysis

Process parameter	Electro sorption reactor		Electro dialysis
	Flat sheet	Tubular	
DC power supply to reactor	0.7 – 1 kWh· kg^{-1} -ground water 500 TDS 2 –3 kWh· kg^{-1} - mine water 3500 TDS 3-6 kWh· kg^{-1} - electroplating effluent 3000 TDS	25 kWh· kg^{-1} – ground water 500 TDS 15 kWh· kg^{-1} – 1500TDS	0.5 kWh· kg^{-1} - ground water 400 TDS 1.2 kWh· kg^{-1} – mine water 3500 TDS
Pumping energy	Requires less than 1 bar pressure 0.1 – 0.3 kWh· kg^{-1}	Requires 1-2 bar Pressure 0.2-0.4 kWh· kg^{-1}	Requires 4 bar pressure 0.5 – 1 kWh· kg^{-1} for brackish water of 1000 TDS
Total energy consumption	Estimated 3 + kWh· kg^{-1} – 3500 TDS	Estimated 15 kWh· kg^{-1} -3500 TDS	1.5 kWh· kg^{-1} – 500 TDS 4 kWh· kg^{-1} – 3500 TDS
Membrane fouling	Ions - can be controlled Gasses – possibly H_2S Silica Colloids Large ions - ? Ions - can be controlled		Ions – heavy metals Gasses – O_2, CO_2, H_2S Silica Colloids Dissolved organics Large ions
Pre-treatment	Suspended solids filters	Precipitation of insoluble species	Suspended solids – filters Precipitation – ion exchange softening
Concentration diluting streams	Limited by ion exchange capacity and regeneration ability		Limited by back diffusion
Concentration of electrode stream	No		Additional operation parameter
Temperature	No effect on membrane life		Negative effect on membrane life
Membrane cost	Support R 120 – R 200 m^2, total cost up to R 300 – R 500 m^2	R 6000 m^2 cost directly related to ceramic support	R 400 – R 2000 m^2
Stack design	No high voltages – low current leakage through supply ducts		High overall voltages require high resistances of supply ducts
Hydraulic staging	Up to 90% removal possible ion one stage		40 – 50% removal in one stage requires several stages
$CaSO_4$ saturation	Controlled electrochemically		Maximum 175%

The 175% of $CaSO_4$ mentioned in table 8.8 means that the solution can be oversaturated by an order of 1.75. Above this value the precipitation will be so fast that clogging and fouling of the membrane is inevitable.

8.5 References

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2. J. Mallevialle, J. P.E. Odendaal, M.R.Wiesner (Eds), *Water treatment membrane processes.* AWWA, Lyonnaise des Eaux", WRC of SA. Mcgraw-Hill: New York (1996).

CONCLUSIONS PART A

A new type of purification unit was developed that is capable of removing ionic species AND micro particles from aqueous solutions. The unit exhibited non-chemical regeneration ability and required low pressure and only electrical energy for the purification of a solution. The developed purification unit is novel since conventional purification systems can only be used for desalination or microfiltration and require chemicals or high pressures during operation.

In the electrosorption system where microfiltration and desalination are combined, energy losses are difficult to avoid. The minimal energy consumption observed was 8 $kWh \cdot kg^{-1}$. It was calculated that roughly 25% of the protons and hydroxyl ions generated were effectively involved in the activation of sorption material.

The purification was based on microfiltration and electrochemically activated sorption. The purification units were prepared by modification of ceramic-based microfiltration units. The main achievements during the modifications were:

- The preparation of electroconductive and permeable coatings of, nickel, gold and carbon on ceramic substrates were optimized to control both permeability and conductivity
- The preparation of electrocatalytic coatings containing Pt-Si-Mo with high catalytic activity for water electrolysis and methanol oxidation
- Preparation, impregnation and optimization of zirconia and zirconium phosphate as sorption material. Maximal reversible sorption capacity of zirconia was $1.8meq \cdot g^{-1}$, maximal sorption capacity of zirconium phosphate was $1meq \cdot g^{-1}$
- A gradient of phosphorized ZrO_2 over the cross sectional diameter of the tube was essential.

Several reactors were manufactured to support the electrosorption unit. The main achievements in this area were:

- Watertight sealings were prepared by partial impregnation of microfiltration substrates with Na-silicate
- Conductive O-rings could be used to establish electrical contact between the sorption electrode and the potentiostat
- A upscalable and easy to assemble multiple tubular electrode reactor was developed

- A fully automated pilot plant was designed, manufactured and tested. The quality of permeating water was determined by measurements of conductivity and pH. The combination of these parameters was used to start or stop the regeneration and adsorption cycles.

During the optimization of the electrosorption process and preparation procedure the following conclusions were drawn:

- The optimal phosphorization time was found to be 4 hours
- Electrodes prepared from Al_2O_3 supports with 0.9μm pores showed better removal efficiencies than electrodes prepared from Al_2O_3 support with 3μm pores
- The electrical connection between a power source and a sorption electrode could be established using an electro conductive O-ring
- Deposition of Pt decreased the potential difference for water electrolysis. The energy consumption per kg salt removed did however not show any improvements
- The optimal potential difference between the sorption electrode and the counter electrode was found to be 4V. Although 5V potential difference resulted in similar energy efficiency, relatively poorer desorption characteristics were obtained
- The permeation flow should be close to $2ml \cdot min^{-1}$ (flux: $0.5\ m^3 \cdot h^{-1} \cdot m^{-2}$) when a potential difference of 5V is applied. Lower permeation flows resulted in lower desorption percentage and higher permeation flows resulted in lower removal efficiencies
- Removal efficiencies of both cations and anions >50% were obtained at a permeate/reject ratio of 0.5. Higher ratios led to lower removal efficiencies. Lower ratios may lead to higher removal efficiencies but will lead to low water recovery
- Using the current density as a control parameter during the electro sorption process instead of the potential difference may increase electrode lifetime. Calculation of the minimal required current density may give an indication of the efficiency of the electro sorption process.

Specific properties of the purification unit for different waters sources:

- The simultaneous adsorption of Ca^{2+} and SO_4^{2-} (93 and 69%, respectively) from a $1.4\ g \cdot l^{-1}$ $CaSO_4$ solution. The simultaneous desorption of Ca^{2+} and SO_4^{2-} was observed after switching the sorption electrode to an anode. Adsorption and desorption efficiencies remained unchanged for several cycles

- The filter efficiency of the electro sorption electrode was higher than a standard 0.45 micrometer filter. The permeate of a standard filter contained 6% of the microbes whereas the concentration in the permeate using the electrosorption filter was as low as 2%
- Ca^{2+} and Cl^- were most efficiently removed. Effluents containing large amounts of Fe, Ni or other elements that can easily be reduced may not be candidate ions for electrosorptive removal. All reactions besides water oxidation and reduction, such as reduction of metal ions and oxidation of Cl^- disturb the development of a pH profile necessary for controlled adsorption and desorption of ions
- With the hybrid system where an electrolysis reactor was placed in series with the electro sorption reactor, it was possible to treat Brugspruit water, an acid mine drainage effluent. Over 99% of Fe was removed by neutralizing the Brugspruit water electrochemically and 30% of Ca^{+2} was removed by a single pass through the electrosorption unit

Besides the preparation and extensive testing and optimization of the electrosorption process the following was done:

- Two mathematical models were developed. Model I showed that ionic diffusion could not be neglected. The predictions made with model II are in excellent agreement with the experimental findings for currents up to 100mA
- An alternative desalination system was described in which 72% of Na^+ and 50% of SO_4^{-2} was removed from 0.01M (1.4g· l^{-1}) Na_2SO_4. The total energy consumption for desalination and regeneration was 23.8kWh/kg. The water recovery was 38%. Simultaneously 0.4 liter of H_2 and 0.2 liter O_2 were produced from every 2 liter solution treated

Since the properties of both microfiltration and desalination could be combined in one unit using an electrochemically activated ion exchange mechanism, the project aims were reached.

PART B

9 ELECTROMEMBRANE REACTORS FOR DISINFECTION OF AQUEOUS SOLUTIONS

Abstract

Current electrochemical methods for the generation of disinfecting agents are dominated by the chlor-alkali industry, based on the electrolysis of brine to produce chlorine, sodium hydroxide and hydrogen. Alternative technologies such as the use of electro membranes could be employed as they may reduce the energy consumption and thus the cost of chlorine production, allowing the production of cheaper chlorine products for all communities and a disinfection technology that is reliable, appropriate and effective for small and rural communities not served by urban infra-structure.

This project focused on hypochlorite generation via the electrolysis of brine and its specific objectives were:

- The development of dimensionally stable anodes with electro catalytic coatings for optimisation of chlorine evolution as opposed to oxygen evolution
- Development of a cell design that allows minimal toxic chlorate generation
- Design cells with good current efficiency for chlorine generation (better than that of existing technologies)
- Low power consumption, less than that in conventional cells
- Facility to control the pH of the hypochlorite solution produced.

Design of cells for electrochemical generation of disinfecting agents

The cell designs separated the anodic and cathodic compartments to prevent mixing of the cathodic and anodic products. A diaphragm, porous to aqueous inorganic ions, was employed to divide the cell. To minimize diffusion of hydroxide ions through the diaphragm back into the anolyte (brine), the catholyte (water) movement was designed as a separate flow stream. Hence brine flowed

through the anode chamber and was converted to low pH hypochlorite whereas water flowed through the cathode chamber and was converted to high pH sodium hydroxide solution. For practical reasons of availability the diaphragm chosen was a porous inorganic tubular membrane (aluminium – zirconium oxide based). The tubular shape allowed a cell to be readily designed and constructed consisting of tubes of different diameters. Two different membrane coatings were utilised in this project, RuO_2, which has a rutile structure and is electrically conducting, and Co_3O_4, a conducting spinel oxide. The RuO_2 coating proved to be unstable and was not further developed here. The Co_3O_4 coating was applied thus: CoO was deposited on a titanium rod 5 mm in diameter. The starting material was Co_3O_4 which, when vaporised in a vacuum above 900°C, loses oxygen and is converted to CoO. The vaporisation was achieved by plasma deposition. However, CoO is non-conducting. It was converted to a conducting form of Co_3O_4 by electrochemical activation (oxidation). Activation was achieved by using the anode in the cell under hypochlorite generation operational conditions with a current density of 6 $mA \cdot cm^{-2}$ for 15 hours. During this period the colour of the coating changed from dark blue to black and a comparison of the galvanostatic polarization curves and hypochlorite current efficiencies were used as indicators of the termination of the oxidation process in the anode coatings. Later experiments found it preferable to pre-coat the titanium substrate with a layer of platinum prior to coating with CoO. This prevented oxidation of the titanium at the CoO/Ti interface during electrochemical activation.

Generation of hypochlorite using the electrolysers

Flows of anolyte and catholyte were controlled by gravity feeds of brine (sodium chloride in water as anolyte) and distilled water (catholyte). Hypochlorite and dissolved chlorine were analysed by back titration of liberated iodine with thiosulphate following addition of excess acidified potassium iodide. Hypochlorite concentrations were converted to *available chlorine* concentrations for comparison purposes. The presence of chlorate was tested by the manganese oxidation test.

Chemical considerations

In the cell, hydrogen is evolved at the steel rod or wire cathodes and OH^- ions accumulate. In the anolyte Cl_2 is evolved at the anode. Overall, two moles of added sodium chloride were converted to one mole of NaOCl. Under conditions of low pH in the anolyte, the hypochlorite existed almost entirely as HOCl, disproportionation to chlorate was suppressed and decomposition to oxygen was slow. Thus the anolyte consisted of dissolved chlorine, HOCl and HCl in water along with any unconverted NaCl. The catholyte consisted of dilute sodium hydroxide solution.

Generation of hypochlorite using the cobalt oxide electrolyser

The best results were obtained at 0.4 A using a low concentration of NaCl (25 g· l^{-1}) with flow rates of 50 ml· h^{-1} for the anolyte and 140 ml· h^{-1} for the catholyte. The *figures of merit* for the electrolyser were comparable to those achieved in chlor-alkali cells. Current efficiencies for Cl_2 were almost the same as those for NaOCl, there was no decrease in conductivity over long periods, the anodes were stable and chlorate was not detected. Duplicate experiments on the Co_3O_4 electrolyser at UWC provided broadly similar results. These results correspond to a production of about 11 g of chlorine per day. Some diffusion of hydroxide ions into the anolyte probably did occur and would have caused a reduction in current efficiency.

Conclusions on generation of disinfecting agents using a hypochlorite generator

The Co_3O_4 electrolyser hypochlorite generator is suitable as a disinfection technology for small and rural communities but is not a viable industrial chlorine generator. The major advantages over existing brine electrolysers include; no generation of toxic chlorate; pH control without the requirement of additional chemicals; and lower power requirements than other systems (suitable for electrical supply from solar panels). At 0.4 A, the electrolyser requires only 32 g of added salt per day to produce 11 g of chlorine, sufficient to disinfect 7200 litres of water at a dose of 1.5 mg· l^{-1} Cl_2. Hence the electrolyser can produce 50 litres of water per person per day for a community of 144 people at a low cost in terms of added chemicals and energy. A cost comparison based on a small community indicated that annual combined costs for a Co_3O_4 electrolyser water treatment plant were considerably less than for other systems currently in use (i.e. Moggod and on-site hypochlorite).

Overall the generation of hypochlorite by electrochemical means was a success. A research product was constructed that met the objectives of the project, i.e. the *cobalt oxide electrolyser*. In addition, the electrolyser has great potential for practical application as an appropriate reactor for generation of disinfecting agents for rural water supplies.

9.1 Introduction

Disinfection of water supplies is essential to the health of the world's population. Water related diseases are still a major cause of death, mainly through water-borne pathogens, in spite of more than a century of water disinfection practice.

The most often-used disinfection technology has been that of chlorination (l) via the addition of chlorine or chlorine compounds to water supplied to domestic users. This method has been successfully and appropriately applied in almost every town and city in the world. However, in rural areas of developing countries a major problem still remains. Also, small towns and peri-urban informal settlements adjacent to cities in such countries suffer from poor quality drinking water with pathogenic organism contamination.

Although water supply infrastructure is spreading slowly from the urban centres, it will be many years before such facilities reach the rural areas.

The problems with the practice of chlorination in rural areas, particularly in the South African context, have been investigated previously by earlier Water Research Commission studies (2, 3).

9.2 Problems that alternative technologies could address

Alternative technologies such as the use of electro membranes could address the following issues:

(a) Reduce the energy consumption and thus the cost of chlorine production, allowing the production of cheaper chlorine products for all communities great and small, urban and rural.

(b) Produce a disinfection technology that is reliable, appropriate and effective to small and rural communities not served by urban infra-structure.

Such a technology must be affordable, be technically simple but allow accurate dosing. It must be easy to maintain and operate. Most importantly, any materials or chemicals required should be readily available in that community.

9.3 Current electrochemical methods for the generation of disinfecting agents

The disinfecting agents considered here are chlorine and hypochlorite only. There are several others such as peracids and permanganate but these currently have only minor application and many associated problems (2, 4). The discussion that follows is in relation to problem 2 (a) above.

The chlor-alkali industry, based on the electrolysis of brine to produce chlorine, sodium hydroxide and hydrogen, is a heavy chemical industry generating in the order of 1×10^7 tons of chlorine in the USA alone (5). Chlorine for water treatment is only one of many uses of electrolytic chlorine (6).

There are three main chlorine cell technologies, mercury, diaphragm and membrane. These technologies can be compared and contrasted in many ways (4, 7) but what concerns this project initially is the scientific data relating to current efficiencies and energy consumption in terms of chlorine production. The reason for this is that any proposed alternative technology must at least equal the above figures of merit for existing technologies. To inspire a change the figures of merit of the new technology have to be significantly advantageous, unless there are other advantages due to unrelated considerations. The figures of merit thus create a baseline for the new technology that must be equalled or bettered.

Typical data for recent commercial chlor-alkali cells:

	Mercury cell	Diaphragm cell	Membrane cell
Cell voltage (v)	4.4	3.45	3.5
Current efficiency for Cl_2 (%)	97	96	93
Energy consumption KWh kg^{-1} of Cl_2	3.43	2.69	2.85

(Data adapted for Cl_2 from reference (4) page 109).

Hypochlorite generation is carried out in undivided electrolytic cells within which hypochlorite forms during the electrolysis of brine:

$$2Cl^- - 2e^- \quad Cl_2$$

$$2H_2O + 2e^- \quad H_2 + 2OH^-$$

$$Cl_2 + 2OH^- \quad H_2O + OCl^- + Cl^-$$

Further oxidation of hypochlorite also readily occurs in the basic solution via disproportionation:

$$3OCl^- \quad 2\,Cl^- + ClO_3^-$$

($K = 3 \times 10^{26}$; rapid reaction at 60°C (4))

In addition, chlorate also forms due to anodic oxidation:

$$6OCl^- + 3H_2O - 6e^- \quad 2ClO_3^- + 4\,Cl^- + 6H^+ + {}^3/_2\,O_2$$

Thus current efficiencies only reach 20% and energy consumption is in the range 4.5–7.0 kWh· kg^{-1} of NaOCl at cell voltages of 4 volts (4).

Divided cells using porous ceramic membranes with MnO_2 coated anodes have been reported (8) which had somewhat improved current efficiencies (but still well below 50%); it seems clear that it is extremely difficult for these to challenge the existing chlor-alkali cell technologies (which have current efficiencies above 90% coupled with relatively low energy consumption). However, greater opportunity exists in the field of hypochlorite generation.

Further opportunity exists to address problem 2 (b): small unit on site generation of hypochlorite can be adapted to meet the disinfection needs of small and rural populations (2).

9.4 Focus of the Project

This project focuses on hypochlorite generation via the electrolysis of brine.

9.5 Problems related to hypochlorite generation

Potential problems include:

(a) Corrosion of electrode materials by the caustic electrolyte, particularly the anode

(b) Anodic oxygen evolution

(c) Chlorate formation via disproportionation of hypochlorite and anodic oxidation of hypochlorite.

Chlorate formation not only affects current efficiency but also contaminates the disinfectant produced with a toxic species, namely the chlorate ion (1).

9.6 Project Objectives

(a) The development of dimensionally stable anodes with electro catalytic coatings for optimisation of chlorine evolution as opposed to oxygen evolution

(b) Development of a cell design that allows minimal toxic chlorate generation

(c) The cell must have good current efficiency for chlorine generation and better than that of existing technologies

(d) Power consumption must be low, less than that in conventional cells

(e) Facility to control the pH of the hypochlorite solution produced

9.7 Project team activities

The objectives of the project were pursued both in South Africa at UWC and in Kiev, Ukraine.

9.8 Development of cell design

In order to address objective 6 (b) it is clear that the cell design must incorporate division of the anodic and cathodic compartments to prevent mixing of the cathodic and anodic products.

During the electrolysis of brine the following reactions take place:

$2H_2O + 2e^-$	$H_2 + 2OH^-$	cathodic
$2Cl^-$	$Cl_2 + 2e^-$	anodic
$2H_2O + 2Cl^-$	$H_2 + Cl_2 + 2OH^-$	cell reaction

In an undivided cell the following reactions occur:

$$Cl_2 + H_2O \qquad HOCl + H^+ + Cl^-$$

$$HOCl + OH^- \qquad OCl^- + H_2O$$

Disproportionation will also occur:

$$3OCl^- \qquad 2Cl^- + ClO_3^-$$

and $$2HOCl + OCl^- \qquad ClO_3^- + 2Cl^- + 2H^+$$

It was therefore decided to incorporate a diaphragm that was porous to aqueous inorganic ions in order to divide the cell. To minimize diffusion of hydroxide ions through the diaphragm back into the anolyte (brine), the catholyte (water) movement was designed as a separate flow stream. Hence brine flowed through the anode chamber and was converted to low pH hypochlorite whereas water flowed through the cathode chamber and was converted to high pH sodium hydroxide solution. (Sodium ions migrated through the diaphragm to the cathode). This also allowed control of the pH of the sodium hypochlorite solution produced by adding only a chosen volume of the catholyte stream to the anolyte stream external to the cell (see objective 6 (e)).

