Electrolytic iron flocculant production with a bipolar electrode in series arrangement

WA Pretorius*, WG Johannes and GG Lempert
Department of Chemical Engineering, University of Pretoria, South Africa

Abstract

The theory of the electrolytic dissolution of metal in water and some electrode and electrolytic cell arrangements are briefly described. The electrolytic dissolution of iron by means of bipolar electrodes in series arrangement is compared with predicted values of a simplified mathematical model. Correlation coefficiencies of $R^2 > 0,85$ and a cell efficiency of 0,87 were obtained. Iron dissolves as the ferrous ion and at low current densities the cost of electrolytically produced iron flocculant compares favourably with commercially available iron salts.

Introduction

Technology for the removal of plant nutrients, nitrogen and phosphorus from waste water has been developed to a high level in South Africa. A wide range of chemical and biological processes and combinations of these are available for upgrading existing works and designing new works. For certain waste-water treatment processes like biological filtration, phosphate removal by chemical precipitation is the only viable option (Wiechers *et al.*, 1984), while the reliability of biological nutrient removal plants is such that chemical back-up systems are recommended (Best, 1986).

The chemicals most commonly used for phosphorus removal include the salts of aluminium and iron (Metcalf and Eddy, 1979). There are, however, two distinct disadvantages associated with these chemicals. Firstly, the nett salinity of the treated water is increased due to the anions remaining after phosphorus removal (Wiechers, 1987; Louw *et al.*, 1988). Secondly, part of all of the alkalinity of the treated water is neutralised as these chemicals are the salts of strong acids (Metcalf and Eddy, 1979). This increase in salinity and decrease of alkalinity will make the water less suitable for domestic, industrial and agricultural reuse (Heynike, 1986).

As South Africa is experiencing high rates of population growth and urbanisation, the direct and indirect reuse of treated waste water becomes important (Botha and Pretorius, 1989). It has become important that alternative purification processes are sought which will produce effluents with a greater reuse potential than existing ones.

A non-conventional process for the production of metal cations suitable for the precipitation of phosphorus and the clarification of turbid water could be the electrochemical dissolution of metals directly in water (Smith, 1972; Grøterud and Smoczynski, 1986b).

In this paper some background theory of the electrochemical dissolution of metals in water and some of the different possible electrode arrangements are briefly described. The experimentally observed electrical energy requirement for the dissolution of iron using bipolar electrodes in series in an electrolytic cell is compared with the theoretically predicted values. A cost comparison between electrolytically produced iron flocculant and commercially available iron salts was made.
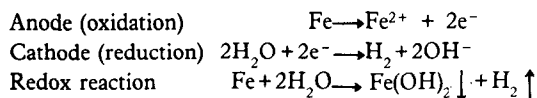
List of symbols

d   = distance between electrodes (m)
E_{eq} = equilibrium *potential* (V)
F   = Faraday's constant (96 487 C)

I   = electric current (A)
i   = current density (A/m²)
κ = specific conductivity of the electrolyte (S/m)
M   = molecular weight of sacrificial electrode (for iron: M = 55,85 g/mol)
n   = number of anodes
R^2 = correlation coefficient
R   = resistance (ohm)
n_{kin} = kinetic overpotential (V)
η = cell efficiency
t   = time (s)
V   = potential needed to overcome cell resistance
V_{ohm} = potential needed to overcome solution resistance (V)
w   = mass of sacrificial electrode dissolved (g)
z   = number of electrons involved in the redox reaction (for iron: z = 2)

Theoretical and practical considerations

Flocculant production

The use of electrochemical methods for flocculant production is not new (U.S. Patent 937 210, 1909; Smith, 1972; Dobolyi, 1978; Grøterud and Smoczynski, 1986(a); 1986(b); 1986(c)). In the process sacrificial metal electrodes are forced to corrode by means of a direct electric current, thus dissolving the anode to form a metal hydroxide flocculant. The dissolution of iron for example, proceeds according to the following oxidation - reduction reactions (Peters *et al.*, 1974):

Anode (oxidation) $Fe \longrightarrow Fe^{2+} + 2e^-$
Cathode (reduction) $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$
Redox reaction $Fe + 2H_2O \longrightarrow Fe(OH)_2 \downarrow + H_2 \uparrow$

