STABILISATION OF
SOFT ACIDIC WATERS WITH LIMESTONE

Final Report to the

Water Research Commission

by

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Final Report

Prepared for
Water Research Commission

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EXECUTIVE SUMMARY

Background and motivation

A significant proportion of the surface waters of South Africa, and all the surface waters of Lesotho, characteristically have low Alkalinity (0-25 mg/ℓ as $CaCO_3$), low calcium (0-25 mg/ℓ as $CaCO_3$) and low pH (4.0 to 7.0). Furthermore, virtually all of the groundwaters of the southern and eastern fringes of South Africa (up to approximately 200 km inland) have similar characteristics. In addition, surface waters of the southern region have variable colour due to the presence of complex Natural Organic Matter (NOM) constituents, the presence of which can further lower pH to as low as 4.0.

The waters described above are aggressive to cement type materials, and corrosive to metals, attacking conduits, pipes and fittings. The financial cost of attack on distribution networks, and on fittings and equipment in private households in South Africa is substantial. Such cost is incurred as a result of lost water and the need to replace and repair pipes, reservoirs, valves, geysers and plumbing. A further cost is that relating to deterioration in chemical water quality as a result of raised levels of dissolved metals, often in excess of SABS 241-1984 Specification for Water for Domestic Supplies. The need to minimize these costs is of equal importance in large scale distribution networks and small community user systems, albeit not always for the same reasons. The principal component of measures to prevent corrosive and/or aggressive attack by soft, acidic waters is the chemical conditioning, or stabilisation, of the water.

Conventionally, stabilisation of soft, acidic waters is achieved via the addition of lime and carbon dioxide. However, for smaller municipalities, stabilisation via lime dosing (with or without carbon dioxide) is problematic, requiring skilled, well trained staff and costly equipment. Furthermore, stabilisation with lime is expensive, comprising about half of the overall chemical cost of treatment. For small volume water users, such as rural communities and small holdings, stabilisation is not readily implementable and the cost of corrosion and aggression can be significant.

An alternative means of stabilising soft, acidic waters is considered in this report, namely contact with limestone ($CaCO_3$). Limestone appears attractive as a stabilising media for both small scale and large scale stabilisation units, principally because of potential simplicity of operation, and reduced chemical costs.

Aims and objectives

This study aimed to assess the suitability of limestone mediated stabilisation of soft, acidic waters, and to develop a better understanding of such stabilisation and its implementation opportunities. The stated objectives of the study were as follows:

(i) Identification of suitable limestone sources

(ii) Kinetic modelling of limestone dissolution

(iii) Development and assessment of limestone stabilisation units for

- Small Users (50 m^3/day)
- Large Users (more than 1000 m^3/day)

(iv) Evaluation of influencing parameters (e.g. raw water characteristics)

(v) Assessment of cost benefits of limestone stabilisation relative to conventional stabilisation methods

Research programme

The research programme was designed to address the objectives, thereby necessitating a combination of elementary test procedures, including pilot plant trials, and more complex, in-depth modelling studies. Suitable laboratory test rigs and pilot plants were designed and constructed, and tests were carried out at laboratories of the University of Cape Town and CSIR, Stellenbosch, and in the field. Data collection, documentation and interpretation were implemented as follows:

(i) Five potentially suitable limestone deposits were identified and evaluated for suitability as stabilisation media. Emphasis was on limestone deposits in the Western Cape, i.e. the region where the laboratory and pilot plant studies were carried out. The deposit identified as most suitable was considered further in terms of laboratory and field assessment. Selection of particle sizing was considered from both a practical and process optimisation perspective.

(ii) A literature study to identify an appropriate kinetic model describing limestone dissolution kinetics was carried out, and a suitable model was identified and assessed.

(iii) Pilot plant units for small users were developed and tested. Whilst initial objectives were to assess a pressure system only, it was realised that use of a pressure system for groundwaters was inappropriate as a result of the role that dissolved carbon dioxide plays. Accordingly, separate systems were considered, developed and tested for, (i), groundwater, and (ii), surface water. Developmental and prototype units for groundwater and surface water were installed and assessed in the laboratory and field. System specifications and construction guidelines were developed for the groundwater and surface water treatment systems. The influence of a range of variables on the performance of the small user systems were assessed by means of pilot tests. These included varying NOM levels, and varying levels of iron and manganese in the water.

(iv) A fluidised limestone bed pilot plant was operated and assessed as to suitability for large systems. In order to design the fluidised bed pilot plant, a theoretical understanding of fluidised bed technology was attained to determine design parameters. Thereafter, a pilot plant was constructed and operated, with tests being carried out on two types of aggressive, corrosive water. Results of the pilot plant development were used to derive design parameters for a 10 Mℓ/d fluidised bed unit.

(v) During preliminary investigation regarding the cost benefit analysis, it became apparent that no competing stabilisation technology for volumes of around 50 m^3/day exist, and therefore a cost benefit analysis on the small user systems was not possible. A comparative cost study was carried out for the fluidised bed system, in which chemical and energy operating costs of the system were compared with those of the lime and carbon dioxide dosing system.

Summary of results and conclusions

Of the five limestone deposits that were assessed for suitability, the Bredasdorp deposit of the Western Cape was found to be the most suitable for use as stabilisation media. The Bredasdorp deposit is actively mined, and has suitable mineral structure, mineral composition and geographical proximity to the study area.

It was established that the dissolution kinetics of limestone can be modelled by a diffusion controlled model formulated by Plummer, Parkhurst and Wigley in 1979. Practical application of the dissolution kinetics requires that the compound rate constant in the above model be known for specific hydraulic conditions. It was shown that the compound rate constant depends on granule size and reactor loading rate. An empirical relationship was developed, describing the compound rate constant for the Bredasdorp deposit as a function of loading rate and nominal mean granule size. It was concluded that the dissolution characteristics of other limestone deposits and gradings may be established using the same methodology.

Two types of small user systems (about 50 m^3/day), designed to treat groundwater and surface waters respectively, were shown to be effective for the stabilisation of a range of soft, acidic waters. The small user groundwater stabilisation unit, called "Spraystab" after the treatment configuration, was found to be highly effective at treating soft, acidic groundwater with no iron or manganese present. It was shown that a limestone bed retention time of about three minutes was sufficient to significantly reduce the calcium carbonate dissolution potential (CCDP), and increase pH, calcium and Alkalinity to desirable levels. The "Spraystab" process was shown also to be effective at treating soft, acidic groundwater with low levels of iron (about 2 mg/ℓ). In this case, the process was shown to stabilise the water satisfactorily and to remove the dissolved iron with a limestone bed retention time of about five minutes. The system was shown to be compact and robust, requiring minimal operator attention and/or maintenance. The "Spraystab" system has proven itself to be an effective and financially attractive water treatment system in a market niche area where there are no viable alternatives.

The small user surface water stabilisation unit, called "Presstab" after the treatment configuration, was found to be effective for the stabilisation of a range of surface waters. Waters tested varied from "white" water, to strongly coloured "brown" water (water with high NOM levels), whilst dissolved iron levels varied between 0 and 2 mg/ℓ. The process was found to be effective, provided that, (i), turbid waters containing suspended matter are filtered prior to stabilisation, and (ii), it is accepted that when treating highly coloured waters there will be a reduction in efficiency owing to the "coating" of the limestone particles with time. It was shown that the "Presstab" process operates effectively at a contact time of around ten minutes for a range of waters. The system was shown to be compact and robust, requiring minimal operator attention and/or maintenance. The "Presstab" system has shown itself to be a financially attractive water treatment system in a market niche area where there are no viable alternatives.

Experimental trials with the fluidised limestone bed pilot plant, showed that the fluidised bed system can significantly reduce the CCDP of aggressive water within reasonably short retention times, thereby almost eliminating aggressiveness to cement and reducing corrosivity. (Two soft, acidic water types were considered, namely Stellenbosch mountain catchment water and a simulated reverse osmosis permeate.) It was shown, however, that the characteristics of the raw water determine both the rate of calcium carbonate dissolution (and hence the retention time required for stabilisation) and the chemical characteristics of the final water. The latter is problematic in that it is not possible to ensure that the final stabilised water will have chemical characteristics which satisfy stabilisation guideline levels for negation of iron corrosion in large distribution networks.

The process was shown, for example, to reduce the CCDP of Stellenbosch mountain catchment water from 53 mg/ℓ to 2.8 mg/ℓ as $CaCO_3$, with associated final Alkalinity and calcium levels of about 15 mg/ℓ as $CaCO_3$. These calcium and Alkalinity values are considerably lower than the iron corrosion prevention guideline levels of ≥ 50 mg/ℓ as $CaCO_3$.

Finally, with regard to the financial attractiveness of limestone mediated stabilisation, it was concluded that, with regards to the small user systems of about 50 m^3/day, no alternate competing technologies exist for comparison. With regards to large user systems of greater than 1000 m^3/day, the fluidised bed process was shown to be able to reduce the CCDP of the test waters at reasonable savings relative to the conventional lime and carbon dioxide dosing process. Such savings ranged between 25 % (simulated reverse osmosis permeate) and ± 44 % (Stellenbosch mountain catchment water), and are influenced significantly by the raw water characteristics. It was concluded, however, that full-scale application of the fluidised limestone bed process for medium to large water treatment works appears unattractive because, (i), the fluidised bed process alone is unable to meet water quality stabilisation guidelines for all aggressive and corrosive waters, and (ii), the capital cost of the fluidised bed process is likely to be an order of magnitude larger than that of the alternate conventional lime and process. Hence, the apparently attractive chemical and energy savings of between 25 % (± R26 000/annum) and 44 % (± R64 000/annum), are relatively insignificant and unlikely to redeem the increased capital cost.

Recommendations for further research

Recommendations for further research were determined by the project team and the Steering Committee as follows:

(i) With regards the small user systems, further research and development is required regarding:

- assessment of the "Spraystab" system for waters containing a wider range of iron and manganese levels and identification of the upper limit in terms of removal thereof,
- scaling up of the "Spraystab" to treat greater volumes of water, say up to 1 000 m^3/day, such that it is suitable for small town purposes,
- identification of the colour level in surface waters at which the NOM coating of the limestone becomes problematic, and
- the information available be collated into a practically oriented guideline for the use of small user limestone mediated stabilisation systems.

(ii) With regards to medium sized stabilisation units (1 000 to 20 000 m^3/day), CSIR has carried out its own research, development and implementation work into fixed bed limestone contactors. To date, nine full scale units have been installed in the Western Cape and have shown the process to be an effective means of partial stabilisation (i.e. significant reduction in CCDP and satisfactory adjustment of pH, but not satisfying iron corrosion prevention guidelines for calcium and Alkalinity). The limestone mediated partial stabilisation process has been shown to provide a significant total running cost saving of about 70 % versus lime and carbon dioxide stabilisation, and is robust and simple in operation. However, limitations in understanding exist as to both, (i), suitability of the process for conditioning acidic waters created by purification processes such as desalination, and (ii), the relative benefit of partial stabilisation versus complete stabilisation. It is recommended that:

- pilot scale tests be implemented to assess the suitability of fixed bed limestone contactors for different types of product water, including reverse osmosis permeate and post-ferric salt clarification,
- a study be undertaken into the relative degree of protection afforded to common conduit materials (copper, cement concrete, iron) by limestone mediated "partial stabilisation" versus "complete stabilisation", and consideration of the relative cost implications thereof,
- the kinetic model be developed further to provide a computer based design package for fixed bed limestone contactors,
- the information available be collated into a guideline for the stabilisation of medium to large user systems with limestone.

(iii) It is recommended that:

- following the completion of (i) and (ii) above, a **Manual for the Stabilisation of Waters with Limestone** be collated, published and distributed,
- an Expert Systems based package be developed to go with the Manual, covering in particular the design/construction of both the small scale and medium to large scale systems,
- a technology transfer programme be implemented, including two regional seminars (Western Cape and Natal), technical papers, and profiling through WISA and the relevant groupings in SAICE and IMIESA.

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The Steering Committee for this project consisted of the following persons:

Dr G Offringa; Water Research Commission (Chairman)
Dr H Saayman; Water Research Commission
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DEFINITIONS AND SYMBOLS

acidity	General term for the proton (H^+) donating capacity relative to some equivalent solution
Acidity	(Capital letter) Proton donating capacity relative to an equivalent solution of CO_3^{2-} - also called CO_3^{2-} acidity or total acidity
alkalinity	General term for the proton (H^+) accepting capacity relative to some equivalent solution
Alkalinity	(Capital letter) Proton accepting capacity relative to an equivalent solution of $H_2CO_3^*$. Also called $H_2CO_3^*$ alkalinity or total alkalinity
CCDP	Calcium carbonate dissolution potential - a characteristic of a water that indicates the theoretical amount of calcium carbonate that the water can dissolve before reaching saturation with respect to calcium carbonate
CCPP	Calcium carbonate precipitation potential - a characteristic of a water that indicates the theoretical amount of calcium carbonate that can precipitate from the water
$H_2CO_3^*$	Chemical formula denoting the sum of carbonic acid, H_2CO_3, and molecularly dissolved carbon dioxide, $CO_{2\,(aq)}$
SI	Saturation Index - an index used for qualifying the saturation state of a water, defined as the difference between the pH and saturation pH (pH_s), if positive, solution is supersaturated, if negative, solution is undersaturated

CHAPTER 1

INTRODUCTION

1.1 Soft Acidic Waters

Approximately forty percent of the surface waters of South Africa, and all the surface waters of Lesotho, characteristically have low calcium, alkalinity and carbonate species concentration (Loewenthal, 1995) (see **Figure 1**). In addition, virtually all of the groundwaters of the southern and eastern fringes of South Africa (up to approximately 200 km inland) have similar characteristics. Typically ground and surface waters have low Alkalinity (0-25 mg/ℓ as $CaCO_3$), low calcium (0-25 mg/ℓ as $CaCO_3$) and low pH. Surface waters rarely have pH greater than 6.5, whilst groundwaters brought to the surface have pH levels ranging between 4.0 and 6.0. Furthermore, surface waters of the southern coastal region have variable colour due to the presence of complex Natural Organic Matter (NOM) constituents; mainly humic and fulvic acids. The presence of these organic acids can further lower pH to as low as 4.0.

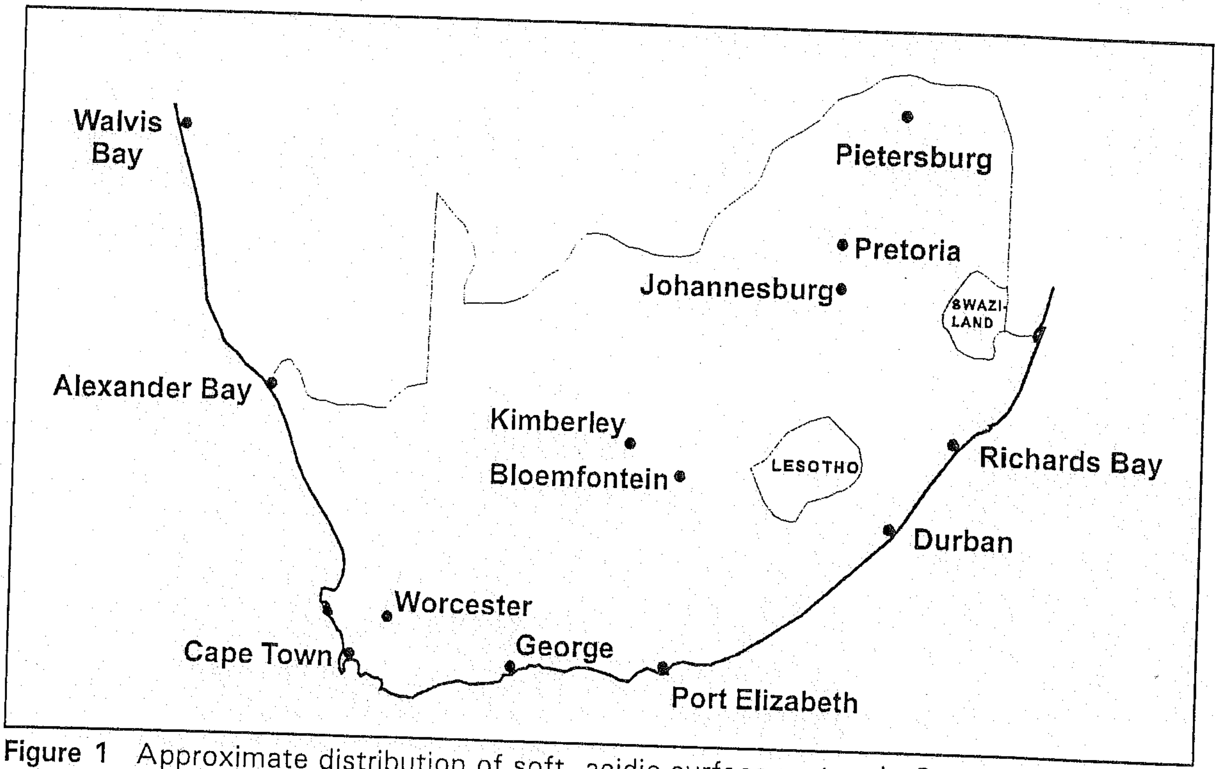


Figure 1 Approximate distribution of soft, acidic surface waters in South Africa

Note that only an approximate overview of the geographical distribution of soft, acidic surface waters in the country is given above. Only regions where soft, acidic surface waters predominate were shaded. Groundwaters, as well as waters that have been subjected to certain treatment processes (e.g. desalination), in the unshaded areas may also be soft and acidic.

Low pH and carbonate species concentrations in surface and groundwaters of these regions cause the water to be both aggressive (to cement type materials) and corrosive (to metals), attacking conduits and pipes. By **aggressive attack** of cementitious materials is meant the leaching of free lime, aluminates and silicates out of the cement matrix into the water. In the case of cement asbestos type pipes, such attack results in eventual collapse of the cement matrix and results in pipe bursts. In the case of reinforced concrete materials, such attack results in corrosion of the reinforcing metal and eventual leakage. By **corrosive attack** of metals is meant the oxidation and reduction reactions between the water and the metal components of the system. The dissolution of metals and precipitation of metal salts results in impaired function and eventual failure of metal pipes, valves and geysers. Such aggressive and corrosive attack has both an economic and potability implication for water supply and usage.

1.2 Cost of Soft Acidic Water Attack

The financial cost of aggressive and corrosive attack on distribution networks and water systems in private households in South Africa has not been quantified. However, discussion with both municipal officials and members of the South African public indicates that the financial cost of aggressive and corrosive attack is substantial. Such costs are categorised below. Brief examples indicate the severity of typical related problems.

Lost water

In many municipalities water lost from pipe bursts and leakages is unquantified, recognised as being higher than acceptable, yet historically regarded as being part of normal operation by local authorities. The cost of lost water resulting from pipe bursts and leakages can be substantial. For example: in the Durban townships of Umlazi, Kwamashu and Ntazuma total water losses from service reservoirs and reticulation systems was "found to be around 50% of the total bulk volume of water purchased from Umgeni Water" prior to rehabilitation. The cost of the lost water amounted to R11 670 000 in 1992 (Deighton and Vawda, 1992).

Repairs

The substantial finances allotted to water reticulation systems for households, villages, towns and cities are very seldom afforded the attention that other more visible investments receive. In the case of conduits and reservoirs, the failure to prevent or ameliorate aggressive and corrosive attack can result in significant cost. For example: in Stellenbosch, prior to the installation of stabilisation units, an average of 30 sections of cement concrete pipe were replaced per month at a cost of between R2 000 and R6 000 per section (Hartzenberg, 1993). Similarly, Umgeni Water had to carry out expensive repair to their Durban Heights Reservoir in 1990 to overcome a leak of 300 m^3/day as a result of aggressive attack (Hakin and Crawford, 1992). At consumer level, corrosive attack can necessitate accelerated replacement of geysers and piping. For example: corrosive attack of internal plumbing in a six year old five star hotel utilising municipal water in Somerset West, necessitated close to one million rand being spent in replacing piping and the installation of an on-site stabilisation unit (Callaghan, 1992).

Potability

Corrosive attack of metal conduits and valves in household and municipal water reticulation systems results in raised level of dissolved metals in household water. In many cases dissolved metal levels resulting from corrosion exceed SABS 241-1984 Specification for Water for Domestic Supplies requirements. Moderately raised levels of copper and iron can lead to stomach complaints, staining of baths, laundry and hair. Severe cases make the water unfit for human consumption and/or other household use. For example:, dissolved iron of 23 mg/ℓ and dissolved copper of 6,7 mg/ℓ at a Southwestern Cape country hotel (de Villiers, 1993).

These examples of the impact of aggressive and corrosive attack reflect a general and serious problem that exists throughout areas where soft, acidic waters are found. To overcome these problems, effective water conditioning is required.

1.3 Stabilisation of Soft Acidic Waters

General guidelines to prevent aggression and/or corrosion exist (Loewenthal *et al*, 1986). The principal component of measures to prevent corrosive and/or aggressive attack by soft, acidic waters is the chemical conditioning, or stabilisation, of the water.

Conventionally, stabilisation is achieved via the addition of lime ($Ca(OH)_2$), to increase calcium (Ca^{2+}) and alkalinity levels, and the addition of carbon dioxide (CO_2), to add carbonate species and adjust pH. Stabilisation of soft, acidic waters will terminate aggression and corrosion. However, whilst such stabilisation is well documented and understood, it requires well trained staff with reliable equipment; both which are seldom available in the many small towns and communities receiving such waters. Hence, in many cases only lime mediated pH adjustment to more desirable pH levels of, say, 8.0, is practised, thereby providing only a partially stabilised water. Even so, for the smaller municipal installation, dosing of lime (with or without carbon dioxide) remains problematic and difficult to control. Furthermore, stabilisation with lime is expensive, often comprising about half of the chemical cost of treating water.

For the independent small volume water users, such as farmers and small holding owners, stabilisation is not possible and the costs of corrosion can be significant. An alternative approach is the use of limestone.

1.4 Stabilisation with Limestone

An alternative means of stabilising soft, acidic waters is by contact with limestone ($CaCO_3$). In this process the natural driving force - calcium carbonate dissolution potential (CCDP) - of the water is used to take up the necessary carbonate and calcium for stabilisation. For example: a water with a CCDP of 35 mg/ℓ $CaCO_3$ will take up 35 mg/ℓ $CaCO_3$ to reach chemical stability; in doing so the pH, alkalinity and calcium levels of the water will increase. Whilst this will not result in a water with a positive calcium carbonate precipitation potential (CCPP), it will result in a water which is essentially non-aggressive to cement concrete, non-corrosive to copper and with a reduced corrosivity to iron.

The first documented attempts to stabilise municipal water were made using limestone in 1906 in Frankfurt, Germany, when domestic water was treated by contacting it with a marble bed. It was shown that with such treatment, corrosion of the distribution network was significantly reduced (Hirsch, 1933). However, the availability of the more readily soluble lime resulted in the use of limestone falling from favour, and by the 1930's, the application of limestone was essentially discontinued (Reijnen, 1979). Nevertheless, limestone stabilisation was further investigated in the Netherlands in the 1960's and a number of pilot studies were carried out (CMCO, 1978). In South Africa, a limited number of small limestone units were installed in the 1960's and 1970's, but these fell into disuse; apparently as a result of poor treatment efficiency and hydraulic failure resulting from both poor design and the use of inappropriate limestone. Although there are few documented cases of full scale use of the technology, it would appear that there has been recent renewed interest in limestone mediated stabilisation and that a number of small plants have been installed in the USA and Canada (Letterman et al,1987).

In South Africa, CSIR reinitiated research into limestone stabilisation in the early 1990's as part of a research programme into low maintenance, robust, small water treatment plants. CSIR successfully ran a number of groundwater treatment units, and found that stabilisation with limestone potentially has significant advantages over the traditional use of lime and carbon dioxide, or dosing of sodium alkali's such as sodium carbonate. These include inter alia:

- Limestone is significantly cheaper than lime (approximately R150/t vs R750/t, 1997 prices).
- pH is controlled naturally at desirable levels as the water approaches chemical equilibrium, and overdosing can not occur.
- The process requires little or no operator skill.
- Lime dosing equipment is notoriously troublesome; and is generally impractical on small scale water treatment plants.

However, negative aspects of stabilisation with limestone had also been identified. In order to concentrate on identifying, qualifying and, ideally, overcoming, the problematic issues, a two year exploratory study contract (1994, 1995) was negotiated between the Water Research Commission and the CSIR, through its former Division of Water Technology (now part of Water, Environment and Forestry Technology). Subsequently the study period was extended to include 1996 and 1997 to allow for the gathering of data from privately funded prototype small user stabilisation units installed during 1996.

1.5 Project Objectives

The project objectives were to investigate and further develop limestone mediated stabilisation such that it could be implemented in a successful and cost effective manner for both small scale and municipal scale utilisation. To achieve these objectives the project was focussed as follows:

(i) **Identification of suitable limestone sources**
A limited number of limestone sources would be investigated for suitability.

(ii) **Kinetic modelling of limestone dissolution**
Kinetic modelling of limestone dissolution would be carried out. A maths model would be developed based on the ruling kinetic parameters.

(iii) **Development and assessment of limestone stabilisation units**
The design, construction and development of stabilisation units suitable for both small users and large users would be investigated. In brief these would be as follows:

Small User (50 m^3/day)
In-line fixed bed pressure units for the stabilisation of both ground and surface water would be developed and studied.

Large User (more than 1000 m^3/day)
A fluidised bed process would be investigated, as it was believed that the fluidising process would significantly reduce the retention time required for treatment.

Where pertinent, basic design criteria would be provided for both of the above..

(iv) **Evaluation of influencing parameters**
The influence of variable water quality would be investigated at a practical level. Water quality variables to be addressed would include surface water, groundwater, and water containing humic acids, iron and manganese.

(v) **Cost benefit analysis of limestone stabilisation**
In order to quantify the benefits of limestone mediated stabilisation, a cost benefit analysis of stabilisation would be carried out.

REFERENCES - CHAPTER 1

Introduction

CALLAGHAN B (1992) Private communication.

COMMISSIE METHODIEKEN CENTRALE ONTHARDING (CMCO) (1978) Kwaliteitseisen In Verband Met De Stabiliteit Van Het Distribüren Drinkwater. Rijswijk. Kiwa, 1978; 57 Blz., Mededeling 54.

DE VILLIERS H (1993) Private communication.

DEIGHTON, ME and VAWDA, MS (1992) Water management in Durban's townships - stopping the snowball. Paper presented at the Young Water Engineers Conference, 5-6 March 1992, Midrand.

HAKIN WD and CRAWFORD CE (1992) The use of a geomembrane in a potable water reservoir to prevent concrete attack. Paper presented at the Young Water Engineers Conference, 5-6 March 1992, Midrand.

HARTZENBERG PSJ (1993). Private communication.

HIRSCH P (1933) Ontzuring van drinkwater door filtratiemethoden. *Water*, 17, pp 255-261.

LETTERMAN RD, DRISCOLL CT, HADAD M AND HSU A (1987) Limestone Contactors for Corrosion Control at Small Water Utilities, Final Research Report submitted to the U.S. Environmental Protection Agency, Water Engineering Research Laboratory, Cincinnati, OH (EPA/600/S2-86/099).

LOEWENTHAL RE (1995), Private communication.