For practical reasons of availability the diaphragm chosen by both the UWC and the Kiev groups was a porous inorganic tubular membrane (aluminium – zirconium oxide based). The tubular shape allowed a cell to be readily designed and constructed consisting of tubes of different diameters.

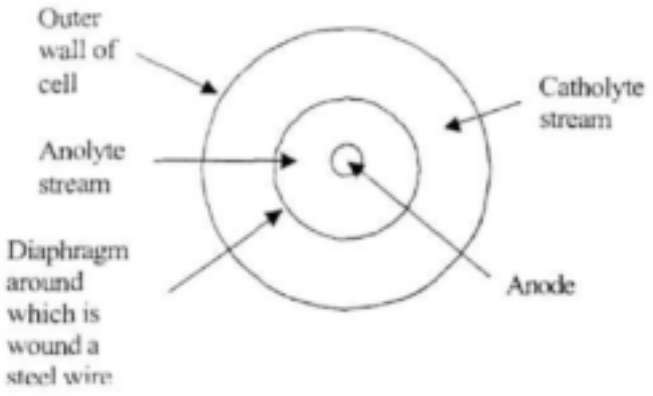


Figure 9.1 Cell designed by the Kiev group

Figure 9.1 depicts the cell designed by the Kiev group. It had an outer catholyte stream, the cathode consisting of a steel wire wound around the diaphragm. The anode chosen was a cylinder of titanium metal.

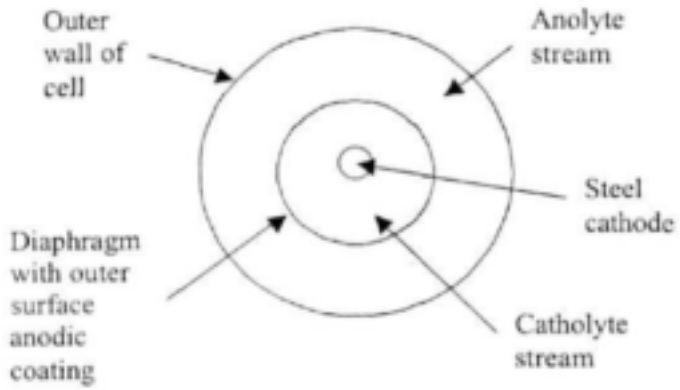


Figure 9.2 Cell used by the UWC group

Figure 9.2 shows the cell used by the UWC group, which followed the design of an anodic electro membrane (9.1). This consisted of an outer anolyte stream. The anodic conducting material was deposited on the outer surface of the diaphragm. The cathode was a steel rod inside the diaphragm. Thus two different designs were investigated based on the same diaphragm.

9.9 Development of anodes and anodic materials

A great deal of work has been done in the area relating to objective 6 (a). The development of the "dimensionally stable anodes" (DSA) anodes began some 30 years ago for application in the chlor-alkali electrolysis industry (10, p522). From a strict thermodynamic point of view, electrolysis of aqueous solutions of chlorides should give rise to the evolution of oxygen not chlorine:

H_2O $O_2 + 2H^+ + 2e^-$

Cl^- $Cl_2 + e^-$

Under equilibrium conditions even at low pH (= 0) the thermodynamic reversible potential for O_2 evolution falls below that of Cl_2. Fortunately chlorine is kinetically preferred at low pH on most materials (10, p537) so that between pH 0 and pH 4 chlorine is preferably evolved. On most materials used, chlorine evolution has a low overpotential whereas oxygen evolution takes place with large overpotentials, and with a marked dependency on the electrode material.

The most studied DSA is a titanium substrate coated with ruthenium dioxide. RuO_2 has a rutile structure and is electrically conducting (11). It has been shown that at low pH, between 2 and 4, and in spite of the oxygen overpotential being relatively low, current efficiencies of more than 90% with very little O_2 evolution can be obtained with RuO_2 anodes (10, p539). Compact RuO_2 layers as opposed to rough porous layers have better corrosion resistance (10, p587). UWC opted to use RuO_2 rather than the more easily obtained MnO_2 due to better current efficiency for Cl_2 evolution and better anode stability; MnO_2 is subject to dissolution in acid solution:

$$MnO_2 + 4HCl \qquad MnCl_2 + Cl_2 + 2H_2O$$

The Kiev group opted for Co_3O_4 (a conducting spinel oxide), which has a high oxygen overpotential and excellent stability to corrosion when deposited on titanium substrates. In addition Co_3O_4 acts as an electro catalyst for chlorine evolution (10, p656):

$Co^{II}O + Cl^-$	$ClCo^{III}O + e^-$	electrochemical step
$ClCo^{III}O$	$Co^{II}O + \frac{1}{2}Cl_2$	catalytic step
Cl^-	$\frac{1}{2}Cl_2 + e^-$	overall

The UWC group opted for the more difficult task of deposition of an oxide layer on the porous membrane rather than using a solid rod anode. The major difficulty was the uniform deposition of an oxide layer that was conducting but that did not block the porous membrane for Na^+ diffusion. The Kiev group had access to plasma deposition technology suitable for deposition of a layer of CoO on a solid substrate, which could then be electrochemically activated (oxidised) to a conducting "Co_3O_4" surface (12).

9.10 Development of the RuO_2 coated membranes at UWC

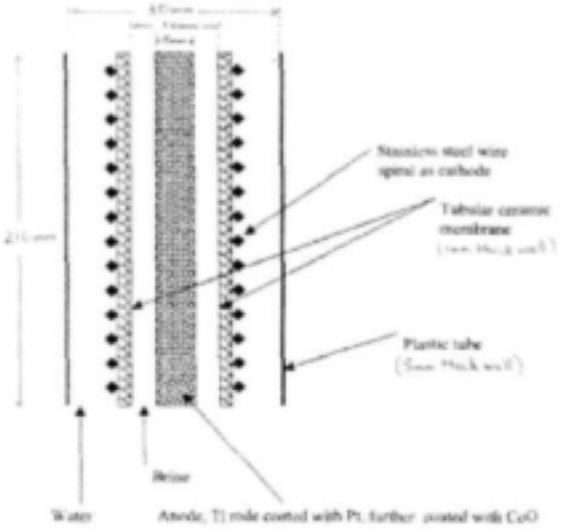
Although a method of coating the membrane with RuO_2 was developed the coatings were unstable when used for brine electrolysis and thus the method was not further developed.

9.11 Development of "Co_3O_4" coated anodes in Kiev

CoO was deposited on a titanium rod 5mm in diameter. The starting material was Co_3O_4 which when vaporised in a vacuum above 900°C, loses oxygen and is converted to CoO (14,15). The vaporisation was achieved by plasma deposition. However, CoO is non-conducting. It was converted to a conducting form of Co_3O_4 by electrochemical activation (oxidation). Activation was achieved by using the anode in the cell under hypochlorite generation operational conditions with a current density of $6mA \cdot cm^{-2}$ for 15 hours. During this period the colour of the coating changed from dark blue to black and a comparison of the galvanostatic polarization curves and hypochlorite current efficiencies were used as indicators of the termination of the oxidation process in the anode coatings (16). In further experiments it was found preferable to pre-coat the titanium substrate with a layer of platinum prior to coating with CoO. This prevented oxidation of the titanium at the CoO/Ti interface during electrochemical activation (16).

9.12 Presentation of the electrolysers

The laboratory membrane reactor for hypochlorite generation is illustrated in the photograph and diagram below.



Schematic diagram of membrane electrolyser with cobalt oxide catalyst

9.13 Generation of hypochlorite using the electrolysers

9.13.1 General

(a) Volumes and flow rates

Flows of anolyte and catholyte were controlled by gravity feeds of brine (sodium chloride (GPR) in distilled water as anolyte) and distilled water (catholyte). Flow rates through the cell were calculated from total volumes delivered and the cell dimensions.

(b) Analytical methods

Hypochlorite and dissolved chlorine were analysed by back titration of liberated iodine with thiosulphate following addition of excess acidified potassium iodide:

$NaOCl + 2HI \rightarrow 2NaCl + I_2 + H_2O$

$Cl_2 + 2HI \rightarrow 2HCl + I_2$

Hypochlorite concentrations were converted to "available chlorine" concentrations for comparison purposes.

The presence of chlorate was tested by the manganese oxidation test:

$ClO_3^- + 6Mn^{2+} + 12PO_4^{3-} + 6H^+ \quad 6[Mn(PO_4)_2]^{3-} + Cl^- + 3H_2O$

Where ClO_3^- ion gives a violet colour, the test having a sensitivity of 0.05 µg of ClO_3^- or concentration limit of 1 in 10^5 (17).

(c) Figures of merit of the electrolysers

These were calculated using the methods described in reference (4).

(d) Chemical considerations

In the cell the following reactions occurred:

$2H_2O + 2e^-$	$H_2 + 2OH^-$	cathodic
$2Cl^-$	$Cl_2 + 2e^-$	anodic
$2H_2O + 2Cl^-$	$H_2 + Cl_2 + 2OH^-$	cell reaction

Hydrogen is evolved at the steel rod or wire cathodes and OH^- ions accumulate.

In the anolyte: Cl_2 is evolved at the anode according to the reaction:

$Cl_2 + H_2O \quad HOCl + H^+ + Cl^-$

And : K acid $4.2 \times 10^{-4} mol^2 \cdot l^{-2}$

On mixing anolyte and catholyte the following reaction occurred:

$Cl_2 + NaOH \quad NaCl + NaOCl + H_2O$

As well as

$2NaOH + HOCl + HCl \quad NaOCl + NaCl + 2H_2O$

Thus, overall two moles of added sodium chloride were converted to one mole of NaOCl in a two electron transfer. Under conditions of low pH in the anolyte the hypochlorite existed almost entirely as HOCl:

$HOCl \quad H^+ + OCl^-$

K acid $2.9 \times 10^{-8} mol \cdot l^{-1}$

Thus the following disproportionation to chlorate is suppressed:

$2HOCl + OCl^- \quad ClO_3^- + 2Cl^- + 2H^+$

Decomposition to oxygen according to the following reaction, is slow :

HOCl HCl + Θ 2

Thus the anolyte should have consisted of dissolved chlorine, HOCl and HCl in water along with any unconverted NaCl. The catholyte should have consisted of dilute sodium hydroxide solution.

9.13.2 Generation of hypochlorite using the cobalt oxide electrolyser in Kiev

Experimental parameters and results obtained using the cobalt oxide electrolyser in Kiev are presented in Table 9.1.

Table 9.1 Sodium hypochlorite production using the cobalt oxide electrolyser (Kiev).

Current Density $mA.cm^{-2}$	*Cell Voltage (V)*	*NaCl Concentration* $(g \cdot l^{-1})$	*Flow Rate NaCl* $(ml \cdot h^{-1})$	*Flow Rate* H_2O $(ml \cdot h^{-1})$	*Concentration NaOCl* $(g \cdot l^{-1})$	*Production Of NaOCl* $(l\text{-}day^{-1})$	*Available Chlorine* $(g \cdot day^{-1})$
12	3.35	25	42	135	2.56	4.25	10.50
12	3.35	50	42	135	2.60	4.25	10.54
12	3.35	100	42	135	2.74	4.25	11.09
12	3.00	150	42	135	2.46	4.25	9.95
24	4.06	25	42	135	3.30	4.25	13.35
24	3.92	15	86	135	3.44	5.30	17.33
24	3.79	50	42	135	3.83	4.25	15.51
39	4.38	25	165	135	5.21	7.20	35.71
39	4.20	50	60	135	6.22	4.70	27.82

Anode Surface area = 33 cm^2.

Figures of merit calculated from the results obtained are presented in Table 9.2. The figures of merit were very encouraging.

Table 9.2 Figures of merit corresponding to results in Table 9.1.

Current Density $mA.cm^{-2}$	*Material yield* %	*kg NaCl per kg NaOCl*	*kg NaCl per kg* Cl_2	*Current efficiency* % for NaOCl	*Energy Consumption* $KWh \cdot kg^{-1}$ *NaOCl*	*Energy Consumption kWh/kg* Cl_2
12	68	2.32	2.44	82	2.96	3.10
12	34	4.56	4.79	83	2.80	2.94
12	18	8.66	9.09	87	2.53	2.66
12	11	14.5	15.1	78	2.75	2.89
24	87	1.80	1.89	53	5.56	5.84
24	55	2.83	2.97	68	4.13	4.33
24	51	3.10	3.25	61	4.62	4.86
39	60	2.66	2.77	87	3.64	3.83
39	64	2.46	2.58	67	4.48	4.70

It can be seen that at 0.4 A and using a low concentration of NaCl (25 $g \cdot l^{-1}$) the figures of merit for the electrolyser are comparable to those achieved in the chlor-alkali cells (see section 8.3 above).

In Table 9.2 current efficiencies for Cl_2 are almost the same (multiply by 0.952) as those for NaOCl. There was no evidence of decreasing conductivity over long periods of use and the anodes were stable. All tests for the presence of chlorate proved negative. The absence of chlorate was probably due to the relatively fast flow rate of the catholyte stream (0.006 $cm \cdot s^{-1}$), which swept away the hydroxide ions formed near the cathode before they could diffuse through the diaphragm into the anolyte (18). Thus all the objectives 6 (a) to 6 (d) were achieved.

9.13.3 Generation of hypochlorite using a cobalt oxide electrolyser at UWC

Following an analysis of the results from UWC and Kiev, it was decided to proceed with the cobalt oxide electrolyser and suspend work on the RuO_2 electrolyser. It was agreed that the "Co_3O_4" electrolyser be tested at UWC to check if the same results were obtainable and to check the possibility of pH control (objective 6 (e)). Table 9.4 presents data obtained for sodium hypochlorite production using the cobalt oxide electrolyser at UWC.

Table 9.3 Sodium hypochlorite production using the cobalt oxide electrolyser at UWC.

Current Density $mA.cm^{-2}$	Cell Voltage (V)	NaCl Conc. ($g \cdot l^{-1}$)	Flow Rate NaCl ($ml \cdot hr^{-1}$)	Flow Rate H_2O ($ml \cdot hr^{-1}$)	Conc. NaOCl ($g \cdot l^{-1}$)	Production of NaOCl ($l.day^{-1}$)	Available Chlorine ($g \cdot day^{-1}$)
12	3.19	25	51.5	141	2.45	4.62	10.76
12	3.20	25	52.5	139	2.51	4.60	10.99
24	4.01	25	49.5	141	3.41	4.57	14.85
24	3.99	25	50.0	142	3.40	4.58	14.84
39	4.45	25	70.0	141	4.51	5.05	21.67
39	4.41	25	71.0	140	4.49	5.06	21.61

Anode Surface Area = 33 cm^2.

Results were obtained using the same electrolyser without backwashing after intervals of two days during which the electrolyser was switched off. Many experiments were carried out with different flow rates and concentrations. The results presented here represent conditions where repeatable results were obtained. Each experiment lasted for two days. No fouling problems were experienced even after several weeks of use but during that time the system was washed with water several times. Figures of merit calculated from the results obtained are presented in Table 9.4. The figures of merit were again encouraging.

Table 9.4 Figures of merit corresponding to results in Table 9.3.

Current Density $mA.cm^{-2}$	Material yield %	kg NaCl per kg NaOCl	kg NaCl per kg Cl_2	Current Efficiency % for NaOCl	Energy Consumption $KWh \cdot kg^{-1}$ NaOCl	Energy Consumption $KWh \cdot kg^{-1} Cl_2$
12	58	2.73	2.87	85	2.71	2.84
12	58	2.73	2.87	87	2.66	2.79
24	82	1.91	2.00	58	4.94	5.19
24	82	1.90	1.99	58	4.90	5.15
39	83	1.87	1.96	53	6.15	6.46
39	84	1.88	1.97	52	6.06	6.36

The results are very comparable to those in Table 9.2 obtained in Kiev except at high current densities where there was deterioration in current efficiency and energy consumption. The best results were obtained at 0.4 A with NaCl concentration 25 g· l^{-1} as with the Kiev results.

9.13.4 Other results obtained with the cobalt oxide electrolyser at UWC

From the results presented above it can be seen that the best conditions obtained are at 0.4 A and 25 g· l^{-1} of NaCl solution with flow rates of 50 ml· h^{-1} for the anolyte and 140 ml· h^{-1} for the catholyte. These results correspond to a production of about 11 g of chlorine (i.e. 10.88 g Cl_2) per day. This yield of chlorine could be increased to about 22 g per day by running the cell at 1.3 A with a consequent loss of current efficiency and increased energy consumption.
Considering the 0.4 A, 25 g· l^{-1} case the expected and obtained pH values are as follows:

	Anolyte pH	Catholyte pH	Combined NaOCl (aq) pH
Expected	1.43	12.96	10.04
Found	3.53	11.73	10.00

The above data implies some diffusion of hydroxide ions into the anolyte and this will therefore have caused a reduction in current efficiency. Nevertheless, the above measured pH values show that objective 6 (e) has been achieved, since by mixing the anolyte (acidic) and catholyte (alkaline) the pH can be adjusted to values between 3.53 and 10.00 as desired.

It is worth noting that the combined NaOCl (aq) also is considerably saline due to only a 58% material yield. This caused an unused NaCl concentration of 10.5 g· l^{-1} and the Cl_2/NaOH reaction yields a further 2.5 g· l^{-1} NaCl. Thus the mixed 2.5 g· l^{-1} NaOCl solution contained 13 g· l^{-1} NaCl.

9.14 Recommendations for applications of the cobalt oxide electrolyser

In terms of addressing the problems outlined in section 9.2 of this report it is clear that the hypochlorite generator described here is not a viable alternative to the present chlor-alkali industrial systems for chlorine production in use today. The current efficiencies and energy consumption of the hypochlorite generator are not as good (although close) as for the chlor-alkali systems.
However the results achieved are much better than those reported for other small scale

hypochlorite generators (2, 4). Thus in terms of addressing problem 2 (b), as a suitable disinfection technology for small and rural communities, the electrolyser described in this report has great potential.

The major advantages over existing brine electrolysers are:

- elimination of toxic chlorate generation
- pH control without the requirement of additional chemicals (all required chemicals (except NaCl) are produced by the electrolyser on site)
- lower power requirements than other systems, and being very suitable for electrical supply from solar panels.

Assuming a raw water demand of 1.0mg $Cl_2 \cdot l^{-1}$ and a required residual of 0.5mg $Cl_2 \cdot l^{-1}$, a disinfecting dose of 1.5mg $Cl_2 \cdot l^{-1}$ is required. At 0.4 A the electrolyser requires only 32 g of added salt per day to produce 11 g of chlorine. This is sufficient to disinfect 7200 litres of water. At 1.3 A, the electrolyser requires 42 g of salt to produce 22 g of Cl_2 per day, sufficient to disinfect 14400 litres of water. Hence the electrolyser can produce 50 litres of water per person per day for a community of 250 people at a low cost in terms of added chemicals and energy. Several electrolysers could be run in parallel to supply larger communities. It is worth noting that on storing, the anolyte in a closed plastic container (without mixing with the catholyte) maintained the chlorine concentration and pH levels for a period of three days.

9.15 Cost comparison

These are based on requirements for a small community of 500 people, namely needing 27 m^3 of disinfected water per day. The figures are compared with those estimated by F. Solsona and I. Pearson in WRC Report No. 449/1/95 (reference 2). It is assumed that installation requirements are similar to those of current "on-site hypochlorite" generation except that, due to low power requirements, solar panel power generation would be appropriate for the cobalt oxide electrolyser described here.