The mass of iron which theoretically dissolves for a particular electrical current flow in an electrolytic cell is quantified by Faraday's law (Vik *et al.*, 1984):

$$w = \frac{I \times t \times M}{z \times F} \qquad (1)$$

The electrical potential difference required for a specific current to flow through an electrolyte in an electrolytic cell is determined as the sum of three components:

$$V = E_{eq} + n_{kin} + V_{ohm} \qquad (2)$$

The first two terms in Eq. (2) depend on the chemical properties of the electrolytic cell and V_{ohm} on certain physical properties, amongst others the conductivity of the electrolyte, the geometry and spacings of the electrodes and the flow conditions prevailing during electrolysis (Johannes, 1989). Complex mathematical models have been proposed to describe V for a specific electric current (Pickett, 1979; Rousar et al., 1986). However, V can be calculated reasonably accurately for a single electrolytic cell with the following equation (Pickett, 1979):

$$V = \frac{i \times d}{\kappa} \qquad (3)$$

For practical applications, multiple cell arrangements would be preferred in which case Eqs. (1) and (3) respectively are corrected as follows (Johannes, 1989).

$$w = \frac{I \times t \times M \times n \times \eta}{z \times F} \qquad (4)$$

$$\text{and } V = \frac{i \times d \times n}{\kappa} \qquad (5)$$

If a reasonable agreement between the theoretically calculated and experimentally measured values for I and V exists, then Eqs. (4) and (5) could be used for the design of an electrolytic cell for any particular effluent if κ is known.

Electrode configuration and cell arrangement

The single electrolytic cell with one anode and one cathode is the simplest of arrangements. This arrangement is generally not considered to be of much practical use in wastewater flocculation due to the large dimensions of the electrodes required for a practical rate of metal dissolution. Variations of multiple cell arrangements have been proposed (Pickett, 1979) such as:

- Monopolar electrodes with cells in series
- Monopolar electrodes with cells in parallel
- Bipolar electrodes with cells in series

The various cell arrangements and their equivalent electric flow diagrams are shown schematically in Fig. 1.

The differences between the different cell arrangements can be seen from the corresponding electric flow diagrams. The difference between the series and parallel cell arrangements (see Figs. 1(a) to 1(c)) is that the series cell arrangement for a given current flow requires a higher potential difference due to the higher resistance for the cells connected in series. The same electric current would, however, flow through all the electrodes. In the parallel arrangement, the electric current is divided between all the electrodes in relation to the resistance of the individual cells, while the potential difference would be that required by a single cell. For practical reasons the cells in series arrangement would be preferred as it is more economical to convert a high potential difference low alternating current to direct current than to a low potential difference high alternating current.

An arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with a multitude of electrodes

and interconnections. On the other hand, an arrangement of bipolar electrodes with cells in series (see Fig. 1(d)) has a practical advantage in that only two monopolar electrodes are connected to the electric power source with no interconnections between the inner (bipolar) electrodes. Furthermore, this cell arrangement gives a simple physical set-up which facilitates ease of maintenance under practical applications.

After considering the advantages and disadvantages of the various cell arrangements described above, an arrangement of bipolar iron electrodes with cells in series was selected for further investigation. The effect of practical changes such as current density, electrode spacing and number of electrodes on the dissolution of iron in water was experimentally evaluated.

Laboratory studies

Materials and methods

Experimental unit

The experimental unit consisted of an electrolytic cell, electrolyte (water) container with recirculation pump and DC power source arranged as shown schematically in Fig. 2.

The electrolytic cell consisted of a 'Perspex' container provided with a continuous flow of electrolyte controlled by the recirculating pump. Inside the electrolytic cell, 200 mm x 200 mm x 3 mm mild steel plates arranged in bipolar configuration were used as sacrificial electrodes. The DC power source had a maximum current rating of 150 A at an open circuit potential of 72 V. The current (and potential) supplied to the electrolytic cell was controlled by a variable transformer. Current and potential were measured with a multimeter. The electrolyte was tap water in which the conductivity was raised to 110 mS/m with NaCl to resemble municipal effluent.

Experimental procedures

Iron dissolution was determined gravimetrically. Before a particular experiment new mild steel electrodes were etched with concentrated hydrochloric acid, brushed with a steel brush to remove scale, rinsed with tap water, degreased with acetone and dried at 150°C for 1 h, cooled in a desiccator and weighed. After a particular experimental run, the electrodes were brushed with a soft nylon brush under running tap water, dried, cooled and weighed as before. The difference between the initial and final mass was considered as the amount of iron dissolved during a particular experimental run. The duration of an experimental run was 2 h. The experimental programme showing the different parameters evaluated with its corresponding test conditions is summarised in Table 1.