LOEWENTHAL RE, WIECHERS HNS and MARAIS GvR (1986) *Softening and Stabilization of Municipal Waters.* Water Research Commission, Pretoria.

REIJNEN GK (1979) Marmerontzuring, een oud proces met nieuwe perspectieven. *H_2O* (Rotterdam), Vol 12, No 13, pp 290-295.

CHAPTER 2

BACKGROUND

2.1 Chemistry of the Carbonate System in the Aqueous, Gaseous and Solid Phases

In terrestrial waters, the carbonate system is the dominating one to such a degree that other weak acid/base systems are usually neglected. The carbonate system in water is comprised of the species molecularly dissolved carbon dioxide, $CO_{2(aq)}$, carbonic acid, H_2CO_3, and the ionic species bicarbonate, HCO_3^-, and carbonate, CO_3^{2-}, and the water species, H^+ and OH^-. The relative concentrations of the dissolved species are governed by chemical equilibrium, and it is the interaction between these species that controls the pH in natural terrestrial waters. Furthermore, consideration needs to be given to inter-phase equilibrium, i.e. water brought into contact with the gaseous phase (carbon dioxide in the air) or a solid phase.

In this investigation, equilibrium between species in the aqueous and solid phases is of primary interest. However, equilibrium between aqueous and solid phase species of a mineral is influenced by aqueous-gaseous interaction. Before assessing quantitatively the changes which occur as inter-phase equilibrium is attained, it is first necessary to briefly consider:

- chemistry of the carbonate system in the aqueous phase,
- chemistry of the carbonate system in the aqueous-gaseous phase, and
- chemistry of the carbonate system in the aqueous-solid phase.

For the consideration of the above carbonate chemistry, particulars will be limited to the requirements of this monograph. For detailed description of the carbonate system, the reader is referred to Loewenthal and Marais, 1976 and Loewenthal et al, 1986.

2.1.1 Aqueous phase system characterisation

Relationships between dissolved carbonate species ($H_2CO_3^*$, HCO_3^- and CO_3^{2-}) and water species (H^+ and OH^-) are governed by a set of thermodynamic equilibrium equations, all of which must be satisfied simultaneously. These complex relationships are well described elsewhere (Loewenthal and Marais, 1976), suffice to note that the use of measurable mass parameters, such as total carbonate species concentration, C_T, the various forms of alkalinity and acidity, and pH are used for the characterisation of the carbonate system in the aqueous phase.

Commonly used parameters are:

$$\text{Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \tag{2-1}$$

$$\text{Acidity} = [HCO_3^-] + 2[H_2CO_3^*] + [H^+] - [OH^-] \tag{2-2}$$

$$C_T = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3^*] \tag{2-3}$$

$$\text{pH} = -\log (H^+) \tag{2-4}$$

where [ ], ( ) = molar concentration and activity of species, and

$(H_2CO_3^*) = (H_2CO_3) + (CO_{2\,(aq)})$.

Measurement of only two of the above four independent parameters allows for characterisation of the carbonate system in the aqueous phase. The two independent parameters most commonly measured to allow characterisation of the carbonate system in the aqueous phase are pH and Alkalinity. Measurement of these will allow determination of Acidity either by, (i) by calculation, or (ii) Deffeyes type diagram.

In order to calculate Acidity, **Equation (2-5)** below must be solved.

$$\text{Acidity} = \text{Alk}\left[\frac{1 + 2\times10^{(\text{pH} - \text{p}K'_{c1})}}{1 + 2\times10^{(\text{p}K'_{c2} - \text{pH})}}\right] - 10^{(\text{pH} - \text{p}K'_{w})} + 10^{(-\text{pH})} \tag{2-5}$$

More conveniently, Acidity can be determined graphically in Deffeyes type diagrams, which are constructed for specific temperatures and ionic strengths (Loewenthal et al, 1986). An example of a Deffeyes type diagram is shown in **Figure 2-1**, whereby Acidity is simply read off for known pH and Alkalinity values. In the diagram, Alkalinity 2 mg/ℓ and pH 6.0 gives Acidity = 11 mg/ℓ.

An important aspect of the Alkalinity-Acidity-pH diagram is that it can be used to predict the change in state of a water due to chemical dosing, and as such, constitutes a single phase conditioning diagram. Fundamental to the use of this diagram as a conditioning diagram are the simple stoichiometric changes in the capacity parameters with dosing.

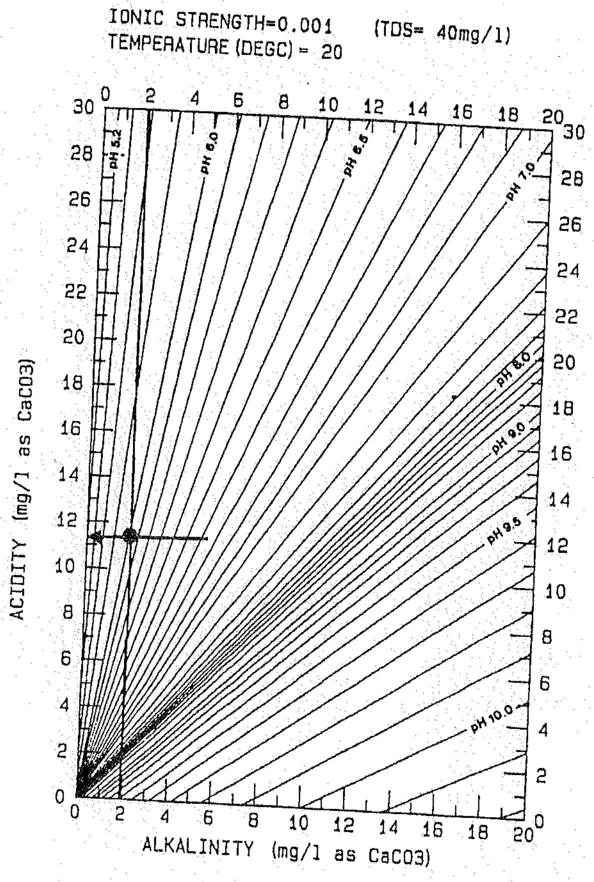


Figure 2-1 Deffeyes type diagram

Alkalinity and Acidity change in a simple stoichiometric manner with the mass concentration of a chemical dosage (or removal). From the definitions of Alkalinity and Acidity above, the changes in the parameters Alkalinity and Acidity with chemical dosage are as follows:

$$\begin{aligned}\Delta\,\text{Alkalinity} &= \text{Alk}_{\text{added}} \\ &= 2[CO_3^{2-}]_{\text{added}} + [HCO_3^-]_{\text{added}} + [OH^-]_{\text{added}} - [H^+]_{\text{added}}\end{aligned} \tag{2-6}$$

$$\begin{aligned}\Delta\,\text{Acidity} &= \text{Acid}_{\text{added}} \\ &= 2[H_2CO_3^*]_{\text{added}} + [HCO_3^-]_{\text{added}} - [OH^-]_{\text{added}} + [H^+]_{\text{added}}\end{aligned} \tag{2-7}$$

where Δ indicates an increase.

These simple stoichiometric changes in the capacity parameters with addition of the various carbonate and water (H^+ and OH^-) species form a useful basis for both predicting either the condition of a water after dosing, or to determine the dosage to achieve a desired resultant condition.

The corresponding changes in pH are however more complex and need to be calculated using equilibrium considerations, or measured off a Deffeyes type diagram.

2.1.2 Aqueous-gaseous phase equilibrium

The in situ dissolved carbon dioxide (CO_2) content of underground waters usually is very high compared with waters in contact with the air, as a result of the raised CO_2 partial pressure at depth. When pumped to surface and exposed to air, a CO_2 exchange takes place until the CO_2 partial pressures in the two phases are equal. Similarly, exchange of CO_2 in surface waters also occurs until CO_2 partial pressures in the two phases are equal.

In the approach to aqueous-gaseous phase equilibrium, the pH in the water changes, and there is a redistribution of the dissolved carbon species, i.e. a change in the dissolved CO_2 concentration occurs as CO_2 is exchanged with the air. The pH at which equilibrium occurs depends on the Alkalinity of the water. Exchange of CO_2 between air and water does not change the Alkalinity, only the Acidity and pH, provided no $CaCO_3$ precipitation occurs.

For equilibrium between dissolved and atmospheric CO_2 at a particular partial pressure of CO_2, ($\bar{p}CO_2$), the concentration of dissolved CO_2 is defined by Henry's Law. Theoretical determination of whether a water is at aqueous-gaseous equilibrium, the equilibrium state the water will attain if allowed to reach equilibrium, and the amount of CO_2 expelled to reach such a state, can be carried out either:

- graphically, using a Modified Caldwell-Lawrence (MCL) diagram, or
- using computer based equilibrium modelling software.

Suffice to note that such theoretical determination is most easily done by using an interactive computer programme such as STASOFT. For detailed description of the use of either of these procedures, the reader is referred to the Water Research Commission publications: *Softening and stabilisation of municipal waters* (Loewenthal et al, 1986), and *Chemical Conditioning of Low and Medium Salinity Waters: STASOFT Version 3.0* (Friend and Loewenthal, 1992).

2.1.3 Aqueous-solid phase equilibrium

Undersaturation, supersaturation and saturation are terms that describe whether the chemical state of a water is such that it causes:

- dissolution of a solid (undersaturation),
- precipitation of a solid (supersaturation), or
- no precipitation or dissolution (saturation).

For soft, acidic waters, the solubility of the mineral $CaCO_3$ is of importance. Theoretically, the saturation state with respect to $CaCO_3$ is identified by comparing the **activity product** of calcium, Ca^{2+} , and carbonate, CO_3^{2-}, species with the **thermodynamic solubility product** constant for calcium carbonate, K_{sp}, where the:

$$\text{Activity Product} = (Ca^{2+})\,(CO_3^{2-}) \qquad \textbf{(2-8)}$$

For the dissolution of $CaCO_3$ (undersaturation):

$$(Ca^{2+})\ (CO_3^{2-}) < K_{sp} \qquad \textbf{(2-9)}$$

For the precipitation of $CaCO_3$ (supersaturation):

$$(Ca^{2+})\ (CO_3^{2-}) > K_{sp} \qquad \textbf{(2-10)}$$

and at saturation:

$$(Ca^{2+})\ (CO_3^{2-}) = K_{sp} \qquad \textbf{(2-11)}$$

The value of the thermodynamic solubility product depends on temperature, pressure and the type of calcium carbonate mineral precipitated. For more detail the reader is referred to Loewenthal and Marais (1976). On a practical level, the saturation state for terrestrial waters is determined by considering the calcium carbonate precipitation/dissolution potential.

2.2 Soft Water Aggression and Corrosion

2.2.1 Aggressive attack

Soft acidic waters attack cementitious material by leaching free lime, calcium aluminates and silicates out of the cement matrix. Where the chemical characteristics of the water are such that it is undersaturated with respect to calcium carbonate, calcium carbonate precipitates, formed on the outer surfaces of the cement mass by the reaction of free lime ($Ca(OH)_2$) and carbon dioxide in the air or water, will dissolve. Under such conditions, progressive leaching of calcium minerals will occur, thereby damaging the integrity of the material, and may result in the eventual failure of the structure. Such attack is termed **aggressive attack** and such waters are called **aggressive**. Conversely, for waters saturated or supersaturated with respect to $CaCO_3$, solid $CaCO_3$ will not dissolve, and free lime in the cement in contact with the water will be transformed with time to solid $CaCO_3$, thereby preventing attack. Therefore, the ability to determine whether a water is aggressive, and the mineral dissolving potential of an aggressive water, clearly is of importance.

In order to prevent aggressive attack of distribution networks, it is important to know the saturation state of a water. In this context it is necessary to obtain both a **qualitative** description of saturation (i.e. whether the water is saturated, undersaturated or supersaturated, with respect to $CaCO_3$), and a **quantitative** description of the saturation state (i.e. the mass of $CaCO_3$ that will dissolve in/precipitate from the water). Use of non-quantitative methods such as the *Langelier Saturation Index* and the *Aggressiveness Index* should be avoided, as their values are often misconstrued as being of quantitative significance (Mackintosh, 1992). The **calcium carbonate precipitation potential (CCPP)** provides an accurate prediction of the amount of solid calcium carbonate that will precipitate from or dissolve into a water.

The CCPP defines the mass of $CaCO_3$ to be precipitated from a water to attain saturation with respect to $CaCO_3$. For example, a water with a CCPP of 35 mg/ℓ as $CaCO_3$ will precipitate 35 mg/ℓ $CaCO_3$, to reach chemical equilibrium. In doing so, the pH, Alkalinity and calcium levels of the water will decrease, whilst the CCPP will decrease eventually to zero. Conversely, a water with a **calcium carbonate dissolution potential (CCDP)** of 10 mg/ℓ as $CaCO_3$ will dissolve 10 mg/ℓ $CaCO_3$ to reach chemical equilibrium.

Consequently these parameters, CCPP or CCDP, give both a quantitative, and qualitative description of the saturation state of a water. The CCPP/CCDP may be experimentally determined with the *Marble Test* (see *Standard Methods*, 1985). However, this method is both labourious and prone to error, and for these reasons, theoretical methods, based on equilibrium chemistry, are preferable.

Theoretical determination of the saturation state and the CCPP/CCDP, using equilibrium chemistry, is carried out very easily, either:

- graphically, using a Modified Caldwell-Lawrence (MCL) diagram, or
- using computer based equilibrium modelling software.

Suffice to note that such theoretical determination is most easily done by using an interactive computer programme such as STASOFT. For detailed description of the use of either of these procedures, the reader is referred to the Water Research Commission publications: *Softening and stabilisation of municipal waters* (Loewenthal et al, 1986), and *Chemical Conditioning of Low and Medium Salinity Waters: STASOFT Version 3.0* (Friend and Loewenthal, 1992).

2.2.2 Corrosive attack

When water is being conveyed, or used for any purpose, interaction with metal components of the water distribution and household systems occurs. The principal metals utilised in these systems are iron (municipal and household) and copper (mainly household). Corrosion of these metals principally results from oxidation and reduction reactions at sites on the metal-water interface. Depending on the characteristics of the water and metal, the reactions may give rise to continuous dissolution of the metal into the water, (corrosion), or precipitation of stable minerals onto the metal surface, thereby reducing the areas of active electro-chemical sites, and the rates of reactions, even eventually stopping the corrosion completely (passivation).

The corrosivity of a water depends mainly on pH, carbonate balance and oxygen levels within the water. However, other factors influencing the corrosion process are: the presence of chlorides and sulphates; velocity of flow; temperature; and the presence of microorganisms. In this monograph, it is sufficient to note that guidelines for iron corrosion passivation are as follows (Loewenthal et al, 1986):

<u>Guideline 1</u>: The bulk water should be saturated, or slightly supersaturated, with respect to $CaCO_3$.

<u>Guideline 2</u>: Calcium and Alkalinity values should not be less than 50 mg/ℓ (as $CaCO_3$).

<u>Guideline 3</u>: Waters be regarded as potentially corrosive when either the chloride or sulphate levels exceed 50 mg/ℓ.

<u>Guideline 4</u>: Design conduits in reticulation systems to maintain a velocity in excess of 0.2 m/s, preferably > 1 m/s, and avoid dead ends. Where

these conditions are not likely to be satisfied, utilise cement type or plastic pipes.

Guideline 5: The dissolved oxygen in the water should be greater than about 4 mg/ℓ (as O_2)

With regards to corrosion of copper in contact with soft acidic terrestrial waters, passivation by the formation of a protective copper oxide layer is generally readily achievable by ensuring pH greater than 7.0.

2.3 Stabilisation of Soft, Acidic Waters

General guidelines to prevent both aggression and/or corrosion exist as described above. The principal component of measures to prevent corrosive and/or aggressive attack by soft, acidic waters, is the chemical conditioning, or stabilisation, of the water. Complete stabilisation of water requires adjusting the chemical characteristics of the water such that:

- calcium and Alkalinity >50 mg/ℓ as $CaCO_3$
- $6.5 < pH < 9.5$
- Calcium Carbonate Precipitation Potential (CCPP) of about 4 mg/ℓ as $CaCO_3$.

Complete stabilisation will terminate aggressive attack of cementitious material and corrosive attack of metals commonly found in water distribution networks. However, prevention of corrosion of iron will only occur if a dense precipitate scale is formed on the metal surface adjacent to the water. Attainment of such a dense precipitate scale in soft acidic waters requires extremely high chemical doses and is, hence, both expensive and impractical. Consequently, where complete termination of corrosive attack by soft, acidic waters of large metal pipes is required, these pipes should be lined with cement mortar, and the water treated to be non-aggressive, ie saturated with respect to $CaCO_3$ (Loewenthal et al, 1986).

Several methods are available for attaining the desired slightly supersaturated water quality, including inter alia dosing of sodium alkali's (such as sodium carbonate, sodium hydroxide or sodium bicarbonate) and the conventional approach of using lime and carbon dioxide. By far the most commonly used process for the stabilisation of soft, acidic waters is the latter, in which stabilisation is achieved via the addition of lime ($Ca(OH)_2$), to increase calcium (Ca^{2+}) and Alkalinity levels, and the addition of carbon dioxide, (CO_2), to add carbonate species and adjust pH.

Whilst such stabilisation is well documented and understood, control of the process requires well trained staff and reliable equipment - both seldom available in the many small towns and communities receiving such waters. Hence, in many cases only lime is dosed, such that pH is adjusted from low levels to more desirable levels of, say, 8.0, thereby providing a partially stabilised water. Even so, for a smaller municipal installation, stabilisation using lime, (with or without carbon dioxide), remains problematic and difficult to control. Furthermore, lime and carbon dioxide mediated stabilisation is expensive. For example, at Heidelberg, Cape, (which has a colour removal, stabilisation and disinfection water treatment works), more than half of the chemical cost of treating water results from stabilisation (Theron, 1993).

For the independent, small volume, water user, such as farmers and small holding owners, stabilisation is not possible, and the costs of corrosion can be significant. An alternative approach is the use of limestone.

REFERENCES - CHAPTER 2

Background

FRIEND JFC and LOEWENTHAL RE (1992) Chemical Conditioning of Low- and Medium- Salinity Waters: STASOFT Version 3. Water Research Commission, Pretoria.

LOEWENTHAL RE and MARAIS GvR (1976) *Carbonate Chemistry of Aquatic Systems: Theory and Application*, vol 1. Ann Arbour Sci. Publishers, Michigan.

LOEWENTHAL RE, WIECHERS HNS and MARAIS GvR (1986) *Softening and Stabilization of Municipal Waters.* Water Research Commission, Pretoria.

MACKINTOSH GS (1992) Aggressive Water: A Quantitative and Qualitative Assessment. Paper presented at the Young Water Engineers Conference, 5-6 March 1992, Midrand.

STANDARD METHODS (1985) *Standard Methods for Examination of Water and Wastewater* (16th ed.). Publ. American Public Health Ass., American Water Works Ass., Water Pollution Control Federation, Washington.

THERON D (1993) Private communication

CHAPTER 3

HISTORICAL REVIEW OF STABILISATION WITH LIMESTONE

3.1 Introduction

The first attempts to stabilise municipal water were made using limestone. The first documented application occurred in 1906 in Frankfurt when domestic water was treated by contacting it with a marble bed to reduce its corrosivity. It was shown that the corrosion of the distribution network was significantly reduced (Hirsch, 1933), and this process was subsequently applied at other sites. In a thesis by Eschenbrenner (1932) the kinetics of the neutralisation reaction of contacting acidic water with calcium carbonate, showed that full stabilisation would only be reached after a very long contact period, if at all. However, during the early 1900's, more easily dosed alkali's, such as sodium carbonate and bi-carbonate and lime, came into use and replaced the use of limestone.

As early as 1912, a publication by Tillmans and Heublin described the stabilising effect of treating acidic water with lime, whereby it would no longer attack iron conduits. In the 1930's, it was found that a much more rapid stabilisation effect was possible by using a "half-burnt dolomitic limestone", with the result that the application of limestone fell further out of favour (Reijnen, 1979).

Although treatment of soft water with limestone has not gained much in popularity, several studies have been conducted into the process. This section serves to highlight the work carried out on limestone mediated stabilisation.

3.2 Literature Overview

Interest in the limestone contact process was evident in the Netherlands from the middle 1960's, and variations of the process were applied. Research on the process, as well as comparisons to other, more conventional stabilisation processes and studies on the practical application of the process, were carried out by KIWA. KIWA's "Commissie Methodieken Centrale Ontharding" (CMCO), published stabilisation recommendations for domestic water supplied in distribution systems (CMCO,1978). The main aims of these recommendations were to minimise dissolution of lead, reduce corrosion of copper and iron pipes and reduce aggression towards concrete and asbestos/cement pipes.

Van Duuren (1967) noted that the method of treatment appears attractive, because limestone is comprised mainly of $CaCO_3$. However, he also noted that various installations using limestone in the process had yielded "indifferent results".

A chemical reagent cost comparison between various stabilisation methods showed that limestone treatment was relatively cheap, and if a large increase in HCO_3^- alkalinity was required, it had a significant advantage over other methods (Reijnen, 1979). Reijnen (1980) concluded that treatment by limestone stabilisation was a viable alternative for very soft waters containing relatively low CO_2 concentrations, and that limestone stabilisation produces a very constant final product, and that the pH cannot increase excessively as it does with some other processes.

In full scale plants in Germany and the Netherlands, it was found that dissolved iron as well as a small amount of manganese was removed by the limestone contact process. The effect of the deposits in reducing the stabilisation capacity was not established (Reinjen, 1979). Reijnen lists a number of experimental and pilot applications, where limestone mediated stabilisation was applied to replace other methods. Generally all of these proved to be more effective than the previously applied method. The following are examples:

- At Apeldoorn Magno-syn media (a dolomitic commercial stabilising material) was replaced in a number of filters by limestone (1.8 to 2.5 mm particles).
- At Wezep, lime dosing and treatment on Akdolit-gran (another commercial dolomitic stabilising material) was replaced by limestone treatment, followed by a small dose of NaOH to achieve full stabilisation (SI ±0) and to remove all iron and manganese present in the raw water.
- At Texel, the product from a sea water distillation plant, which contains no bicarbonate alkalinity and is highly aggressive and corrosive, was treated by CO_2 addition, followed by limestone contact filtration to achieve an acceptably stable water.
- At Dordrecht, sewage water reclaimed by reverse osmosis, the product of which contains a large amount of CO_2, was treated on a "dry" limestone filter with counter-current aeration.
- At Valtherbos weakly buffered water containing about 20 mg/ℓ iron was treated on a "dry" limestone filter to remove the iron. Numerous other methods tried were unsuccessful in achieving effective iron removal and increasing the stability of the treated water (Beeftink,1976).
- At Waalwijk water treated on rapid gravity filters, still containing 14 - 20 mg/ℓ CO_2 and more than 0.1 mg/ℓ iron, was treated on limestone filters to achieve a pH of 7.7 to 7.9, a bicarbonate alkalinity of 95 mg/ℓ and an SI of zero.

It was recommended that the water to be treated should not contain more than 0.2 - 0.3 mg/ℓ iron, and no suspended material or manganese (Krachtwerktuigen, 1971; Humphrey, 1964). In full-scale plants in Germany and the Netherlands it was found that iron as well as a small amount of manganese was removed by the limestone contact process.

Reijnen (1980) concluded that no guidelines have been established for the application of limestone. He recommended pilot scale testing of the raw water to obtain reliable estimate of contact time and the effect of other variables. Other conclusions were:

- Treatment by limestone stabilisation was an excellent alternative stabilisation method for very soft waters containing relatively low CO_2.
- Limestone stabilisation produces a very constant final product. The pH cannot increase excessively, as it does with some processes.
- Treatment of a water containing iron and manganese on a limestone filter does not pose a problem, provided that the bed is regularly flushed with air and water to remove the deposits.

Contact processes with calcium bicarbonate is apparently frequently used in the erstwhile USSR, for the stabilisation of corrosive water produced by distillation plants. Problems related to this process is discussed in a paper by Vakhnin et. al. (1986a). Certain large plants stabilising distillate use contact filters containing "crushed marble" of 0.5 to 5.0 mm particle size with a bed depth of 3 to 4 metres. The water produced was still highly corrosive as it contained a significant quantity of free (unreacted) carbon dioxide.

Another paper by Vakhnin et. al. (1986b) describes a process whereby the distillate produced by thermal desalting aboard ships is stabilised by contact with calcium carbonate produced during the thermal softening process ahead of the distillation units. The carbon dioxide required to intensify the dissolution of the solid calcium carbonate is also obtained from the thermal softener.

3.3 Dissolution Kinetics

Many water treatment handbooks and papers on water stabilisation to minimise corrosion contain a rule of thumb generalisation that limestone stabilisation can only be employed if the sum of the free and bound CO_2 does not exceed 50 to 60 mg/ℓ . Generally it is stated that the reaction rate is unacceptably slow (Krachtwerktuigen, 1971; Humphrey,1964).

The generalisation regarding the limits of free and bound CO_2 was carried over from the work on the kinetics of limestone stabilisation by Eschenbrenner, (1932). It concluded that the reaction time increased as the CO_2 content of the water increases. This was confirmed by Anderlohr, (1976). Other significant findings from these studies include that the use of smaller sized limestone pebbles reduces contact period due to increase in specific surface area, that the required contact period is not affected by an increase in the filtration rate above 0.14 m/h, and that the reaction rate is increased by an increase in temperature.

Plummer, Parkhurst and Wigley (1979) proposed that calcium carbonate dissolution kinetics may be dominated by either or both the proton activity and carbonic acid species concentrations in the bulk solution, i.e. when either H^+ concentration and or $H_2CO_3^*$ concentration in the bulk solution are sufficiently high, these species accelerate reactions at the crystal surface thereby accelerating the overall dissolution reaction. This dissolution model is described in more detail in Chapter 5.

Reijnen (1980) concluded that no definite guidelines have been established for the application of limestone. He recommends pilot scale testing of the raw water to obtain reliable estimate of the contact time and the effect of other variables.

3.4 Acidic Effluent Neutralisation

Several researchers have reported the use of $CaCO_3$ as a neutralising agent for acid waters (Braley, 1954; Barnes and Romberger, 1968; Henzen and Pieterse, 1978; Thompson, 1980). The use of limestone to replace lime for the neutralisation of acidic effluent such as acid mine water is described in a publication by Maree et. al. (1992). Although the purpose of this process is somewhat different from the stabilisation of potable water, some of the observations are relevant. It was established that the rate of $CaCO_3$ neutralisation depends on the $CaCO_3$ dosage, the particle size and the presence of iron. The rate of neutralisation was not affected by the presence of iron (III), whereas iron (II) dramatically retarded the rate of acid water neutralisation, as the iron deposited on the surfaces of the limestone particles. It was established that the capital costs of lime and limestone neutralisation in a fluidised bed reactor were similar, but that the chemical costs (in South Africa) of the limestone process amounted to only 29 % of that of lime.

The problem of long reaction time as a result of the low reactivity of limestone is solved in the fluidised-bed reactor because an excessive amount of limestone is in contact with the acid water (Maree and Du Plessis, 1993). Scaling of limestone particles is prevented due to the attrition between the particles under fluidised conditions.

Maree, Van Tonder and Millard (1996) showed that underground mine water could be neutralised effectively with the limestone neutralisation process. The pH of the water can be increased from less than 3 to levels above 7, while 97 % acidity, 95 % iron and 83 % uranium can be removed. The alkalinity of the treated water was greater than 120 mg/ℓ (as $CaCO_3$). Chemical savings of 66 % could be achieved, compared to conventional processes, when the cost of limestone and lime amounts to R100/t and R400/t respectively.