(a) Capital Cost of Equipment

These would be similar to those "on-site hypochlorite" installations except gravity feed would substitute for a feeding pump thus reducing cost.

Moggod	R5 400
On-site hypochlorite	R3 700
Co_3O_4 electrolyser	R3 300

(b) Annual Manpower Costs

All systems R2 400

These are based on costs for 1995 as in reference 2, as for all costs quoted here for comparison purposes.

(c) Annual Chemical Costs

40.5 g/Cl_2 per day are required to disinfect 27 m^3 of water (reference 2).

Amount of NaCl required per day

Moggod	69 g
On-site hypochlorite	220 g
Co_3O_4 electrolyser	77 g

Annual Chemical Costs

Moggod	R40
On-site hypochlorite	R220
Co_3O_4 electrolyser	R45

(d) Annual Power Costs

The cobalt oxide (Co_3O_4) electrolyser uses much less power than the other systems *i.e.* other systems 2 kWh· day^{-1}, Co_3O_4 electrolyser 0.25 kWh· day^{-1}.

Moggod	R100
On-site hypochlorite	R100
Co_3O_4 electrolyser	R13

(e) Annual Equipment Costs

Assuming the lifespan of the systems in five years (*c.f.* (a) above).

Moggod	R1 080
On-site hypochlorite	R740

Co_3O_4 electrolyser R660

(f) Annual Maintenance Costs

It is assumed that these are the same as for "on-site hypochlorite".

Moggod	R420
On-site hypochlorite	R240
Co_3O_4 electrolyser	R240

(e) Annual Combined Costs

Moggod	R4 240
On-site hypochlorite	R3 950
Co_3O_4 electrolyser	R3 358

Thus the Co_3O_4 electrolyser system is significantly cheaper than other systems currently in use.

9.16 Conclusions part B

Overall the project was a success. A research product was constructed that met the objectives of the project, i.e. the *cobalt oxide electrolyser*. The Co_3O_4 electrolyser hypochlorite generator is suitable as a disinfection technology for small and rural communities but is not a viable industrial chlorine generator. The major advantages over existing brine electrolysers include; no generation of toxic chlorate; pH control without the requirement of additional chemicals; and lower power requirements than other systems (suitable for electrical supply from solar panels). At 0.4 A, the electrolyser requires only 32 g of added salt per day to produce 11 g of chlorine, sufficient to disinfect 7200 litres of water at a dose of 1.5 mg l^{-1} Cl_2. Hence the electrolyser can produce 50 litres of water per person per day for a community of 144 people at a low cost in terms of added chemicals and energy. A cost comparison based on a small community indicated that annual combined costs for a Co_3O_4 electrolyser water treatment plant were considerably less than for other systems currently in use (i.e. 26% cheaper than Moggod and 18% cheaper than on site hypochlorite).

Overall the generation of hypochlorite by electrochemical means was a success. A research product was constructed that met the objectives of the project, i.e. the *cobalt oxide electrolyser*. In addition, the electrolyser has great potential for practical application as an appropriate reactor for generation of disinfecting agents for rural water supplies.

9.17 References

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Appendix A: ELECTROLESS AND ELECTRO DEPOSITED PT ON ELECTRODE SYSTEMS MODIFIED WITH SI-MO AND SI-W

Preparation procedure

Three different types of electrodes, namely Pt-Ru, Pt/Si-Mo and Pt/Si-W were prepared. The first aim in the preparation of the electrode was to obtain a support with appropriate electro conductive properties.

Support preparation

The base of the support was a ZrO_2/metal composite membrane (Z100S Degussa, Germany). The Z100S support was coated with carbon by pyrolytic decomposition of LPG gas (Afrox) in order to obtain more homogeneous conductive properties of the support. The coatings procedure was similar to the procedure described in chapter 2. Briefly: Up to 10 strips of Z100S (1cm x 5cm, 0.1cm thick) were placed in the middle of a tube furnace. LPG gas was flowed over the Z100S strips at a rate of 5ml· min^{-1} whilst heating the furnace at a rate of 25°C· min^{-1}. When the furnace reached 900°C, the flow rate of the LPG gas was increased to a rate of 50ml· min^{-1}. The furnace was kept at 900°C for 30 minutes. After this period of time, the membrane strips were taken out of the tube furnace and cooled down in open air. The conductivity of the carbonised and plain supports was measured by means of impedance spectroscopy.

Preparation of the electrodes

To prepare the Pt-Ru electrode, 50mg of 40wt.% Pt-Ru on Vulcan (E-TEK) was suspended in 0.95g of ultra pure water and agitated in an ultrasonic bath. The suspension was spray coated onto the carbonised support and dried at 100°C for 1 hour.

To obtain the Pt-SiW and Pt-SiMo containing electrodes, the carbonised supports were first spray coated with a 5wt% carbon suspension. This suspension was prepared by mixing 500mg Vulcan XC72 with 10ml ultra pure water in an ultrasonic bath for 20 minutes. The spray coated carbon support was dried at 100°C for 1 hour. Subsequently the spray coated (and previously carbonised) supports were immersed into either a 5% silicomolybdic acid solution or a 10% silicotungstic acid solution and dried at 100°C for one hour. This immersion and drying procedure was repeated once for each support. Pt was finally deposited onto these supports using two different techniques namely

electro plating [19] and electroless plating [20]. Experimental details of the Pt deposition are listed in Table A1.

Table A1. Characteristics for Pt plating solutions

	Electroplating	Electroless plating
H_2PtCl_6 (Sigma Aldrich) ($g \cdot l^{-1}$)	10	40
Methanol vol.%	-	20
Formaldehyde Sigma 39% vol%	-	40
Supplied current ($mA \cdot cm^{-2}$)	8	-
Anode material	Pt foil	
Temperature (°C)	25	25
Time	3 minutes	1 day

Appendix B: MODIFICATION FOR WATERTIGHT MEMBRANE PARTS

Introduction

However favourable the connection using conductive O-ring might be, a further problem had to be solved. The conductive O-rings that were used appeared to be unstable under experimental conditions. The O-rings showed signs of corrosion resulting in a loss of electro-conductance. The combination of the high current density through the O-ring and the presence of water was most likely the cause of the instability of the O-ring material. More stable O-rings (such as platinum loaded O-rings), if commercially available, are not likely to be economically feasible. Available carbon loaded Orings may possibly be less sensitive to the presence of water but the conductivity is an order of magnitude lower. Use of such O-rings would lead to a significant potential drop between the power source and the sorption electrode, which was undesirable. Hence, a way had to be found to avoid the presence of water in order to prevent corrosion.

Because of the porous nature of the sorption electrode, Viton O-rings at both sides of the conductive O-ring did not prevent water from making contact with the conductive O-ring. A thin coating of impermeable material on the tip of the sorption electrode was not an option either since the O-ring had to make direct contact with the electro conductive phase of the sorption electrode. Water contact could be avoided only if the edge of the membrane was made impermeable as illustrated in Figure B1.

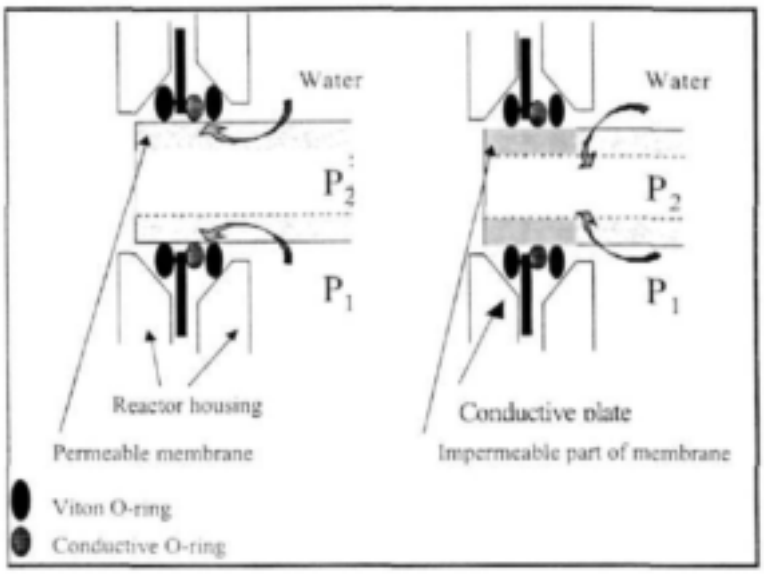

Figure B1. Schematic representation of how water contact could be avoided by making parts of the membrane impermeable

Experimental

Several experiments were conducted in order to prepare totally impermeable supports or support-edges. The experiments included total and partial impregnation with 40% Na-silicate solution (provided by Dr. Scott Khuel Stellenbosch University) followed by calcination procedure up to 1100°C.

The optimal method found to prepare a support with an impermeable edge and a minimal decrease of permeability for the rest of the support was the following:

A support was placed in a test tube with 1 ml of Na-silicate at the bottom.

Due to the capillary forces, the solution was sucked upwards. The impregnation height of the solution in the support could be monitored visually by the slight colour difference between the impregnated and the dry support

The support was taken out of the Na-silicate when the desired level of impregnation was reached (e.g. 1cm). The excess of Na-silicate on the inner and outer side of the support was wiped dry with a paper towel

The calcining procedure followed was to place the support in the furnace and ramp up the temperature to 120°C at 60°C· h^{-1}. Subsequently, a temperature ramp up to 1100°C at 600° C· h^{-1} was performed and thereafter the furnace was shut off and allowed to cool.

When the supports were once again at room temperature the impregnation procedure with Na-Silicate solution was repeated

Results and discussion

Na-silicate is a solid that starts to melt at 1100°C. Support impermeability after impregnation is most probably caused by a film of molten Na-silicate. In Table B1 the permeability of the support as a function of calcination time and temperature can be seen.

Table B1. Permeability as function of calcination temperature and time

Membrane Type	No	treatment	Temp °C	Duration min	Permeability (m3/m2/bar/h)	D* %
I	1	no			2.64	
		immersed in Na-silicate	900	60	0.81	69
		immersed in Na-silicate	1000	60	0.18	93
		immersed in Na-silicate 2x	1000	60	0.02	99.2
I	2	no			2.76	
		no	1100	60	2.14	22
		immersed in Na-silicate	1100	60	0.01	99.9
I	54	no			2.64	
		part impreg with Na-silicate	1100	0	0.20	92
		2nd impreg with Na-silicate	1100	0	**(Tip) 0.00**	100
I	55	no			2.88	
		Na-silicate tip 1x impregnated	1100	0		
		part 2x not impregnated	1100	0	2.42	16
		part 2x impreg with Na-silicate	1100	0	**(Tip) 0.00**	100

*Decrease in permeability

The results show that the supports that were impregnated twice and heated up to 1100°C in between (calcination time 0) were totally impermeable. A second impregnation and calcination procedure was preferred not only because total impermeability could be obtained but because the calcination times could also be reduced. This resulted in the highest permeability of the non-impregnated part of the support (comparing tube-no 2, with 22% decrease of permeability after heating up to 1100°C and holding at temperature for 60 min, and tube-no 55, with a 16 % decrease in permeability when twice heated up to 1100 for 0 hours).

Finally, the stability of the sodium silicate was tested. The supports treated with Na-silicate remained non-permeable after submerging in a 0.01M NaOH solution for 7 days (the pH of this solution is comparable with the pH of the solution during a cathodic cycle of an electro sorption experiment). However it is known that the silica in Na-silicate can be dissolved in alkaline solutions. It is not known yet how long this coating of Na-silicate could prevent contact of water with the conductive O-ring.

Appendix C: WATER PURIFICATION PILOT PLANT

Design features

The primary stage of the pilot plant shown in Figure C1 comprises a high pressure water circulation loop which incorporates a 120 litre storage tank, re-circulation pump, 1 micron depth filter and a pressure regulating valve with indicating gauge (0-4 bar).

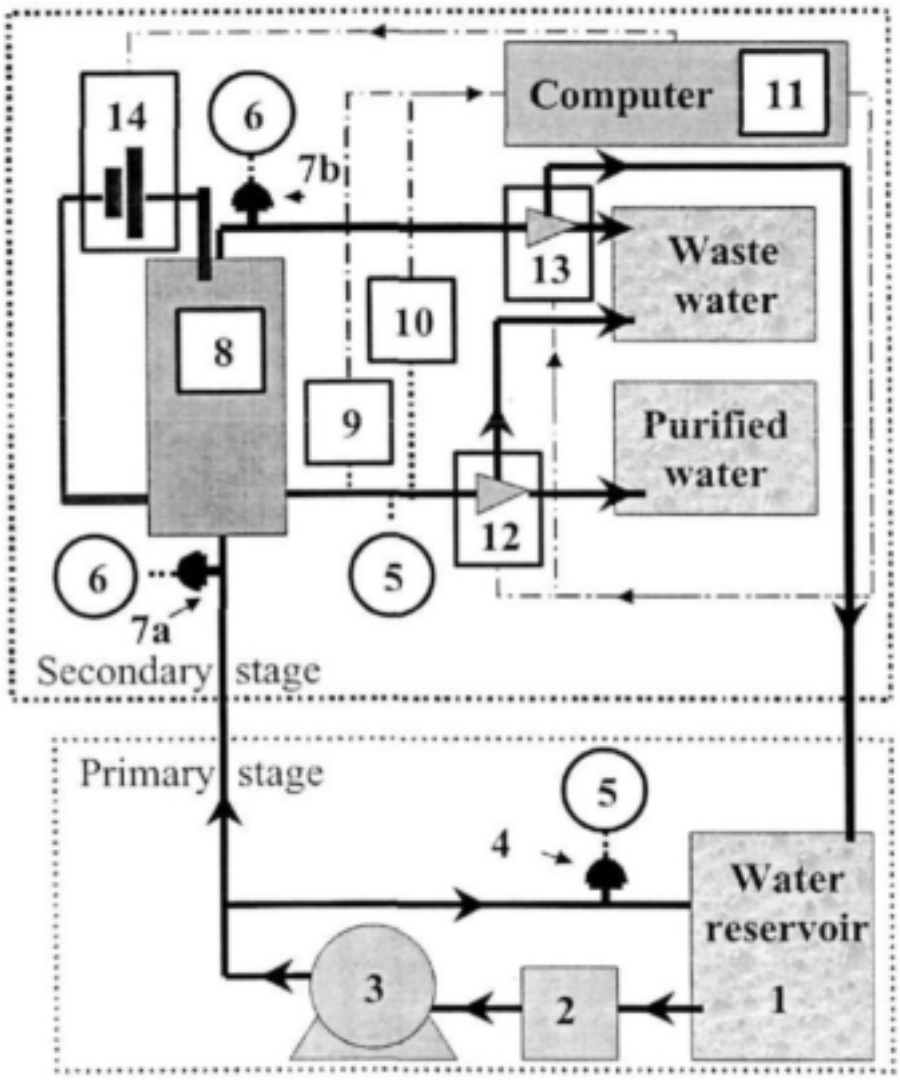

Figure C1. Schematic drawing of pilot plant for electro sorption

The secondary stage comprises a flow indicating rotameter with flow control valve on either side of the membrane reactor, an in-line conductivity probe connected to a meter, an in-line pH probe

connected to a meter, a normally open solenoid valve controlling outflow of purified water, a normally closed solenoid valve regulating outflow of wastewater, and a potentiostat (0-24V DC, 0-5 A) with reversible polarity for supplying current to the reactor membranes. Two relays (220v AC/24V DC) are energized via TTL relays situated on the Borwin A/D board and this operation is controlled via the I/O commands in the Borwin Software. The relay controlling the two solenoid valves is situated within the main switchboard enclosure. The relay controlling the polarity switching of the potentiostat is housed within the potentiostat unit itself. The third rela y (220v AC/24V DC) is energized via the 24V DC output from the potentiostat and switching of this relay is achieved via the red level switch situated in the storage tank. This relay circuit controls the power supply to the re-circulation pump. When the storage tank is more than 1/3 full the relay is energized and the pump will operate. However, should the water level drop below 1/3, the relay coil will no longer be energized and hence the pump will cease to operate. This safety mechanism is important, as the Pro-Con pump head fitted to the system cannot operate without water circulating through it.

The Pilot plant is supplied with 220v AC power via a double pole 15A main switch in which both live and neutral lines are broken. Voltage (220v) is supplied to a series of switches (LED indicating) which control the power supply (220v) to the re-circulation pump, pH meter, Conductivity Meter, potentiostat, and solenoid valves. There is one spare switch for the addition of another relay should the system require modification to include a stop flow option. All units drawing line voltage (220v) are earthed and will trip a functional earth-leakage relay system should either the live or neutral line leak to earth. Circuits that could be directly exposed to water (level switch) carry a line voltage of only 24V DC.

The pH meter has a signal voltage output of 0-10V DC. This means that each pH unit in the dynamic range of this meter (2-12 pH units) corresponds to a voltage output of approximately 1V or 1000mV. The Conductivity meter also has a signal voltage output of 0-10V DC and the range of this meter is 0-500uS· cm^{-1}, which means that each uS· cm^{-1} corresponds to approximately 20mV or 0.02V. Both these units can be connected to the Borwin A/D Board and the Borwin Software can be configured such that the solenoid valves can be controlled based on individual or combined signal output values (see below).

Operational instructions

Before you start the experiment:

The Storage tank should be at least ½full and the pressure -regulating valve should be fully open. The flow control valve between the filter housing and the membrane reactor should be fully closed and the flow control valve after the reactor should be fully open. The solenoid relay should be in the off or non-energized position (see below for instructions on how this is achieved). The main switch as well as the switches for pump, pH, conductivity, potentiostat and solenoid relay should be on. Ensure that electrical cables between the potentiostat and the reactor are connected. Confirm that water is circulating back into the tank via the pressure-regulating valve. Slowly close the pressure-regulating valve until the pressure gauge reads 3 bar (300Kpa). Lock the regulating valve using the grey locking ring. Open the initial flow control valve slowly until flows through the reactor and to the solenoid valves are suitable. The unit can now be used for experimentation.

Programming the I/O relay commands

The Borwin-4 Software and A/D Board provide a total of four programmable TTL relays which can be configured to control both the polarity of the potentiostat as well as the direction of water outflow from the reactor based on pH and/or conductivity. In order to achieve this, the software has to be configured to a) accept two 10V data input channels and b) control two or possibly three output relays based on the input signal levels.

This is achieved as follows:-

Ensure that the Conductivity data input is plugged into channel 3 on the Borwin A/D Board and the pH data input is plugged into channel 4. Plug the potentiostat relay into channel 2. Launch the Borwin Software. Go to **File**, **Configuration Set-up**, **Advanced Hardware Configuration** Click on any one of the **Parameters** buttons. Change the signal voltages for channel's 3 & 4 to 10V and check that the data acquisition rate is 1m point per second. It is also advisable to rename System_3 and System_4 to read as Conduct and pH respectively. Click on **OK**. The system is now ready to accept data input from both instruments.