Results

Applicability of theory

The experimentally obtained results for iron dissolution and power used were compared. Fig. 3 shows the correlation between mass of iron dissolved experimentally and the mass predicted by Eq.(4) which is a variation of Faraday's law.

The correlation between measured potential for a specific current and that predicted by using Eq. (5) is shown in Fig. 4.
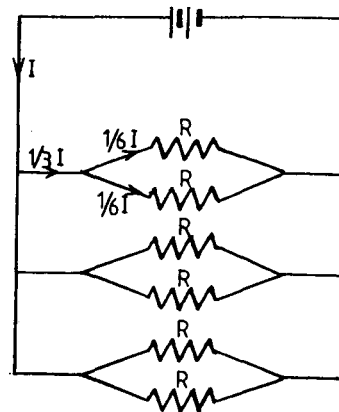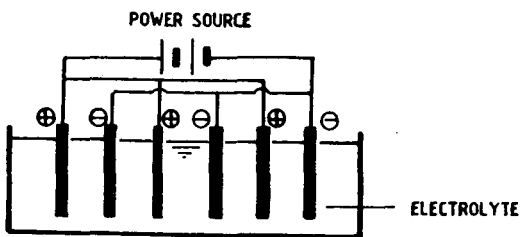
The efficiency factor (η) (see Eq. 4) which gives a direct correlation between the measured power consumption to dissolve 1 g iron and
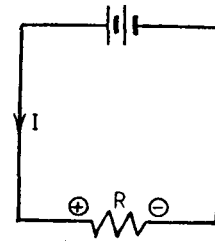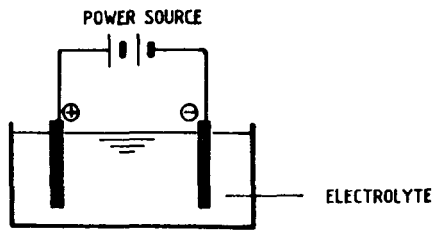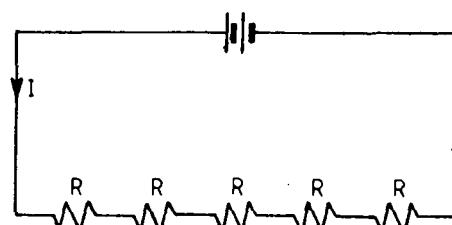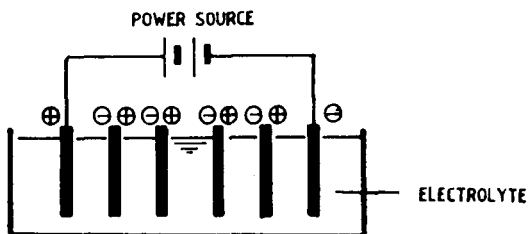
(a) Monopolar electrode — single cell
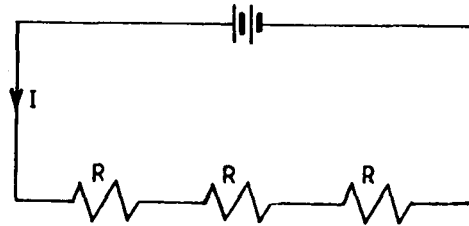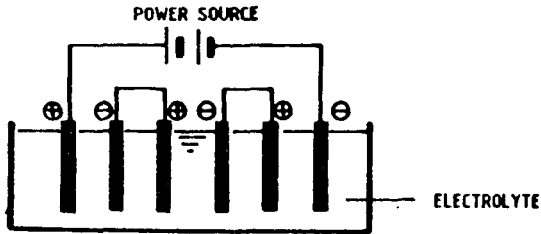
(b) Monopolar electrodes with cells in series