REFERENCES - CHAPTER 3

Historical review of stabilisation with limestone

ANDERLOHR A (1976) Experimentelle Untersuchungen zur Anflösung von Calciumkarbonat durch Kohlensäurehaltige Wässer in Schüttungen. In: Veröffentl. der Ber. und des Lehr st. für Wasserchemie. Diplomarbeit Karlsruhe, Engler Bunte Inst. (1976) Heft 10, 104 blz.

BARNES HL and ROMBERGER SB (1968) Chemical aspects of acid mine drainage. *Journal WPCF*, **40** (3), 371 - 384.

BEEFTINK WG (1976) Grondwaterzuiwering pompstation Valtherbos. *H_2O (Rotterdam)*, Vol.9, No.24, pp 500-502.

BARLEY SA (1954) A Pilot Plant Study of the Neutralisation of Acid Drainage from Bituminous Coal Mines, Commonwealth of Pensylvania, Dept. of Health.

COMMISSIE METHODIEKEN CENTRALE ONTHARDING (CMCO) (1978) Kwaliteitseisen in verband met de stabiliteit van het distribueren drinkwater. Rijswijk. KIWA, 1978; 57 blz., Mededeling 54.

ESCHENBRENNER AE (1932) Ueber die Geschwindigkeit der Entsäuerung Kohlensäurehaltiger Wässer beim Marmorrieselungsverfahren. Reprint from: Vom Wasser VI (1932). Dissertation.

HENZEN MR and PIETERSE MJ (1978) Acidic Mine Drainage in the Republic of South Africa. *Progress in Water Technology*, 9, 981-992.

HIRSCH P (1933) Ontzuring van drinkwater door filtratiemethoden. *Water*, 17, pp 255-261.

HUMPHREY WH The Removal of Aggressive Carbon Dioxyde From Potable Waters. *Water and Water Eng.* (1964) Aug., pp 324-327.

KRACHTWERKTUIGEN: Water voor de industrie. Deventer, Kluwer, 1971. 639 blz.

MAREE JP, DU PLESSIS P and VAN DER WALT CJ (1992) Treatment of acidic effluents with limestone instead of lime. *Wat. Sci. Tech.* Vol. 26, No. 1-2, pp. 345-355.

MAREE JP, VAN TONDER GJ and MILLARD P (1996) Underground neutralisation of mine water with limestone. WRC Report, File No K5/609/0/1

MAREE JP, DU PLESSIS P and VAN DER WALT CJ (1992) Treatment of acidic effluents with limestone instead of lime. *Wat. Sci. Tech.*, **26** (1-2), 345-355.

MAREE JP and DU PLESSIS P (1993) Neutralization of acid mine water with calcium carbonate. Proc. IAWQ Conf. on Pre-treatment of Industrial Wastewaters, Athens, 399-411.

PLUMMER LN, PARKHURST DL and WIGLEY TML (1979) Critical Review of the Kinetics of Calcite Dissolution and Precipitation, *Chemical Modelling in Aqueous Systems: Am. Chem. Soc. Symposium Ser.* pp 537 - 573.

REID IK and LOEWENTHAL RE (1989) Investigation into Requirements for Research in Surface Water Treatment in South Africa. Final Report to the Water Research Commission of South Africa. Department of Civil Engineering, University of Cape Town.

REIJNEN GK (1979) Marmerontzuring, een oud proces met nieuwe perspectieven. *H_2O (Rotterdam)*, Vol.12, No.13, pp 290-295.

REIJNEN GK (1980) Conditionering van water door filtratie over marmer.*H_2O (Rotterdam)*, Vol.13, No.25, pp 618-621.

THOMPSON JG (1980) Acid Mine Waters in South Africa and their Amelioration, *Water SA,* **6** (3), 130-134.

TILLMANS J and HEUBLIN O (1912) Ueber die kohlensäure Kalk angreifende Kohlensäure der natürlichen Wasser. *Gesundh. Ing.* 35 (1912) p. 669.

VAKHNIN I G, MAKSIN V I, SKOROBOGACH E V and STANDRITCHUK O Z (1986b) Use of calcium carbonate granules produced by thermal softening of sea water for mineralization of desalted water. *Khimiya i Tekhnologiya Vody,* Vol 8, No. 4, pp. 90-92. UDC 663.63:614:777:546.212

VAKHNIN IG, GORONOVSKII IT, EGOROV AI, IPATV PF and LAZAREV IP (1986a) Stabilization treatment of water by desalting distillation. *Khimiya i Tekhnologiya Vody*, Vol 8, No. 1, pp. 56-59. UDC 663.632.7

CHAPTER 4

LIMESTONE SOURCES

Prior to proceeding with pilot plant studies, it was necessary to investigate the availability and suitability of limestone. This was necessary, as limestone is a broad term, covering a wide range of mineral make-up. The objective of this part of the investigation was to identify the most suitable, commercially available limestone for the development and assessment of limestone stabilisation units.

4.1 Limestone Characteristics

Limestone is composed of calcium carbonate, with variable amounts of impurities, and with diverse types of crystalline structures. The mineral and crystalline characteristics of a deposit determine how suitable it would be for drinking water stabilisation purposes.

Mineral composition
Limestone, when pure, is composed almost entirely of calcium carbonate, but may contain variable amounts of impurities such as dolomite, quartz, silicates and iron oxides. The magnesium content varies from nil to as high as about fifty percent, the magnesium being present in a carbonate form. Where calcium and magnesium are both present in appreciable quantities, the rock is termed dolomite.

Crystalline structure
A further consideration is the crystalline structure of the limestone. In Southern Africa, calcium carbonate rock types are particularly diverse and include inter alia sedimentary carbonates, soil precipitates, travertine, cave limestone, calcite veins and magmatic carbonates.

4.2 Suitability for Stabilisation

Past experience in this regard had shown that not all purer limestone is suitable for use as water stabilisation media. In particular, dense crystalline structured "marble type" deposits, although almost pure $CaCO_3$, show very slow rates of dissolution.

For the purposes of water stabilisation, desirable qualities of limestone can be simplified and summarised as:

- high calcium carbonate purity,
- porous structure,
- high solubility,
- low iron and manganese content,
- low silica and acid insoluble mineral content.

4.3 Experimental Investigation

Five potentially suitable limestone deposits were tested - four from the Western Cape, and one from deposits near Rustenburg, Northwest Province. The Western Cape deposits included limestone from Bredasdorp, the Cape Flats and two commercially mined deposits, denoted as "A" and "B". The commercially mined deposit near Rustenburg was denoted as "C". **Figure 4-1** shows the location of the five different limestone deposits. First, analyses for the mineral composition of the various deposits were carried out. A preliminary assessment of the suitability of the deposits were made, based on the criteria set out above. Next, laboratory scale dissolution tests were carried out, to confirm the conclusions from the chemical analyses. Using these results, the most suitable deposit was identified for use in stabilisation of soft, acidic, aggressive waters.

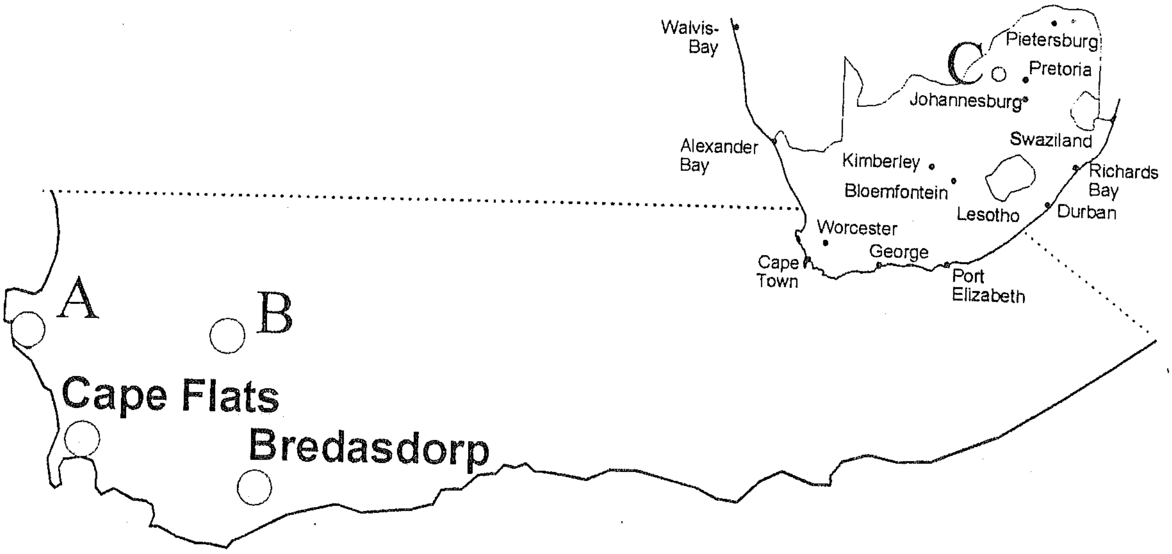


Figure 4-1 Location of evaluated limestone deposits

4.3.1 Mineral composition analyses

The mineral composition of the limestones was tested and the results are shown in **Table 4-1** below.

Table 4-1 **Mineral composition of various limestones (all results reported in mg/g on a dry basis)**

	Cape Flats	A	B	Bredasdorp	C
Ca	178	294	221	370	330
Mg	3.3	4.4	121	4.6	23.6
Na	3.3	1.8	0.1	2.9	0.1
Fe	1.3	1.9	1.1	0.7	2.3
Mn	0.01	0.02	0.03	0.01	0.27
SO_4	3	3	2	2	2
Cl	0.2	0.2	0.1	0.1	0.2
Acid Insoluble*	456	544	34	14	88

* Insoluble in acid, therefore this fraction will be very insoluble in water. This fraction probably mainly comprises silica (SiO_2).

Observations from these results and visual inspection include:

- The high acid insoluble content of the Cape Flats and Deposit A makes these unsuitable for use as stabilisation media.
- Deposit B has high levels of magnesium and is therefore not ideal.
- The Bredasdorp deposit is the most suitable deposit of those tested in terms of mineral content.
- Deposit C has nominally higher iron, manganese, magnesium and acid insoluble fractions than the Bredasdorp deposit. Nevertheless, the levels at which these occur in Deposit C are not expected to be problematic.
- The Bredasdorp deposit is of a soft, porous nature, whilst Deposit C is of a hard, crystalline nature.

4.3.2 Laboratory scale dissolution tests

Test rig

A test rig was designed for the purpose of practical assessment of the suitability of limestone deposits for stabilisation media (see **Figure 4-2**). This plant was designed such that it could be used for both laboratory and on-site pilot scale tests. The unit consists of three vertical columns constructed from clear PVC. The columns are of height 102 cm and diameter 16 cm. The columns are connected in parallel to a raw water feed pump. The flow through each column is measured by a rotameter and controlled by a diaphragm valve. Flow can be set between 12 ℓ/h and 125 ℓ/h.

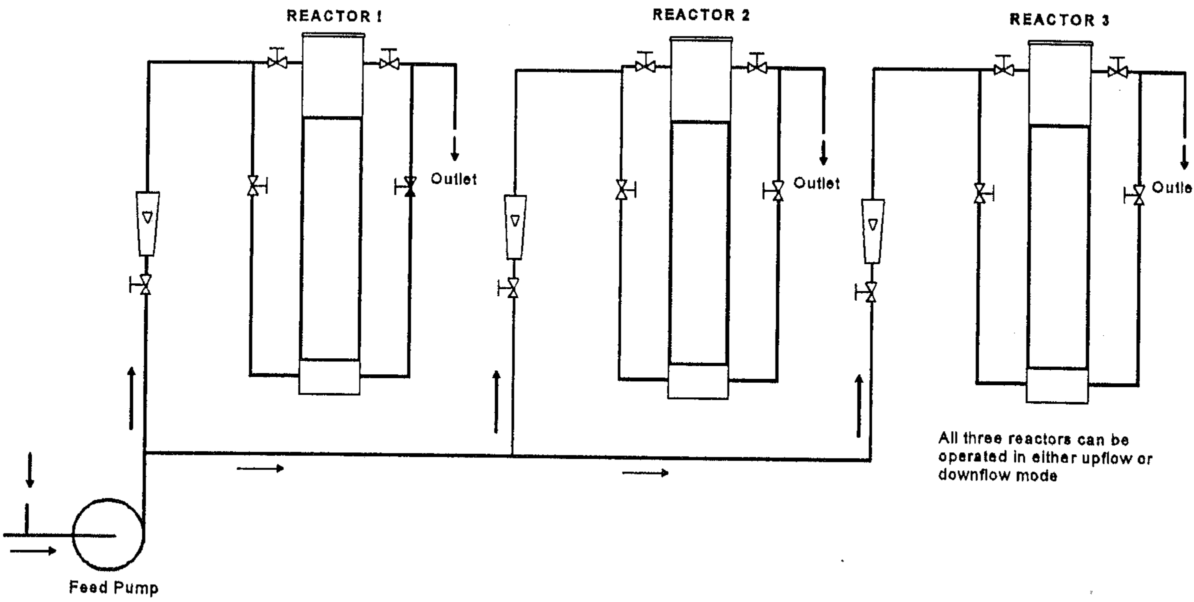


Figure 4-2 Test rig for limestone studies

Raw water

A synthetic raw water of an aggressive nature was produced for the tests. The water was made up using Stellenbosch tap water, and adding both hydrochloric acid and sodium carbonate. The synthetic raw water characteristics were: pH 5.8, Alkalinity 10 mg/ℓ as $CaCO_3$, Acidity 85 mg/ℓ as $CaCO_3$, conductivity of 24 mS/m, and calcium 4 mg/ℓ as $CaCO_3$. The raw water had a CCDP of 65 mg/ℓ, as determined with the STASOFT software package.

Limestone

Three different limestone sizings were used. The sizings were - 9 mm + 6mm, - 6 mm +1.7 mm and - 1.7 mm + 1mm.

Procedure

Void volumes were measured in situ, and flow rates were calculated such that retention times of 3, 4, 5, 10, 15 and 20 minutes were obtained. Following an initial flushing of the units, samples were taken after a period of time 30 % longer than the respective retention times. Samples were filtered and bottled. All were tested for pH, Alkalinity, calcium and conductivity. From these, the CCDPs were calculated. Such tests were carried out for the Bredasdorp limestone, and Deposits B and C. The Cape Flats deposit and Deposit A were considered not worth further investigation as a result of high silica levels.

4.3.3 Results and discussion

The effectiveness of the various limestone sources at stabilising an aggressive water was determined by assessing the decrease in the driving force of aggressive attack, namely the CCDP. Further criteria considered were increase in pH, Alkalinity and calcium levels.

Experimental results were similar for the Bredasdorp deposit and Deposit C and showed that both limestones are suitable for use in water stabilisation. Deposit B gave poor results. Typical results of the laboratory tests with the Bredasdorp water are shown below in **Table 4-2** and **Figure 4-3**.

Table 4-2 Fixed bed test results for Bredasdorp limestone

	- 9 mm + 6 mm				- 6 mm + 1.7 mm				- 1.7 mm + 1 mm			
Ret Time	pH	Alk	Ca	CC DP	pH	Alk	Ca	CC DP	pH	Alk	Ca	CC DP
0	5.8	10	4.8	62.6	5.9	10	4.8	62.6	5.9	10	4.8	62.6
3	7.3	40	38.0	9.2	7.7	55	51.0	4.9	7.8	59	54.5	3.59
4	7.4	45	42.3	8.7	7.9	57	52.5	3.1	7.9	62	54.8	2.31
5	7.5	48	44.3	7.4	7.8	58	53.0	3.94	8.0	71	61.3	1.24
10	7.5	52	48.3	8.0	7.6	60	56.3	5.7	8.0	74	65.8	1.02
15	7.6	62	57.0	5.8	7.8	70	64.0	3.1	8.0	77	65.8	1.28
20	7.6	68	65.0	5.5	7.7	74	68.3	3.6	8.1	79	70.8	0.23

Calcium, Alkalinity and CCDP all reported in mg/ℓ as $CaCO_3$

Inspection of **Table 4-2** shows that, for the synthetic water, stabilisation with limestone is successful with significant increase in pH, Alkalinity and calcium levels being achieved. Satisfactory reduction of CCDP was achieved within reasonably short retention times.

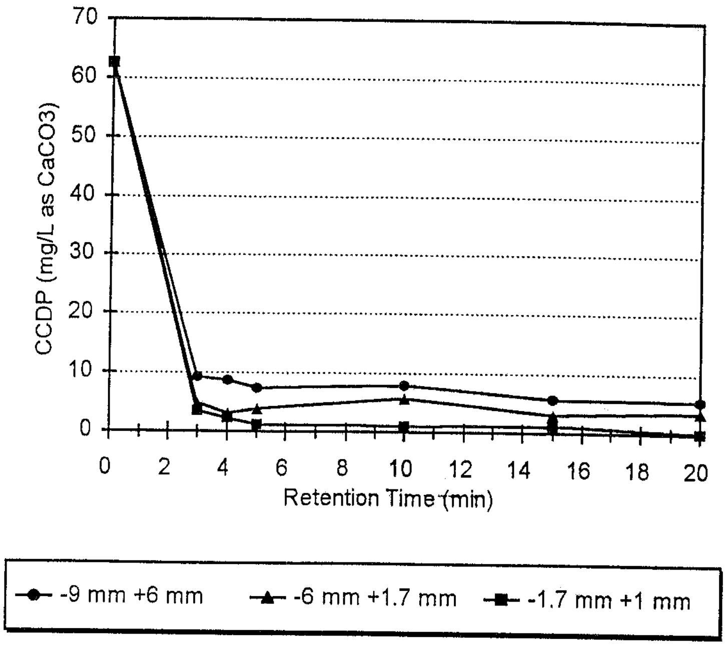


Figure 4-3 Dissolution tests - Bredasdorp limestone

The following general observations were made:

- Particle size influences reaction rates - reaction rate increasing with decreased particle size.
- Acceptable reduction in CCDP was readily achieved with reasonable retention times for both the Bredasdorp deposit and Deposit C.
- Retention times required to achieve significant reduction in CCDP were acceptable. With the Bredasdorp deposit, particle size range - 1.7 mm + 1 mm achieved a 94 % reduction in CCDP with a 3 minute retention time. A 5 mininutes retention time resulted in 98 % reduction and 20 mintes resulted in a 99.6 % reduction. With Deposit C, particle size range - 4 mm + 1.5 mm achieved a 96 % reduction in CCDP with a 3 minute retention time.

4.4 Conclusions

Of the deposits evaluated, the Bredasdorp deposit in the Western Cape, and the deposit mined near Rustenburg, appear suitable for stabilisation of drinking water. The Bredasdorp deposit was considered the most suitable for further consideration in the investigation, due to its mineral composition, geographical location and commercial availability.

CHAPTER 5

KINETIC MODELLING

5.1 Chemistry of Calcium Carbonate Dissolution

The literature on the equilibrium between the aqueous calcium and carbonate species and solid calcium carbonate was investigated and thoroughly assessed (Kornmüller, 1995). After consideration of the various models available in the literature, the validity of the equation suggested by Plummer, Parkhurst and Wigley (1979) to model calcium carbonate dissolution, was investigated.

Plummer, Parkhurst and Wigley (1979) proposed that calcium carbonate dissolution kinetics may be dominated by either or both the proton activity and carbonic acid species concentrations in the bulk solution, i.e. when either H^+ concentration and or $H_2CO_3^*$ concentration in the bulk solution are sufficiently high, these species accelerate reactions at the crystal surface thereby accelerating the overall dissolution reaction. By including terms describing the dissolution of calcium carbonate due to high concentrations of H^+ and/or $H_2CO_3^*$, the dissolution model is :

$$\frac{d[Ca^{2+}]}{dt} = k_1\, S\, f_d \left\{ K'^{\frac{1}{2}}_{spc} - [Ca^{2+}]^{\frac{1}{2}}\, [CO_3^{2-}]^{\frac{1}{2}} \right\} + k_2\, S\, [H^+] + k_3\, S\, [H_2CO_3^*] \qquad \textbf{(5-1)}$$

where:

$\frac{d[Ca^{2+}]}{dt}$ = rate of dissolution reaction

$[Ca^{2+}]$ = concentration of Ca^{2+} in the bulk solution
$[CO_3^{2-}]$ = concentration of CO_3^{2-} in the bulk solution
S = surface area of $CaCO_3$ crystals in the solution
f_d = activity coefficient for the divalent ion
$K'_{sp\,c}$ = apparent solubility product for $CaCO_3$
k_1, k_2, k_3 = rate constants

Each of the three rate constants in the above equation (i.e. k_1, k_2 and k_3) depend on a number of factors including the physical characteristics of the dissolving mineral and the hydraulic flow characteristics, i.e. flow rate. As far as the physical characteristics of the mineral are concerned calcium carbonate occurring in natural deposits may vary from a dense metamorphosed marble, through a pure non-metamorphosed chalk, to a friable impure permeable form. In general each calcium carbonate deposit will give rise to different rate constants.

According to Plummer, Parkhurst and Wigley the second term in **Equation (5-1)** is significant only for pH less than about 5, and the last term for $\bar{p}CO_2$ greater than 0.1 atm. For natural terrestrial waters usually only the first term is of any significance and it is this term which was investigated in this work.

In Section 5.2 the validity of the use of **Equation (5-1)** to model calcium carbonate dissolution into typical soft Cape waters is investigated.

5.2 Experimental Investigation

Researchers investigating dissolution kinetics of calcium carbonate minerals have used a number of laboratory systems in order to investigate the kinetics of the process. Principally, three systems are identified:

(i) *pH stat method.* In this method pH of the solvent is kept constant by addition of standard mineral acid.

(ii) *Free drift batch test method.* In this method investigation is conducted by monitoring pH of the solution containing known quantities of finely ground calcium carbonate in suspension.

(iii) *Semi-plug flow reactor method.* In this method investigations are carried out by allowing the solvent to pass through a reactor containing calcium carbonate granules. Samples are drawn at intervals along the length of the reactor and the calcium concentration (and pH, Alkalinity etc.) measured. The spacial changes in water quality can be related to calcium carbonate dissolution kinetics. The hydraulic conditions and mineral surface area are not as easily defined as in the two systems above, but can be altered by changing the flow rate through the system and the mean particle size of the reactor contents respectively.

The investigation reported here utilised calcium carbonate obtained from Bredasdorp, Western Cape, South Africa. The porous friable nature of the Bredasdorp deposit ruled out the possibility of making use of the pH stat and free drift batch test methods. As transport mechanisms were expected to be rate controlling, the complexities of determining and varying the hydraulic conditions in systems of type (ii) above rendered it unsuitable for this investigation. The semi-plugflow reactor method was considered to be most representative of the full scale application of the system to partial stabilisation with limestone. Some measure of control over the surface area could be obtained by uniformly packing the reactor with a range of "single size granules" for the different experiments.

Having selected the most appropriate method of investigation, it was then necessary to identify system parameters to be measured so that rates could be determined. As an inorganic carbon analyser was not available, choice of which parameters should be measured to determine CO_3^{2-} concentration was any two of the three Alkalinity, pH and Acidity. Alkalinity is accepted as a reliable and relatively easily measurable parameter. The second parameter selected was pH.

To ensure that Alkalinity and pH measurement could be used to give an accurate description of the in situ CO_3^{2-} concentration in the reactor, one needs to identify factors which may cause the values of these parameters to change during sampling and measurement. In this regard the principal factor would appear to be loss or gain of CO_2 from the sample.

The effect of CO_2 exchange with the atmosphere will have no effect on the value of the Alkalinity parameter. However, Acidity will change. Consequently pH will change with CO_2 exchange and affect the calculated value for CO_3^{2-}. Clearly it would be advantageous to measure pH directly inside the reactor. This was achieved using a sampling unit described later.

A further possible problem arising from loss of CO_2 from solution was escape of dissolved CO_2 within the reactor forming gas pockets; alternatively introduction or loss of CO_2 into the reactor during sampling procedure.

The former was obviated by selecting an upflow reactor configuration. This ensured that any CO_2 dissolved in the water remained within the bulk liquid in its path through the reactor. This also provided contact opportunity for redissolution should gas release occur at the bottom of the reactor. The second problem was overcome by adhering to a contra-flow sampling sequence.

Ionic strength effects were taken into account simply via change in TDS.

5.2.1 Equipment and analyses

The equipment common to most of the investigations is described in this section followed by a short description of the analytical chemistry methods that were used during the investigation.

Reactor and accessories

The overall arrangement of the test equipment is shown in **Figure 5-1**. The basic elements comprised of:

- A vertical upflow reactor together with its accessories;
- A flow meter, overhead constant head tank, pipework and valves to supply the reactor with a constant flow of water;
- Two supply tanks of 1 m^3 and 2 m^3 capacity each, a pump and an air compressor.

Reactor

Reactor
The reactor consisted of a vertical, 105 mm internal diameter clear PVC tube 1500 mm in length. The inner end caps were conically shaped to distribute the flow evenly into the reactor. Fourteen sampling ports were spaced equally, 100 mm apart, along the length of the reactor.

Sampling unit
The sampling unit consisted of a clear PVC cylinder with 185 mℓ volume. In order to obtain meaningful in situ pH measurements it was necessary to measure this parameter before the sample was exposed to the atmosphere. This was effected by allowing the sampling stream to flow through a sealed sampling container with only a very small outlet area open to the atmosphere. Sampling was always effected sequentially from the top port downwards (i.e. counterflow) to obviate interference between successive samples.

Manometer tubes
Two 9 mm internal diameter clear PVC tubes were vertically mounted and extended above the constant head tank.

Conductivity recording equipment
To determine the rate at which a plug of fluid passes through the packed bed, conductivity readings with respect to time were required. These readings were obtained at the upper end cap of the reactor, i.e. as close as possible to where the water emerges from the packed bed.