The next step is to configure, describe and test the two I/O relays that control the Solenoid valves and the potentiostat respectively. Proceed as follows. In the Borwin software select **Control**, **Edit Run/Control Method** . Double click on the yellow **In/Out Time Control** Bar. Click on the Definitions button. Click on In/Out **Label #6** and type in SOLEN1. Click on **Label #8** and type in SOLEN2 Click on **Label #4** and type in POLARITY. Click on **OK** and **Exit** buttons. Save file as **Pplant,** click on **OK** and **Exit** buttons. The relay outputs have now been named and it is necessary to test them. This is done by ensuring that the solenoid valve and the potentiostat main switches are

on, and that a DC voltmeter is plugged into the positive and negative output points (red and black banana plug sockets on front panel of potentiostat). Now in the Borwin Software click on **Control**, **Input/Output Control**. Click on the square red button next to label #4 POLARITY and observe the voltmeter. The Polarity should change from positive to negative. Click on he square red button next to label #6. SOLEN1 The solenoid valves should emit a loud click to indicate activation of both valves. If nothing happens, click on the button next to label #8 SOLEN2 and listen for the click. Once this is heard click on the **Exit** button to return to the main menu. The relays are now working and controlling the potentiostat and solenoid, as they should. All that remains is to create a control method in which the relay definitions are used along with some logical programming language to turn the units on and off based on signal outputs from the pH and conductivity meters (Channel 4 and Channel 3). This is done as follows:-

Click on **Control**, **Edit Run Control Method**, Select **System_3**. Double click on the yellow In/Out Time Control Bar and the In/Out Timed Event table will appear. This table has four columns, all of which require entries. On line 1 of the table in the Time_B column enter the analysis start time i.e. 0.00. In the Time_E column enter the analysis end time e.g. 100 (minutes). In the test column it is necessary to enter the logical statement that will control the solenoid valves and the potentiostat polarity. For the type of analysis being done here it will be best to use the CROSSUP and TIME logical operators and link these directly to the signal output being received from the conductivity and pH meters.

The logical statement that should be entered if only conductivity readings are being used to switch valves is:-

CROSSUP (3) = *signal (3) max*

If only pH is being used to switch valves then the statement should read:-

CROSSUP (4) = *signal (4) max*

If both conductivity and pH are being used then the statement should read:-

CROSSUP (3) = *signal (3) max* AND CROSSUP (4) = *signal (4) max*

Where *signal () max* refers to the maximum signal value in V or mV that you would allow the purified water to reach, before regeneration of the membranes was required.

The Action Column in any of the above cases would read:-

SOLEN1 (or SOLEN2 depending on which one was working) = ON_TIME (*time value in seconds*)

Line 2 of the table would have the same Time_B & Time_E values and the same logical statement as above. The Action column would read POLARITY = ON_TIME (*time value in seconds*).

Line 3 of the table would have the same Time_B & Time_E values. The Test column would contain the following:- SOLEN1 = ON. The Action column would read SOLEN1 = OFF_TIME (*time value in seconds set by user*)

Line 4 of the table would have the same Time_B & Time_E values. The Test column would contain the following:- POLARITY = ON. The Action column would read POLARITY = OFF_TIME (*time value in seconds set by user*)

The logic behind all of the above is as follows. Between time 0.00 and the user defined end time 999 (minutes max) the software monitors the incoming conductivity and pH signal voltages and when these reach a value in excess of that set in the logical statement the software will trigger the relays to activate by pulsing on for a user defined time period and the reactor will automatically go into regeneration mode, after a user specified time delay (in seconds), with the product water being redirected to waste (or the tank) and the polarity of the current across the membranes being reversed. When the time pulse is over (set by user defined OFF_TIME value in seconds) the relays will return to their original state and the system will continue to purify water. If for some reason the pulse time selected was not long enough to cause the conductivity and/or pH values to return to signal levels below the preset values, the software will again energize the relays and repeat the regeneration procedure until such time as the product water is within specified limits. One potential problem that could arise due to the nature of the reactor/solenoid design is the following:- During the regeneration stage water from the storage tank which has a relatively high conductivity is used to flush the membranes and as a result, the conductivity signal will more than likely not go below the preset level in the software and the system will continually try to regenerate with no resultant decrease in the product water conductivity. One way around this is to fit two normally closed cut-out relays into the data signal lines from the conductivity and pH meters. These can be set to cut the signal from the meters for a user defined time period AFTER the user defined regeneration period to enable the system to begin producing product water with a lower (than specified limit)

conductivity. The software will then not keep trying to regenerate, as it will only begin monitoring real signal levels once the cut-out relays are deactivated.

The In/Out Time Event table for this application should read as follows:-

Line	Time_B	Time_E	Test	Action
1	0.00	999.00	CROSSUP(3)=1200 AND CROSSUP(4)=500	SOLEN1=ON_TIME (10)
2	0.00	999.00	CROSSUP (3)=1200 AND CROSSUP (4)=500	POLARITY=ON_TIME (10)
3	0.00	999.00	SOLEN1=ON	SOLEN1=OFF_TIME (30)
4	000	999.00	POLARITY=ON	POLARITY=OFF_TIME (30)

Possible extra lines to avoid constant regeneration due to high input signals just after regeneration would read like this:-

5	0.00	999.99	SOLEN1=ON	CUTOUT=ON_TIME (10)
6	0.00	999.99	CUTOUT=ON	CUTOUT=OFF_TIME (60)

Where CUTOUT referred to two normally closed relays connected to the signal output lines from the conductivity and pH meters.

Appendix D THE STANDARDIZED PREPARATION PROCEDURE OF THE ELECTRO SORPTION UNITS

The optimised electro sorption unit is prepared in seven subsequent steps as illustrated in Figure D1. The most important steps have been discussed separately in chapters 2 and 4.

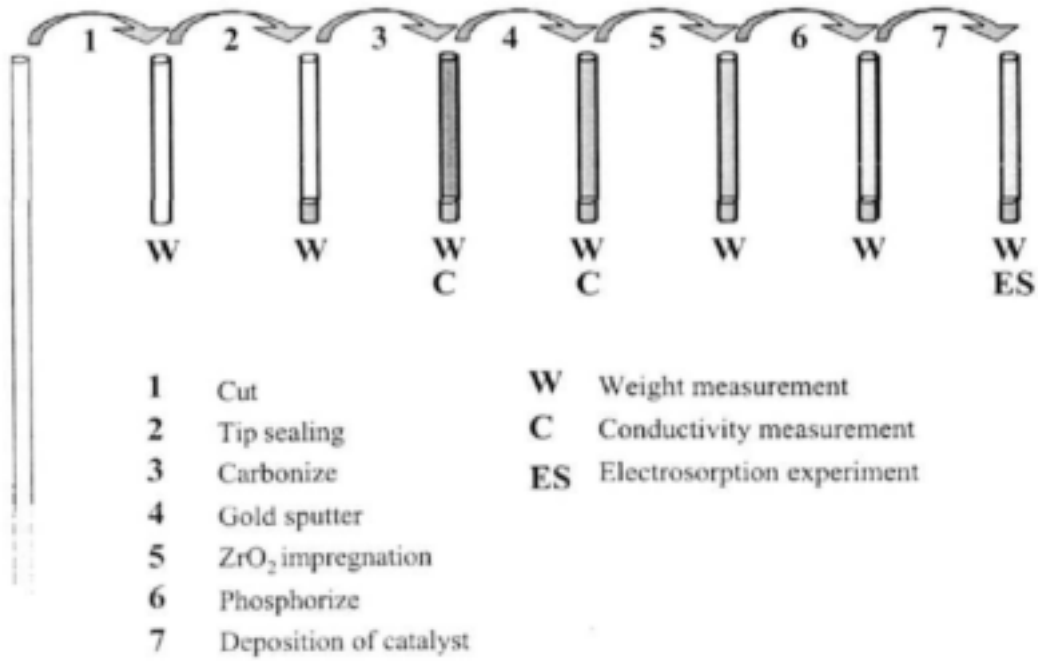

Figure D1. Preparation procedure for electro sorption unit

In step 1 the 50cm long tubular Al_2O_3 supports (type I or II, see Table 2.1 for support details) were cut to size, each piece with a length of 10.2cm using a diamond saw. The support was rinsed with ultra pure water and dried at 120°C after which the weight and subsequently the permeability were measured. In step 2 the support was heated to 1100°C after the edge of the support had been impregnated with 40% Na-silicate as described in Appendix B. In step 3 the porous support was carbon coated by pyrolytic decomposition of liquid petroleum gas (LPG) at 900°C as described in chapter 2.1.4.1. The LPG flow was set to 50ml· min^{-1} and was flowed over the support for 30 minutes. The carbonised supports were gold sputtered (see chapter 2.4.3) in step 3 after which weight, and conductivity were once again measured. In step 4 the carbonised and gold coated support type I or type II was impregnated with commercial available ZrO_2 sol (10% or 20% respectively) and heat treated at 200°C for 1 hour as described in section 2.3. Again the weight was

measured. The impregnated support ends were both plugged and submerged into 15% H_3PO_4 solution for 4 hours, and subsequently rinsed with ultra pure water, then heat treated at 200°C for 1 hour as described in chapter 7. After phosphorization, the weight was measured.

For the deposition of Pt particles the electrode was first submerged in a 10% Si-Mo solution as described in Appendix A. This was repeated once. Then the electrode was submerged in the plating solution (composition in Appendix A, Table 1), dried for a day at room temperature and heated to 100 degrees for 1 hour. This step was necessary to create active sides on the surface of the electrode. These active sides were necessary to start the electroless plating of Pt at 25°C is (= reduction of Pf^{4+} to Pt using methanol a formaldehyde as reducing agents. Subsequently the electrode was electroless plated during one day at room temperature in 4ml plating solution (composition in Appendix A, Table 1). Both sides of the electrode were plugged to prevent the solution entering the lumen side. After plating the electrode was heated to 100°C for one hour to dry the electrode. After the weight measurement, the electrode can be used for further experiments.

APPENDIX E: EXPERIMENTAL ELECTROSORPTION DATA

List of abbreviations used in this Appendix:

Carb:	Carbonized at 900°C for 30 minutes using 50 ml· min^{-1} LPG
Ger 0.9:	Ceramic support type I see Table 2.1
Gold:	Gold sputtered
Phosphor 1h from outside	Treated with phosphoric acid according to procedure in chapter 4
Sample number	Portion of solution collected from retentate
Sample P numbers	Portion of solution collected from permeate
Rate of ion removal	Decrease in ion concentration as % of ion concentration in the feed solution, 50% means the sample contains 50% of the feed solution, 0% means the sample contains the same ion concentration and −50% means that the sample has 50% higher concentration than the feed solution.
Atomic adsorption	The slope and intercept of the calibration line for the specific ion

Electrochemically activated sorption experiment. Date: 20-03-2000

Experiment Experiment No A Ger0.9 carb gold ZrO2 Phosphorized from outside 1 hour

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,022 slope
-0,0010435 intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Rate of ion removal Ca (%)	flowrate (ml/min)	Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
0	0	0	0.0			6,5	0	0		50	6	0,17	168	7,82	1008	391
1	1	5,0	-220,0	3	4	3,5	-8	4	3,0	50	6	0,17	182	7,50	1092	375
2	3	5,0	-200,0	7	4	3	-9	5	4,7	50	6	0,16	183	7,45	1098	373
3	6	5,0	-180,0	9	4	2	-19	9	3,0	50	6	0,16	200	7,09	1200	354
4	7	0,0	0,0	4	4	6	2	-1	2,7	50	6	0,17	165	7,86	990	393
5	10	-5,0	180,0	7	4	12	19	-17	2,3	50	6	0,20	136	9,14	816	457
6	14	-5,0	160,0	8	4	12	18	-16	2,3	50	6	0,20	138	9,04	828	452
7	15	0,0	0,0	3	4	5	-8	-3	2,0	50	6	0,18	181	8,04	1086	402
8	19	5,0	-125,0	9	4	2,5	-29	2	2,3	50	6	0,17	216	7,64	1296	382
9	24	5,0	-100,0	11	4	2	-18	6	2,2	50	6	0,16	198	7,36	1188	368
10	30	5,0	-60,0	12	4	2	-23	8	2,0	50	6	0,16	206	7,18	1236	359
11	36	5,0	-40,0	13	4	2	-15	-1	2,4	50	6	0,17	193	7,91	1158	395
12	37	0,0	0,0	3	4	6	-5	-3	2,0	50	6	0,18	176	8,04	1056	402
13	43	-5,0	120,0	13	4	13	28	-28	2,2	50	6	0,22	121	10,00	726	500
p1	1	5	-220	2	4	3	95	28	2,0	50	6	0,12	8	5,59	48	279
p2	3	5	-200	4	4	3,5	83	30	2,3	50	6	0,12	28	5,45	168	273
p3	6	5	-180	6	4	3	50	22	2,0	50	6	0,14	84	6,14	504	307
p4	7	0	0	2	4	3	39	13	1,3	50	6	0,15	102	6,77	612	338
p5	10	-5	180	4	4	2,5	-26	-10	1,3	50	6	0,19	211	8,64	1266	432
P6	14	-5	160	6	4	2,5	-34	-16	1,7	50	6	0,20	225	9,09	1350	454
P7	15	0	0	2	4	2,5	-13	-5	1,3	50	6	0,18	189	8,18	1134	409
P8	19	5	-125	6	4	4	60	30	1,5	50	6	0,12	67	5,45	402	273
P9	24	5	-100	12	4	4	48	10	2,4	50	6	0,16	88	7,04	528	352
p10	30	5	-60	14	4	6	35	6	2,3	50	6	0,16	109	7,32	654	366
p11	36	5	-40	8	4	7	27	10	1,5	50	6	0,16	123	7,04	738	352
p12	37	0	0	2	4	7	7	7	1,3	50	6	0,16	157	7,27	942	364
p13	43	-5	130	11	4	4	-30	-5	1,5	50	6	0,18	218	8,18	1308	409

Electrochemically activated sorption experiment. Date: 22-03-2000

Experiment: Experiment No B, Ger3 carb gold ZrO2 Phosphorized from outside 12hours

Solution: 0,01 M
Cation: Ca
Anion: SO4

Atomic Adsorption: 0,021 slope
-0,0010435 intercept

Sample No	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	1	5,0	-160,0	2	4	3	-9	6	2,3
2	3	5,0	-140,0	6	4	2,5	-11	8	3,0
3	6	5,0	-130,0	10	4	2	-16	7	3,3
4	7	0,0	0,0	3	4	5	1	1	3,0
5	10	-5,0	180,0	10	4	12	16	-14	3,3
6	14	-5,0	170,0	9	4	12	16	-14	2,6
7	15	0,0	0,0	4	4	4,5	3	-2	2,5
8	19	5,0	-140,0	11	4	2	-21	14	2,6
9	24	5,0	-120,0	13	4	2	-19	9	2,6
10	30	5,0	-80,0	13	4	2	-23	12	2,1
11	36	5,0	-67,0	13	4	3	-22	6	2,4
12	37	0,0	0,0	5	4	6	1	-5	3,0
13	43	-5,0	-170,0	20	4	13	14	-12	3,3
p1	1	5	-160	1	4	1,5	33	70	1,4
p2	3	5	-140	3	4	2	22	75	1,5
p3	6	5	-130	4	4	2	19	69	1,4
p4	7	0	0	1	4	2,5	8	11	1,2
p5	10	-5	180	3	4	1,5	-11	-25	1,1
P6	14	-5	170	5	4	2	-19	-16	1,4
P7	15	0	0	2	4	2,5	-30	-19	1,3
P8	19	5	-140	6	4	3	20	68	1,5
P9	24	5	-120	7	4	3	34	67	1,4
p10	30	5	-80	9	4	4,5	32	41	1,5
p11	36	5	-67	7	4	7	7	40	1,3
p12	37	0	0	2	4	8	1	9	1,3
p13	43	-5	130	10	4	3	-25	-21	1,3

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	167	8,05	1002	402
50	6	0,16	182	7,57	1092	379
50	6	0,16	186	7,43	1116	371
50	6	0,16	194	7,48	1164	374
50	6	0,17	165	7,95	990	398
50	6	0,19	141	9,14	846	457
50	6	0,19	140	9,14	840	457
50	6	0,17	162	8,19	972	409
50	6	0,15	202	6,95	1212	348
50	6	0,15	198	7,33	1188	367
50	6	0,15	205	7,05	1230	352
50	6	0,16	204	7,57	1224	379
50	6	0,18	166	8,43	995	421
50	6	0,19	144	9,05	864	452
50	6	0,05	112	2,38	672	119
50	6	0,04	130	2,05	779	102
50	6	0,05	135	2,48	810	124
50	6	0,15	153	7,14	918	357
50	6	0,21	166	10,09	1116	505
50	6	0,20	199	9,33	1194	467
50	6	0,20	176	9,57	1056	479
50	6	0,05	133	2,57	798	129
50	6	0,06	110	2,67	660	133
50	6	0,10	114	4,76	684	238
50	6	0,10	156	4,86	936	243
50	6	0,15	165	7,28	996	364
50	7	0,20	208	9,71	1456	486

Electrochemically activated sorption experiment. Date: 23-03-00

Experiment: Experiment No C1 Ger3 carb gold ZrO2 Phosphorized from outside 4hours

Solution: 0,01 M
Cation: Ca
Anion: SO4

Atomic Adsorption: 0,02252062 slope
-0,0010435 intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Rate of ion removal Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	1	5,0	-260,0	8	4	3	-8	3	8,0
2	3	5,0	-240,0	17	4	2,5	-8	5	8,5
3	6	5,0	-190,0	18	4	2	-20	9	6,0
4	7	0,0	0,0	8	4	5	3	-1	8,0
5	10	-5,0	200,0	20	4	12	21	-17	6,7
6	14	-5,0	180,0	20	4	12	22	-16	5,7
7	15	0,0	0,0	9	4	4,5	-8	-3	6,0
8	19	5,0	-130,0	20	4	2	-36	6	5,0
9	24	5,0	-110,0	16	4	2	-29	10	3,2
10	30	5,0	-70,0	14	4	2	-25	8	2,3
11	36	5,0	-40,0	20	4	3	-16	-1	3,7
12	37	0,0	0,0	8	4	6	-2	-3	5,3
13	43	-5,0	130,0	16	4	13	32	-35	2,7
p1	1	5	-260	3	4	2,5	30	87	3,0
p2	3	5	-240	7	4	3	28	67	3,5
p3	6	5	-190	9	4	3	34	56	3,0
p4	7	0	0	2	4	3	34	47	2,0
p5	10	-5	200	5	4	2	-56	-27	1,7
P6	14	-5	180	5	4	2	-87	-48	1,4
P7	15	0	0	2	4	2	-30	-19	1,3
P8	19	5	-130	6	4	4,5	63	67	1,5
P9	24	5	-110	10	4	4,5	56	55	2,0
p10	30	5	-70	12	4	6	38	33	2,0
p11	36	5	-40	7	4	6,5	35	29	1,3
p12	37	0	0	2	4	6,5	17	17	1,3
p13	43	-5	130	10	4	2,5	-62	-48	1,3

Dillution factor AA	Dillution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	5	0,17	149	7,64	747	382
50	5	0,17	162	7,37	809	368
50	5	0,16	161	7,28	805	364
50	5	0,16	179	6,93	896	346
50	5	0,17	145	7,68	724	384
50	5	0,20	118	8,92	589	446
50	5	0,20	117	8,84	585	442
50	5	0,18	162	7,86	808	393
50	5	0,16	204	7,15	1019	357
50	5	0,15	193	6,84	964	342
50	5	0,16	186	7,01	931	351
50	5	0,17	173	7,73	866	386
50	5	0,18	153	7,86	764	393
50	5	0,23	102	10,30	511	515
50	5	0,02	105,32	1,02	527	51
50	5	0,06	107,77	2,53	539	126
50	5	0,06	98,73	3,33	494	166
50	5	0,09	98,61	4,04	493	202
50	5	0,22	233,69	9,68	1168	484
50	5	0,25	279,64	11,28	1398	564
50	5	0,20		9,06	0	453
50	5	0,06	54,65	2,53	273	126
50	5	0,08	65,57	3,42	328	171
50	5	0,12	92	5,11	460	255
50	5	0,12	97,75	5,42	489	271
50	5	0,14	123,35	6,35	617	317
50	5	0,26	241,71	11,32	1209	566