(c) Monopolar electrodes with cells in parallel

(d) Bipolar electrodes with cells in series

Figure 1
Schematic electrolytic cell arrangements with corresponding electric
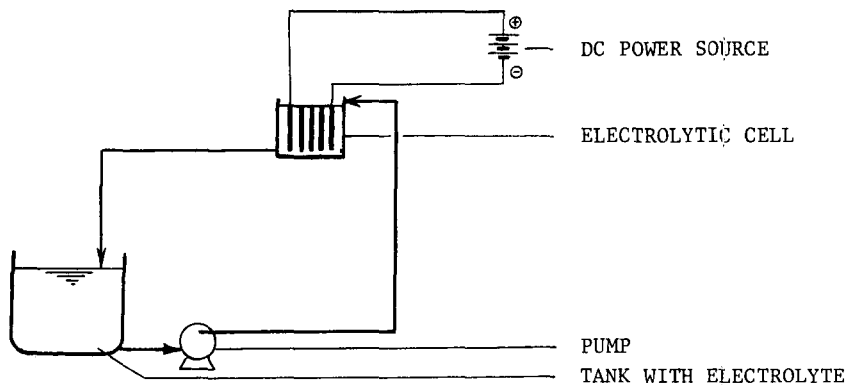flow diagrams

DC POWER SOURCE

ELECTROLYTIC CELL

Figure 2
Lay-out of laboratory electrolytic experimental unit

PUMP

TANK WITH ELECTROLYTE

Calculated Fe
dissolved (g)

$R^2 = 0,94$

Measured Fe dissolved (g)
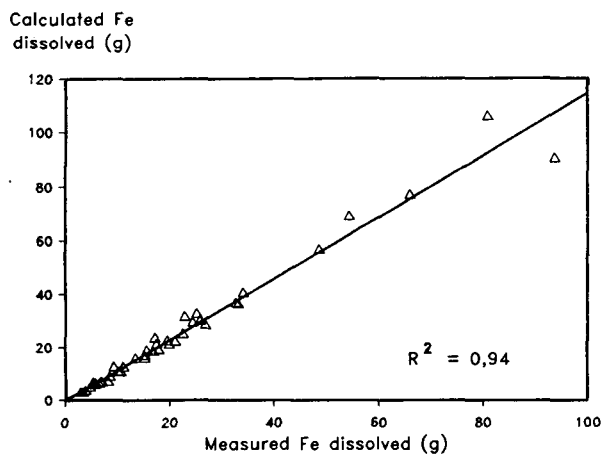
Figure 3
Linear correlation between mass of iron dissolved and calculated mass

Calculated power con=
sumption (kW.h/gFe)

$R^2 = 0,90$
$\eta = 0,865$

Measured power consumption (kW.h/gFe)
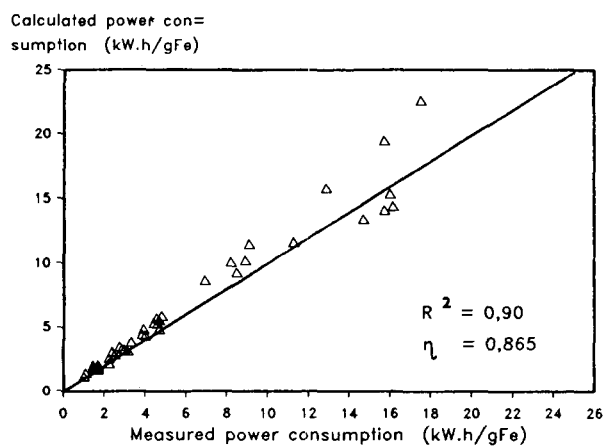
Figure 5
Correlation between measured and calculated power consumption

Calculated
potential (V)

$R^2 = 0,83$

Measured potential (V)
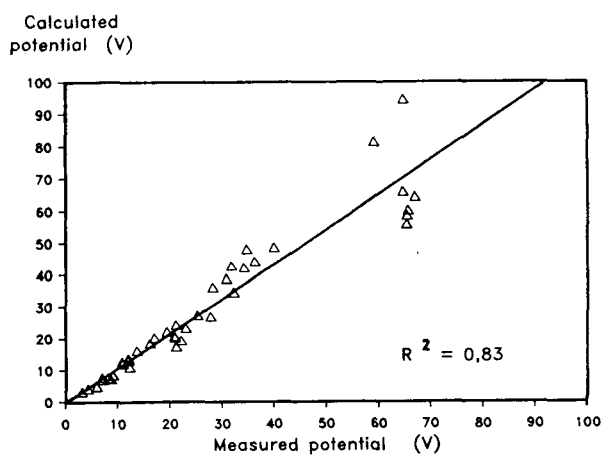
Figure 4
Correlation between measured electrical potential and that theoretical-ly predicted