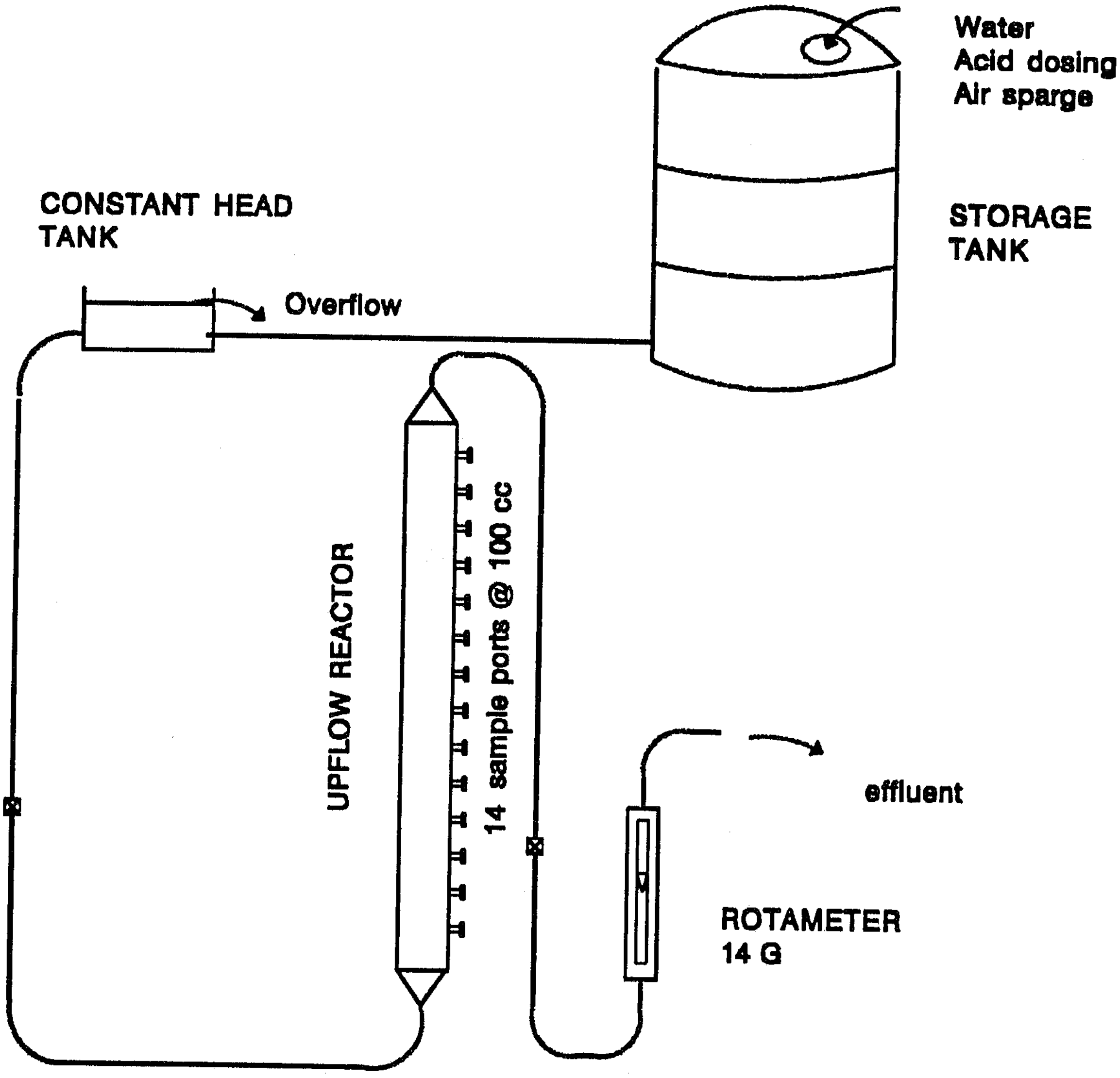


Figure 5-1: Diagrammatic representation of upflow reactor system.

Flow control

Flow meter
A rotameter was mounted downstream from the reactor just prior to the discharge point from the system.

Constant head tank
In order to reduce the effect of flow surges through the system a PVC constant head tank of 15 ℓ capacity was used.

Outlet
The outlet consisted of a 15 mm diameter galvanized metal pipe located immediately after the flow meter and fixed directly to it. This pipe was allowed to discharge horizontally to

the atmosphere. A nonflexible pipe was used to prevent inadvertent hydrostatic head changes during experiments.

Miscellaneous

Tanks
Tanks of a 2.5 m^3 and a 1 m^3 capacity were used to provide storage for the feed water.

Aeration
A 0.25 kW electric motor driven compressor acted as an air source for a sparging device in the 2.5 m^3 storage tank.

Sizing of calcium carbonate granules
Standard laboratory test sieves were used to size the calcium carbonate granules. Sieve sizes used were 9.4 mm, 6.7 mm, 4.7 mm, 2.4 mm, 1.7 mm and 1.168 mm.

Chemical analyses

Parameters that were routinely measured in any particular experiment included temperature, pH, conductivity, calcium concentration and Alkalinity. Alkalinity was determined using Gran titrations in the pH range 4≥pH≥3 (Gran, 1952).

5.2.2 *Experimental investigation - general comments and objectives*

Kinetics of calcium carbonate dissolution can be modelled by an equation of the form given by **Equation (5-1)**, provided that the mechanism is diffusion controlled. Further, for pH in the region $5 \leq pH \leq 9$ and $\bar{p}CO_2 \leq 0.1$ atm., the first two terms are negligible so that the rate equation now becomes **Equation (5-2)** below.

$$\frac{d[Ca^{2+}]}{dt} = k_1 f_d \left\{ K'_{spc}{}^{\frac{1}{2}} - [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} \right\} \qquad \textbf{(5-2)}$$

The rate constant, k_1, varies with temperature, granule size, physico-chemical properties of the mineral and the hydraulic characteristics (flow rate).

Alternatively if the mechanism is surface controlled the rate equation in the region $5 \leq pH \leq 9$ and $\bar{p}CO_2 \leq 0.1$ atm. reduces to **Equation (5-3)** i.e.

$$\frac{d[Ca^{2+}]}{dt} = k_{(D+J)} f_d^2 \left\{ [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} - \left(\frac{K_{spc}}{f_d^2} \right)^{\frac{1}{2}} \right\}^2 \qquad \textbf{(5-3)}$$

where the rate constant $K_{(D+J)}$ varies with temperature, granule size and the physico-chemical properties of the mineral but *not* with the hydraulic characteristics.

The initial investigation involved determining whether the process is diffusion or surface controlled. Clearly this requires determining whether dissolution kinetics in the system are controlled by hydraulic characteristics. That is whether the rate constants in **Equation (5-2)** and **Equation (5-3)** above vary with flow rate, if so then the process is diffusion controlled and **Equation (5-2)** is valid, if not then it is surface controlled and **Equation (5-3)** applies.

The experimental investigation therefore was divided into two sections. The first, an investigation into the mechanism of rate control. The second, determination of the effects of limestone granule size and flow rate on the rate constant (for limestone from one particular quarry). In both of the objectives outlined above, the same experimental apparatus was used.

5.2.3 Determination of the rate constant

The upflow reactor described in the previous section was used to investigate the dissolution behaviour of calcium carbonate granules under various flow conditions for specific initial water quality parameters. During the course of the investigation a range of different conditions was held constant while others were varied and vice versa, but in essence the experimental and analytical procedure remained unchanged throughout.

Experimental procedure

Experimental procedure involved preparing a water to a predetermined specific initial state, loading the reactor with calcium carbonate granules and then allowing the water to pass through the reactor at a certain predetermined flow rate. Samples were taken at various ports along the side of the reactor during the run.

Raw water

A number of waters were used in the investigation.

Tap water
For economic reasons many of the experiments were carried out using tap water which was adjusted prior to its use to Acidity and Alkalinity values (and hence pH) approximating a soft, acidic Cape water. Pretreatment involved filling the 2.5 m^3 tank with the tap water and then dosing it with mineral acid to reduce Alkalinity, followed by aeration to reduce Acidity by removing CO_2.

The raw water tap supply varied slightly in quality with time. In order to ensure some measure of consistency in water quality from one batch to another, pH of the water, after aeration was maintained at approximately pH 4.

Rain water
A limited amount of rainwater was collected from the roof of the laboratory during the winter months (the high rainfall season in the Western Cape).

Table Mountain water
A few experiments were conducted making use of a typical soft, acidic water representative of that found in the Western Cape. This water was transported to the laboratory from Constantia Nek water treatment plant supply.

Preparation of calcium carbonate granules

Crushed, pre-sieved granular calcium carbonate was obtained from a limestone quarry near Bredasdorp in the Western Cape.

In any particular dissolution test conducted, the calcium carbonate granules used were of some nominal mean diameter. Sizing to obtain mean diameter was effected using standard soil analysis sieves and a sieve shaker. Four mean granular sizes were obtained, they were - 9.40 mm + 6.70 mm, - 6.70 mm + 4.70 mm, - 4.70 mm + 2.40 mm and -1.70 mm + 1.18 mm.

Starting and operating the reactor

A number of precautions were taken prior to start-up and during each experimental run.

Prior to startup the pipes leading to the upflow reactor where cleared of any entrapped air by flushing to waste. Effects of air entrainment through sampling was prevented by the contra-flow sampling procedure described previously.

The reactor was run for at least an hour before samples were taken to ensure that the reactor was operating at a steady state condition. The pH at the uppermost sampling port was continuously monitored during this period. When the pH showed a constant value a steady state was assumed. The time taken to reach this steady value varied but rarely took longer than twenty minutes.

The sampling unit allowed in situ pH measurements to be taken, thereafter the contents of the sampling unit was filtered immediately through 0.45 μm membrane filters. This was done to prevent continued dissolution of any grains of calcium carbonate that may have been inadvertently washed into the sampling unit.

Estimation of contact time

In order to determine dissolution kinetics from the water quality data gathered during each experiment, the contact time between the water and calcium carbonate has to be known. This time depends inter alia on flow rate, flow behaviour and porosity of the packed bed.

With regard to flow behaviour, in all probability the flow is likely to be pseudo plug flow. However, for the sake of convenience true plug flow is assumed in order to facilitate modelling the calcium carbonate dissolution behaviour.

With regard to the porosity, n, of the in situ granules, this is the ratio of the total volume of voids in the reactor to the total volume occupied by the granules and voids. The total volume of voids in the reactor was determined assuming that all voids were occupied by water. By draining and measuring the amount of water contained within the volume of reactor occupied by the calcium carbonate granules the volume of voids in this space was determined. The porosities determined are shown listed in the table below. A porosity based on the volume of drained water alone also is shown.

Table 5-1 Limestone porosity

Nominal granule size (mm)	Porosity (by oven drying)	Porosity (by drip drying)
1.43	59.6 %	45.3 %
3.55	64.1 %	47.2 %
5.7	63.9 %	44.5 %
8.05	65.1 %	45.2 %

Once porosity is known, it is possible to determine average flow velocity through the medium. In view of the potential complexities of the flow behaviour through the packed bed, tracer studies were undertaken in an attempt to obtain a direct measurement of flow velocities through the reactor.

Measurement of flow velocity
A tracer KCℓ solution was injected at a lower port of the reactor while recording the conductivity with time at the upper end cap. Data logging with time was effected using a Personal Computer, which provided an accurate measure of time. On injection of tracer, a signal was sent to the computer to indicate the start of the observations. *Conductivity -time* plots were produced for the various flow rates and tracer injection at the different ports. The time taken by a plug to flow from injection point to the detector was measured from the electronic marker indicating the moment of injection to the centroid of the *conductivity - time* plot (Levenspiel, 1972).

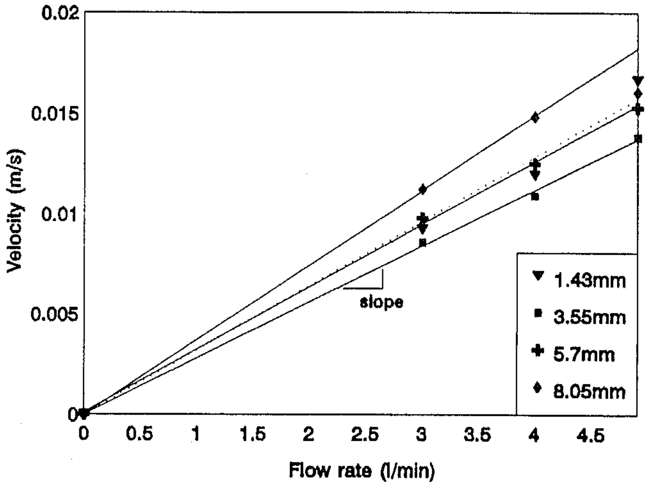


Figure 5-2 *Velocity - flow* rate plot for the various calcium carbonate granules investigated.

Examining the *velocity - flow rate* plots for the various granule sizes under investigation, it can be seen that the slopes of these plots, (corresponding to mean granule diameters of 8.05 mm, 5.7 mm and 3.55 mm), decrease with decreasing granule size. However, investigation of the corresponding porosities revealed that the proportion of voids in each case is closely constant (regardless of whether one examines the porosity obtained before or after oven drying, see **Table 5-1**). This is to be expected as single size particles of similar shape would probably pack in similar proportions. Consequently, the observed differences in velocities with granule size would indicate a significant flow component through the granules arises from the mineral porosity.

The total porosity of the granules in the reactor has been determined from the volume of voids obtained by oven drying the granules.

The equation for porosity, n in terms of other parameters, is:

$$n = \frac{q}{\bar{v} \times A \times 1000} \qquad \textbf{(5-4)}$$

The quantity $q/\bar{v}$ is the inverse of the slope of the *velocity - flow rate* plot, thus by multiplying by the cross sectional area of the reactor, the apparent porosity is obtained.

A relationship linking total surface area of granules per unit volume, (S_a), to mean granule diameter, (D_m), was formulated.

Having determined the flow velocities through the reactor at the various flow rates for each of the granule sizes, the average contact time can be calculated.

Estimate of average contact time

The contact time between successive sampling ports, which is required for the subsequent kinetic studies, is derived from the flow velocity. As the distance between ports is known, the time taken for the fluid plug to pass through this distance can be calculated and is taken to be the contact time.

Analytical considerations

By examining **Equations (5-2)** and **(5-3)**, a certain commonality between the two forms of the equation can be detected. Taking this into account, the calcium carbonate dissolution rate can be expressed as;

$$\text{Dissolution rate} = k \, . \, S \, . \, f([Ca^{2+}], [CO_3^{2-}]) \qquad \textbf{(5-5)}$$

where k = rate constant and is influenced by different parameters, depending on the mechanism proposed.
S = surface area
$f([Ca^{2+}], [CO_3^{2-}])$ = a model function incorporating the products of the concentrations of the two species

It is apparent that if the surface area term is held constant, it can incorporated into the rate constant to give a "compound rate constant" for a particular set of experimental conditions. This compound constant is given by the slope of a plot of *dissolution rate vs the model function*. Thus for a particular set of experimental conditions, the value of k depends on the choice of model used to describe the dissolution reaction.

Dissolution rate vs model function plot

In order to effect a plot of calcium carbonate dissolution rate against the model function, values for each of these need to be determined from some set of measurements at the sample ports.

Dissolution rate determination

Dissolution rate can be determined either from calcium and/or Alkalinity measurement at successive ports along the reactor, provided that time of flow between ports is known.

The calcium carbonate dissolution rate at any port can be approximated by the difference between the calcium/Alkalinity concentration of the port immediately downstream of the port in question and the one immediately upstream, divided by the time it takes a plug of water to pass through the distance between these ports. This determination assumes plug a flow regime between ports.

Model function determination

The two model functions investigated here included that where the process is diffusion controlled, i.e.

$$f(\text{diffusion model}) \propto \left\{ K'^{\frac{1}{2}}_{spc} - [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} \right\} \tag{5-6}$$

and, that where the process is surface controlled, i.e.

$$f(\text{surface model}) \propto \left\{ K'^{\frac{1}{2}}_{spc} - [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} \right\}^2 \tag{5-7}$$

Value of the model function at any particular port therefore requires knowing the values $[Ca^{2+}]$, $[CO_3^{2-}]$, temperature and ionic strength at that port. The calcium concentration, temperature and ionic strength can be measured as set out in the appropriate sections. The value of CO_3^{2-} is determined indirectly from Alkalinity and pH measured at a particular port.

Compound rate constant determination

In general determination of the compound rate constant from the slope of the plot of *rate vs model function* at each port was unsatisfactory. This arises because small errors in the values of any parameters measured lead to large variability.

Consequently the observed data for calcium concentration, Alkalinity and pH, were first plotted and smoothed. Thereafter using the rate equation, known flow rate and the initial characteristics of the water, a value for the rate constant was assumed and calcium concentration, Alkalinity and pH determined at each port. The value of the rate constant was varied to obtain the best fit between the calculated and smoothed data.

5.2.4 Determination of the controlling mechanism of dissolution kinetics

Mineral dissolution phenomena usually are controlled by a diffusion mechanism (Stumm and Morgan, 1981). In Section 5.1 it was shown that for calcium carbonate dissolution a diffusion controlled mechanism in the region 5 ≤ pH ≤ 9 leads to an equation of the form;

$$\frac{d[Ca^{2+}]}{dt} = k_{D.C.\ compound}\ f_d \left\{ K'^{\frac{1}{2}}_{spc} - [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} \right\} \tag{5-8}$$

where $k_{D.C.\ compound}$ = compound rate constant for a diffusion controlled reaction, which varies with temperature, ionic strength, physico-chemical properties of the mineral and hydraulic characteristics (flow rate) and includes a surface area term.

However, for calcium carbonate dissolution, some investigators have either explicitly postulated a surface controlled mechanism (Sjöberg, 1976) or implicitly accepted a surface controlled mechanism by their choice of the equation describing kinetics (Mills, 1984). Such a mechanism leads to an equation of the form utilized by Mills (1984), i.e.;

$$\frac{d\,[Ca^{2+}]}{dt} = k_{S.C.\ compound}\ f_d^2 \left\{ [Ca^{2+}]^{\frac{1}{2}}\ [CO_3^{2-}]^{\frac{1}{2}} - \left(\frac{K_{sp\,c}}{f_d^2} \right)^{\frac{1}{2}} \right\}^2 \qquad \textbf{(5-9)}$$

where $k_{S.C.\ compound}$ = compound rate constant for a surface controlled reaction, which varies with temperature, ionic strength, physico-chemical properties of the mineral and includes a surface area term.

(Both these equations representing kinetics in regions where $5 \leq pH \leq 9$ and $\bar{p}CO_2 \leq 0.1$ atm., see Section 5.2.3).

To identify which of these two mechanisms controls dissolution, one needs to identify some measurable parameter which separates them. In this regard, a mineral dissolution phenomenon in which the kinetics varies with mixing energy (all other parameters being kept constant) is considered diffusion controlled. That is, where the compound rate constant in **Equation (5-8)** varies with mixing energy between otherwise identical experiments, the process is diffusion controlled. This approach was used to identify the rate controlling mechanism in the investigation reported here.

Method

The reactor was loaded with single size granules of a nominal mean diameter. Acidified tap water was prepared and a set of experiments was carried out as described in the previous section. Mixing energy was varied by changing flow rates between experiments. The compound rate constant was determined for both model functions (i.e. $k_{D.C.\ compound}$ and $k_{S.C.\ compound}$) and plotted against the loading rates.

The loading rate, which is not dependent on the cross sectional area of the reactor, was used in preference to the flow rate. In this way the results are presented in a general format. Loading rate is defined as follows;

$$LR = \frac{q \times 60}{A \times 1000} \qquad \textbf{(5-10)}$$

where
LR = loading rate (ms^{-1})
A = reactor cross sectional area (m^2)
q = flow rate through reactor (ℓ/min)

Results

The rate constants, making use of the diffusion model, were calculated for the set of experiments conducted on the 5.7 mm mean size Bredasdorp calcium carbonate granules and plotted against their respective reactor loading rates in **Figure 5-3** below. From **Figure 5-3** it can be seen that the rate constant varies with loading rate, ie mixing energy, indicating that the process is diffusion controlled. Consequently, an equation of the form shown in **Equation (5-8)** is considered to represent the dissolution process. At this stage it is noted that the compound rate constant varies with both mixing energy and granule size.

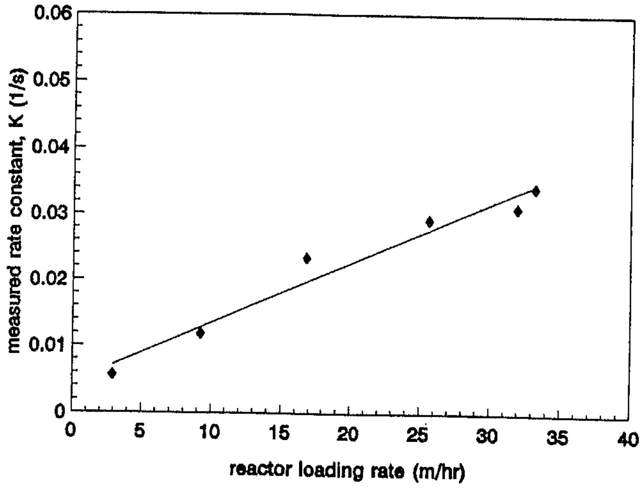


Figure 5-3 *Compound rate constant - loading rate* plot for 5.7 mm mean size Bredasdorp calcium carbonate granules in acidified tap water.

5.2.5 *Effects of granule size on the compound rate constants*

The discussion above shows the dependence of the compound rate constant on loading rate for a single granule size. However, from **Equation (5-8)** the mineral dissolution rate is proportional to a rate constant which incorporates a surface area term. It is expected that the effects of surface area per unit volume of reactor would be inversely proportional to the mean granules diameter. From this, it is expected that as the granule diameter increases/decreases the surface area term and hence the compound rate constant decreases/increases (i.e. decrease/increase in mineral dissolution rates). This interdependency was investigated by experiment.

Acidified tap water was prepared as set out above and a set of dissolution rate experiments was carried out on two extra granule sizes (3.55 mm and 8.05 mm) in the packed beds. In each case mixing energy was varied by changing the flow rates between experiments.

In **Figure 5-4** is shown plotted the compound rate constant versus the loading rate for the three granule sizes 3.55 mm, 5.7 mm and 8.05 mm. This plot indicates a closely linear relationship between the compound rate constant and the loading rate for each nominal mean granule size. Linear regressions were carried out on this data in order to obtain the best fit line representing each of the data sets and are plotted in the diagram. Experimental data gives a compound rate constant which increases with decrease in granule size.

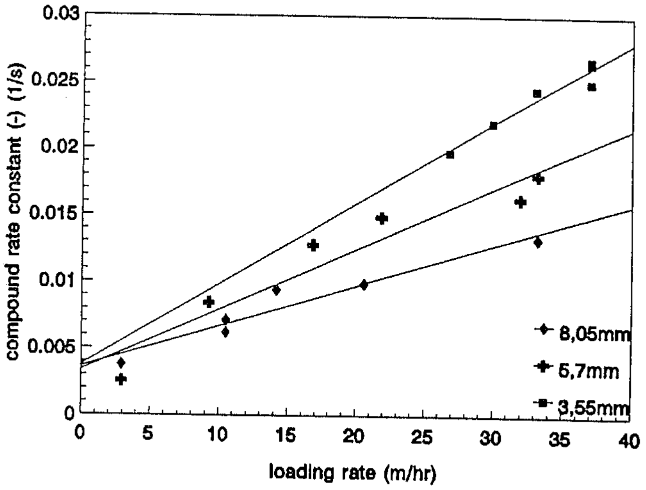


Figure 5-4 *Compound rate constant versus loading rate* plot for 3.55 mm, 5.7 mm and 8.05 mm mean size Bredasdorp limestone granules in acidified tap water (T = 22.5 °C ± 2 °C).

A linear dependence of the apparent porosity (and hence the flow characteristics of the reactor) on the inverse of the mean granule diameter was established in a previous section. This made it possible to simultaneously present the effects of both granule size and loading rate on the compound rate constant. A plot of $k_{compound}$ versus the ratio of loading rate to mean granule diameter is shown in **Figure 5-5**. In this form experimental data of all three granule sizes is closely linear. A linear regression was carried out to obtain an equation representing the effects of both granule size and loading rate on the compound rate constant giving,

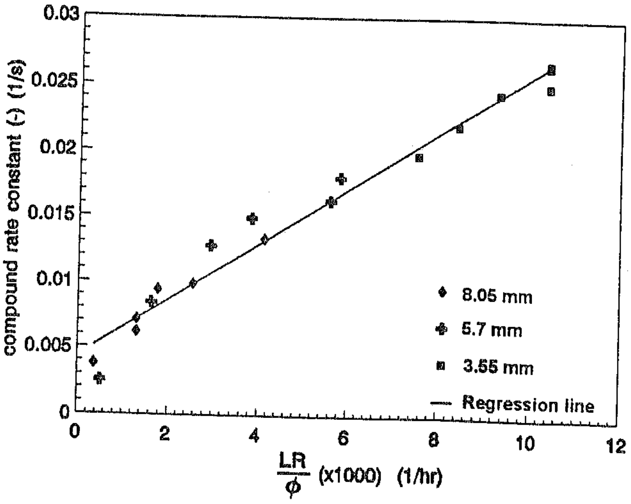


Figure 5-5 *Compound rate constant versus LR/ϕ for all* limestone granules investigated in acidified tap water (T = 22.5 °C ± 2 °C).

$$k_{D.C.\ compound\ (\phi)} = 0.0021 \frac{LR}{\phi} + 0.0044 \qquad (5\text{-}11)$$

where ϕ = nominal mean granule size (mm)
LR = loading rate (m hr^{-1})

It is reiterated that **Equation (5-11)** is valid only for granules obtained from the Bredasdorp deposit and within the mean nominal granule size range of 8.05 mm to 3.55 mm.

5.2.6 Comments on the experimental results

In a number of experiments the calculated Acidity value increased with flow through the granule bed. This is contrary to what is to be expected from basic theory. The increase in calculated Acidity may arise either from some external source of Acidity (e.g. CO_2 or mineral acid) or it may result from errors in measurement of either or both Alkalinity and pH.

With respect to an external source of Acidity, great care was taken to avoid CO_2 interaction with air and this interference effect was therefore rejected. A second alternative is that the Bredasdorp limestone is contaminated with a source of Acidity released on dissolution on waters with high redox potential. In this regard obvious sources are the minerals Fe_3O_4 and/or $FeCO_3$ and/or $MnCO_3$ entrapped in the limestone matrix. Dissolution of these minerals may release carbonates which do not affect Acidity, and manganese and ferrous species which would be oxidized and subsequently precipitate $Fe(OH)_3$ and/or MnO_2. This would result in Acidity increase and concomitant Alkalinity decrease. This hypothesis was discarded for two reasons. First, the Alkalinity and calcium concentrations (on the equivalent scale) increased by closely equal amounts with dissolution through the bed. Second, X-ray fluorescence analysis of the limestone, see **Table 5-2**, indicated that Mn and Fe^{2+} exist only in trace amounts in the mineral.

Table 5-2 **Mineralogical analysis by X-ray fluorescence of the Bredasdorp limestone deposit.**

Mineral	Sample A % by weight	Sample B % by weight	Average % by weight
SiO	6.23	6.83	6.50
TiO_2	0.02	0.03	0.025
Al_2O_3	0.21	0.30	0.255
Fe_2O_3	0.25	0.35	0.30
MgO	0.59	0.64	0.615
Na_2O	0.02	0.03	0.025
K_2O	0.08	0.10	0.09
P_2O_5	0.05	0.05	0.05
CaO	~54*	~54*	~54*
CO_2	not analysed		
	parts / million	parts / million	parts / million
Mn	10	14	12
Cr	14	17	15.5

* outside calibration range

With respect to errors arising in Alkalinity and/or pH measurement, an apparent increase in Acidity would require either an over estimate of Alkalinity or an under estimate of pH or both. With respect to Alkalinity measurement this was effected using Gran titration and there is no reason to suppose that a continuously increasing overestimate in measured Alkalinity should occur up the reactor.

With respect to pH measurement there is the possibility of a sluggish probe response arising in the very poorly buffered waters investigated. During a particular experimental run, pH observations were taken from the top of the reactor downwards (i.e. in a direction against the flow) with observations moving from high pH zone with low buffer (i.e. pH ≈ 8) through a zone of better buffer capacity (i.e. pH ≈ 6.5) into a lower zone again with poor buffer capacity (pH ≈ 5). There is a possibility that the responsiveness of the probe is linked to buffer capacity (i.e. slower response with lower buffer capacity). In the high pH region of lower buffer capacity an error of ± 0.3 pH units would have negligible effect on the calculated Acidity value whereas in the lower pH region, also with low buffer, an error of ± 0.3 pH units would have very significant effect on the calculated Acidity value. This type of trend is not observed with the troublesome experimental data and hence it is unlikely that sluggish pH response causes the observed Acidity increase trend on these particular experiments. This matter was not satisfactorily resolved.