Electrochemically activated sorption experiment. Date: 14-4-2000

Experiment Experiment No D Ger3 carb gold ZrO2 Phosphorized from outside 4hours

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,02252062 slope
-0,0010435 intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	P (bar)	pH	Rate of ion removal SO4 (%)	Rate of ion removal Ca (%)	flowrate (ml/min)
0	0	0	0,0				6,5	0	0	
1	1	5,0	-260,0	8	4	-	3	-8	3	8,0
2	3	5,0	-240,0	17	4	-	2,5	-8	5	8,5
3	6	5,0	-190,0	18	4	-	2	-20	9	6,0
4	7	0,0	0,0	8	4	-	5	3	-1	8,0
5	10	-5,0	200,0	20	4	-	12	21	-17	6,7
6	14	-5,0	180,0	20	4	-	12	22	-16	5,7
7	15	0,0	0,0	9	4	-	4,5	-8	-3	6,0
8	19	5,0	-130,0	20	4	-	2	-36	6	5,0
9	24	5,0	-110,0	16	4	-	2	-29	10	3,2
10	30	5,0	-70,0	14	4	-	2	-25	8	2,3
11	36	5,0	-40,0	20	4	-	3	-16	-1	3,7
12	37	0,0	0,0	8	4	-	6	-2	-3	5,3
13	43	-5,0	130,0	16	4		13	32	-35	2,7
p1	1	5	-260	3	4		2,5	30	87	3,0
p2	3	5	-240	7	4		3	28	67	3,5
p3	6	5	-190	9	4		3	34	56	3,0
p4	7	0	0	2	4		3	34	47	2,0
p5	10	-5	200	5	4		2	-56	-27	1,7
P6	14	-5	180	5	4		2	-67	-48	1,4
P7	15	0	0	2	4		2	-30	-19	1,3
P8	19	5	-130	6	4		4,5	63	67	1,5
P9	24	5	-110	10	4		4,5	56	55	2,0
p10	30	5	-70	12	4		6	38	33	2,0
p11	36	5	-40	7	4		6,5	35	29	1,3
p12	37	0	0	2	4		6,5	17	17	1,3
p13	43	-5	130	10	4		3,5	-62	-48	1,3

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	149	7,64	956	382
50	6	0,17	162	7,37	1035	368
50	6	0,16	161	7,28	1031	364
50	6	0,16	179	6,93	1147	346
50	6	0,17	145	7,68	926	384
50	6	0,20	118	8,92	754	446
50	6	0,20	117	8,84	749	442
50	6	0,18	162	7,86	1034	393
50	6	0,16	204	7,15	1304	357
50	6	0,15	193	6,84	1234	342
50	6	0,16	186	7,01	1192	351
50	6	0,17	173	7,73	1109	386
50	6	0,18	153	7,86	978	393
50	6	0,23	102	10,30	654	515
50	6	0,02	105,32	1,02	674	51
50	6	0,06	107,77	2,53	690	126
50	6	0,08	98,73	3,33	632	166
50	6	0,09	98,61	4,04	631	202
50	6	0,22	233,68	9,66	1496	484
50	6	0,25	279,64	11,28	1790	564
50	6	0,20		9,06	0	453
50	6	0,06	54,85	2,53	350	126
50	6	0,08	65,57	3,42	420	171
50	6	0,12	92	5,11	589	255
50	6	0,12	97,75	5,42	626	271
50	6	0,14	123,35	6,35	789	317
50	6	0,26	241,71	11,32	1547	566

Electrochemically activated sorption experiment. Date: 29-03-01

Experiment Experiment No F Ger0.9 carb gold ZrO2 Phosphorized from outside 4hours

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,0212 slope
-0,0019435 intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	1	-4,9	-100,0	3	4	2	-15	9	2,5
2	3	-5,0	-100,0	8	4	2	-17	16	4,1
3	6	-5,1	-100,0	9	4	2	-14	10	3,0
4	7	0,0	0,0	4	4	4	0	-2	4,3
5	10	4,6	100,0	12	4	12	16	-24	4,0
6	14	4,8	100,0	13	4	12	16	-13	3,7
7	15	0,0	0,0	6	4	10	-2	2	4,1
8	19	-4,9	-100,0	16	4	2	-19	12	4,0
9	24	-5,0	-100,0	17	4	2	-22	10	3,4
10	30	-5,0	-100,0	20	4	2,5	-25	15	3,2
11	36	-5,1	-100,0	24	4	3	-20	16	4,5
12	37	0,0	0,0	7	4	6	1	-3	4,7
13	43	4,8	100,0	22	4	12	25	-15	3,7
p1	1	-5	-100	2	4	2	32	36	1,5
p2	3	-5	-100	4	4	3,5	35	48	2,1
p3	6	-5	-100	5	4	5	33	37	1,7
p4	7	0	0	2	4	4	31	1	1,8
p5	10	5	100	6	4	2	-34	-40	1,8
P6	14	5	100	6	4	2	-40	-55	1,8
P7	15	0	0	3	4	5	-14	-5	2,1
P8	19	-5	-100	6	4	6	66	44	1,4
P9	24	-5	-100	8	4	5,5	35	38	1,6
p10	30	-5	-100	11	4	5,5	29	39	1,7
p11	36	-5	-100	8	4	5,5	14	37	1,5
p12	37	0	0	2	4	6,5	4	1	1,6
p13	43	-5	100	13	4	2,5	-42	-54	1,7

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	167	8,11	1002	406
50	6	0,16	192	7,36	1152	368
50	6	0,15	195	6,84	1170	342
50	6	0,15	190	7,26	1140	363
50	6	0,18	167	8,30	1002	415
50	6	0,21	141	10,05	846	502
50	6	0,19	140	9,15	840	457
50	6	0,17	170	7,97	1020	399
50	6	0,15	198	7,17	1188	358
50	6	0,15	203	7,26	1218	363
50	6	0,15	208	6,89	1248	344
50	6	0,15	201	6,84	1206	342
50	6	0,18	166	8,35	996	417
50	6	0,20	126	9,34	756	467
50	6	0,11	113	5,19	678	259
50	6	0,09	109	4,24	654	212
50	6	0,11	112	5,09	672	255
50	6	0,17	115	8,02	688	401
50	6	0,24	223	11,32	1338	566
50	6	0,27	234	12,59	1404	630
50	6	0,18	190	8,49	1140	424
50	6	0,10	91	4,53	546	226
50	6	0,11	109	5,00	654	250
50	6	0,11	118	4,95	708	248
50	6	0,11	144	5,14	864	257
50	6	0,17	161	8,02	966	401
50	6	0,27	237	12,50	1422	625

Electrochemically activated sorption experiment. Date: 12-02-01

Experiment Experiment No G Ger0.9 carb gold ZrO2 Phosphorized from outside 4hours

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,0219 slope
-0,0016435 intercept

Sample No	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Rate of ion removal Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	1	-3,9	-100,0	2,3	4	2	-14	14	2,3
2	3	-4,1	-100,0	7,4	4	2	-16	12	3,7
3	6	-4,2	-100,0	9,9	4	2	-13	11	3,3
4	7	0,0	0,0	3,8	4	5	2	-3	3,8
5	10	3,7	100,0	11,4	4	12	17	-18	3,8
6	14	3,9	100,0	13,2	4	12	15	-15	3,8
7	15	0,0	0,0	5,5	4	9	4	3	3,7
8	19	-3,8	-100,0	14,5	4	2	-28	14	3,6
9	24	-4,2	-100,0	16,8	4	2	-20	13	3,4
10	30	-4,3	-100,0	21,5	4	2	-19	11	3,5
11	36	-4,4	-100,0	18,0	4	2	-18	9	3,3
12	37	0,0	0,0	5,0	4	6	0	1	3,3
13	43	3,9	100,0	20,1	4	12	28	-15	3,4
p1	1	-3,9	-100	3,1	4	2,5	31	17	3,1
p2	3	-4,1	-100	3,5	4	3	41	45	1,8
p3	6	-4,2	-100	5,2	4	4	32	24	1,7
p4	7	0,0	0	2,0	4	4	-4	2	2,0
p5	10	3,7	100	5,1	4	2	-34	-32	1,7
P6	14	3,9	100	5,5	4	2	-40	-52	1,6
P7	15	0,0	0	2,9	4	4,5	-14	-2	1,9
P8	19	-3,8	-100	5,5	4	5	46	44	1,4
P9	24	-4,2	-100	7,2	4	5,5	35	37	1,4
p10	30	-4,3	-100	9,5	4	6	29	40	1,6
p11	36	-4,4	-100	7,6	4	6	20	37	1,4
p12	37	0,0	0	2,4	4	3,5	4	-2	1,6
p13	43	-5,0	133	10,6	4	2,5	-42	-41	1,4

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	167	7,94	1002	397
50	6	0,15	190	6,85	1140	342
50	6	0,15	193	6,99	1158	349
50	6	0,16	189	7,08	1134	354
50	6	0,18	164	8,17	984	409
50	6	0,21	139	9,41	834	470
50	6	0,20	142	9,13	852	457
50	6	0,17	160	7,67	960	384
50	6	0,15	213	6,80	1278	340
50	6	0,15	200	6,94	1200	347
50	6	0,15	198	7,03	1188	352
50	6	0,16	197	7,21	1182	361
50	6	0,17	167	7,85	1002	393
50	6	0,20	121	9,13	726	457
50	6	0,14	115	6,57	690	329
50	6	0,10	99	4,34	594	217
50	6	0,13	113	6,03	678	301
50	6	0,17	173	7,76	1038	388
50	6	0,23	223	10,50	1338	525
50	6	0,26	234	12,05	1404	603
50	6	0,18	190	8,08	1140	404
50	6	0,10	91	4,47	546	224
50	6	0,11	109	4,98	654	249
50	6	0,11	118	4,79	708	240
50	6	0,11	134	4,98	804	249
50	6	0,18	161	8,13	966	406
50	6	0,25	237	11,23	1422	562

Electrochemically activated sorption experiment. Date: 26-05-01

Experiment: Experiment No H Ger0.9 carb gold ZrO2 Phosphorized from outside 4hours
Conductive O-ring

Solution: 0,01 M
Cation: Ca
Anion: SO4

Atomic Adsorption: 0,021 slope
-0,0010435 intercept

Sample No	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Rate of ion removal Ca (%)	flowrate (ml/min)
0	0	0	0			6	0	0	
1	1	-3,7	-100	2,5	4	2	-14	13	2,5
2	3	-3,8	-100	8,1	4	2	-14	15	4,1
3	6	-3,9	-100	9,0	4	2	-15	7	3,0
4	7	0,0	0	4,3	4	3,5	-1	1	4,3
5	10	3,2	100	12,1	4	12	13	-10	4,0
6	14	3,5	100	12,9	4	12	11	-14	3,7
7	15	0,0	0	6,1	4	10	-2	3	4,1
8	19	-3,8	-100	15,8	4	2	-12	13	4,0
9	24	-3,9	-100	17,2	4	2	-11	13	3,4
10	30	-3,9	-100	19,7	4	2,5	-14	13	3,2
11	36	-4,0	-100	24,1	4	3	-9	9	4,5
12	37	0,0	0	7,0	4	6	0	-3	4,7
13	43	3,4	100	22,0	4	12	13	-16	3,7
p1	1	-3,7	-100	1,4	4	2	32	36	1,4
p2	3	-3,8	-100	3,2	4	4	34	25	1,6
p3	6	-3,9	-100	4,8	4	4	33	24	1,6
p4	7	0,0	0	2,0	4	5	7	-3	2,0
p5	10	3,2	100	5,5	4	2	-22	-34	1,8
P6	14	3,5	100	6,3	4	2	-36	-28	1,8
P7	15	0,0	0	2,0	4	5	-5	-5	1,3
P8	19	-3,8	-100	6,3	4	6	28	26	1,6
P9	24	-3,9	-100	7,5	4	6	25	28	1,5
p10	30	-3,9	-100	9,8	4	6	24	25	1,6
p11	36	-4,0	-100	8,8	4	6	22	30	1,6
p12	37	0,0	0	2,4	4	6	1	-5	1,6
p13	43	-5,0	100	12,0	4	2	-21	-21	1,6

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	166	8,19	996	409
50	6	0,15	189	7,14	1134	357
50	6	0,19	190	6,95	1140	348
50	6	0,16	191	7,62	1146	381
50	6	0,17	168	8,09	1008	405
50	6	0,19	145	9,05	870	452
50	6	0,20	148	9,33	888	467
50	6	0,17	169	7,95	1014	398
50	6	0,15	186	7,09	1116	355
50	6	0,15	184	7,14	1104	357
50	6	0,15	189	7,09	1134	355
50	6	0,16	181	7,43	1086	371
50	6	0,18	166	8,48	996	424
50	6	0,20	145	9,52	870	476
50	6	0,11	113	5,24	678	262
50	6	0,13	109	6,14	654	307
50	6	0,13	112	6,19	672	309
50	6	0,18	155	8,43	930	421
50	6	0,23	202	11,00	1212	550
50	6	0,22	225	10,48	1350	524
50	6	0,18	175	8,57	1050	429
50	6	0,13	119	6,05	714	302
50	6	0,12	124	5,90	744	295
50	6	0,13	126	6,14	756	307
50	6	0,12	130	5,71	780	286
50	6	0,18	165	8,57	990	429
50	6	0,21	201	9,90	1206	495

Electrochemically activated sorption experiment. Date: 11-11-00

Experiment Experiment No J Ger0.9 carb gold ZrO2 Phosphorized from outside 4hours

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,022 slope
-0,0010435 intercept

Sample No	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate (pump) (%)	pH	Rate of ion removal SO4 (%)	Ca (%)	flowrate (ml/min)
0	0	0	0.0			6,5	0	0	
1	1	-4,0	-100,0	3,2	4	2	-7	13	3,2
2	3	-4,0	-80,0	5,7	4	2,5	-10	10	2,8
3	6	-4,0	-75,0	7,1	4	2,5	-14	10	2,4
4	7	0,0	0,0	3,6	4	5	0	-2	3,6
5	10	4,0	110,0	8,5	4	11,5	8	-9	2,8
6	14	4,0	100,0	10,7	4	11,5	13	-12	3,1
7	15	0,0	0,0	4,6	4	7	-2	2	3,1
8	19	-4,0	-95,0	11,0	4	2,5	-8	9	2,8
9	24	-4,0	-75,0	13,6	4	2,5	-12	14	2,7
10	30	-4,0	-72,0	16,5	4	2,5	-8	9	2,7
11	36	-4,0	-70,0	16,2	4	2,5	-14	8	3,0
12	37	0,0	0,0	4,1	4	6	1	-1	2,7
13	43	4,0	95,0	16,2	4	12	16	-12	3,0
p1	1	-4,0	-100	1,2	4	2,5	40	25	1,2
p2	3	-4,0	-80	2,8	4	2,5	40	37	1,4
p3	6	-4,0	-75	4,0	4	3	32	36	1,3
p4	7	0,0	0	1,2	4	3	-4	2	1,2
p5	10	4,0	110	4,4	4	2,5	-34	-25	1,5
P6	14	4,0	100	4,7	4	2,5	-39	-46	1,3
P7	15	0,0	0	2,4	4	5	-14	-2	1,6
P8	19	-4,0	-95	5,6	4	5	38	30	1,4
P9	24	-4,0	-75	6,9	4	5,5	35	35	1,4
p10	30	-4,0	-72	7,9	4	6	28	34	1,3
p11	36	-4,0	-70	8,0	4	6	20	29	1,5
p12	37	0,0	0	2,2	4	5	0	-2	1,5
p13	43	4,0	130	8,5	4	2,5	-42	-32	1,1

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	167	7,91	1002	396
50	6	0,15	178	6,91	1068	346
50	6	0,16	184	7,09	1104	355
50	6	0,16	190	7,14	1140	357
50	6	0,18	167	8,04	1002	403
50	6	0,19	154	8,64	924	433
50	6	0,20	145	8,86	870	444
50	6	0,17	171	7,73	1026	387
50	6	0,16	180	7,23	1080	362
50	6	0,15	187	6,82	1122	342
50	6	0,16	181	7,18	1086	360
50	6	0,18	190	7,27	1140	364
50	6	0,18	166	8,00	996	401
50	6	0,20	141	8,86	846	444
50	6	0,13	100	5,91	600	296
50	6	0,11	100	5,00	600	250
50	6	0,11	113	5,09	678	255
50	6	0,17	173	7,73	1038	387
50	6	0,22	223	9,91	1338	496
50	6	0,25	232	11,54	1392	578
50	6	0,18	190	8,04	1140	403
50	6	0,12	103	5,50	618	275
50	6	0,11	109	5,14	654	257
50	6	0,12	120	5,23	720	262
50	6	0,12	134	5,59	804	280
50	6	0,16	167	8,09	1002	405
50	6	0,23	237	10,41	1422	521

:hemically activated sorption experiment. Date: 24-03-00

ıent **Experiment No. K Ger0.9 carb gold ZrO2 Phosphorized from outside**

	0,01	M
Cation	Ca	
Anion	SO4	

ıorption: 0,023 slope
-0,0033478 intercept

time	dU	Current	Volume	flowrate pump	P	pH	Rate of ion removal SO4	Ca	flowrate
(min)	(V)	(mA)	(ml)	(%)	(bar)		(%)	(%)	(ml/min)
43	0	0,0					0	0	
49	3,0	13,0	6	4	-	7	23	0	1,1
53	3,0	13,0	9	4	-	7	0	-5	2,0
54	0,0	0,0	2	4	-	7	-15	-9	1,5
59	-3,0	-30,0	10	4	-	3	-21	-3	2,0
63	-3,0	-26,0	6	4	-	3	-11	-2	1,5
68	-3,0	-22,0	15	4	-	3,5	5	-9	3,0
71	0,0	0,0	7	4	-	7	12	-6	2,8
75	3,0	45,0	8	4	-	6,5	4	2	2,0
78	3,0	28,0	10	4	-	6,5		-2	2,9
49	3	13	11	4	2	4,5	-2	-7	0,2
53	3	13	13	4	1,6	6	0	-6	2,9
54	0	0	5	4	1	4,5	-10	-3	5,0
59	-3	-30	20	4	0,9	6	9	-1	4,0
63	-3	-26	18	4	0,8	6,5	2	-2	4,5
68	-3	-22	17	4	0,7	6,5	-11	0	3,4
71	0	0	8	4	0,5	6	-7	-8	3,2
75	3	45	12	4	0,6	4,5	-10	-11	3,0
78	3	28	17	4	0,3	4,5			4,9

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,18	149	7,91	956	395
50	6	0,18	115	7,91	735	395
50	6	0,19	149	8,34	956	417
50	6	0,20	172	8,61	1104	430
50	6	0,19	181	8,13	1161	406
50	6	0,19	167	8,08	1066	404
50	6	0,20	142	8,65	907	432
50	6	0,19	131	8,39	837	419
50	6	0,18	143	7,74	916	387
50	6	0,19		8,04	0	402
50	6	0,19	151,98	8,43	973	422
50	6	0,19	148,87	8,39	953	419
50	6	0,19	164,89	8,13	1055	406
50	6	0,18	135,68	7,95	868	398
50	6	0,19	147,08	8,04	941	402
50	6	0,18	165,62	7,91	1060	395
50	6	0,20	160,59	8,52	1028	426
50	6	0,20	164,06	8,78	1050	439
		0,19		8,43	0	0