Current density
(A/m^2)

IRON   ENERGY

$Fe_2(SO_4)_3$

$FeCl_3$

Chemical costs (R/d)

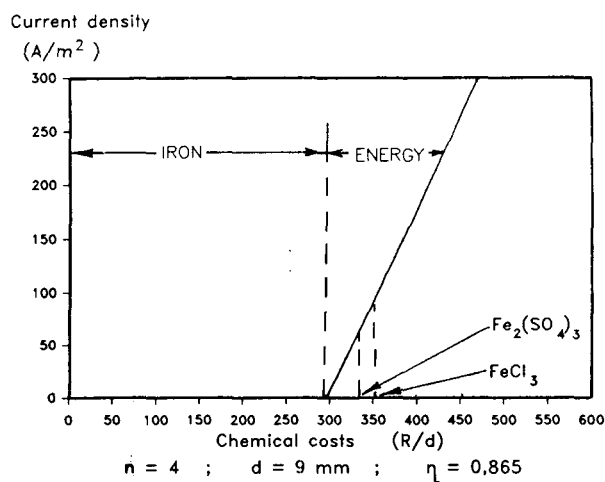n = 4 ;   d = 9 mm ; $\eta = 0,865$

Figure 6
Cost comparison of commercial and electrolytically produced iron coagulants for a 10 Ml/d treatment plant

TABLE 1
EXPERIMENTAL PROGRAMME

Parameter evaluated	Current density (A/m²)	Number of electrodes (n + 1)	Electrode spacing (mm)
Electrode spacing	15-300	5	5, 9, 15, 20
Number of electrodes	20-70	3, 5, 7, 9	9

TABLE 2
COST COMPARISON OF COMMERCIAL AND ELECTROLYTICALLY PRODUCED IRON COAGULANTS FOR A 10 Mℓ/d TREATMENT PLANT

Coagulant	Iron cont. % Fe	Unit cost of chemicals* R/t	Unit cost of chemicals* c/m³	Dosing equipm R	Production costs** c/m³
Ferric chloride	14,8	260	3,51	19 000	3,73
Ferric sulphate	10,5	175	3,33	19 000	3,55
Iron (Electrol.)	100	1 581***	3,16	46 000	3,69

* Dosage — 20 mg/ℓ as Fe; chemical prices as in February 1990.
** Includes capital redemption of dosing equipment at 20% interest over a 10-year period
*** Includes electricity costs at R16,5/kVA per month plus R0,0396/kWh

that calculated by Eqs. (4) and (5) is $\eta = 0,87$. This efficiency factor gives a correlation coefficient $R^2 = 0,90$ as shown in Fig. 5.

The experimental results were used to compare the cost of the electrolytically produced iron floc with comparable floc from commercially available iron salts (Table 2). For this purpose a 10 Mℓ/d capacity waste-water treatment plant requiring a 20 mg/ℓ dose of iron (as Fe) was used as basis for the comparison. Fig. 6 shows how the production cost increases with an increase in current density during the electrolytic process for iron coagulant production.

Discussion and conclusions

Although the mathematical modelling of the electrolytic dissolution of iron is complicated by the evolution of a gas (hydrogen) (Johannes, 1989), relatively good correlations (see Figs. 3 and 4) were found between experimental data obtained with bipolar electrodes in a cells in series arrangement and the simplified mathematical models described by Pickett (1979). These relationships also indicate that iron dissolves in the ferrous form. With this electrolytic cell arrangement a relatively high effective use of electric power $\eta = 0,865$) was obtained as shown in Fig. 5. These results indicate that once the effectivity of the electrolytic cell (η) and the specific conductivity (κ) of the waste water are known, the electrode sizes, spacings and numbers as well as the electric power required for a given iron dissolution rate could be calculated using Eqs. (4) and (5).