5.2.7 Calcium carbonate dissolution kinetics - practical considerations

Practical application of the dissolution kinetics requires that the kinetic constant be known for both flow rate and granule size. Furthermore the kinetics is valid only for a mineral from a particular deposit. The work reported here constitutes preliminary results for calcium carbonate derived from Bredasdorp. However, practical application is clearly hindered by the fact that a packed bed reactor invariably will be comprised of a graded granule size resulting from differential dissolution through the filter. In this regard use of the kinetic equation proposed here to a particular granule size (based on granules added to the filter) will give a conservative estimate of dissolution rates. This information nevertheless suffices for an initial design.

Note: Perhaps most important, the work reports in detail preliminary investigation methodology to be adopted to determine the rate constant for a particular geological deposit. In this sense the work highlights that it is not possible to supply to the user general design charts that can be adopted throughout the country for these dissolution processes.

5.3 General Summary

It was established that the dissolution process in fixed bed upflow limestone contactors is diffusion controlled and the following general equation models the rate:

$$\frac{d[Ca^{2+}]}{dt} = k_1 S f_d \left\{ K_{spc}^{\prime\,\frac{1}{2}} - [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} \right\} + k_2\, S\, [H^+] + k_3\, S\, [H_2CO_3^*] \qquad \textbf{(5-1)}$$

S = surface area

The first term of the equation is dominant in natural terrestrial soft water environments (in the range 5 ≤ pH ≤ 9). The second and third terms of the equation represent dissolution phenomena dominated by high proton (low pH, pH ≤ 4) and carbonic acid concentration ($pCO_2 \geq 0.1$ atmospheres) respectively.

Each of the rate constants depends on a number of factors including the physico-chemical characteristics of the mineral, flow characteristics, temperature and ionic strength. The physico-chemical characteristics of the mineral vary according to the geological history of the limestone deposit, hence these rate constants must be determined for a particular limestone (calcium carbonate) deposit. To this end the procedures described in Section 5.2 should be followed.

The model was applied to the dissolution of limestone from the Bredasdorp deposit in the soft waters representative of those found in the Western Cape. The last two terms of the model above, do not play a significant role in the dissolution of limestone in the natural waters relevant to this study, and were therefore not investigated further. The first term in the above rate equation thus became the focus of this study. For practical purposes, the surface area, S, and rate constant, k_1, were combined to form a compound rate constant, $k_{DC\ compound}$, which was found to vary with mixing energy (i.e. hydrological conditions) for a specific granule size - an observation consistent with the diffusion controlled model. Thus the equation investigated is

$$\frac{d[Ca^{2+}]}{dt} = k_{D.C.\ compound}\, f_d \left\{ K_{spc}^{\prime\,\frac{1}{2}} - [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} \right\} \qquad \textbf{(5-8)}$$

where $k_{D.C.\ compound}$ = compound rate constant for a diffusion controlled reaction, which varies with temperature, ionic strength, physico-chemical properties of the mineral and hydraulic characteristics (flow rate) and includes a surface area term.

Limestone from the Bredasdorp deposit is friable and porous. The porosity influences the flow characteristics through the reactor. The velocity at which a plug of water progresses through the reactor was found to decrease with increase in the granule surface area per unit volume of reactor (i.e. decrease in mean nominal granule size).

The dependence of the compound rate constant (for Bredasdorp limestone) on granule size and hydraulic conditions was investigated, and leads to the following empirical relationship,

$$K_{D.C.compound} = 0.0021 \frac{LR}{\Phi} + 0.0044 \qquad \textbf{(5-11)}$$

where ϕ = nominal mean granule size (mm) in the range
$3.55 \text{ mm} \leq \phi \leq 8.05 \text{ mm}$
LR = loading rate (m/hr)

A limited number of tests using rain water and Table Mountain water (i.e. containing dissolved organic carbon), showed that use of the results obtained from the acidified tap water was justified when considering the soft waters of the Western Cape. Long term effects of humic substances, such as precipitation of humics and consequential armouring effects, were not investigated. However, long term tests (± 100 days) conducted at the University of Cape Town into the dissolution of concrete pipes in humic waters, showed no armouring effects (Mackintosh, 1990).

In practice a reactor will contain particles of varying and changing size, and a grading will occur from small to large up the reactor. Design using the findings for the rate constant based on size of granules added to the reactor will yield a conservative result. This is because reactions in practice may be expected to occur faster than those based on "startup" granule size.

In a number of experiments the calculated Acidity value increased with flow through the granule bed. This is contrary to what is to be expected from basic theory. The reason for this anomaly is at present still elusive.

REFERENCES - CHAPTER 5
Kinetic Modelling

GRAN G (1952) Determination of the Equivalence Point in Potentiometric Titrations. Part 2. *The Analyst*. Vol. 77,.pp 661-671.

KORNMÜLLER UR (1995) Limestone dissolution kinetics in upflow systems, *MSc Dissertation*, Dept Civil Engineering, Univ Cape Town.

LEVENSPIEL O (1972) *Chemical reaction engineering 2nd ed.*. Wiley, New York.

MACKINTOSH GS (1990) Aggressive water attack on carbonated cement materials. *MSc Dissertation*, Dept Civil Engineering, Univ of Cape Town.

MILLS RDWB (1984) Stabilization of Calcium Carbonate deficient waters. *MSc Dissertation,* Dept Civil Engineering, Univ of Cape Town.

PLUMMER LN, PARKHURST DL and WIGLEY TML (1979) Critical Review of the Kinetics of Calcite Dissolution and Precipitation, *Chemical Modelling in Aqueous Systems: Am. Chem. Soc. Symposium Ser.* pp 537 - 573.

SJÖBERG E L (1976) A fundamental equation for calcite dissolution kinetics. *Geochimica et Cosmochimica Acta* vol. 40, pp 441-447.

STUMM W and MORGAN JJ (1981) *Aquatic Chemistry 2nd ed.* Wiley, New York.

CHAPTER 6

SMALL USER SYSTEM STUDIES

6.1 Introduction

Small scale private water users using soft, acidic waters usually fail to stabilise the water prior to introduction to household and other piping systems. The resulting corrosive attack has substantial cost implications in terms of replacement of piping and geysers, washing machines and the like, and not insignificant inconvenience resulting from the staining of baths, clothes and hair. Furthermore, failure to stabilise results in an associated decrease in water quality resulting from raised dissolved metal levels (such as iron, copper and zinc). In many cases dissolved metal levels resulting from corrosion exceed SABS 241-1984 domestic supply requirements.

These small scale users usually utilise between 5 m^3/day and 500 m^3/day. About seventy percent of small users utilise **ground-water** (pumped from boreholes, or collected from springs) with the remainder utilising **surface waters** (collected from mountain streams). In both cases these waters have characteristics that require special consideration.

Failure to stabilise usually results from a combination of both ignorance regarding the need to stabilise, and the lack in availability of suitable, low cost, low maintenance stabilisation technology for small scale users.

This chapter reports on the development and operation of pilot plant small user systems for the stabilisation of both groundwater and surface water. The systems developed are shown to be effective for the particular application. Sufficient detailed design information is provided for replication of the units, and operating guidelines are given.

6.2 Small User System Plant Requirements

Two systems were investigated for the small scale user. The two basic systems investigated were for, (i), the stabilisation of groundwater, and (ii), the stabilisation of surface water. In both instances the unit was required to satisfy the following criteria:

- Easily transportable by a LDV, and easily erectable on site.
- Simple. The aim of these units is not to evaluate detailed scientific factors, but basic factors, such as configuration, retention (contact) time, flow rates and backwash (or other cleaning) requirements.
- If possible, the units should require no additional pumps, electrical control systems etc.
- An appreciable level of stabilisation should take place.
- The plant should be able to treat between 25 m^3/day and 50 m^3/day.
- Most importantly, the units must be able to operate reliably with minimum operator attention.

6.3 Groundwater System

6.3.1 Special considerations

Special considerations for the stabilisation of groundwater are excess dissolved carbon, dioxide, the presence of iron and manganese, and pumping requirements.

Excess carbon dioxide

Groundwater abstracted via boreholes will always be more aggressive/corrosive than its surface water counterpart. This is as a result of the high levels of dissolved carbon dioxide present, resulting from the increased CO_2 partial pressure at depth. Typically, these high levels of dissolved carbon dioxide, or carbonic acid, can result in very low pH of, say, 5.5. The same water, brought to aqueous-gaseous phase equilibrium, will have a pH of 7.5. This excess carbon dioxide will be unstable once the water has been brought to the surface, and needs to be removed prior to stabilisation.

- The system is required to effectively aerate the water.

Iron and manganese

Water abstracted from boreholes in soft water regions frequently contains iron and manganese in their dissolved state. In areas such as the Western Cape the presence of, say, iron of 2 mg/ℓ and manganese of 1 mg/ℓ is fairly common. These levels are in excess of SABS 241-1984 Recommended and Maximum Allowable limits, impacting on taste and staining clothes, walls etc. CSIR receives numerous requests from farmers, small communities and other users of groundwater, for help in removing iron in particular. Hence, it would be beneficial if, in addition to stabilisation, the process was able to operate as a simple iron (and possibly manganese) removal process.

- The system should ideally be able to treat water with an iron content of 1 to 2 mg/ℓ, and manganese of 1 mg/ℓ.
- Dissolved iron and manganese must be oxidised and removed to comply with the SABS 241-1984 Maximum Allowable Limit (1.0 mg/ℓ) at worst, or preferably the Recommended Limit (0.1 mg/ℓ for iron, and 0.05 mg/ℓ for manganese).

Pumping requirements

An initial project objective for small user systems was that the pressure head provided by the water source, be it borehole, river or reservoir, be maintained through the stabilisation process to overcome the need for secondary pumping. However, this is not possible with groundwater because of the excess carbon dioxide present. Groundwater can not be readily stabilised by simple limestone contact in a pressure vessel as the excess carbon dioxide will result in excessive dissolution of calcium carbonate. In turn, as the excess carbon dioxide comes out of solution further on within the distribution network, the "stabilised water" will become supersaturated and precipitate significant amounts of calcium carbonate thereby calcifying pipes, geysers, kettles, etc.

As in most cases groundwater can be pumped to a high point on the property - it was felt that the stabilisation system could in most cases be located at such a high point. The water can then be stabilised and gravity fed into the distribution system, the only other pumping related constraint then being that any filter incorporated in the system should be designed such as to be back washable with the borehole pump.

- The filter must be back washable by the borehole pump.

Limestone usage

As a general rule, the limestone usage per unit of water stabilised can be estimated from the average CCDP of the unstabilised water, according to the formula below. The calcium carbonate purity of the limestone (approximately 94 % for the Bredasdorp deposit) and percentage limestone wastage should also be taken into account:

$$Usage = \frac{CCDP}{(x_{purity}).(1-x_{wastage})} \cdot \frac{1}{1000} \qquad \textbf{(6-1)}$$

where:

Usage	=	Limestone usage	[kg limestone per m^3 water]
CCDP	=	Average calcium carbonate dissolution potential of the unstabilised water	[mg/ℓ as $CaCO_3$]
x_{purity}	=	Fraction $CaCO_3$ purity of limestone	
x_{waste}	=	Fraction limestone wastage	

Example
An unstabilised water with an average CCDP of 100 mg/ℓ as $CaCO_3$ will use 0.107 kg limestone per m^3 water, if the limestone purity is 94 %, and if limestone wastage is 1 %.

6.3.2 Groundwater treatment unit design

Mark One unit

Groundwater treatment pilot plants were designed, installed and operated. A preliminary "Mark One" unit was used to gather initial design data. Two updated units, termed "Spraystab" units, were installed for long term test work. The groundwater treatment units were required to fulfill three main functions, namely:

- *aeration*, to strip excess carbon dioxide and assist in oxidising iron and manganese,
- *stabilisation*, via providing sufficient contact time with limestone, and
- *filtration*, to remove limestone fines and other insolubles such as iron and manganese floc.

The "Mark One" pilot plant was constructed such that it could be used to evaluate flow and retention data from tests on typical "small user" rural boreholes, delivering up to 35 ℓ/min (48 m^3/day), as shown in **Figure 6-1**. The unit was designed such that it could operate in two modes, namely:

- *Flooded Mode*: With the limestone bed fully flooded during operation.
- *Cascade Mode*: In cascade mode, with the feed water sprayed directly on the limestone pebbles and draining down over the pebbles to the manifold in the base of the column.

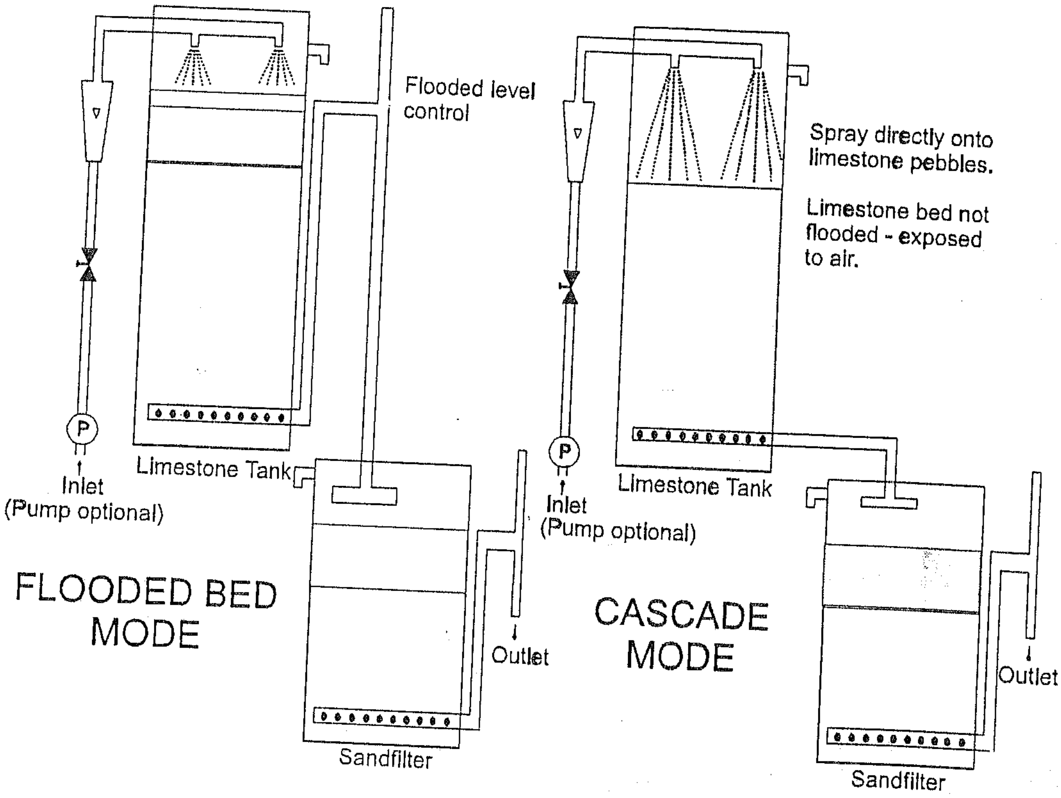


Figure 6-1 "Mark One" pilot plant - groundwater

Design details

The general configuration of the unit is shown in **Figure 6-1**. Basic details of the components are given below.

(i) *Aeration and limestone contact unit*

Internal diameter:	565 mm
Total depth:	1750 mm
Limestone bed depth	1300 mm
Limestone material:	-15 mm +12 mm
Spray nozzles (1 or 2):	Fulljet 1/4 G SS 10
Distance of nozzle to bed;	300 mm
Construction:	Steel, epoxy coated

(ii) *Sand filter*

Internal diameter:	565 mm
Total depth:	865 mm
Total filter area:	0.251 m^2

Effective bed depth:	360 mm
Sand grading:	0.35 to 0.50 mm
Available backwash rate:	28 m/h

Sampling

Flow rate measurements and pH (field) readings were taken on site. Analyses for iron, manganese, pH (laboratory), calcium, Alkalinity and conductivity were performed at the CSIR analytical laboratory, Stellenbosch on samples collected at the required intervals.

Limestone source and sizing

Limestone used was the Bredasdorp limestone with particle size -15 mm +12 mm. (This size had been shown to be most practical for transportation purposes, with smaller particle size distributions breaking down into fines and being difficult to handle).

Raw water quality

The unit was run on a borehole with raw water quality as shown in **Table 6-1** and **Table 6-2.**

Table 6-1 **"Mark One" unit - flooded mode**

Date of Test	23/02/94
Time after Start (minutes)	60
Type of Limestone Contact	Flooded mode
Flow Rate (ℓ/h)	423
Retention Time (minutes)	18.4

Determinant		**Feed from Borehole**	**After Limestone**	**After Sandfilter**
Iron	mg/ℓ	1.17	0.39	0.07
Manganese	mg/ℓ	0.36	0.26	0.28
Calcium	mg/ℓ as $CaCO_3$	32	78.5	81.3
Alkalinity	mg/ℓ as $CaCO_3$	43.5	88.5	89.3
pH (Field)		5.9	7.3	7.3
pH (Laboratory)		6.7	7.7	7.8
pHs		7.3	8.1	8.1
Electrical Conductivity	mS/m	86	93	93
TDS (Calculated)	mg/ℓ	550	595	595
CCDP	mg/ℓ as $CaCO_3$	177	14.3	14.2

Table 6-2 "Mark One" unit - cascade mode

Date of Test	04/03/94
Time after Start (minutes)	180
Type of Limestone Contact	Cascade mode
Flow Rate (ℓ/h)	423
Retention Time (minutes)	18.5* (see note below)

Determinant		Feed from Borehole	After Limestone	After Sandfilter
Iron	mg/ℓ	0.64	<0.05	0.05
Manganese	mg/ℓ	0.39	0.11	0.11
Calcium	mg/ℓ as $CaCO_3$	32.5	67.8	66.8
Akalinity	mg/ℓ as $CaCO_3$	43.3	77.3	76.5
pH (Field)		5.8	7.8	7.9
pH (Laboratory)		6.4	8	8.1
pHs		7.2	8.3	8.3
Electrical Conductivity	mS/m	87	92	93
TDS (Calculated)	mg/ℓ	557	589	595
CCDP	mg/ℓ as $CaCO_3$	208	3.5	2.4

Operation of unit

Following the initial flushing of the unit to remove limestone fines, a number of initial orientation runs were carried out to familiarise the operators with the apparatus and to establish a standard test procedure. Thereafter, the unit was run at various flow rates to provide limestone bed retention times of between 4 and 20 minutes.

Note: The "retention times" given for all the tests runs are for the unit operating in the flooded mode. In the cascade mode the real retention time is far shorter, but for ease of reference this nomenclature has been adopted.

A comparative set of tests were done with the limestone column operating in cascade mode versus flooded mode. Between each series of tests, the sand filter was backwashed and drained to remove limestone fines, and iron and manganese deposits. Although the limestone bed became discoloured, there was no evidence of build-up on the surfaces of the limestone pebbles during these relatively short tests. The limestone unit was also backwashed and drained, but very little removal of deposits occurred.

The unit was run for a period of eight weeks.

Results

Typical results are shown in **Tables 6-1** and **6-2**. The results obtained showed inter alia:

- The cascade mode is more efficient than the flooded mode with regard to pH adjustment, iron removal and manganese removal
- Dissolved iron is effectively removed from borehole water by spray aeration, limestone contact and sand filtration.
- Dissolved manganese is partly removed by the system.
- A considerable degree of stabilisation occurs.

However, *shortcomings* with the system and tests were identified as:

- The sand filter requires more development. In its present configuration most borehole pumps would not have sufficient capacity to backwash the filter.
- Long term tests are required to establish efficiency of the system, and in particular with regard to establishing effective backwashing procedures for both the limestone unit and the sand filter.
- The Mark One system is ungainly, and could be made more compact.

"Spraystab" unit

To overcome the shortcomings of the Mark One unit, a Mark Two unit was designed and has become colloquially referred to as "Spraystab". Two "Spraystab" units were constructed and installed for field trials. The units were installed at two separate sites, both with characteristic soft, acidic groundwaters. Site A has no dissolved iron or manganese, and the unit was installed in February 1995. Site B had dissolved iron of 1.55 mg/ℓ, and the unit was installed during April 1996.

The three basic components of the "Spraystab" unit are as follows: (i) the aeration system housed in the lid of the unit, (ii) the limestone contact section, and (iii) the gravity dual media filter at the base.

Design details

The configuration of the unit is shown in **Figure 6-2**. **Figure 6-3** shows more detailed sketches of the components with the main dimensions, and **Figure 6-4** photographs of the unit. Dimensions for the units are given below.

Details of the individual components are as follows:

(i) *Aeration unit*

The spray nozzles are housed in ducts and air outlets are included in the lid, both features are to promote air circulation and, hence the degree of aeration. Ingress of leaves and other windblown matter is prevented by fitting 10 mm stainless steel mesh screens to the air duct ends and the air outlets in the lid.

Spray nozzles:	It is critical that the spray nozzles are sized according to pump, pressure and flow characteristics. The spray nozzles must be of a stainless steel type. Two Fulljet ⅜" SS 15's were used. These are located with nozzle outlet 200 mm above the lower edge of the duct.
Air ducts:	Comprised UPVC pipe sections welded to lid. OD 250 mm, 5 mm wall thickness, covered with 10 mm stainless steel wire mesh.
Air outlets:	As per **Figure 6-3**, directly in lid. Covered with 10 mm stainless steel wire mesh.

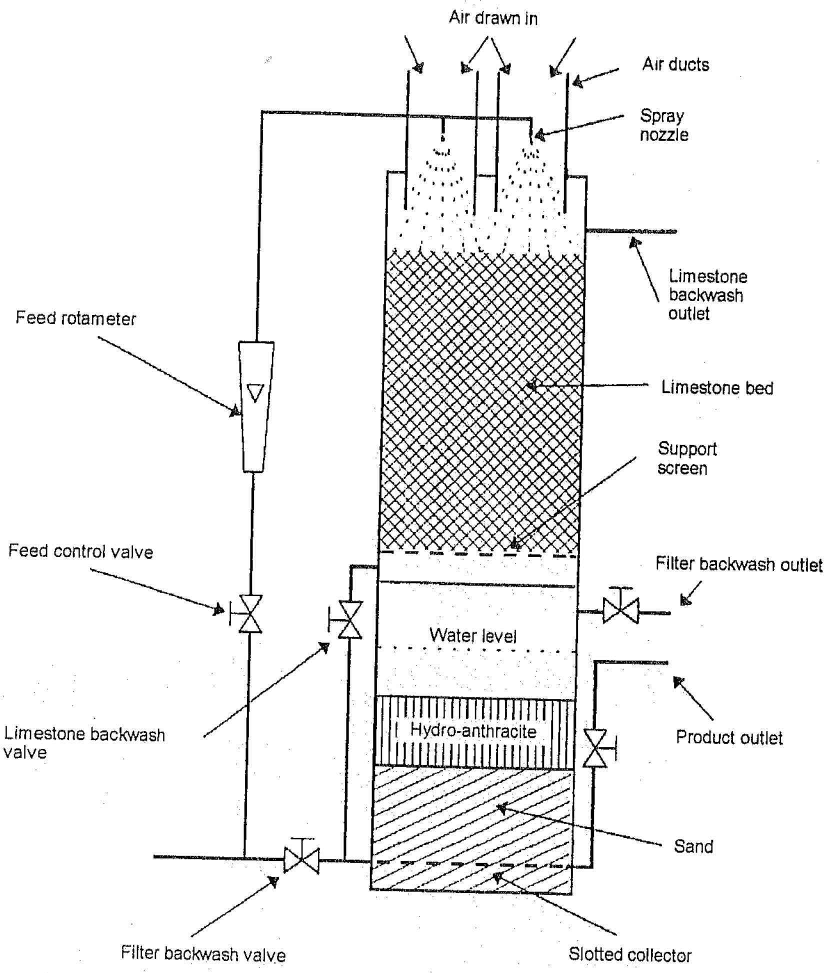


Figure 6-2 Configuration of "Spraystab" unit

(ii) *Limestone contact unit*

The limestone contact unit is an open ended fabricated UPVC cylinder having the following specifications:

Internal diameter:	600 mm
Wall thickness:	6 mm
Wall height:	1100 mm
Limestone bed depth:	800 mm
Limestone material:	-15 mm +12 mm Bredasdorp limestone
Total limestone bed volume:	0.226 m^3
Mean void ratio:	45 %