Electrochemically activated sorption experiment. Date: 16-3-2000

Electrode Experiment No L Ger0.9 carb gold ZrO2 Phosphorized from outside

Solution: 0,01 M
Cation: Ca
Anion: SO4

Atomic Adsorption: 0,01830642 slope
-0,0042609 intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Rate of ion removal Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	16	-5,0	240,0	32	6	2	-26	6	2,0
2	28	-5,0	200,0	29	6	2	-31	21	2,4
3	48	-5,0	150,0	16	6	1	-35	19	0,8
4	56	0,0	0,0	8	6	6,5	10	-14	1,0
5	72	5,0	-310,0	22	6	12	23	-20	1,4
6	82	5,0	-200,0	22	6	12	19	-22	2,2
7	88	0,0	0,0	21	6	8	-3	-18	3,5
8	106	-5,0	190,0	29	6	3	-26	-14	1,6
9	122	-5,0	170,0	14	6	1,5	-43	10	0,9
10	144	-5,0	160,0	27	6	2	-30	5	1,2
11	154	0,0	0,0	16	6	3,5	-18	-2	1,6
12	172	5,0	-240,0	8	6	7		-24	0,4
p1	16	-5	240	10	6	2	59	93	0,6
p2	28	-5	200	8	6	3,5	69	93	0,7
p3	48	-5	150	8	6	3,5	65	82	0,4
p4	56	0	0	4	6	4,5	-37	34	0,5
p5	72	5	-310	10	6	1,5	-91	-25	0,6
P6	82	5	-200	5	6	2	-79	-48	0,5
P7	88	0	0	3	6	2		-23	0,5
P8	106	-5	190	11	6	3	55	62	0,6
P9	122	-5	170	8	6	3	64	62	0,5
p10	144	-5	160	8	6	3,5	59	62	0,4
p11	154	0	0	4	6	5		27	0,4
p12	172	5	-240	8	6	2	-42	-20	0,4

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	7	0,15	152	8,03	1063	401
50	7	0,14	192	7,53	1341	377
50	7	0,12	199	6,33	1390	317
50	7	0,12	206	6,50	1439	325
50	7	0,17	137	9,12	959	456
50	7	0,16	116	9,61	814	480
50	7	0,16	123	9,83	862	491
50	7	0,17	156	9,45	1090	472
50	7	0,17	191	9,17	1340	459
50	7	0,13	217	7,21	1520	360
50	7	0,14	198	7,64	1387	382
50	7	0,15	180	8,19	1257	409
50	7	0,16	-	9,94		497
50	7	0,01	62,03	0,54	434	27
50	7	0,01	47,38	0,54	332	27
50	7	0,03	53,56	1,47	375	74
50	7	0,10	207,79	5,29	1455	265
50	7	0,18	289,8	9,99	2029	500
50	7	0,22	271,9	11,85	1903	592
50	7	0,18	-	9,88		494
50	7	0,06	68,99	3,05	483	153
50	7	0,06	55,08	3,05	386	153
50	7	0,06	61,92	3,05	433	153
50	7	0,11	-	5,84		292
50	7	0,18	215,15	9,61	1506	480

Electrochemically activated sorption experiment. Date: 1-3-01

Experiment Experiment No M Ger0.9 carb gold ZrO2 Phosphorized from outside 4hours

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,0193 slope
0 intercept

Sample No	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	1	5,0	-120,0	9,6	10	3	1	4	9,6
2	3	5,0	-105,0	17,0	10	3	-2	1	8,5
3	6	5,0	-100,0	21,4	10	3	-5	1	7,1
4	7	0,0	0,0	10,8	10	5	-2	-2	10,8
5	10	-5,0	120,0	25,4	10	11	-3	1	8,5
6	14	-5,0	110,0	32,2	10	11	3	-2	9,2
7	15	0,0	0,0	13,9	10	8	-4	2	9,3
8	19	5,0	-110,0	33,1	10	3	0	-1	8,3
9	24	5,0	-100,0	40,8	10	2,5	-4	5	8,2
10	30	5,0	-95,0	49,4	10	3	0	0	8,1
11	36	5,0	-80,0	48,7	10	3	-5	-1	9,0
12	37	0,0	0,0	12,2	10	5	-1	-1	8,2
13	43	-5,0	115,0	54,5	10	11	5	-2	9,1
p1	1	5,0	-120	3,6	10	2,5	24	25	3,6
p2	3	5,0	-105	7,4	10	2,5	18	14	3,7
p3	6	5,0	-100	11,0	10	3	24	29	3,7
p4	7	0,0	0	3,6	10	3	-5	2	3,6
p5	10	-5,0	120	12,2	10	2,5	-24	-14	4,1
P6	14	-5,0	110	12,1	10	3	-29	-32	3,5
P7	15	0,0	0	7,2	10	5	-16	-2	4,8
P8	19	5,0	-110	16,8	10	5	22	24	4,2
P9	24	5,0	-100	20,6	10	5,5	24	18	4,1
p10	30	5,0	-95	23,8	10	6	20	27	3,9
p11	36	5,0	-80	24,0	10	7	10	22	4,4
p12	37	0,0	0	6,7	10	7	-2	-2	4,5
p13	43	-5,0	130	25,4	10	3	-31	-20	3,4

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,16	164	8,11	984	407
50	6	0,15	162	7,80	971	391
50	6	0,15	167	8,00	1004	401
50	6	0,16	173	8,05	1036	403
50	6	0,16	167	8,25	1002	414
50	6	0,16	169	8,05	1016	404
50	6	0,16	160	8,27	957	414
50	6	0,15	171	7,93	1026	397
50	6	0,16	164	8,16	982	409
50	6	0,15	170	7,69	1020	385
50	6	0,16	165	8,10	987	406
50	6	0,16	173	8,21	1036	411
50	6	0,16	166	8,21	996	411
50	6	0,16	155	8,27	931	414
50	6	0,12	124	6,06	744	304
50	6	0,14	134	6,99	804	350
50	6	0,11	124	5,75	746	288
50	6	0,15	173	7,93	1038	397
50	6	0,18	203	9,24	1216	463
50	6	0,21	212	10,73	1272	537
50	6	0,16	190	8,25	1140	414
50	6	0,12	128	6,21	770	311
50	6	0,13	124	6,68	744	335
50	6	0,11	132	5,90	792	296
50	6	0,12	147	6,31	884	316
50	6	0,16	167	8,36	1002	418
50	6	0,19	215	9,71	1293	486

Electrochemically activated sorption experiment. Date: 30-3-00

Experiment **Experiment No N Ger0.9 carb gold ZrO2 Phosphorized from outside 4hours**

Solution: 0,01 M
Cation Ca
Anion SO4

Atomic Adsorption: 0,022 slope
0 intercept

Sample No	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	pH	Rate of ion removal SO4 (%)	Ca (%)	flowrate (ml/min)
0	0	0	0,0			6,5	0	0	
1	1	5,0	-260,0		4	1,5	-52	13	
2	3	5,0	-230,0		4	1,5	-40	10	
3	6	5,0	-230,0	2,0	4	1,5	-37	10	0,3
4	7	0,0	0,0		4	3	-16	1	
5	10	-5,0	320,0		4	13	-3	-13	
6	14	-5,0	150,0	1,2	4	13	4	-7	0,3
7	15	0,0	0,0		4	11	-4	-5	
8	19	5,0	-210,0		4	2,5	-49	15	
9	24	5,0	-160,0		4	1,5	-41	14	
10	30	5,0	-145,0		4	1,5	-34	9	
11	36	5,0	-140,0	7,9	4	2	-28	8	0,4
12	37	0,0	0,0		4	3	1	-2	
13	43	-5,0	150,0	1,8	4	12,5	7	-13	0,3
p1	1	5,0	-260	3,3	4	4	35	51	3,3
p2	3	5,0	-230	9,0	4	4,5	29	30	4,5
p3	6	5,0	-230	11,2	4	5	26	19	3,7
p4	7	0,0	0	3,0	4	4	-4	2	3,0
p5	10	-5,0	320	6,1	4	2,5	-21	-4	2,0
P6	14	-5,0	150	12,1	4	2,5	-27	-20	3,5
P7	15	0,0	0	7,2	4	5	-14	3	4,8
P8	19	5,0	-210	12,8	4	5	23	48	3,2
P9	24	5,0	-160	15,4	4	5,5	26	34	3,1
p10	30	5,0	-145	13,0	4	6	21	24	2,1
p11	36	5,0	-140	12,9	4	7	12	22	2,4
p12	37	0,0	0	4,4	4	7	0	7	2,9
p13	43	-5,0	130	14,1	4	2	-29	-9	1,9

Dilution factor AA	Dilution factor IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ca (AA) (ppm)	SO4 experiment (ppm)	Ca experiment (ppm)
50	6	0,17	167	7,82	1002	392
50	6	0,15	254	6,84	1524	343
50	6	0,15	234	7,02	1404	352
50	6	0,16	229	7,07	1374	354
50	6	0,17	194	7,73	1164	387
50	6	0,19	172	8,82	1032	442
50	6	0,18	160	8,36	957	419
50	6	0,18	174	8,18	1044	410
50	6	0,15	249	6,64	1494	332
50	6	0,15	235	6,75	1410	338
50	6	0,16	224	7,11	1344	356
50	6	0,16	213	7,20	1278	361
50	6	0,18	166	7,95	996	399
50	6	0,20	155	8,86	931	444
50	6	0,08	108	3,82	648	191
50	6	0,12	119	5,45	714	273
50	6	0,14	124	6,36	746	319
50	6	0,17	173	7,64	1038	383
50	6	0,18	203	8,11	1216	406
50	6	0,21	212	9,41	1272	471
50	6	0,17	190	7,55	1140	378
50	6	0,09	128	4,09	770	205
50	6	0,11	124	5,18	744	259
50	6	0,13	132	5,91	792	296
50	6	0,14	147	6,14	884	307
50	6	0,16	167	7,28	1002	365
50	6	0,19	215	8,52	1293	427

Electrochemically activated sorption experiment. Date: 17-11-2000

Experiment Experiment Q German0.9; Carbon,Gold, ZrO2 com,gradient phosphate, 4 hours

Solution:

		initial
Cation	Ca	155
	Mg	74
	Na	218
	Fe	0
Anion	SO4	172
	Cl	699

Atomic Adsorption:

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	P (bar)	pH
0	0	-5	0,0				5,5
1	8	-5,0	250,0	8	27	-	2,3
2	23	-5,0	100,0	10	27	-	2,5
3	31	-5,0	90,0	17	27	-	2,5
4	38	-5,0	75,0	14	27	-	2,6
5	46	5,0	170,0	14	27	-	11,1
6	53	5,0	150,0	13	27	-	10,5
7	59	-5,0	100,0	10	27	-	2,4
8	69	-5,0	50,0	13	27	-	2,1
9	80	-5,0	40,0	12	27	-	2,2
10	94	5,0	130,0	28	27	-	10,9
11	106	5,0	100,0	15	27	-	11
p1	8	-5	250	9	27	1,35	5
p2	23	-5	100	11	27	1,75	6,3
p3	31	-5	90	11	27	1,85	6
p4	38	-5	75	10	27	2,25	6,3
p5	46	5	170	9	27	2,15	3,2
P6	53	5	150	8	27	2,15	2,5
P7	59	-5	100	7	27	2,15	2,3
P8	69	-5	50	10	27	2,15	4,4
P9	80	-5	40	11	27	2,15	5,4
p10	94	5	130	12	27	2,15	3,2
p11	106	5	100	9	27	2,15	2,3

Rate of ion removal SO4 (%)	Ca (%)	Cl (%)	Mg (%)	Na (%)	flowrate (ml/min)
0	0	0	0	0	
-6	10	6	7	-8	1,0
-8	10	3	3	-5	0,7
-3	5	5	1	-1	2,1
-1	5	4	1	-5	2,0
6	52	-3	92	-24	1,8
5	19	-6	91	-22	1,9
-6	5	2	-2	-2	1,7
-11	14	3	3	0	1,4
-6	10	3	1	-1	1,1
5	48	-5	93	-24	1,9
-10	91	-7	31	-15	1,3
35	71	49	75	10	1,1
12	86	54	42	-10	0,7
-1	43	24	8	-6	1,4
-10	24	16	3	-6	1,4
-17	-67	-34	14	-6	1,1
-15	-95	-40	-1	16	1,1
17	86	47	75	-7	1,2
6	48	42	38	-15	1,1
-5	33	43	15	-10	1,0
-13	-110	-27	-44	13	0,8
-3	-38	-24	22	-5	0,8

Electrochemically activated sorption experiment. Date: 5-12-2000

Experiment **Experiment no R, commercial sol, phosphorized from outside 4h**
c

Solution:

		initial
Cation	Ca	155
	Mg	74
	Na	218
	Fe	0
Anion	SO4	172
	Cl	700

Atomic Adsorption:

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	P (bar)	pH
0	0	4	0,0				5,5
1	6	-4,0	100,0	6	27	-	2
2	12	-4,0	40,0	3	27	-	1,8
3	19	-4,0	30,0	7	27	-	2,1
4	28	4,0	150,0	16	27	-	11,6
5	33	-4,0	50,0	8	27	-	2
6	41	-4,4	50,0	7	27	-	1,7
7	51	4,0	80,0	10	27	-	11,6
8	59	-4,0	50,0	7	27	-	1,8
9	68	4,5	50,0	6	27	-	1,7
10	78	4,0	80,0	14	27	-	9,7
11	97	-4,6	50,0	14	27	-	2
p1	6	-4,0	100	9	27	2	5,8
p2	12	-4,0	40	9	27	2	8,7
p3	19	-4,0	30	10	27	2	8,8
p4	28	4,0	150	11	27	2	2,6
p5	33	-4,0	50	7	27	2	3,1
P6	41	-4,4	50	9	27	2	6,4
P7	51	4,0	80	11	27	2	2,5
P8	59	-4,0	50	9	27	2	2,5
P9	68	4,5	50	8	27	2	6,6
p10	78	4,0	80	12	27	2	2,5
p11	97	-4,6	50	14	27	2	6,5

Rate of ion removal SO4 (%)	Ca (%)	Cl (%)	Mg (%)	Na (%)	flowrate (ml/min)
0	0	0	0	0	
-18	9	-21	3	9	1,1
-16	8	-25	4	6	0,6
-12	8	-23	5	6	1,0
12	12	10	97	-12	1,8
-12	-4	-18	-27	10	1,5
-8	5	-20	1	5	0,9
13	28	11	27	-15	1,0
-18	-4	-24	-25	9	0,9
-21	8	-26	7	11	0,7
2	-4	-14	-5	-1	1,4
-7	3	-17	6	6	0,7
14	36	26	23	1	1,6
4	20	24	5	-1	1,4
5	19	14	6	-2	1,4
-11	-64	-32	-16	16	1,2
11	25	21	54	-3	1,2
8	40	14	24	-9	1,1
-15	-41	-26	-8	12	1,1
11	35	14	50	-6	1,1
10	41	-23	23	-7	0,9
-7	-21	3	3	14	1,2
1	41	-5	33	-17	0,7

Electrochemically activated sorption experiment. Date: 25-06-2001

Experiment No S German 0.9 no46, commercial sol, phosphorized from outside 4h

Solution:

		initial
Cation	Ca	89,4
	Mg	18,7
	Na	91,6
Anion	SO4	73,9
	Cl	158,1

Atomic Adsorption:

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	P (bar)	pH
0	0		0.0				5,5
1	6	4,7	130,0	9,9	30	-	2
2	12	5,0	130,0	9,2	26	-	2,1
3	19	5,2	130,0	7,1	20	-	2
4	28	-4,2	-130,0	12,2	20	-	11,8
5	33	-4,4	-130,0	7,1	18	-	12
6	41	4,8	130,0	8,2	18	-	3,2
7	51	5,0	130,0	10,2	18	-	2,2
8	59	5,3	130,0	7,9	18	-	2,1
9	68	-4,2	-130,0	6,6	18	-	11,5
10	78	-4,4	-130,0	11,5	18	-	12
11	84	-4,7	-130,0	8,7	18	-	12
p1	6	4,7	130	8,8	30	2,5	5
p2	12	5,0	130	8,0	26	2,2	7,5
p3	19	5,2	130	7,6	20	2	8
p4	28	-4,2	-130	7,2	20	1,8	2,5
p5	33	-4,4	-130	6,3	18	1,8	2,5
P6	41	4,8	130	7,7	18	1,9	6,5
P7	51	5,0	130	9,2	18	1,9	7,5
P8	59	5,3	130	9,3	18	2	8
P9	68	-4,2	-130	9,7	18	1,9	2,5
p10	78	-4,4	-130	10,5	18	1,9	2,5
p11	84	-4,7	-130	6,5	18	1,9	2

Rate of ion removal SO4 (%)	Ca (%)	Cl (%)	Mg (%)	Na (%)	flowrate (ml/min)
0	0	0	0	0	
-16	9	-19	3	-3	1,8
-14	8	-23	4	7	1,5
-4	8	-21	5	6	1,9
8	-5	9	90	5	1,4
6	-4	-16	97	5	1,3
-20	8	-18	1	-5	1,0
-16	5	10	8	-15	1,0
-13	6	-22	5	-10	1,0
9	-5	-23	85	5	1,0
8	-4	-13	95	-1	1,2
7	-3	-15	94	6	1,5
23	56	54	45	1	1,6
8	75	70	15	-12	1,3
-4	68	64	6	-2	1,1
2	-76	-55	-16	16	0,8
-5	-72	-44	-14	-3	1,1
35	58	65	45	-9	1,0
20	75	57	-8	12	0,9
10	67	54	-5	-6	1,2
2	-68	-64	-45	-7	1,1
-4	-58	-57	3	14	1,1
-6	-45	-46	33	-17	1,1

Electrochemically activated sorption experiment. Date: 14-3-2001

Experiment No T Electrode T, German0.9 carbonized; commercial sol, Phosphorized 4hours
outside

Solution:

Cation Ni
Anion SO4

Atomic Adsorption: 0,00039 slope
intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	P (bar)	Rate of ion removal SO4 (%)	Ni (%)	flowrate (ml/min)	Dillution factor AA	IC	Adsorp. (AA) (fraction)	SO4 (IC) (ppm)	Ni (AA) (ppm)	SO4 experiment (ppm)	Ni experiment (ppm)
0	0	0	0,0				0	0		9	5	0,25	216	635,00	1080	5715
1	2	-5,0	-400,0	12,5	43	-	-7	16	6,2	9	5	0,21	232	534,74	1159	4813
2	7	-3,5	-400,0	15,7	43	-	-11	18	3,1	9	5	0,20	240	519,31	1201	4674
3	13	-3,6	-400,0	12,4	43	-	-21	20	2,2	9	5	0,20	261	509,03	1306	4581
4	18	5,0	400,0	15,5	43	-	14	19	3,1	9	5	0,20	186	516,74	930	4651
5	23	5,0	400,0	11,3	43	-	10	15	2,1	9	5	0,21	194	539,88	969	4859
6	29	-3,0	-400,0	10,3	43	-	1	-15	1,8	9	5	0,29	213	732,69	1064	6594
7	39	-3,7	-400,0	9,2	43	-	-15	7	1,0	9	5	0,23	248	588,72	1240	5299
8	48	5,0	400,0	13,9	43	-	9	10	1,5	9	5	0,22	197	573,30	983	5160
9	60	5,0	400,0	12,7	43	-	12	3	1,1	9	5	0,24	191	614,43	954	5530
10	74	-3,2	-400,0	17,7	43	-	-6	10	1,3	9	5	0,22	228	573,30	1142	5160
p1	2	-5,0	-400	2,3	43	1,4	76	69	1,2	9	5	0,08	53	195,38	264	1758
p2	7	-3,5	-400	7,7	43	1,4	56	54	1,5	9	5	0,11	96	290,51	474	2615
p3	13	-3,6	-400	9,9	43	1,4	41	45	1,8	9	5	0,14	127	352,21	633	3170
p4	18	5,0	400	9,0	43	1,45	3	11	1,8	9	5	0,22	209	568,16	1045	5113
p5	23	5,0	400	11,9	43	1,45	-23	12	2,2	9	5	0,22	267	560,45	1333	5044
P6	29	-3,0	-400	8,1	43	1,45	20	57	1,3	9	5	0,11	174	272,51	869	2453
P7	39	-3,7	-400	6,9	43	1,45	12	68	0,8	9	5	0,08	190	203,10	951	1828
P8	48	5,0	400	9,0	43	1,45	-10	2	0,9	9	5	0,24	238	622,15	1188	5599
P9	60	5,0	400	27,8	43	1,45	10	6	2,3	9	5	0,23	195	596,44	976	5368
p10	74	-3,2	-400	20,9	43	1,5	7	59	1,5	9	5	0,10	200	262,23	1001	2360