More sophisticated equipment is required to produce an iron coagulant electrolytically than the dosing equipment used for commercial coagulants. The electrolytic process is, however, electronically controlled with no moving parts, thus requiring less maintenance than dosing equipment. It will only be necessary to replace individual electrodes as the iron is used up during electrolysis (for coagulant production). As discussed, replacement of an electrode is easily accomplished if the bipolar cell configuration is used. Production costs for the different coagulants compare well. The costs to produce the iron coagulant electrolytically are higher than ferric sulphate costs, but lower than ferric chloride (Table 2). Fig. 6 shows that electrolytically produced iron flocculant has two major cost components, namely the cost of the electrode material (steel) and electricity cost. The cost of the electrode material is fixed, while the current density determines the cost of the required electricity. For the dissolution of high quality plate steel the equivalent costs compared to iron salt dosing occurs at current densities below 100 A/m² for $Fe_2(SO_4)_3$ and 140 A/m² for $FeCl_3$ respectively. It thus seems that electrolytically produced iron coagulant is only more economical than commercial iron salts at relatively low current densities. However, since the metal (iron) represents the major part of the overall cost, some cost savings could be realised by using scrap steel or steel with a lower quality grade.

With increasing emphasis on the reuse of treated waste water, the additional use of electrolytically produced metal flocculants could be favoured since no additional salts are added, as is the case with commercial metal flocculants.

Acknowledgement

References

BEST, HJ (1986) The Department of Water Affairs' approach to a phosphate management strategy for the Republic of South Africa. Paper presented at the Congress for Municipal Engineers, Randburg. 12-15 May.

BOTHA, J and PRETORIUS, WA (1989) Eerste- en tweedegraad watervoorsiening in woongebiede - 'n Fantasie? Paper presented at the 1st Biennial WISA Conference, Cape Town. 30 March.

DOBOLYI, E (1978) Experiments aimed at the removal of phosphate by electro-chemical methods. *Water Research* 12 1113-1116.

GRØTERUD, O and SMOCZYNSKI, L (1986a) Phosphorus removal from water by means of electrolysis. *Water Research* 20(5) 667-669.

GRØTERUD, O and SMOCZYNSKI, L (1986b) Phosphorus removal from wastewaters by electrolysis. *Vatten* 42(1) 33-35.

GRØTERUD, O and SMOCZYNSKI, L (1986c) Removal of phosphorus and residual aluminium by recirculating electrolysis of wastewater. *Vatten* 42(4) 293-296.

HEYNIKE, JJC (1986) The Economic Effects of the Mineral Content Present in the Vaal River Barrage on the Community of the PWVS-complex. Water Research Commission, Pretoria.

JOHANNES, WG (1989) Elektrochemies-geproduseerde Metaalkoagulante vir die Verwydering van Fosfaat uit Rioolwater. M. Eng.-dissertation. University of Pretoria.

LOUW, AS, BASSON, HJ and ALEXANDER, WV (1988) Evaluation and Optimisation of Full-scale Chemical Phosphate Removal in Biological Sewage Treatment Processes. Water Research Commission, Pretoria.

METCALF and EDDY (1979) *Wastewater Engineering: Treatment Disposal Reuse* (2nd edn.). McGraw-Hill Book Company, New York.

PETERS, DG, HAYES, JM and HIEFTJE, GM (1974) *Chemical Separations and Measurements.* WB Saunders Company, Philadelphia.

PICKETT, DJ (1979) *Electrochemical Reactor Design* (2nd edn.) Elsevier Scientific Publishing Company, Amsterdam.

ROUSAR, I, MICKA, K and KIMLA, A (1986) *Electrochemical Engineering.* Elsevier Science Publishing Company, Inc., New York.

SMITH, CE (1972) Waste water treatment through electrochemistry. *Progress in Water Technology, Volume I. Applications of new Concepts of Physical-chemical Wastewater Treatment.* Pergamon Press, Inc.

U.S. PATENT 937 210 (1909) In: MILLER, HC and KNIPE, W (1976) *Electro-chemical Treatment of Municipal Waste Water.* Public Health Service Publication No. 9990WP-19. U.S. Department of Health, Education and Welfare.

VIK, EA, CARLSON, DA, EIKUM, AS and GJESSING, ET (1984) Electrocoagulation of potable water. *Water Research* 18(11) 1355-1360.

WIECHERS, HNS (1987) Guidelines for Chemical Phosphate Removal from Municipal Wastewaters. Water Research Commission, Pretoria.

WIECHERS, HNS, LOUW, AS, THIRION, NV and BRODISH, KEU (1984) Upgrading of biological filter sewerage purification processes for phosphate and nitrogen removal. *Water SA* 10(4) 205-210.