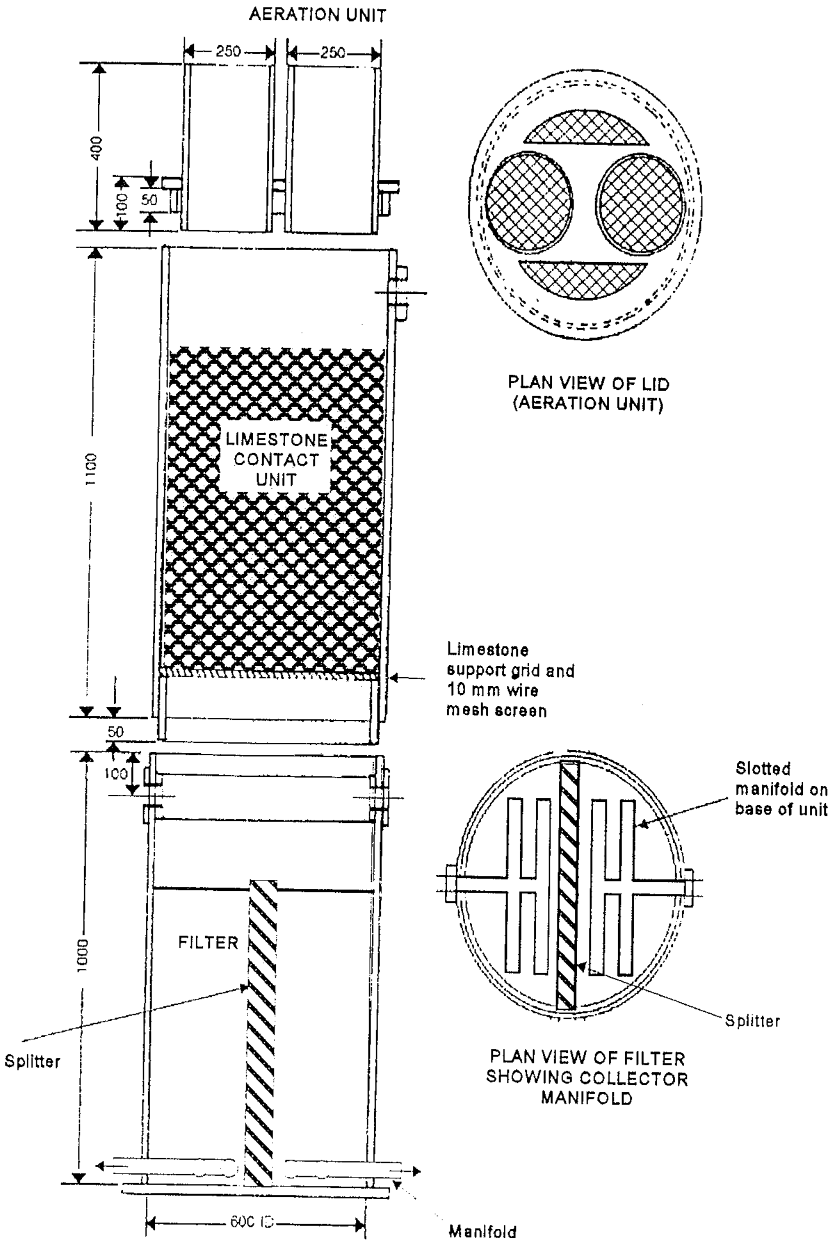
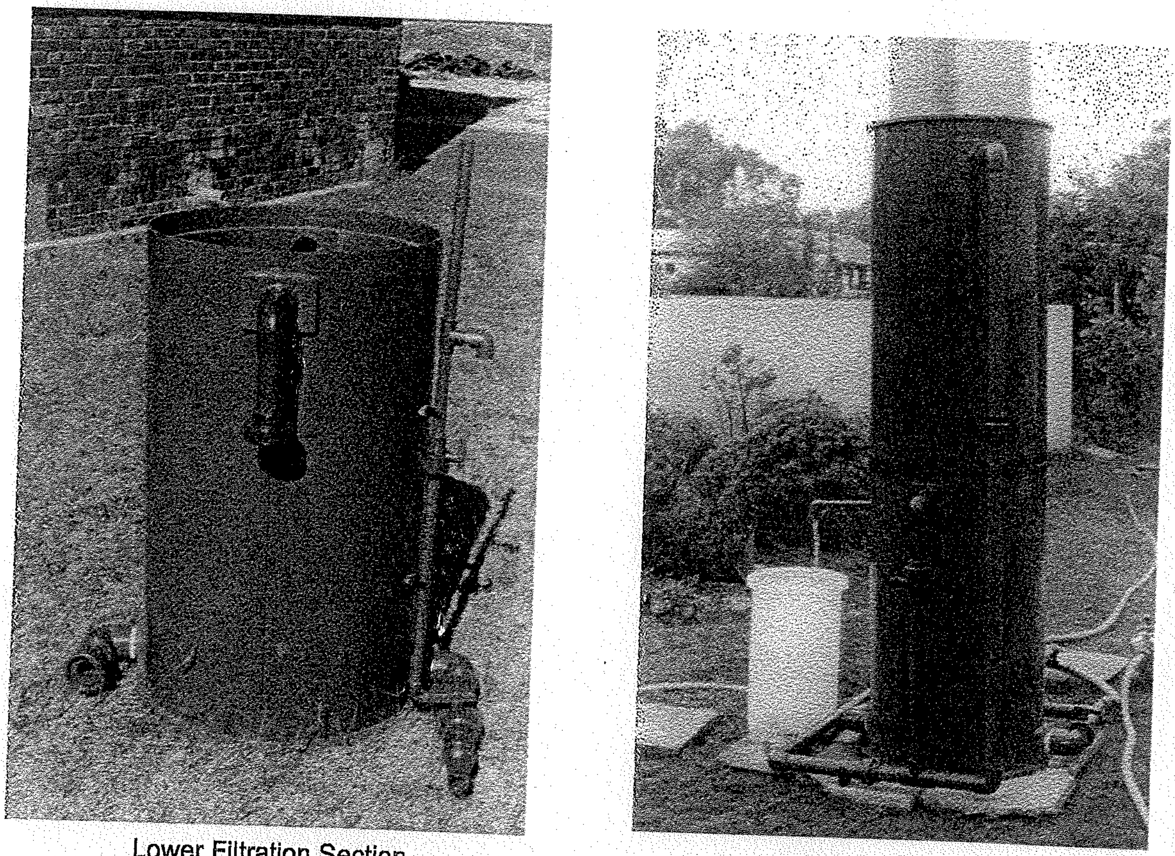


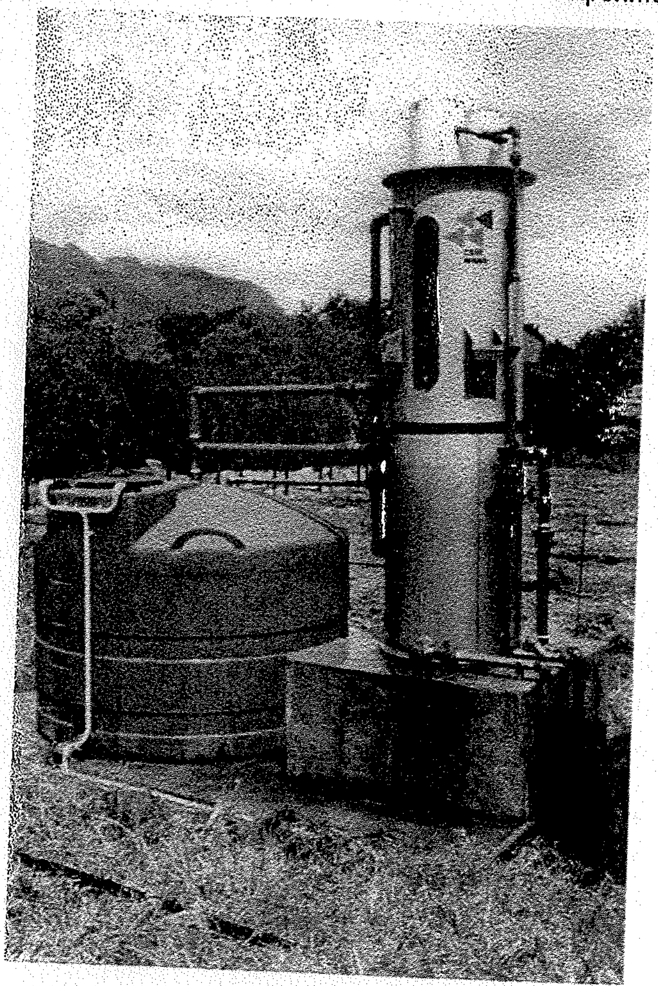
Figure 6-3 Sketch of main component dimensions of "Spraystab" unit

Support screen:	Stainless steel wire mesh screen with 10 mm apertures, supported on a 8 mm diameter stainless steel fabricated support grid, 100 x 100 mm apertures.
Backwash outlet fitting:	2" BSP



Lower Filtration Section

Experimental Unit



Installed Production Unit

Figure 6:4 "Spraystab" unit

(iii) *Multi-media filter*

The filter used is essentially a crude shallow gravity filter. The filter unit supports the limestone contact unit, which fits into it (see **Figure 6-3**) and the joint is sealed by both silica sealant and sealing adhesive tape ("Duct Tape"), the latter applied on the outside around the joint. The bed is divided into two by a "splitter" in order to allow backwashing of half the filter area at a time. The specifications of the sand filter are:

Internal diameter:	600 mm
Wall thickness:	6 mm
Wall height:	1000 mm
Total filter area:	0.283 m^2
Bed depth above manifold:	600 mm
Sand depth:	400 mm
Sand grading:	0.35 to 0.50 mm
Hydro-anthracite depth:	200 mm
Hydro-anthracite grading:	0.8 to 1.6 mm
Backwash head clearance:	200 mm
Collector manifold:	Slotted nozzle fingers, constructed with filter insert sections glued together
All inlet/outlet fittings:	2" BSP
Max Filtration rate:	
Iron removal and stabilisation:	(at 1.4 m^3/h), 4.95 m/h
Stabilisation only:	(at 2.3 m^3/h), 8.14 m/h
Minimum Backwash rate:	
Full area:	8.5 m^3/h, 30 m/h
Half area:	4.0 m^3/h, 28 m/h

(iv) *Sundry equipment*

Feed Rotameter	300 to 3000 ℓ/h clear plastic unit
Feed Control valve	25 mm PVC Saunders type diaphragm valve
Other valves	50 mm PVC ball valves
Feed and product piping	25 mm PVC Class 9
Backwash and drain piping	50 mm PVC Class 9
Flushing hose	25 mm flex hose

Sampling

Flow rate measurements, pH (field), calcium and Alkalinity readings were taken on site. Analyses for iron, conductivity and checks on pH (laboratory), calcium, Alkalinity and conductivity were performed at the CSIR analytical laboratory, Stellenbosch, on samples taken at the appropriate times.

Operation of "Spraystab" units

Following the installation and commissioning of the units, the units were left to run at retention times of about ten minutes for a week or two. Thereafter, a number of visits to the sites were carried out during which:

- Samples were collected.
- A general inspection was carried out for leaks, etc, to ensure that everything was functional.
- The spray nozzles were inspected for blockage.
- The limestone bed was inspected for discolouration and iron sludge build-up (if any), and topping up requirements.
- The filter bed was inspected for accumulation of fines and iron oxides.
- The filter was backwashed, sectionally.
- The two day tests were initiated for a range of retention times (3 minutes to 20 minutes).

Results

The unit was run on boreholes with raw water quality as shown in **Table 6-3**.

Table 6-3 "Spraystab" unit: raw and treated water quality

Determinant		SITE A		SITE B	
		Raw	Final	Raw	Final
pH		6	8.5	4.7	8.2
Calcium	mg/ℓ as $CaCO_3$	6.5	26.3	0	40
Alkalinity	mg/ℓ as $CaCO_3$	19	39	6	39.8
Conductivity	mS/m	22.5	26	18	24
CCDP	mg/ℓ as $CaCO_3$	80.3	1.4	332	1.6
Iron	mg/ℓ	<0.05	<0.05	1.55	0.05

Note: No manganese was detected in the raw waters

Typical results are shown in **Figure 6-5** and **Figure 6-6**. The results obtained showed inter alia :

- In the case of stabilisation only, the "Spraystab" unit proved to be highly effective. A retention time of 3 minutes (2 m^3/h) was found to be sufficient, reducing CCDP from about 80 to about 1.4 mg/ℓ as $CaCO_3$, and increasing pH from about 6.0 to about 8.5. Longer retention times gave improved results.

- In the case of iron removal and stabilisation, the "Spraystab" unit proved to be highly effective. At a recommended retention time of 5 minutes (1.1 m^3/h) the CCDP was reduced from about 322 to about 1.6 mg/ℓ as $CaCO_3$, and pH was increased from about 4.7 to about 8.2. Dissolved iron was reduced from about 1.55 to 0.05 mg/ℓ.

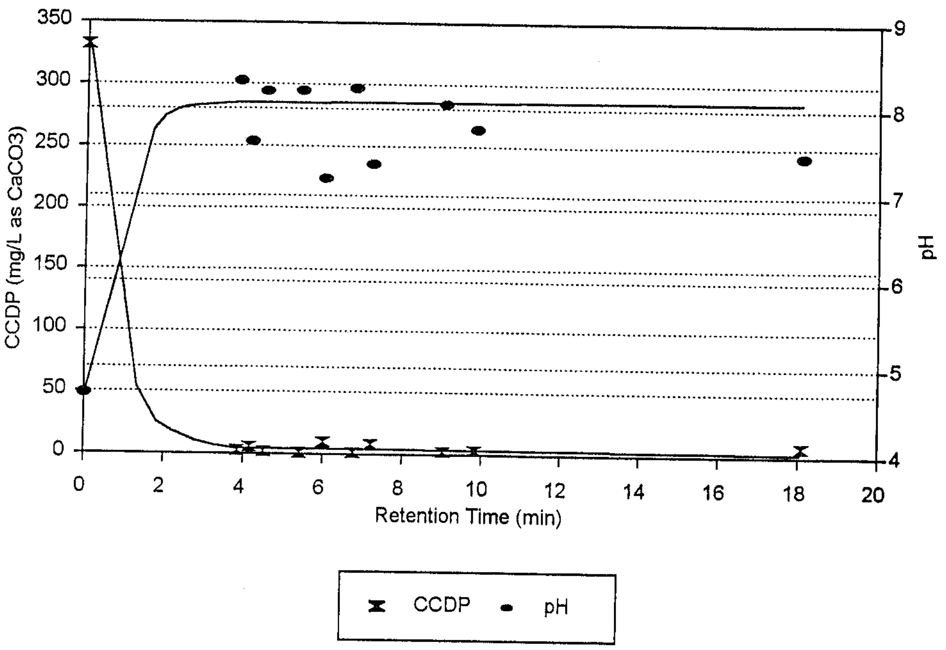


Figure 6-5 Typical changes in CCDP and pH for "Spraystab" unit (Site B)

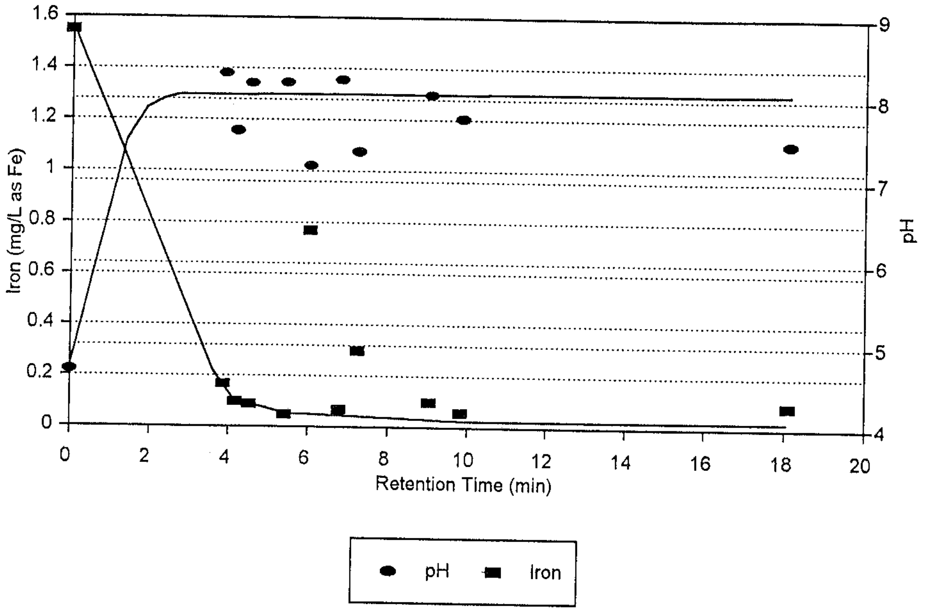


Figure 6-6 Typical changes in dissolved iron and pH for "Spraystab" unit (Site B)

Practical observations

The "Spraystab" unit requires very little operator attention or maintenance. No carry-over of fine silica particles into the treated water was observed. Service requirements are minimal and can be summarised as follows:

Iron removal and stabilisation "Spraystab":

- Backwashing must be carried out on a weekly basis.
- The limestone bed must be thoroughly sprayed down with the flushing hose to dislodge any loose iron carbonate particles and fines prior to backwashing.
- The limestone bed must be topped up on a monthly basis.

- The flowmeter and the spray nozzles should be cleaned on a monthly basis.

Stabilisation only "Spraystab":

- Backwashing must be carried out on a fortnightly basis.
- The limestone bed must be thoroughly sprayed down with the flushing hose to dislodge any loose iron carbonate particles and fines prior to backwashing.
- The limestone bed must be topped up on at least a monthly basis.
- The flowmeter and the spray nozzles should be cleaned on a monthly basis.

6.4 Surface Water System

6.4.1 Special considerations

The requirements for the surface water stabilisation pilot plants were more straight forward than that for groundwater. It was accepted that few surface waters have unstable contaminants such as iron, manganese or excess carbon dioxide and that generally the water chemistry is stable. It was also accepted that it was not the purpose of a stabilisation unit to be an "all-in-one" water treatment plant so in instances where high turbidity, algae, bacteria, etc were present, initial conventional treatment, say filtration, would be required prior to stabilisation.

Nevertheless, with regard to the so-called "brown waters" of the Western-Cape, it was required that the influence of varying amounts of DOM be investigated. Furthermore, some of the DOM rich waters have low levels of iron and it was required that the influence of this also be investigated. Hence, considerations were as follows:

Dissolved organic matter
The presence of DOM is highly variable. Waters of, say Stellenbosch, have a colour of about 10 to 30 mg/ℓ as Pt, whilst waters of George have a colour of 800 to 1000 mg/ℓ as Pt. Broad observation as to the influence of DOM at a practical level was undertaken.

Iron
Coloured surface waters can contain low levels of iron. This iron is complexed with the DOM and as such is stable and not readily removable. Generally, these levels are within SABS 241-1984 Recommended and Maximum Allowable limits. However, in some instances levels can be as high as 2 mg/ℓ. Broad observation as to the influence of iron at a practical level was undertaken.

Pumping requirements
A project objective was that the pressure head provided by the water source, be it river or reservoir, be maintained through the stabilisation process to overcome the need for secondary pumping. This requires that the surface water stabilisation unit be a pressure vessel. For cost and ease of study purposes preliminary pilot scale tests were run with "pressure-loss" systems. A single long term pressure unit was installed.

6.4.2 Test sites for surface water plant tests

Preliminary pilot scale tests, of at least three months, were run on the following waters:

White water:	Soft, acidic, non-coloured water, with low iron. (Withoogte Dam, Wellington)

Lightly coloured brown water:	Soft, acidic, lightly coloured brown water, with no objectionable materials or unstable constituents. (Eerste River, Stellenbosch)
Brown water:	Soft, acidic, highly coloured brown water, with appreciable iron. (Garden Route Dam, George)

The test units used for these investigations were fixed bed "pressure-loss" systems (**Figure 6-7**). A single **long term field unit** was installed to treat soft, acidic, lightly coloured water with low levels of iron at Paradyskloof, Stellenbosch.

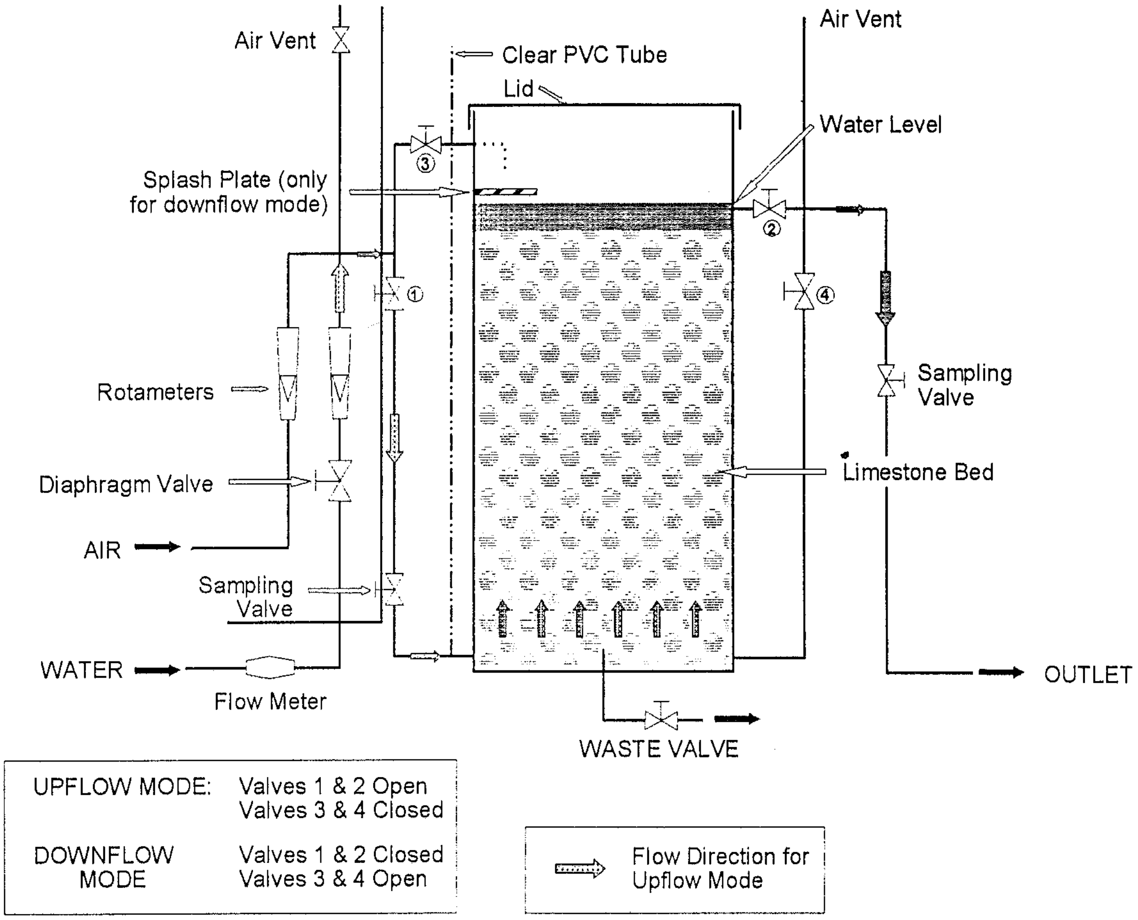


Figure 6-7 Preliminary "pressure-loss" pilot plant

6.4.3 Surface water pilot plant design

Pilot plants were designed, installed and operated. The pilot plant's only function was stabilisation via contact with limestone. Preliminary "pressure-loss" pilot plants were used to gather initial design data. A pressure vessel pilot plant was installed for long term test work. Relevant information relating into the design, operation and observations for both of these are given below.

Preliminary "pressure-loss" pilot plants

A preliminary pilot plant was constructed such that it could be used to evaluate flow and retention data from tests on surface waters. The unit was capable of treating between

10 and 120 m^3/day, with retention time varying between 2 and 30 minutes.

Basic design details
A diagram of the test unit is shown in **Figure 6-7**. The unit was constructed out of clear PVC of 6 mm wall thickness. The inner diameter was 600 mm, the total height was 2000 mm and the limestone bed height was 1600 mm. This gave limestone bed volume of 0.452 m^3 with a void volume of 0.204 m^3. The unit was designed such that it could operate in **two modes**, namely upflow and downflow. A facility for backwashing for water and air was provided. A dual distribution and abstraction manifold was located in the bottom, acting in abstraction mode for downflow, and distribution mode for upflow.

Raw water quality
Raw water quality for the three waters is shown in **Table 6-4.**

Table 6-4 Raw water quality for three surface waters

		White Water	Lightly Coloured Brown Water	Brown Water
Calcium	mg/ℓ as $CaCO_3$	2.8	1	5.3
Alkalinity	mg/ℓ as $CaCO_3$	8.6	2.5	2.3
pH		6.9	6.1	4.3
CCDP	mg/ℓ as $CaCO_3$	11.6	14.3	443
Conductivity	mS/m	5.7	2.9	8.4
Iron	mg/ℓ	0.1	<0.05	2
Colour	mg/ℓ as Pt	3-10	10-30	700-1000

Sampling
Flow rate measurements and pH (field) readings were taken on site. Analyses for iron, pH (laboratory), calcium, Alkalinity and conductivity were performed at the CSIR analytical laboratory, Stellenbosch, on samples taken at the appropriate times.

Limestone source and sizing
Limestone used was the Bredasdorp limestone with particle size -15 mm +12 mm. (This size had been shown to be most practical for transportation purposes, with smaller particle size distributions breaking down to fines and being difficult to handle).

Operation of unit
Following the initial flushing of the unit to remove limestone fines, a number of initial orientation runs were carried out to familiarise the operators with the apparatus and to establish a standard test procedure. The unit was run at various flow rates to provide limestone bed retention times of between one and 20 minutes.

At the initial test site, comparative tests were done with the limestone column operating in upward and downflow mode.

Units were run for a period of between eight and twelve months on respective sites.

Results
Typical results for each of the three water types considered, and for various retention times, are shown in **Figure 6-8** to **Figure 6-11**.