Electrochemically activated sorption experiment. Date: 15-3-2001

Experiment Experiment No U, German0.9 Carbonized 60 min

Solution:

Cation Ni
Anion SO4

Atomic Adsorption: 0,00048031 slope
0 intercept

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	Rate of ion removal SO4 (%)	Ni (%)	flowrate (ml/min)
0	0	0	0,0			0	0	
1	7	-5,0	-400,0	14	30	-12	17	2,0
2	14	-4,0	-400,0	21	30	-6	26	3,0
3	20	-4,5	-400,0	22	30	-2	30	3,7
4	23	4,7	400,0	9	30	7	21	2,6
5	27	4,9	400,0	11	30	5	-5	3,1
6	36	-3,9	-400,0	21	30	-11	5	2,2
7	43	5,0	400,0	15	30	8	36	2,1
8	46	4,9	400,0	8	30	5	18	2,7
9	48	4,9	400,0	6	30	2	31	3,0
10	50	-4,5	-400,0	5	20	-11	-3	3,3
11	55	-4,0	-400,0	18	20	-11	-2	3,6
12	57	-4,3	-400,0	9	20	-7	2	3,6
13	63	5,0	400,0	8	20	3	46	1,4
p1	7	-5,0	-400	10	30	15	52	1,4
p2	14	-4,0	-400	11	30	9	43	1,6
p3	20	-4,5	-400	12	30	4	51	2,0
p4	23	4,7	400	6	30	-5	8	2,0
p5	27	4,9	400	7	30	-1	20	2,0
P6	36	-3,9	-400	15	30	14	50	1,6
P7	43	5,0	400	13	30	-5	56	1,9
P8	46	4,9	400	7	30	-3	7	2,3
P9	48	4,9	400	4	30	0	25	2,0
p10	50	-4,5	-400	3	20	13	51	2,0
p11	55	-4,0	-400	9	20	7	48	1,8
p12	57	-4,3	-400	4	20	12	51	1,6
p13	63	5,0	400	11	20	-6	31	1,8

Dillution factor AA	IC	Adsorption (AA) (fraction)	SO4 (IC) (ppm)	Ni (AA) (ppm)	SO4 experiment (ppm)	Ni experiment (ppm)
10	5	0,31	209	635,00	1045	6350
10	5	0,25	234	524,66	1170	5247
10	5	0,23	221	468,44	1106	4684
10	5	0,22	213	447,62	1065	4476
10	5	0,24	195	499,67	975	4997
10	5	0,32	198	666,23	990	6662
10	5	0,29	232	603,77	1160	6038
10	5	0,19	192	403,90	960	4039
10	5	0,25	199	520,49	995	5205
10	5	0,21	206	437,21	1028	4372
10	5	0,32	232	655,82	1160	6558
10	5	0,31	232	645,41	1160	6454
10	5	0,30	224	624,59	1120	6246
10	5	0,17	202	343,52	1010	3435
10	5	0,15	178	301,89	890	3019
10	5	0,17	190	360,18	950	3602
10	5	0,15	201	312,30	1005	3123
10	5	0,28	220	582,95	1100	5830
10	5	0,24	212	505,92	1060	5059
10	5	0,15	180	320,62	900	3206
10	5	0,14	219	281,07	1095	2811
10	5	0,29	215	593,36	1075	5934
10	5	0,23	209	478,85	1045	4789
10	5	0,15	182	312,30	910	3123
10	5	0,16	194	333,11	970	3331
10	5	0,15	184	312,30	920	3123
10	5	0,21	221	437,21	1105	4372

Electrochemically activated sorption experiment. Date: 23-03-2001

Experiment **Experiment No. V. German0.9C com ZrO2, phosphorized 4h from outside**

Solution:

		initial
Cation	Ca	438
	Mg	196
	Na	320
	Fe	297
Anion	SO4	2742
	Cl	198,1

Atomic Adsorption:

Sample No.	time (min)	dU (V)	Current (mA)	Volume (ml)	flowrate pump (%)	P (bar)	pH
0	0	-5,0	0,0				6
1	2	-3,4	-130,0	16	20	-	6,5
2	5	-3,6	-130,0	23	20	-	6,5
3	9	3,3	130,0	27	20	-	4,5
4	13	3,4	130,0	22	20	-	3
5	17	-3,4	-130,0	27	20	-	7
6	23	-3,4	-130,0	32	20	-	6,5
7	29	3,4	130,0	23	20	-	3,5
8	42	3,6	130,0	19	20	-	2,5
9	55	-3,9	130,0	26	20	-	6
10	72	-3,9	130,0	29	20	-	6,5
p1	2	-3	-130	6	20	0,2	2
p2	5	-4	-130	15	20	0,2	2
p3	9	3	130	14	20	0,3	3
p4	13	3	130	9	20	0,3	5
p5	17	-3	-130	12	20	0,4	3,5
P6	23	-3	-130	12	20	0,4	2
P7	29	3	130	14	20	0,4	3
P8	42	4	130	18	20	0,4	6
P9	55	-4	130	15	20	0,4	3
p10	72	-4	130	13	20	0,4	2

Rate of ion removal SO4 (%)	Ca (%)	Cl (%)	Mg (%)	Na (%)	Fe (%)	flowrate (ml/min)
0	0	0	0	0	0	
6	-2	4	5	2	27	10,9
7	5	6	-1	-5	51	7,7
-21	-11	-9	-4	4	30	6,6
-22	-2	-13	3	7	23	4,9
7	5	7	-1	29	56	6,7
4	7	7	0	-3	56	5,3
-4	-11	-13	-11	10	34	3,9
-20	-5	-18	4	11	31	1,6
6	0	11	-2	1	61	1,9
2	-2	5	0	1	55	1,7
1	68	-1	60	32	89	4,0
-2	7	4	21	16	93	4,9
-8	5	-4	3	10	68	3,4
7	5	-11	16	2	69	2,0
-9	-32	-12	7	-6	71	2,9
-5	-16	-4	20	14	70	2,1
29	7	2	20	12	63	2,3
12	-7	12	18	7	62	1,5
-20	-46	8	30	-14	76	1,1
-21	-9	-16	38	12	85	0,8

University of the Western Cape
Chemistry Department
Inorganic Porous Media Group

APPLICATION OF ELECTROCHEMICALLY ACTIVATED SORPTION FOR CONCENTRATION OF BRINES

SASOL RESEARCH REPORT

March 5, 2000

Presented by:

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TABLE OF CONTENTS

1. INTRODUCTION

Results of investigations carried out in 1998 revealed that the method of electrochemically activated sorption could possibly be used for the removal of ionic impurities. An electrochemical reactor with a tubular inorganic membrane, which was to be used as a sorption active element, was designed, developed and tested.

During our investigations it was found that the removal of ionic impurities from solution, by the reactor, took place not only according to the mechanism of electrochemically activated ionic-exchange sorption. It was established that under the application of an electric field to solutions containing ions of calcium, manganese and chloride, most of the ions were removed by another mechanism completely. The significant dependence of the degree of removal of these ions on the potential difference between the reactor electrodes and the current revealed the electrochemical nature of the process.

The removal of chloride ions in the anode chamber of an electrolyzer took place according to the following reaction:

$2Cl^- \rightarrow Cl_2 + 2e.$

The reaction which took place at cathode was the following:

$2H_2O+2e \rightarrow H_2 + OH^-.$

The result was the removal of calcium and manganese ions from solution due to the formation of hard calcium and manganese hydroxides, soluble in alkaline media, *in the volume of the porous membrane:*

$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 \downarrow$ and
$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow$.

The formation of precipitates of these hydroxides also took place in the solution which flowed out of the cathode volume of the reactor. This was proved by the fact that if the solution from the cathode volume was fed through a rather fine filter then the degree of purification could be as high as 80%.

As a result of our investigations it was shown that electrochemically activated sorption in combination with other electrochemical processes could be used to purify solutions with salt contents of up to 5 $g \cdot l^{-1}$, by up to 90%. Such a high degree of purification could only be achieved by using specially developed inorganic sorption membranes based on porous ceramic.

The possibility to perform the non-chemical regeneration of sorption active elements used in the electrochemical reactor is of great importance for the electrochemically-activated removal of ionic impurities. It has been shown earlier that the regeneration of a sorption active membrane is carried out by

changing the electrode polarity in an electrochemical reactor. Compared to the initial solution, the subsequent regeneration solution has a 45 times higher concentration of salts. Hence, a regeneration solution obtained after the purification of a feed solution with a 5 g · l^{-1} salt content has a salt content of higher than 20 g · l^{-1}.

The investigations which were carried out in 1999 were a continuation of the study which commenced in 1998. The main principles of electrochemically activated sorption and also the suitability of its application have been described in the 1999 report. The present report therefore contains only experimental data, results and discussions. Corresponding conclusions and recommendations have also been made.

The main goal of the investigations carried out in 1999 was to determine the possibility of applying the method of electrochemically activated sorption for the concentration of solutions containing rather large amount of salts (brines). The main emphasis of this work was not to provide for a high degree of purification but rather to increase the sorption capacity of an electrochemical system and possibly regenerate it by an electric current.

2. EXPERIMENTAL

2.1. PREPARATION OF INITIAL SALT SOLUTIONS

The composition of the solution to be considered in the investigations, referred to as the technological solution, was supplied by SASOL and is shown in Table 2.1. It was a highly mineralized solution; the content of salt components was as high as 14000 $mg \cdot l^{-1}$. The main cationic components of the solution were sodium (Na+), magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions. The main anionic component was sulfate (SO_4^{2-}) ions, while the content of chloride (Cl) ions in the solution was significantly lower.

In all our experiments we made use of a model solution of the technological solution. The former contained only a few main components (simple inorganic salts) of the technological solution and its salt content is given in Table 2.2. In order to compare the ionic concentrations of the model solution with those in the technological solution, the former have also been included in Table 2.1. It is seen in Tables 2.1 and 2.2 that only three simple inorganic salts were required to make up a solution which closely modeled the main ionic composition of the technological solution.

Table 2.1: Composition of the technological solution proposed by SASOL for investigation, and upon which the model solution was based.

	Solution	
Constituent	Technological	Model
Sodium	3300	3236
Potassium	25	-
Calcium	650	685
Magnesium	445	300
Nitrate	109	-
Sulfate	7950	7954
Chloride	1200	1215
TDS	13800	13400

All values are expressed as mg/l.

Table 2.2: Salt composition of the model solution

Salt	Concentration, g/l
Na_2SO_4	10.0
$MgSO_4$	1.5
$CaCl_2$	1.9
Total:	13.4

The salts of calcium and mangnesium were added in the form of the crystalline hydrates $MgSO_4 \cdot 6H_20$ and $CaSO_4 \cdot 0.5H_20$.

2.2. METHODS OF ANALYSIS

2.2.1. Sodium

The content of sodium ions was determined by flame photometry with the aid of a PAZ-1 (Ukraine) apparatus.

2.2.2. Magnesium and calcium

The concentrations of magnesium and calcium ions were determined as the sum of hard salts, by titration of the solution with the Disodium Salt of Ethylenediaminetetraacetic Acid (EDTA) in the presence of Eriochrome Black T as indicator, according to a well-known method [1] or by an atomic adsorption method, using a «Pye Unicam SP 6800» (Great Britain) apparatus.

2.2.3 Sulfate ions

The content of the sulfate ions was determined by titration of the solution with Barium Chloride ($BaCl_2$) in the presence of Rhodizonate as indicator, according to [2].

2.3. EXPERIMENTAL APPARATUS USED TO INVESTIGATE THE ELECTROCHEMICALLY ACTIVATED SORPTION REMOVAL OF IONIC COMPONENTS FROM THE MODEL SOLUTION

The main elements of the experimental apparatus used in the present investigation were the electrochemical reactors. Their schematic representations are given in Figures 2.1 and 2.2.

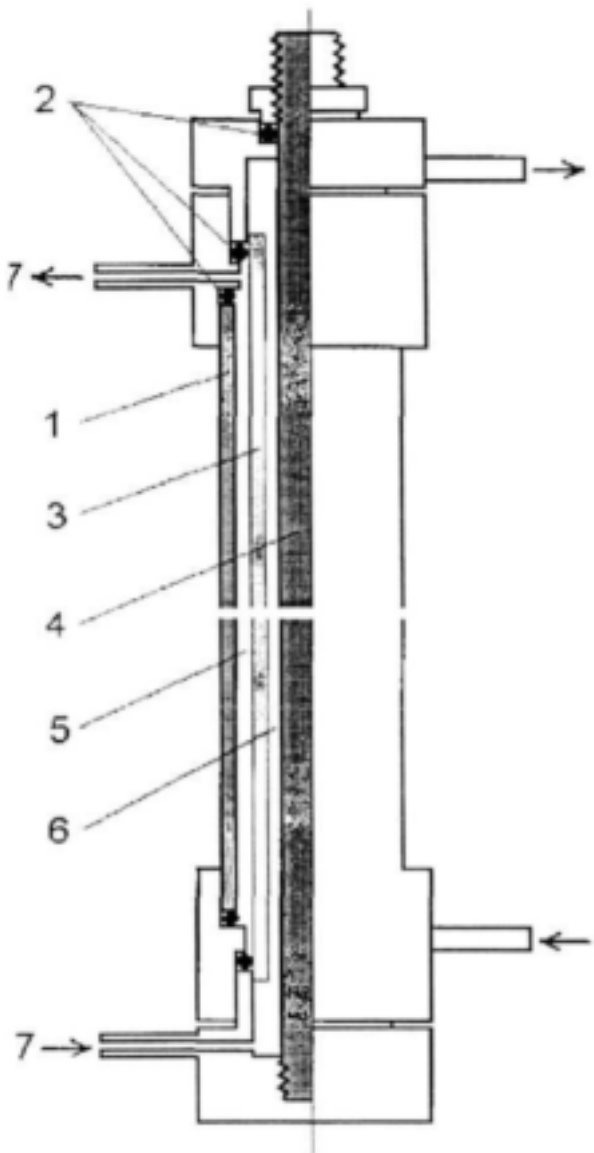

Figure 2.1: Schematic representation of the electrochemical reactor with a sorption active membrane, modified by zirconium dioxide, for the electrochemically activated sorption purification of aqueous solutions from ionic components.
(metallic cylinder plate - 1;. sealing rubber O-rings - 2; tubular ceramic sorption membrane element - 3; rod electrode - 4; electrode volumes - 5 and 6; input and output sleeves - 7).

The reactor shown in Figure 2.1 had a cylindrical construction which was optimal for the distribution of liquid flow. The main elements of this construction were the tubular ceramic membrane and electrodes. They were placed co-axially (one inside another). At the base of the construction was a metal cylinder plate (1), which was also one of the electrodes of the electrochemical reactor. It was made from titanium and covered with platinum on the inside. The tubular ceramic sorption active membrane element (3) and the titanium rod-like electrode coated with platinum (4) were sequentially fixed inside the reactor by two rubber rings (2). The reactor had two electrode spaces which were separated from each other (5 and 6). The introduction and removal of solutions to and from the electrode spaces were carried out through the sleeves (7).

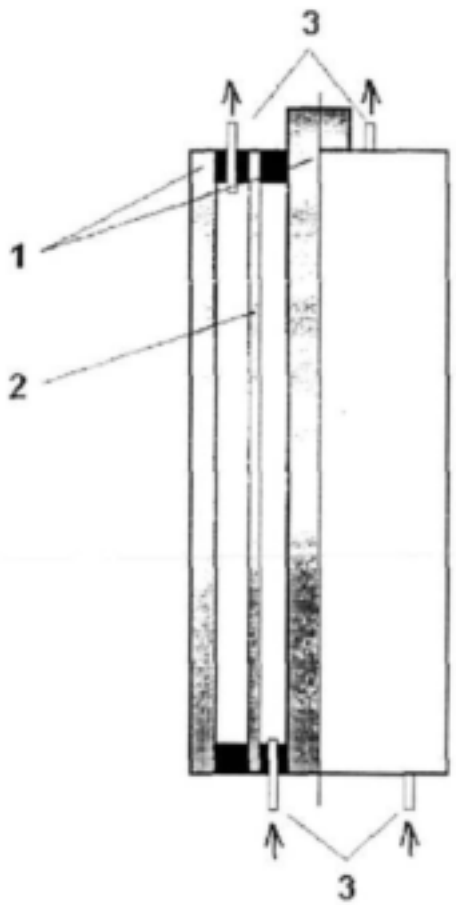

Figure. 2.2: Schematic representation of the electrochemical reactor with a sorption active membrane and ceramic sorption electrodes, modified by zirconium dioxide, for the electrochemically activated sorption purification of aqueous solutions from ionic components.

(electrodes - 1; tubular ceramic sorption membrane element - 2; input and output sleeves - 3).

The reactor shown in Figure 2.2 performed as a modified electrochemical sorption cell. Sorption electrodes were also introduced on the inside of the reactor to increase the sorption capacity. The construction of this cell also had a co-axial configuration (placement) of electrodes (1) and sorption-active membrane (2). Here, the porous ceramic elements which contained additionally introduced zirconium dioxide (sorption component) and pyrolytically precipitated carbon (electrical conducting component) were used as electrodes. The internal electrode was in the form of a porous ceramic rod and the external one was prepared as a porous ceramic tube. It should be mentioned here that the outer electrode was also the outer jacket of the electrochemical sorption cell. The electrode was made impermeable by covering it from the outside with a layer of water-impermeable polymer film.

During the series of experiments carried out to increase the sorption capacity of the electrochemical reactor the free electrode spaces which were separated by the ceramic membrane were filled with a layer of inorganic sorbent – granulated, hydrated zirconium dioxide.

The electrochemical reactor was then attached to the experimental device (Figure 2.3).

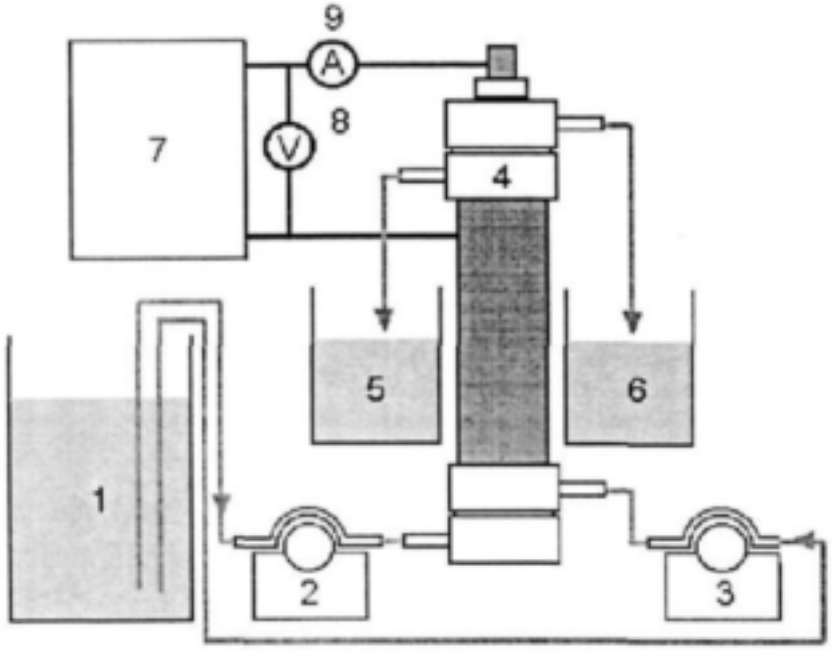

Fig.2.3: Schematic representation of the apparatus used for the investigation of the electrochemically activated sorption purification of aqueous solutions from ionic components.

(vessel containing initial solution - 1; peristaltic pumps - 2 and 3; electrochemical reactor - 4; collecting vessels - 5 and 6; stabilized power supply device - 7; voltmeter - 8; ammeter -9).

The initial solution in vessel (1) was fed by peristaltic pumps (2 and 3) into the electrode spaces of the electrochemical reactor (4) and collected in the vessels (5 and 6). A stabilized power supply device (7) was used to create the potential difference. This allowed us to perform experiments both in the mode of constant voltage (potentiostatic mode) and in the mode of constant current (galvanostatic mode). The current and voltages were controlled by a voltmeter (8) and an ammeter (9).

2.4. PREPARATION OF SORPTION ACTIVE INORGANIC MEMBRANES

Tubular elements made from porous ceramic (produced by JV «INMA», Ukraine) were used for the preparation of sorption active membranes. The characteristics of the initial ceramic elements are presented in the Table 2.3.

Table 2.3: Main characteristics of the porous ceramic elements which were used for the preparation of sorption active inorganic membranes

Length, mm	211
Outer diameter, mm	11
Wall thickness, mm	1
Composition	70% Al_2O_3+ 30% ZrO_2
Average pore size, m 10^6	0.19
Specific surface , $m^2 \cdot g^{-1}$	4.5-5.0

To increase the sorption capacity of the initial porous ceramic materials, disperse zirconium dioxide was incorporated into their structure. This was done by immersing the initial ceramic material in a 1M solution of zirconium hydroxide sol for 1h. The solution was prepared according to the method of Clearfield [3]. The surface of the initial ceramic material was washed with distilled water, then treated with a 25% solution of ammonia for 1h, and dried in air at 200°C. This resulted in an increase in the specific surface of the ceramic material from 5 to 7.5 $m^2 \cdot g^{-1}$, with almost no decrease in pore size.

2.5. PREPARATION OF CERAMIC SORPTION ELECTRODES

To prepare the sorption electrodes, special rods and tubes made from porous ceramic, based on alumina, were produced in the laboratory by extrusion, drying

and sintering. The diameter of the ceramic rods was 5 mm. The ceramic tubular elements had an internal diameter of 15 mm and an outer diameter of 20 mm. The average pore size of the prepared ceramic elements was 10^{-6}m and the total porosity was 50%.

To make the porous ceramic materials electrically conductive a layer of an electrically conductive component - pyrolytic carbon - was precipitated upon them. The precipitation was carried out under vapor-phase conditions in an atmosphere of natural gas [4]. The ceramic materials were placed in the quartz reactor, and natural gas fed through it. After that they were treated at the required temperature.

During our experiments it was found that the electrical conductivity of the ceramic materials with pyrolytic active carbon depended on the temperature and duration of natural gas pyrolysis. Increasing the pyrolysis temperature resulted in a significant increase in the conductivity of the prepared ceramic materials. An abrupt decrease in resistance was observed only at short pyrolysis times. On increasing the pyrolysis time, the resistance achieved its limit (about 0.2 Ohm/cm of ceramic tube length), with no further change. Naturally, decreasing the pyrolysis temperature resulted in an increase in the time required to prepare an electrode with maximal conductivity. So, if at 900°C the time required was 5-6 h, it was half that (2-3h) at 1000°C and at 1100°C it was reduced to 1h. The optimal conditions for the present work were considered to be 2h at 1000°C.

An additional sorption active component (hydrated zirconium dioxide) was incorporated into the porous ceramic material after the incorporation of pyrolytic precipitated carbon in its structure. The method of zirconium dioxide incorporation was similar to that described in section 2.4.

2.6. PREPARATION OF THE INORGANIC SORBENT - HYDRATED ZIRCONIUM DIOXIDE

The inorganic sorbent, hydrated zirconium dioxide, was selected as a sorption active filling component for the electrode spaces in the electrochemical reactor. The main criteria for its selection were its high chemical stability in acidic and alkaline media and the possibility of its effecting the sorption of both anions and cations. The last criterion is a requirement for water desalination processes, which require the removal of both positively and negatively charged ionic species.

The preparation of the sorbent in the form of spherical granules of 0.5-1.0 mm was performed under laboratory conditions by the method of volume thermal neutralization. According to this method, a 25% solution of ammonia (0.6 mole per 1mole of zirconium) was added to a 1M solution of zirconium oxychloride and then hexamethylentetraamine (0.7 mole per 1 mole of zirconium) was also added. The prepared solution was fed through a column containing mineral oil at 90°C. The formed spherical granules of the hydrogel of zirconium dioxide were washed free from oil and excess chemical reagents, then dried in air at 80°C.

The main characteristics of prepared sorbent are listed in Table 2.4.

Table 2.4: Main characteristics of the inorganic sorbent based on zirconium dioxide

Sorption pore volume, $cm^3 \cdot g^{-1}$	0.2
Specific surface, $m^2 \cdot g^{-1}$	120
Sorption capacity for sodium cations, mg-eqv/g	2.8
Sorption capacity for sulfate ions, mg-eqv/g	3.2

3. RESULTS AND DISCUSSION

During the first phase of the present study the electrochemically activated sorption process for the removal of ionic components from a model solution by sorption-active inorganic membranes which were modified by disperse zirconium dioxide was carried out. For this purpose an electrochemical reactor, as shown in Figure 2.1, was used. The main variable change in these experiments was in the potential difference which was applied to the electrodes of the electrochemical reactor. The introduction of the feed solution to the electrode volumes was performed in parallel. Fractions of solutions removed from the cathode (catholyte) and from anode (anolyte) reactor spaces were sampled. The ionic component content of these fractions was analyzed and pH values also determined. The rate of feed of the solution through the reactor electrode spaces was 350 ml $\cdot$ h^{-1}. The total feeding rate of solutions through the electrochemical reactor was 700 ml$\cdot$ h^{-1} or 70 volumes per hour. The reactor volume was equal 10 ml. The experimental results obtained are presented in the Table 3.1 and from them, the following conclusions made:

a) An electrochemical reactor with a sorption active membrane was able to remove about 30% of salts from 100 ml model solution (decreasing the Na^{+} and SO_4^{2-}).

b) As was expected, based on the electrochemical nature of the process, an increase in the degree of removal of Ca^{2+}, Mg^{2+} and Cl^{-} ions was observed not only in the first 100ml of solution leaving the reactor, but also in the subsequent fractions. As the potential difference between the electrodes increased, so did the degree of removal.

c) An increase in the potential difference between the electrodes resulted in an increase in the degree of purification of the model solution and the value of the current. However, if the potential difference was higher than 8V then the energy consumption of process increased abruptly and its efficiency also abruptly decreased.

It can be seen from Table 3.1 that the degree of desalination of the solution was not high - its value was about 50%. In the 1998 research report it was mentioned that the degree of purification depended on the number of interconnected (sequentially and in parallel) electrochemical reactors with sorption membranes. Hence, it should be possible to increase the overall degree of desalination to 90%.

The main objective of the present study was to investigate the possibility of concentrating the model solution, and hence research was not carried out into increasing the degree of purification here.

The process of the electrochemical regeneration of a sorption active membrane, modified by disperse zirconium dioxide, was studied in the following way.

Different quantities of model solution were fed through the electrochemical reactor at a potential difference of 8V.

Table 3.1: Influence of the applied potential difference on the cation and anion contents in the model solution after feeding it through the electrochemical reactor with a sorption active ceramic membrane.

U, V	I, A	V, mL	Content of ions, mg/l					Removal of ions, %				
			Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
2	0.12	0–50	2850	580	165	960	6950	12	16	17	21	13
		50–100	3110	600	175	990	7590	4	13	13	19	5
		100-150	3230	620	175	1010	8000	0	11	13	17	0
		150-200	3250	610	180	1020	7970	0	12	10	16	0
4	0.22	0–50	2660	500	140	740	6400	18	28	30	39	20
		50–100	3010	520	150	790	7500	7	24	24	35	6
		100-150	3240	550	155	820	8000	0	21	22	33	0
		150-200	3220	530	160	810	7950	0	23	21	34	0
6	0.35	0–50	2360	360	95	520	5670	27	48	51	57	29
		50–100	2950	410	120	570	7350	9	40	41	53	8
		100-150	3170	440	130	620	7950	2	36	33	49	0.5

		150-200	3260	430	125	600	8000	0	36	37	51	0
8	0.54	0–50	2300	270	70	510	5830	29	61	64	58	27
		50–100	2970	310	95	580	7270	8	55	52	52	9
		100-150	3220	350	105	630	8010	0	49	48	48	0
		150-200	3250	360	110	600	8000	0	47	45	51	0

After feeding of the solution to the reactor was stopped, the polarity of the electrodes was changed and the electrochemical treatment carried out for a predetermined time. The electric current was then switched off and the solutions from the different chambers of the reactor were replaced by fresh model solution. As was reported for the preliminary experiments, a change in electrode polarity resulted in a change in the ionic content, subject to the applied potential difference. At 8V there was a significant change in ionic content. Increasing the treatment time to 5 min resulted in a significant increase in concentration. At a treatment time greater than 5 min the concentration would start to decrease.

The compositions of the regenerated solutions obtained at a potential difference of 8 V and a treatment time of 5 min are presented in Table 3.2. When these results are compared with the composition of the initial solution it is seen that there was an increase in the content of 'insignificant ions' in the regeneration solution. The greatest increase in concentration (by up to 2 times) was observed after feeding 400ml of solution through the electrochemical reactor. Comparing the salt content of the regeneration solutions with the amount of sorbated ions one could conclude that the almost complete regeneration of the sorption active membrane took place under the established conditions.

The comparatively low degree of concentration of the model solution in the electrochemical reactor with a sorption active membrane was probably a result of its low sorption capacity. The small volume of desalinated solution was also evidence of a low sorption capacity.

In order to increase the sorption capacity of the electrochemical reactor its construction was changed. A composite sorption electrode replaced the metal ones. The schematic representation of such an electrochemical reactor and a description of the sorption electrodes have been given in Section 2. The electrochemical reactor with sorption electrodes and a sorption active membrane was used for the treatment of the model solution under conditions similar to those described for the electrochemical reactor with the sorption active membrane alone. The obtained results are presented in the Table 3.3.

Comparison of the data in Table 3.3 with the data in Table 3.1 showed that the introduction of sorption electrodes in the construction of the electrochemical reactor did not result in a change in the degree of desalination of the model solution. The increase in sorption capacity did, however, result in a significant increase in the volume of purified solution and, as a result, there was a marked increase in the salt content (2 times higher) in the regeneration solution (see Table 3.4).

To further increase the sorption capacity of the electrochemical reactor the free spaces between the sorption electrodes and the inorganic membrane were filled with granulated, inorganic sorbents based on zirconium dioxide. This reactor was tested for the electrochemically-activated desalination of the model solution and the results presented in Table 3.5. Inclusion of the additional sorbent resulted not only in an increase in the volume of desalinated solution, but also an increase in the degree of purification. The degree of concentration of the model

solution did , however, not increase; it even decreased slightly (Table 3.6). Results of additional experiments have shown that this was caused by kinetic features of the inorganic sorbent which was included in the reactor. As has been mentioned, the process of the electrochemical regeneration of sorption active membrane depended on time. Increasing the time of electrochemical treatment by a sorption system results firstly in a significant increase in the salt content in the regeneration solution, followed by a decrease in the salt content. The time of regeneration of the additional sorbent was much longer. Further, it did not correspond to the time for the maximal regeneration of sorption electrodes and the sorption active membrane. This 'mismatch' results in a decrease in the degree of concentration of the model solutions.

Table 3.2: Electricity consumption per kg salt removed (P), concentration factor (N) and composition of regeneration solutions prepared after the electrochemical regeneration of a ceramic membrane modified by zirconium hydroxide (saturation at 6V).

Volume of purified solution, ml	Removal of ions, %	P, Khw kg^{-1}	Content of ions in regeneration solution, mg l^{-1}					N
			Na^{+}	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}	
50	31.6	0.71	4350	1250	360	1100	11500	1.39
100	23.4	0.95	5850	1200	440	1200	14500	1.73
150	18.1	1.23	6200	1220	400	1150	15000	1.79
200	15.3	1.45	6250	1150	390	1250	14800	1.78
250								

Table 3.3: Influence of applied potential difference on the cation and anion contents in the model solution after feeding it through an electrochemical reactor with sorption electrodes and a sorption active ceramic membrane.

U, V	I, A	V, mL	Content of ions, mg/l					Removal of ions, %				
			Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
4	0.16	0–50	2850	510	140	830	6950	12	26	30	32	13
		50–100	2880	520	145	850	7200	11	25	28	30	10
		100-150	2920	510	145	890	7270	10	26	28	27	9
		150-200	3200	530	150	880	7550	1	23	25	28	3
		200-250	3250	550	155	920	7920	0	20	22	25	1
6	0.26	0–50	2620	400	105	620	6450	19	42	47	49	19
		50–100	2750	410	110	660	6700	15	40	45	46	16
		100-150	2790	450	120	680	7200	14	35	39	44	10
		150-200	2690	455	135	670	7450	7	34	32	45	7
		200-250	3250	460	140	710	8000	0	33	30	42	0
8	0.37	0–50	2430	260	65	380	5500	25	62	67	69	31

		50–100	2600	320	80	360	6550	20	53	60	70	18
		100-150	2800	350	85	410	6700	14	50	58	66	16
		150-200	2850	370	100	460	7100	12	46	50	62	11
		200-250	3200	390	120	520	7980	1	43	40	57	0
10	0.48	0–50	2140	200	50	180	5500	34	70	75	85	31
		50–100	2600	240	55	220	6500	20	65	72	82	19
		100-150	2950	270	60	260	6950	9	60	70	79	13
		150-200	3100	330	85	240	7450	4	52	57	80	7
		200-250	3250	340	100	280	8000	0	51	50	77	0

Table 3.4: Electricity consumption per kg salt removed (P), concentration factor (N) and composition of regeneration solutions prepared after the electrochemical regeneration of sorption electrodes and a ceramic membrane modified by zirconium hydroxide (saturation at 8V).

Volume of purified solution, ml	Removal of ions, %	P, Khw kg^{-1}	Content of ions in regeneration solution, mg l^{-1}					N
			Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	
50	35.1	0.87	4100	950	400	950	12300	1.40
100	30.4	1.03	7200	1300	500	1600	17370	2.09
150	27.7	1.13	9600	1850	750	2150	25500	2.97
200	25.3	1.24	11500	2150	850	2500	2800	3.36
250	21.9	1.43	11550	2400	950	2400	30400	3.56

Table 3.5: Influence of applied potential difference on the cation and anion contents in the model solution after feeding it through an electrochemical reactor with sorption electrodes, a sorption active ceramic membrane and an additional inserted inorganic sorbent.

U, V	I, A	V, mL	Content of ions, mg/l					Removal of ions, %				
			Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
4	0.10	0–50	2800	550	150	950	6550	12	21	25	23	18
		50–100	2850	550	165	960	6950	12	20	18	21	13
		100-150	2750	570	160	950	7200	15	18	20	22	10
		150-200	3050	580	160	980	7600	6	15	19	20	5
		200-250	3000	590	160	990	7830	6	16	20	19	2
6	0.14	0–50	2500	490	130	850	5600	22	29	35	31	25
		50–100	2600	490	135	870	6500	19	29	34	29	19
		100-150	2650	520	130	860	7000	19	25	36	30	12
		150-200	2800	530	135	890	6800	12	23	34	27	15
		200-250	2950	520	135	890	7350	9	24	35	27	8
8	0.22	0–50	2250	410	90	610	5200	31	41	55	50	35
		50–100	2600	400	100	660	6550	19	42	50	46	18
		100-150	2600	430	125	700	6400	19	38	38	43	20

		150-200	2550	440	120	670	6800	22	36	40	45	15
		200-250	2750	470	135	710	7200	15	32	32	42	10
10	0.27	0–50	2050	300	50	730	4400	37	57	75	60	45
		50–100	2350	370	90	720	6000	28	46	55	60	25
		100-150	2250	400	100	550	6550	31	42	49	55	18
		150-200	2750	390	110	590	7000	15	43	46	52	12
		200-250	2850	430	120	550	7400	12	38	40	55	7

Table 3.6: Electricity Consumption per kg salt removed (P), concentration factor (N) and composition of regeneration solutions prepared after the electrochemical regeneration of sorption electrodes, a sorption active ceramic membrane modified by zirconium hydroxide and an additional inserted inorganic sorbent (saturation at 10 V).

Volume of purified solution, ml	Removal of ions, %	P, Khw kg^{-1}	Content of ions in regeneration solution, mg l^{-1}					N
			Na^{+}	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}	
50	45.4	0.63	3900	920	450	800	12800	1.41
100	37.9	0.76	7100	1200	600	1450	16500	2.00
150	34.0	0.85	8500	1750	720	1900	24300	2.77
200	30.1	0.96	10900	2050	780	2350	26400	3.15
250	27.0	1.07	11200	2300	930	2200	2850	3.37

4. CONCLUSION

The results of experiments carried out to concentrate the model solution by three different types of electrochemical reactors are consolidated in Table 4.1.

Table 4.1: Summary of the removal of salts from the model solution (content of salts – 13400 mg l^{-1}) obtained after using three different types of electrochemical reactors.

Sorption-active element	Volume of purified solution, ml	Removal of ions, %	P, Khw kg^{-1}	Content of salts in regeneration solution, mg l^{-1}	N
Sorption active membrane	100	23.4	0.95	23190	1.73
	200	15.3	1.45	23840	1.78
Sorption active membrane + sorption electrodes	100	30.4	1.03	27970	2.09
	200	25.3	1.24	45000	3.36
Sorption active membrane + sorption electrodes + inorganic sorbent	100	37.9	0.76	26850	2.00
	200	30.1	0.96	42480	3.15

Taking this data and other data presented in this report into consideration, we reached the following conclusions:

1. The use of electrochemically activated sorption process for the removal of ionic components from solutions enabled us to further concentrate not only low mineralized solutions, but also brines which contained rather high amount of salts (up to 15 gl^{-1}).

2. The highest degree of concentration of a model solution (3.4) could be achieved by using an electrochemical reactor with sorption electrodes and a sorption active inorganic membrane.

3. Although the degree of purification of the model solution obtained in the current study was not high, it should be possible to increase it still further using multistage process.

4. The degree of concentration achieved for the model solution was possibly the limit value for the applied method of the electrochemically activated ionic-exchange sorption.

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Polymeric and ceramic-based membranes for use in electromembrane reactors

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(Completed 2000)

The fouling of ion-exchange membranes by large organic anions together with their low chemical, mechanical and thermal stability, impose serious limitations on electromembrane separation processes. Chemical and electrochemical pretreatment techniques are promising means by which to reduce these problems. A novel procedure for the coating of standard (Ionics) polymeric-electrodialysis membranes was developed by the project team in conjunction with Eskom. This coating renders the membranes more resistant to fouling by organic material. The modified membranes will be very useful in applications where organic material is present together with inorganic salts, such as the situation that exists in many industrial water and effluents from Sasol, Eskom and others. As another product from the project, a significant step was taken toward the development of ceramic membranes possessing conductive and catalytic properties for the oxidation of unwanted organic material. These properties of ceramic membranes, together with their high stability in aggressive media, allow their potential use for plating-effluent treatment, extraction of non-ferrous metals by electrodialysis, treatment of mine waters, electrochemical synthesis of acids and alkalis, and for the preparation of sodium hypochlorite disinfectant.

Report Number 844/1/99 **ISBN 1 86845 539 4**

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