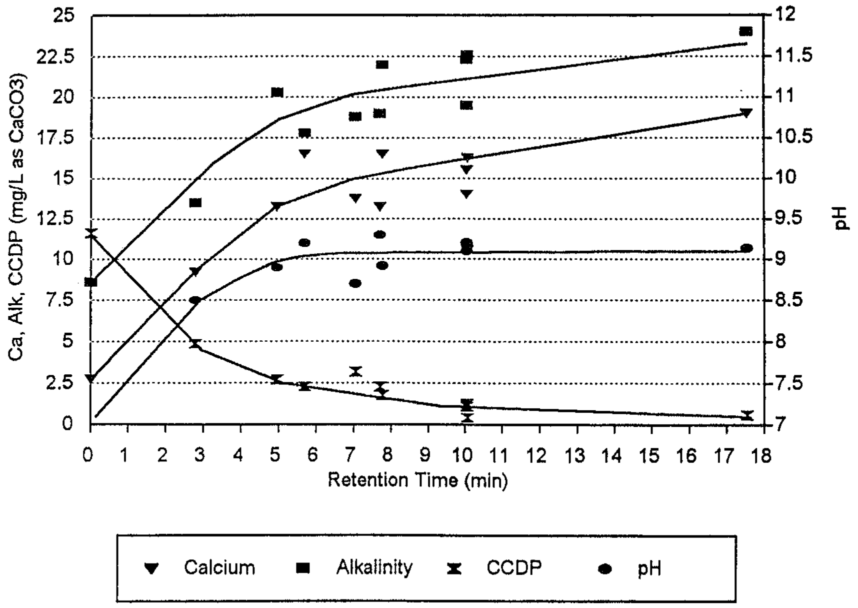


Figure 6-8 White water - increase in pH, calcium and Alkalinity, reduction in CCDP

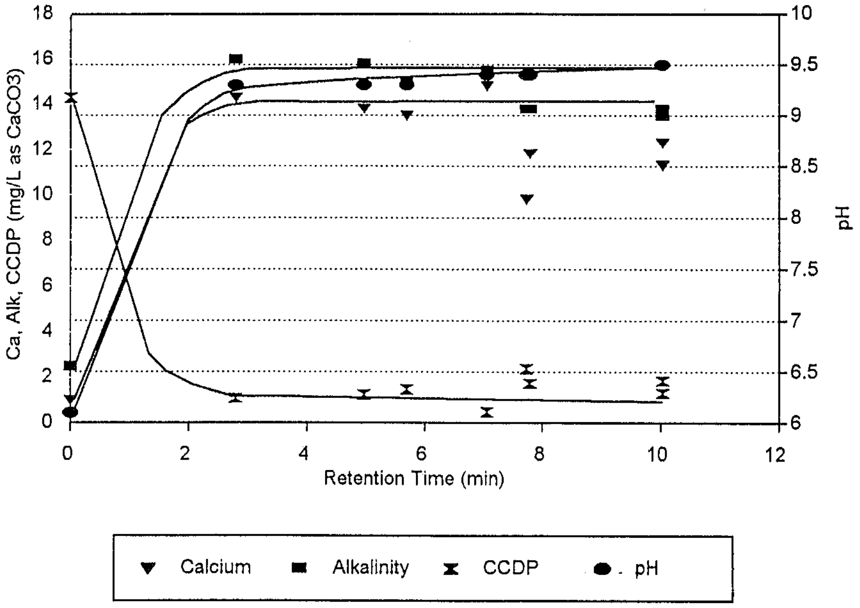


Figure 6-9 Lightly coloured brown water - increase in pH, calcium and Alkalinity, reduction in CCDP

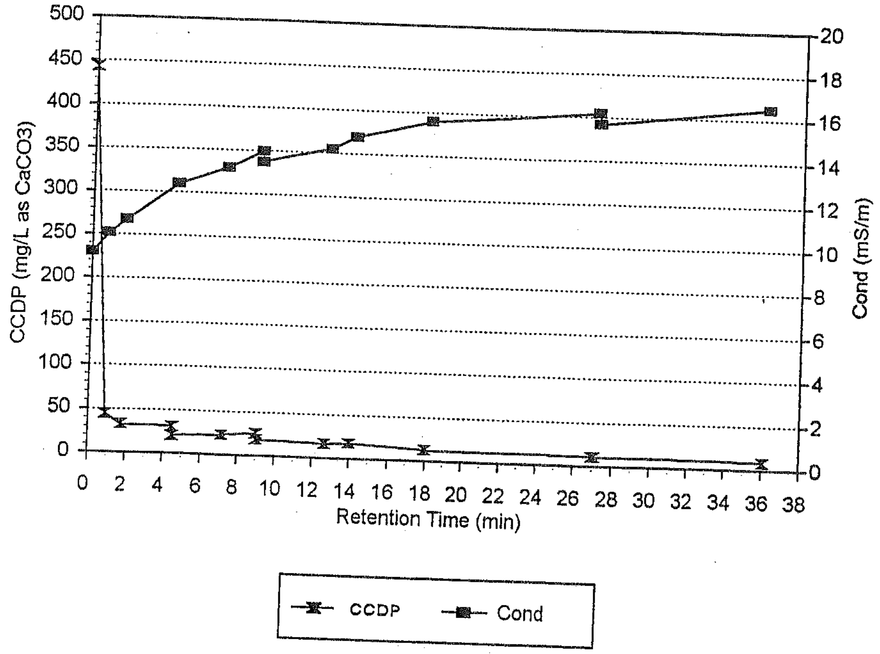


Figure 6-10 Brown water - reduction in CCDP

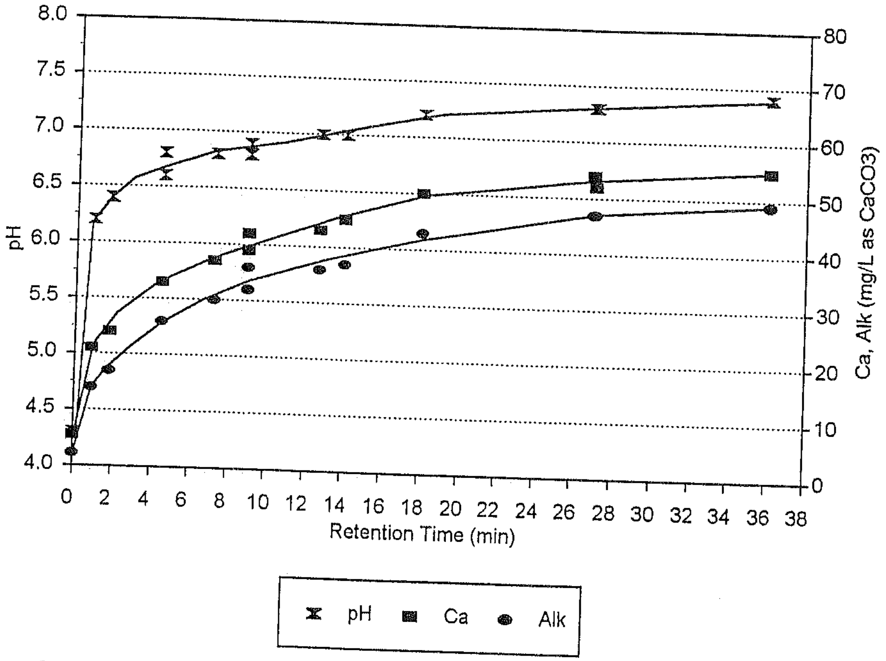


Figure 6-11 Brown water - increase in pH, calcium & Alkalinity

Generalised observations are as follows:

- It was found in initial trials that the unit operated better in an upflow mode in terms of flow distribution and blockage prevention. In the downflow mode the unit was observed to suffer far more rapid increase in head loss with time. Thereafter all tests were conducted in an upflow mode.
- The process readily stabilises soft, acidic white waters achieving, e.g., a reduction in CCDP from 11.6 to 0.9 mg/ℓ as $CaCO_3$ (92.2 %) , and an increase in pH from 6.9 to 9.2 with a ten minute contact time.
- The process stabilises soft, acidic lightly coloured brown waters achieving, e.g., a reduction in CCDP from 14 to 2 mg/ℓ as $CaCO_3$ (85.7 %), and an increase in pH from

6.1 to 9.4 with a ten minute contact time.

- The process stabilises soft, acidic highly coloured brown waters achieving, e.g., a reduction in CCDP from 75 to 3 mg/ℓ as $CaCO_3$ (96 %), and increase in pH from 5.5 to 7.6 with a ten minute contact time.
- In the presence of colour, iron was not removed by the system.

Practical considerations and observations with the system and tests were identified as:

- With highly coloured brown waters it was observed that, with time, significant levels of dissolved organic matter came out of solution, coating the surface of the limestone pebbles and blocking the bed. This was problematic in terms of both reduced reaction rates and flow.
- The system is prone to blockage by floating debris and algae. Waters containing suspended matter require filtration prior to stabilisation.
- The unit should be closed to light, to prevent growth of micro-organisms and algae.

"Presstab" unit

A pressure stabilisation long term field unit was installed on-site at a farm near Paradyskloof, Stellenbosch. This unit treats a lightly coloured water, containing about 0.15 mg/ℓ iron. The unit has been colloquially referred to as a "Presstab" unit. The unit was installed in January 1996.

Raw water quality

The unit was run on mountain catchment stream water which had passed through a "strainer" with 1.1 mm apertures. Raw water and post-stabilisation water quality is as shown in **Table 6-5**.

Table 6-5 Pressure stabilisation unit - raw and post stabilised water quality

Determinant		May		August		October	
		Raw	Post Stab	Raw	Post Stab	Raw	Post Stab
Alkalinity	mg/ℓ as $CaCO_3$	1	14.8	1.3	26	0.5	13.8
Calcium	mg/ℓ as $CaCO_3$	0.6	7.1	0.4	9.3	0.4	6.4
CCDP	mg/ℓ as $CaCO_3$	129	2.2	134	0.9	159	4.21
TDS	mg/ℓ	42	55	41	67	39	47
pH		4.8	9	4.8	8.8	4.7	8
Iron	mg/ℓ	0.19	0.19	0.18	0.29	<0.05	<0.05

Design details

The configuration of the "Presstab" unit is shown in **Figure 6-12.**

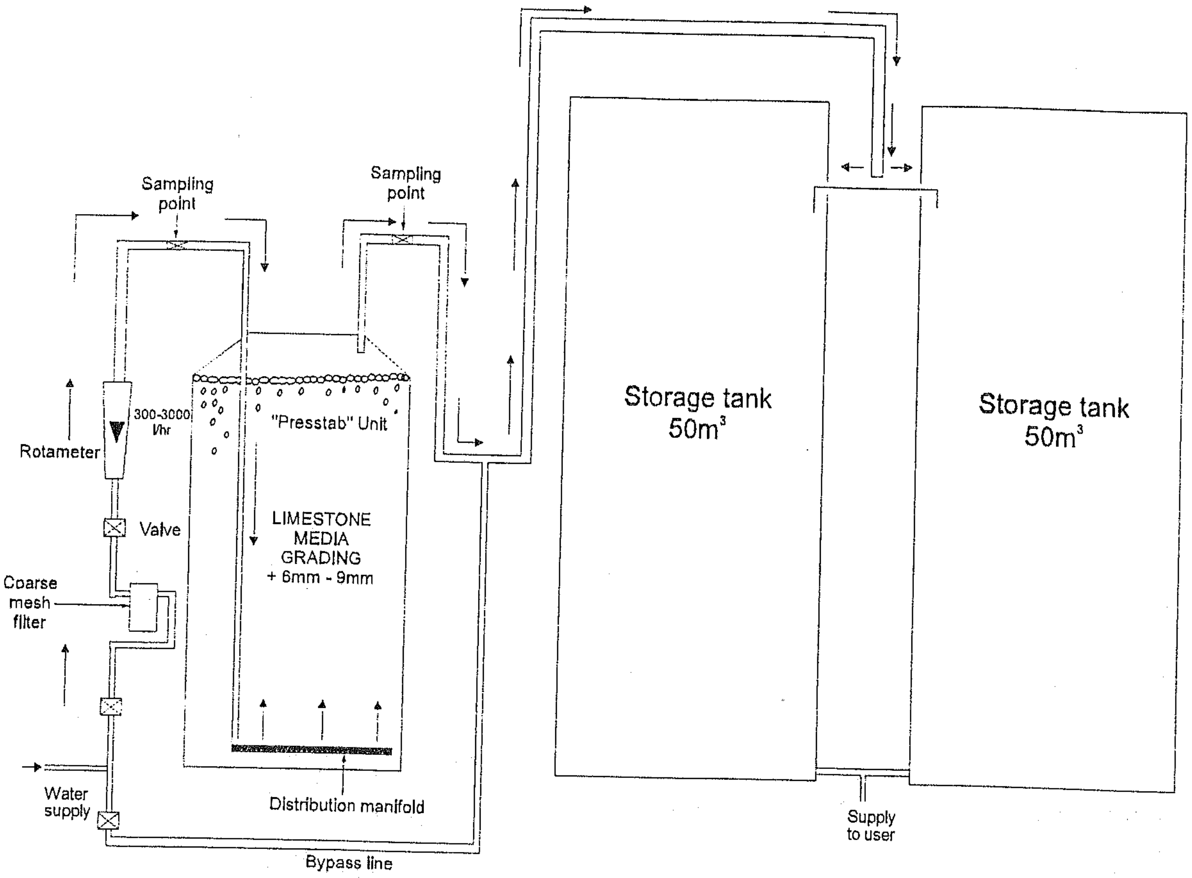


Figure 6-12 Configuration of "Presstab" unit

The stabilised water is fed into two 50 m^3 fibreglass storage tanks, providing a system pressure of about 0.8 bar on the outlet end of the "Presstab". The limestone contact unit is an adapted glass fibre filter (commercially available). General specifications for the completed unit are as follows:

Diameter:	700 mm
Wall thickness:	± 9 mm
Overall height:	1275 mm
Limestone bed depth:	1100 mm
Limestone material:	-12 mm +9 mm Bredasdorp limestone
Total limestone bed volume:	0.383 m^3
Mean void ratio:	45 %
Total void volume:	0.173 m^3
Total filter area:	0.342 m^2
Distribution manifold:	Slotted nozzle fingers

All inlet/outlet fittings:	2" BSP
Max rate:	3.02 m^3/h
Retention time at max rate:	10 minutes
Feed Rotameter:	300 to 3000 ℓ/h clear plastic unit
Feed Control valve:	25 mm PVC diaphragm valve
Other valves:	50 mm PVC ball valves
Feed and product piping:	25 mm PVC Class 9

Sampling
Flow rate measurements and pH (field) were taken on site. Analyses for iron, calcium, Alkalinity and conductivity and checks on pH (laboratory) were performed at the CSIR analytical laboratory, Stellenbosch, on samples taken at the appropriate times.

Operation of "Presstab" unit
Following the installation and commissioning of the unit, the unit was left to run at a retention time of about ten minutes for a week. It is important to note that this is a functional water treatment unit, and its purpose is to test the system with regard to long term application. Hence, flow rate/retention time variations are limited to those inherent in the water supply system. Thereafter, site visits were carried out at three monthly intervals during which:

- A general inspection was carried out for leaks, etc and to ensure that everything was functional.
- Sample collection was carried out.
- The limestone bed was inspected for discolouration and topping up requirements
- The system was flushed.

Results and practical observations
Typical results are shown in **Table 6-5**. The results obtained show inter alia:

- Operating at an average retention time of 10 minutes, the "Presstab" unit proved to be highly effective. In both of the first two site visits CCDP was reduced from about 130 to about 1 mg/ℓ as $CaCO_3$, and pH increased from about 4.8 to about 8.9.
- The low levels of iron passed through the system with no reduction in iron level occurring.
- On the third site visit it was noted that stabilisation efficiency was reduced, with pH increase to 8.0 and CCDP decrease from 160 to about 4 mg/ℓ as $CaCO_3$. Further investigation showed that this decreased stabilisation efficiency was, to some extent, linked to a lowering of the limestone bed, which resulted in a reduced retention time of about 6 minutes only.

Practical observations
With a lightly coloured brown water such as this, the "Presstab" units requires very little attention. Service requirements are minimal and can be summarised as follows:

- Flushing should be carried out on a weekly basis.
- The coarse mesh filter should be cleaned on a weekly basis.

- The limestone bed should be topped up on a monthly basis.
- The flowmeter should be cleaned on a monthly basis.

6.5 Summary and Conclusions

The following conclusions were made:

With regard to the groundwater treatment system:

- A small user system for the treatment of soft, acidic groundwaters needs to combine the treatment processes of aeration, stabilisation and filtration in a compact, robust, low maintenance manner.

- The groundwater was shown to stabilise more efficiently in a "cascade" mode of contact with the limestone.

- The "Spraystab" unit was shown to be highly effective at treating groundwater in an effective manner, being able to both stabilise and remove iron from the water. With regards to water with no iron present it was shown that a retention time of as little as 3 minutes was sufficient to achieve satisfactory reduction of CCDP. With regards to water with dissolved iron levels of around 2 mg/ℓ it was shown that a retention time of 5 minutes was sufficient to achieve satisfactory reduction of CCDP and iron.

- The "Spraystab" unit was also shown to be inexpensive to build and operate, compact, robust, requiring minimal operator attention and/or maintenance.

- The Bredasdorp limestone of particle size -15 mm +12 mm was found to be both practically suitable and effective as a stabilisation media.

- Further investigation is required into:

  (i) water with higher dissolved iron levels, to identify the ceiling level for the "Spraystab" system.

  (ii) scaling up of the unit to treat greater volumes of water.

  (iii) commercial production of the system so that it is available as an "off the shelf item".

With regard to the surface water treatment system:

- A small user system for the treatment of soft, acidic surface waters should preferably be a pressure system, so that pressure head from the water source can be maintained and the need for an additional pump, as would be necessitated by a "pressure-loss" system, negated.

- A stabilisation system is not expected to be an "all in one" treatment system, and where high turbidity, algae, etc. are present, pre-treatment is required. Furthermore, the stabilisation unit must be closed to light to prevent growth of algae.

- Tests on waters ranging from "white" water to highly coloured "brown" water, and a range of dissolved iron levels between 0 and 2 mg/ℓ, showed the upflow fixed bed limestone stabilisation process to be effective with a contact time of about ten minutes.

- With highly coloured brown waters, a significant organic "coating" of the limestone pebbles occurred with time. This coating had a deleterious effect on stabilisation efficiency.

- The "Presstab" unit was shown to be highly effective in stabilising a lightly coloured brown water. The process was also shown to be inexpensive to build and operate, compact, robust, requiring minimal operator attention and/or maintenance.

- Further investigation is required into:

  (i) long terms tests of a broader range of coloured waters to identify the colour level at which DOM coating of the limestone becomes problematic.

  (ii) means of dealing with highly coloured brown waters.

  (iii) commercial production of the "Presstab" system so that it is available as an "off the shelf item".

CHAPTER 7

FLUIDISED BED STUDIES

7.1 Introduction

The small user stabilisation systems described in Chapter 6 were developed to provide low cost, robust and reliable stabilisation for water volumes of around 50 m^3/day. For larger water users, (> 1 000 m^3/day), conventional stabilisation, e.g. by means of lime and CO_2 dosage, is generally being practised. Potential operating cost savings as a result of the significantly lower cost of limestone compared to lime and potentially lower maintenance and operation costs provided incentive to investigate the feasibility of replacing conventional water stabilisation with limestone mediated stabilisation at works treating large volumes of water.

For limestone mediated stabilisation for such larger water users, an increased calcium carbonate dissolution rate is required in order to minimise the required limestone contact time, and hence to avoid the need for very large contactor volumes. Use of a fluidised limestone bed appeared to be an attractive means of increasing dissolution rates, and is a CSIR patented process (Mackintosh and De Villiers, 1995). The feasibility of stabilising large volumes of water by means of a fluidised limestone bed was therefore assessed.

In order to design a fluidised bed stabilisation plant, a theoretical approach had to be developed to determine the design parameters. A literature survey was conducted to identify suitable mathematical equations to model the fluidising process. Furthermore, the theory had to be validated by experimental data gathered from a fluidised limestone bed pilot plant. Two different aggressive raw waters were assessed, namely Stellenbosch water and a simulated RO permeate. The results of these tests were used to derive design parameters for a preliminary design of a 10 Mℓ/d stabilisation unit. Finally, a comparative study was carried out on chemical and energy running costs of the fluidised bed system versus that of the lime and carbon dioxide dosing system.

7.2 Pilot Plant Description

7.2.1 Layout

A pilot plant was constructed to test the fluidised bed process and to establish design parameters. The plant consisted of two vertical columns designed to fluidise two beds of limestone particles. A schematic representation of the pilot plant is given in **Figure 7-1**. A description of the components of the plant is given below.

A distribution plate was fitted at the bottom of each column. The function of the distribution plates was to support the limestone beds, and to ensure an evenly distributed flow through the beds. Sampling ports were spaced at 150 mm intervals along each cylinder. The plant was served by one feed pump and two recirculation pumps, one for each column. The recirculation circuits were used to regulate the flow rate through the beds, in order to achieve different percentages of bed expansion. The raw feed was pumped by the feed pump into the recirculation circuit of Column 1. A diagonal gravity pipe fed water from the top of Column 1 into the bottom part of Column 2. Flow rates in the recirculation circuits and the feed line were measured by four rotameters. The raw feed was supplied from two storage tanks (not shown in diagram).

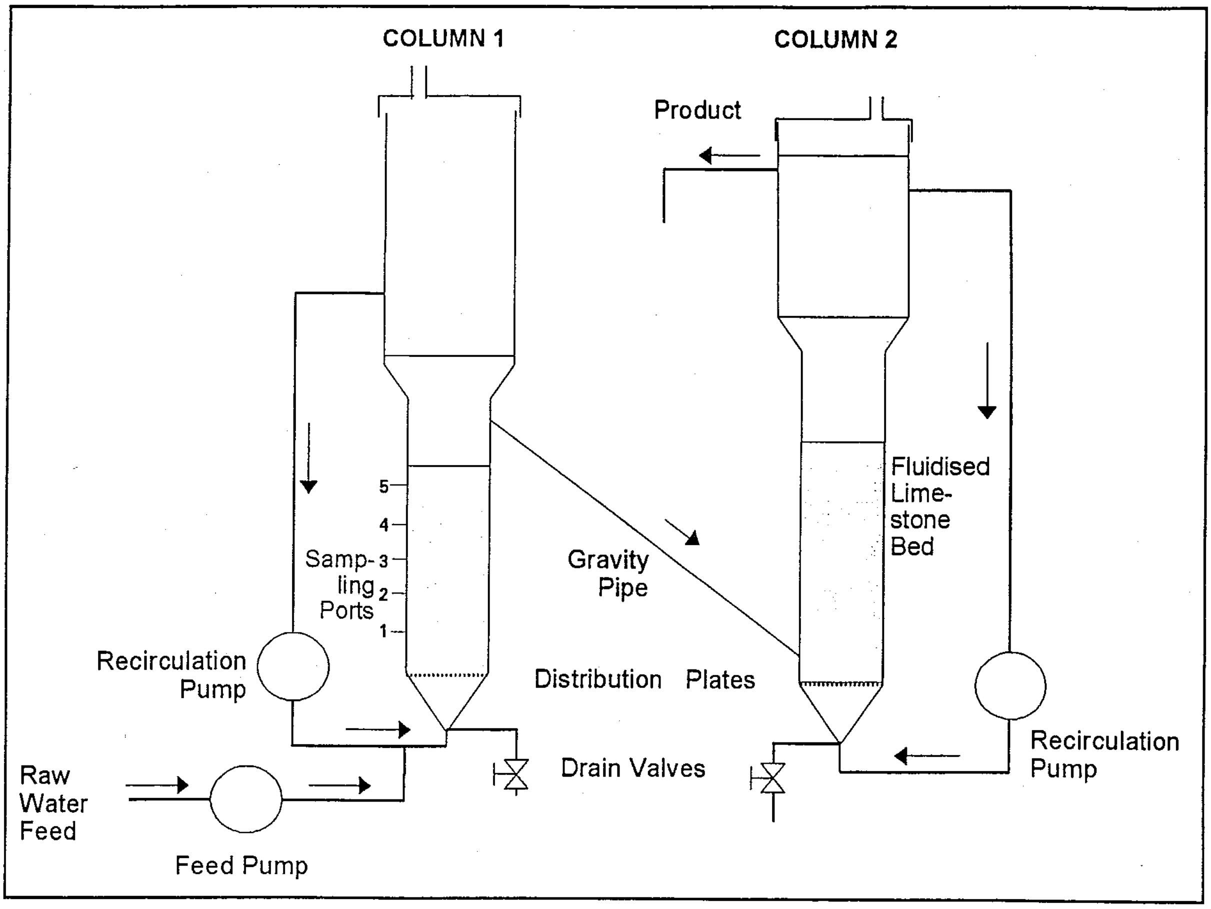


Figure 7-1 Diagram of fluidised bed pilot plant

7.2.2 Design and operating conditions

Particle size distribution

The pilot plant was designed to suspend two fluidised beds with the following size ranges:

Table 7-1 Theoretical size distribution

	Column 1	Column 2
Fluidised Particles - Diameters (mm) smaller than:	5.3	1.7
Flushed Particles - Diameters (mm) smaller than:	1.7	0.7

It was evident from literature that the optimum voidage ratio (porosity) for maximum calcium carbonate dissolution rate would be ± 0.7 (Section 7.3.4). The relationship between expanded porosity and percentage bed expansion is given by **Equation (7-8)**. The optimum percentage bed expansions for the abovementioned coarse and finer grades of limestone particles was determined by calculation, namely ± 30 % for Column 1, and ± 40 % for Column 2. The respective recirculation rates were chosen such that particles with sizes larger than the upper size limit were fluidised, and particles with sizes smaller than the lower size limit were flushed. The required recirculation rates were determined experimentally, but were also compared with theoretically determined rates (Sections 7.3.1 and 7.3.2). Note that recirculation rate in this report refers to the total flow rate at which water approaches the limestone beds in the respective columns.

The two columns of the fluidised bed pilot plant were filled with crushed and graded Bredasdorp limestone. The first column was filled with a relatively coarse grade (-6.7 mm +4.75 mm), and the second column with a finer grade (-1.7 mm +1.0 mm). Particles smaller than 1.7 mm will automatically flush from Column 1 into Column 2 during operation, therefore it was not necessary to top up Column 2. The distribution of particles sizes in the two columns was maintained more or less as indicated in **Table 7-1**. The only deviation from the theoretical size distribution was in Column 1, which contained a percentage of unfluidised particles with diameters of up to 6.7 mm, because the column was regularly topped up with coarse grade limestone. The actual particle sizes in the two columns were therefore approximately within the ranges indicated in **Table 7-2.**

Retention time

The amount of stabilisation achievable at different retention times was determined. The retention times in the two columns were varied by varying the raw feed rate. Note that the recirculation rates through the columns did not affect the retention times. Retention time was only affected by the raw feed rate. The recirculation rates could therefore be controlled in such a way that the optimum bed expansion could be maintained during all the tests.

Table 7-2 gives a summary of the operational parameters that were maintained during the tests.

Table 7-2: Operational characteristics of fluidised bed pilot plant

	Column 1	**Column 2**
Limestone Grade	- 6.7 mm + 4.75 mm	-1.7 mm + 1.0 mm
Fixed Bed Height ℓ_o (m)	0.500	0.635
Fixed Bed Porosity p_0	0.613	0.505
Bed Expansion Percentage	30	40
Recirculation Rate F (ℓ/h)	11 500	4 400
Column Diameter D (m)	0.234	0.212
Velocity at expansion v_e (m/s)	0.0743	0.0346
Expanded Bed Porosity p_e	0.702	0.646
Expanded Bed Height ℓ_e (m)	0.650	0.889

Geometry of Column 2

From the schematic diagram of the pilot plant (**Figure 7-1**) can be seen that the cross-sectional area of Column 2 widens above the fluidised limestone bed - a lower velocity was therefore maintained in this section. The outlet from the column was positioned above the widened region. The column had been designed like this to keep fine particles flushed from the second limestone bed in suspension. This ensured that only the very fine particles left the plant with the product stream. The amount of fine particles suspended in the wider section increased as the trials progressed. A sample was taken from this section, after the fluidised bed had been running on Stellenbosch water for a period of approximately 10 days. After drying and acid treatment of the filtered residue, the calcium content of the fines was determined as 78.2 mg Ca (as $CaCO_3$)/100 mg residue. Comparing this with the calcium content of "fresh" unused Bredasdorp limestone, namely 91.3 mg Ca (as

$CaCO_3$)/100 mg, it was evident that the suspended particles contained a lower percentage of calcium carbonate, and higher percentage of insolubles (mainly silica).

7.3 Characteristics of Particle Motion in a Fluidised Bed

In order to design a fluidised bed, a theoretical approach had to be developed to determine design parameters. Furthermore, the theory had be validated by experimental data gathered from the pilot plant. A literature survey (Scharfetter and Frehse, 1993; Schutte, 1994) was conducted to identify suitable mathematical equations to model the fluidising process.

Fluidised bed technology was found to be widely researched. Unfortunately, the majority of the work reported in literature was directed at gas-solid fluidisation. For the purpose of this study, only liquid-solid fluidisation was considered. The work of a number of authors was studied, including Amirtharajah, 1972, Howard, 1989, and Cairns and Prausnitz, 1960. For the purpose of this report, only the conclusion of the unified theoretical basis from the literature survey is presented. This was used as the basis for the design of the experimental pilot plant, which in turn was used to determine the envisaged design parameters of an industrial-sized fluidised bed stabilisation plant.

Four basic parameters that are important in the design of fluidised beds (Scharfetter and Frehse, 1993) are:

- the *minimum fluidising velocity* - the minimum velocity at which the particles in a certain type of bed will be fluidised (Section 7.3.1),
- the *terminal, or flushing, velocity*, at which particles of a certain size will be flushed from a fluidised bed (Section 7.3.2),
- the relationship between the *percentage of bed expansion* and the velocity of the fluid (Section 7.3.3), and
- the *porosity* of the expanded bed (Section 7.3.4).

7.3.1 Minimum fluidising velocity

When the velocity with which a fluid approaches a bed of particles is gradually increased, a velocity will be reached at which the hydrodynamic shear between the particles and the fluid will start to lift the bed from its fixed position, i.e. fluidise the bed. This velocity is termed the minimum fluidising velocity.

The volumetric flow rates through the two columns of the fluidised bed pilot plant could be varied independently by means of throttling valves in the respective recirculation circuits. The flow rates through the respective columns, as well as their cross-sectional surface areas, determined the velocity at which water approached the two limestone beds. The bed approaching velocity was calculated as follows:

$$v = \frac{F}{A} \qquad \textbf{(7-1)}$$

where:

v	:	Approaching velocity	[m/s]
F	:	Volumetric flow rate	[m^3/s]
A	:	Cross-sectional area	[m^2]

The minimum fluidising velocity v_{mf} was determined from the modified Ergun equation (Howard, 1989):

$$\frac{\rho(\rho_f-\rho)gd^3}{\upsilon^2} = \frac{150(1-p_o)\rho v_{mf} d}{\phi^2 p_o^3 \upsilon} + \frac{1.75(\rho v_{mf} d)^2}{\phi p_o^3 \upsilon^2} \qquad \textbf{(7-2)}$$

where:

v_{mf}	:	minimum fluidising velocity	[m/s]
ρ	:	density of fluid (water)	[kg/m^3]
ρ_f	:	density of particles	[kg/m^3]
g	:	gravitational acceleration	[m/s^2]
d	:	diameter of particle	[m]
υ	:	dynamic viscosity	[kg/m.s]
p_o	:	voidage ratio or porosity of fixed bed	
ϕ	:	sphericity of particles	

This Ergun equation is backed up and checked by Amirtharajah's (Amirtharajah, 1972) equation:

$$v_{mf} = \frac{4.05\ d_{60}^{1.82}(SG-1)^{0.94}}{\upsilon^{0.88}} \qquad \textbf{(7-3)}$$

where:

d_{60}	:	60 % particle size	[m]
SG	:	specific gravity of particles	

7.3.2 Flushing velocity

The flushing velocity v_{flush} is the velocity at which particles of a certain size will be flushed from a fluidised bed (Howard, 1989; Kunii & Levenspiel, 1969), for *Reynolds numbers* ranging between 500 to 200 000 :

$$v_{flush} = \left(\frac{3.1\ g(\rho_f-\rho)d}{\rho}\right)^{0.5} \qquad \textbf{(7-4)}$$

where v_{flush} is the flushing velocity in [m/s].

The *Reynolds number* is calculated as follows:

$$Re = \frac{\rho v d_{60}}{\upsilon} \qquad \textbf{(7-5)}$$

where v is the bed approaching velocity in [m/s].

For large *Reynolds numbers* (turbulent flow conditions), v_{flush} in the above equations should be multiplied by a correction factor for non-spherical particles, η, where:

$$\eta = 5.31 - 4.88\phi \tag{7-6}$$

7.3.3 Bed expansion

At different fluid flow velocities greater than the *fluidising velocity* for a specific bed of particles, different levels of bed expansion will occur. To determine flow velocities for required percentages of bed expansion, Amirtharajah and Cleasby's method (Amirtharajah, 1972) may be used.

(i) Required expansion, ε is defined as:

$$\varepsilon = \frac{\ell_e}{\ell_o} \tag{7-7}$$

where ℓ_0 and ℓ_e are the heights (in m) of the fixed and expanded beds respectively.

The expanded bed's porosity p_e is calculated as follows:

$$p_e = 1 - \frac{\ell_o}{\ell_e} \cdot (1 - p_o) \tag{7-8}$$

where p_e is the voidage ratio or porosity of expanded bed.

(ii) The minimum fluidising velocity v_{mf} is determined by **Equation (7-2)** or **(7-3)**.

(iii) The *Reynolds number* at the minimum fluidising velocity Re_{mf} is calculated with **Equation (7-5)**, with v the minimum fluidising velocity (v_{mf}).

(iv) If $Re_{mf} > 10$, v_{mf} is corrected by multiplying with Kr, where:

$$Kr = 1.775\, Re_{mf}^{-0.272} \tag{7-9}$$

(v) The unhindered settling velocity of a particle, v_s, is calculated from:

$$v_s = 8.45\, v_{mf} \tag{7-10}$$

(vi) The *Reynolds number* at v_s, Re_s, is calculated with **Equation (7-5)**, with v the unhindered settling velocity v_s.

(vii) The expansion coefficient n is determined as follows:

$$n = 4.45\ Re_s^{-0.01} \tag{7-11}$$

(viii) The constant k in the following equation can now be found:

$$v_{mf} = k.p_o^n \tag{7-12}$$

(ix) An equation is now available for calculating the porosity of the expanded bed, and the velocity at the expansion, v_e :

$$v_e = k.p_e^n \tag{7-13}$$

7.3.4 *Porosity of expanded bed*

Another aspect which is important for modelling a fluidised bed is the matter of the bed porosity and the way it changes with expansion of the bed. Fluctuating fluid and particle velocities are at a maximum in the same voidage range as that in which the intensity of interparticle mixing is the greatest. This occurs at an expanded voidage (p_e) of ca. 0.7. Maximum hydrodynamic shear occurs at expanded porosities of about 0.7. Maximum interaction and movement of particles occur at expanded porosities of 0.70 to 0.72 (Cairns & Prausnitz, 1960). For a graded material, these expanded porosities occur at expansions of 30 to 40 %.

7.3.5 *Design parameters for a fluidised bed*

The following were identified as the main parameters that will affect the level of stabilisation in a fluidised bed reactor:

- the type of limestone used in the fluidised beds,
- the grades (particle sizes) of the limestone,
- the percentage of bed expansion, and
- the retention time in the fluidised beds.

Limestone type

In previous studies, a variety of available limestone sources were evaluated in terms of suitability for stabilisation. The two predominant requirements that would make a source suitable were:

- a high calcium carbonate purity, and
- a porous structure.

High calcium carbonate purity ensures that problems with insolubles are minimised. Intra-particle pores increase the reaction surface area, and hence the overall reaction rate. In previous fixed bed studies, crushed and graded limestone from the Bredasdorp source was found to be ideally suitable for stabilisation of drinking water, due to its high calcium carbonate purity, and its friable structure.

Limestone particle sizes

In previous calcium carbonate dissolution tests, higher dissolution rates were achieved by using smaller particle sizes. However, smaller particle sizes will result in a higher pressure drop over a fluidised bed, and hence higher energy costs. The driving force for calcium carbonate dissolution (i.e. the CCDP) of the aggressive raw water that enters Column 1 is high, therefore the dissolution rate in Column 1 will be relatively high, even with larger particle sizes. Water that enters Column 2 has already been stabilised to a large extent. In effect, Column 2 functions as a "polishing" unit, and was therefore designed for finer limestone particles.

Percentage bed expansion

When designing a fluidised bed for water stabilisation, reaction rates should be maximised by designing the bed for a fluidising velocity that will cause a percentage bed expansion at which the interaction between the particles and the fluid will be at a maximum. In the case of fluidised bed limestone stabilisation, the dissolution rate of calcium carbonate will be maximised.

Retention time

The only remaining significant design parameter for a fluidised bed is the retention time of the fluid (water) with the fluidised medium (limestone). The retention time in a cylindrical fluidised bed, at a specific feed rate, can be calculated from:

$$Ret\ time = \frac{150\ \pi d^2\ \ell\ (100\ p_o + z)}{F} \qquad \textbf{(7-14)}$$

where:

d	:	Column diameter	[m]
ℓ	:	Fixed bed height	[m]
F	:	Raw water feed rate	[ℓ/h]
p_o	:	Voidage ratio or porosity of fixed bed	
z	:	Bed expansion %	

7.4 Initial Tests

7.4.1 Background

It is important to make the right assumptions regarding reactor characteristics if a full-scale plant is to be designed. Hence, the objective of these initial tests was to investigate the plug-flow versus completely mixed-reactor characteristics of the fluidised bed reactors. These characteristics depend inter alia on the hydraulic characteristics of the fluidised bed, e.g. the amount of turbulence, as well as the recirculation ratio. In a cylindrical completely mixed reactor, the concentration of reaction products will be similar along the longitude of the reactor, whereas in a plug-flow reactor, concentrations will be higher at the outlet of the reactor. A well designed plug-flow reactor would be more efficient in terms of required reactor volume than a completely-mixed reactor.

The feed rate to the first column was set at 940 ℓ/h, and the recirculation rate set to achieve a bed expansion of 30 % (± 11 500 ℓ/h). After an hour, samples were taken from the five equally spaced sampling ports along the length of the column (see **Figure 7-1**). The samples were filtered immediately and then analysed.

7.4.2 Results of initial tests

The results from the analyses and STASOFT evaluations are presented in **Table 7-3**. Sample 1 was taken from the lowest, and Sample 5 from the highest sampling port.

Table 7-3 Results of analyses from sampling ports, Column 1

Sample	Temperature oC	pH	Alkalinity mg/ℓ as $CaCO_3$	Acidity mg/ℓ as $CaCO_3$	Calcium mg/ℓ as $CaCO_3$	Conductivity mS/m	CCDP mg/ℓ as $CaCO_3$
Raw Water Feed (at 940 ℓ/h)							
Feed	14	4.68	0.5	228.31	2	4.38	177
Samples From Ports - Column 1							
1	17	8.99	22	19.71	19	7.58	1.1
2	17	9.01	24	21.44	19	7.92	0.8
3	17	8.98	21	18.84	20	7.75	1.1
4	17	8.75	12	11.16	16	7.42	3.4
5	17	8.59	12	11.49	14	7.09	4
Product - Top of Column 1							
Product	15	8.77	17	16.01	16	7.51	2.8

From the results it was evident that the $CaCO_3$ content was higher at the bottom of the bed, in contrast to the expected situation in an up-flow plug-flow reactor, where the water at the top of the reactor should have had the most time to react with the fluidised medium.

A test was also carried out to determine whether there was a significant difference between the amount of stabilisation before and after the widened region of Column 2, which contained very fine suspended particles. During two different runs, at raw water feed rates of 1 000 and 2 000 ℓ/h respectively, water samples were taken at the bottom, and above the region of fine suspended particles. From the results shown in **Table 7-4** below, it was evident that the water characteristics did not differ significantly below and above the region, if related to the initial CCDP in the feed of 177 mg/ℓ as $CaCO_3$.

Table 7-4: Effect of bed of fine suspended solids

Sample	Temperature oC	pH	Alkalinity mg/ℓ as $CaCO_3$	Acidity mg/ℓ as $CaCO_3$	Calcium mg/ℓ as $CaCO_3$	Conductivity mS/m	CCDP mg/ℓ as $CaCO_3$
FLOWRATE: 1 000 ℓ/h							
Bottom of Region	14	9.45	21	15.78	13	6.13	0.1
Above Region	14	9.48	18	13.05	12	6.33	0.8
FLOWRATE: 2 000 ℓ/h							
Bottom of Region	14	9.45	20	14.96	12	6.20	0.6
Above Region	14	9.40	16	12.10	11	6.52	1.9

7.4.3 Conclusions

It was concluded that the difference between stabilisation levels (as measured by the CCDP) at the bottom and the top of the columns was insignificant, if compared to the original CCDP of the raw water feed (177 mg/ℓ as $CaCO_3$). For practical design purposes, therefore, the experimental fluidised beds were regarded as completely-mixed reactors.

From the tests on samples below and above the widened region in Column 2, it was concluded that the fine limestone particles suspended in this region did not significantly contribute to the stabilisation of the water, and was therefore not very important for the gathering of information for a cost assessment of a full-scale unit.

7.5 Fluidised Bed Stabilisation Tests

7.5.1 Objective

The objective of these tests was to assess the suitability of the fluidised bed process for the stabilisation of aggressive waters. Experimental determination of retention time and chemical dosing requirements would allow consideration of design parameters for full-sized fluidised beds, and a cost comparison between stabilisation with a fluidised bed and conventional methods.

7.5.2 Characteristics of raw waters

Pilot plant tests were carried out on two basic raw waters types, namely:

- Stellenbosch water, and
- Simulated reverse osmosis permeate (two different batches).

The purpose of using these waters was to assess the efficiency of the fluidised bed process to stabilise two common types of soft, acidic water, namely (i), a typical soft, acidic Cape water, with naturally low pH, Alkalinity, calcium and buffer capacity, and (ii), a reverse osmosis (RO) permeate with low pH, Alkalinity and calcium, but higher buffer capacity.

The simulation of RO permeate was achieved by dosing alkali and acid to Stellenbosch water, a single batch being sufficient for a complete run. The findings relating to two representative batches (Batch #1 and Batch #2) are reported here. Analyses of the feed waters are shown in **Table 7-5**.

Stellenbosch water

At the time of testing, the Stellenbosch water was a typical soft, acidic mountain catchment water. Average quality included pH of ± 5, Alkalinity and calcium of ± 1 mg/ℓ as $CaCO_3$ and a CCDP of about 50 mg/ℓ as $CaCO_3$.

Simulated RO permeate

Batches of simulated RO permeate were prepared to determine the feasibility of the process for the treatment of a typical permeate produced by a reverse osmosis plant (RO permeate). The simulated RO permeate had a CCDP similar to that of the Stellenbosch water, but a higher Alkalinity, Acidity and buffer capacity.

Batches of simulated RO permeate were prepared in two feed tanks (2 500 ℓ and 5 000 ℓ tanks). These tanks were initially filled up with Stellenbosch water. The simulated RO permeate was prepared by adding soda ash (Na_2CO_3) to the water to raise the Alkalinity to approximately 10 mg/ℓ as $CaCO_3$. The water was constantly circulated to ensure proper mixing. The pH was adjusted to approximately 5.8 by adding hydrochloric acid (HCℓ).

Note: In an actual RO permeate, high Acidity would exist as a result of high dissolved CO_2, whilst in the simulated RO permeate, high Acidity was attained by adding a mineral acid.

Analyses of the different raw feeds used are shown in **Table 7-5**.

Table 7-5 Analyses of different raw feeds

Determinant		Typical Stellenbosch Water	Simulated RO permeate	
			Batch #1	Batch #2
pH		5.13	5.61	5.96
Alkalinity	mg/ℓ as $CaCO_3$	1	5	9
Acidity	mg/ℓ as $CaCO_3$	54	69	60
Calcium	mg/ℓ as $CaCO_3$	1	2	2
Temperature	°C	15	14	13
Conductivity	mS/m	4.02	16	23
CCDP	mg/ℓ as $CaCO_3$	52.6	62.8	50.9

7.5.3 *Experimental procedure*

Raw feed rates were varied between 100 ℓ/h and 4 000 ℓ/h. Each test was run for a period of at least three times the total retention time before the following samples were taken:

- the raw water (feed) (sampled from the feed tank),
- the product from Column 1 (from a sampling port at the top of Column 1), and
- the final product from Column 2 (sampled at the outlet of the pipe from the top of Column 2).

During each test run, analyses for the following determinants were carried out:

- pH
- Electrical Conductivity
- Alkalinity
- Calcium concentration
- Temperature.

Samples taken from the fluidised beds were filtered before analysis, using Whatman 1 filterpaper, to remove suspended limestone fines. The raw water was sampled each time the products from Column 1 and 2 were sampled. This was done to ensure that the trends detected from the final water analyses were indeed the result of stabilisation by the plant, and not a result of changes in the quality of the raw feed to the plant. The retention times were calculated from the raw feed rates using **Equation (7-14)**. The analyses of the raw water and the final water were plotted against retention time.

The measured calcium carbonate dissolution rates were also plotted against the various reactor loading rates. The reactor loading rate (in m/h) was calculated as the raw feed rate over the cross-sectional area of the bed (loading rate and retention time are inversely proportional). The measured dissolution rates were compared with rates calculated with the diffusion controlled rate equation developed in Chapter 5. The compound rate constant used in this rate equation, $k_{D.C.\ compound}$, was determined from the following equation, formulated in Chapter 5 from experimentally obtained data:

$$K_{D.C.} = \frac{0.0021}{d}.LR + 0.0044 \qquad \textbf{(7-15)}$$

where $K_{D.C}$ = compound rate constant for a diffusion controlled reaction, which varies with temperature, ionic strength, physico-chemical properties of the mineral and hydraulic characteristics (flow rate) and includes a surface area term [s^{-1}]
d = particle diameter [mm]
LR = reactor loading rate in [m/h]

Note: This equation was established for particles diameters ranging between 3.55 and 8.05 mm. Extrapolation outside this range should not be attempted.

The reaction kinetics tests (Chapter 5) were conducted on fairly narrowly graded (single sized) limestone particles, whereas the limestone used in the pilot studies fell within a wider range of particle sizes. For the purpose of comparing the experimentally determined reaction rates with the theoretical rates, a nominal particle diameter was used, namely the mean of the maximum and minimum particle diameters in Column 1, namely 5.7 mm.

Using **Equation (7-15)**, the expected compound rate constants and reaction rates for the smaller particles in Column 2 were also calculated, using data from the Batch #1, Simulated RO permeate run. **Equation (7-15)** did not adequately predict the compound rate constant for the smaller particles in Column 2. This was to be expected, because the relationship between compound rate constant and particle diameter had been determined experimentally for particle sizes ranging between 3.55 and 8.05 mm. This relationship could therefore not be expected to be valid for the small particles in Column 2 (diameters ranging between 1.0 and 1.7 mm). **Equation (7-16)** was therefore formulated from the calcium dissolution data obtained from the pilot plant tests, for particle diameters in the 1.0 to 1.7 mm range:

$$K_{D.C.} = \frac{0.0004185}{d}.LR + 0.00291 \qquad \textbf{(7-16)}$$

For comparison purposes, reaction rates and compound rate constants were determined from **Equation (7-15)** and **(7-16)**, and plotted against the reactor loading rates, on the same axes as the experimentally determined rates and constants (see next section). A nominal particle diameter of 1.35 mm was assumed for Column 2 (mean of estimated maximum and minimum diameters).

7.5.4 Results of retention time runs

The results of the runs at various retention times, with the two waters, (Stellenbosch water and two batches of Simulated RO permeate), are presented in this section. For each water, the following data are presented graphically in **Figure 7-2** to **Figure 7-21** (pp 14 to 17):

- *Raw feed quality*
  This shows variation in the determinants of aggressiveness of the raw feeds at the various total retention times (total time in both Column 1 and 2).
- *Final water quality*
  The pH, Alkalinity and calcium of the final water are shown at the different total retention times.
- *CCDP from Column 1*
- *CCDP from Column 2*
- *Calcium carbonate dissolution rate*
  These graphs show the rate of calcium carbonate dissolution in Column 1, at the various reactor loading rates.
- *Compound rate constant*
  These graphs show the experimentally determined compound rate constants for a diffusion controlled reaction, at the various reaction loading rates, and also the constant determined from theoretical considerations (using inter alia **Equation (7-15)** and **(7-16)**).

Stellenbosch Water

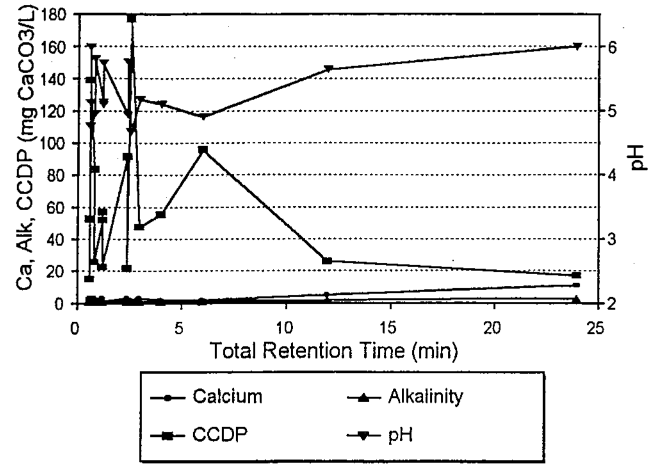


Figure 7-2: Raw feed quality

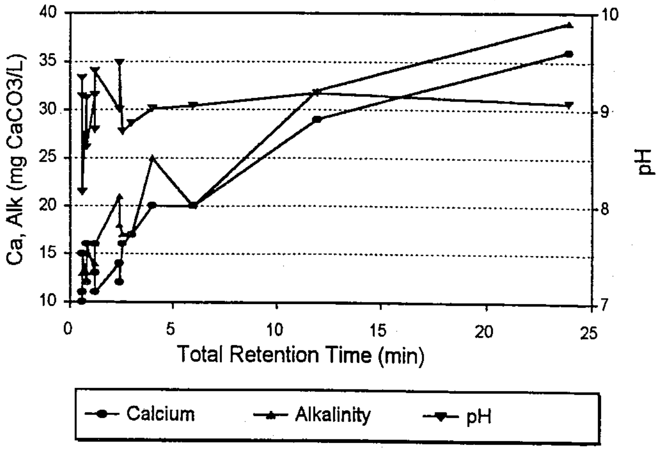


Figure 7-3: Final water quality

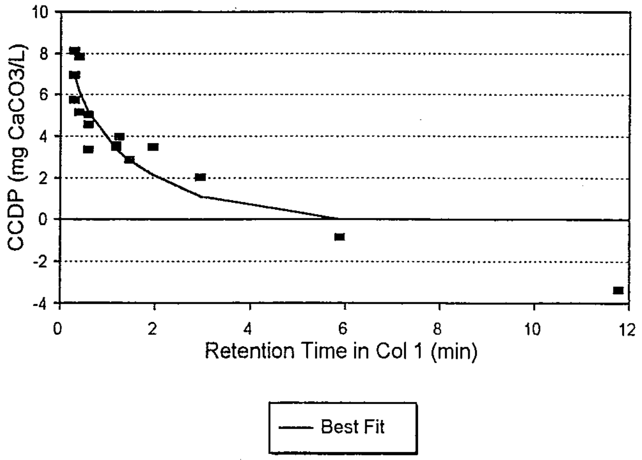


Figure 7-4: CCDP from Column 1

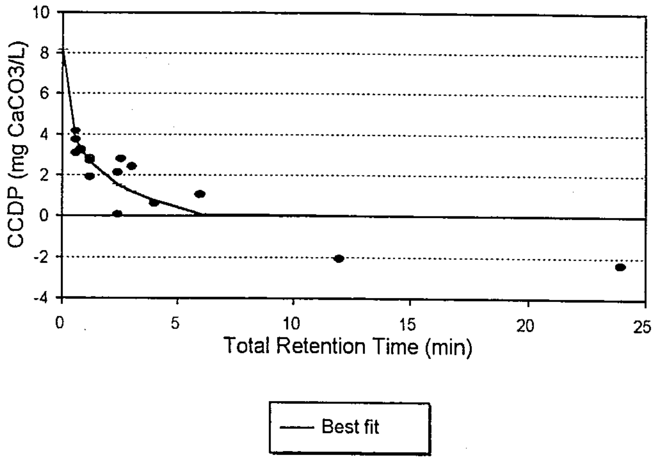


Figure 7-5: CCDP from Column 2

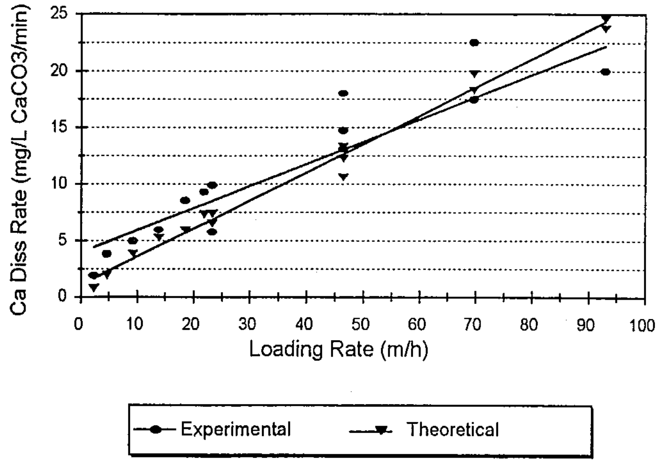


Figure 7-6: Calcium carbonate dissolution rate

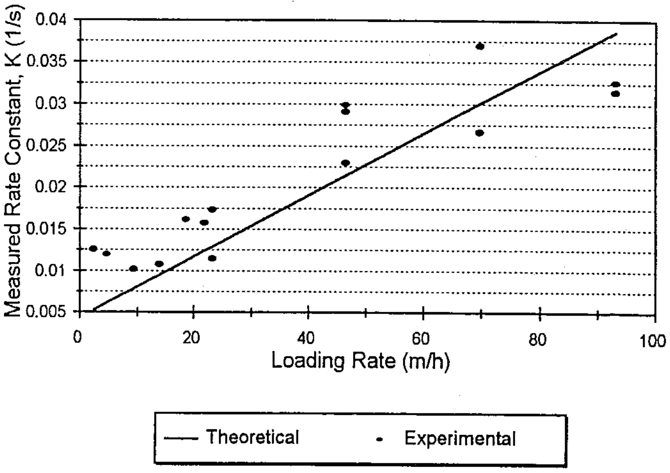


Figure 7-7: Compound rate constant

Simulated RO permeate: Batch #1

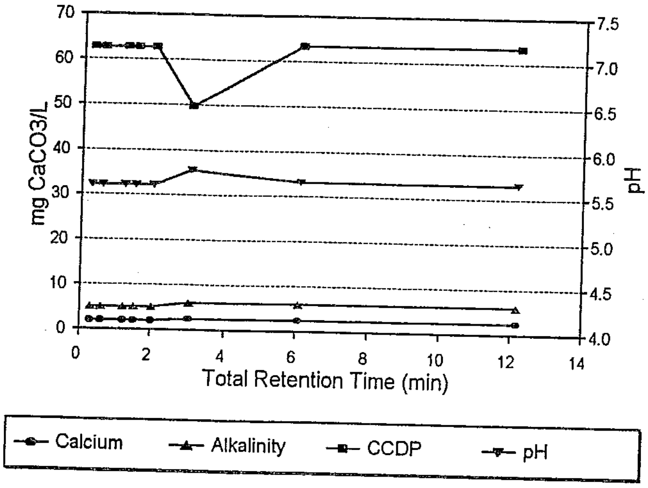


Figure 7-8: Raw feed quality

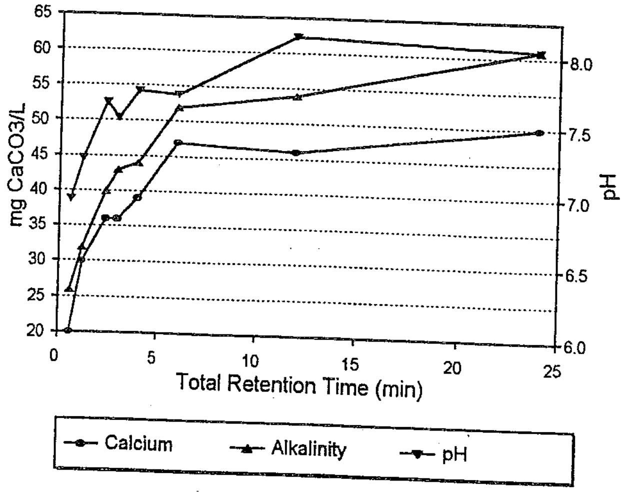


Figure 7-9: Final water quality

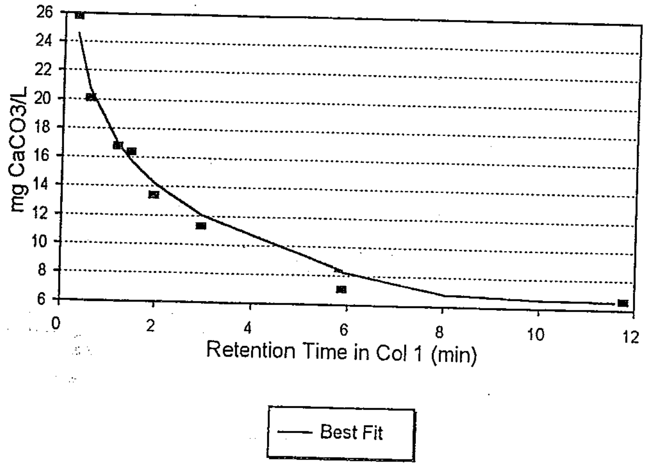


Figure 7-10: CCDP from Column 1

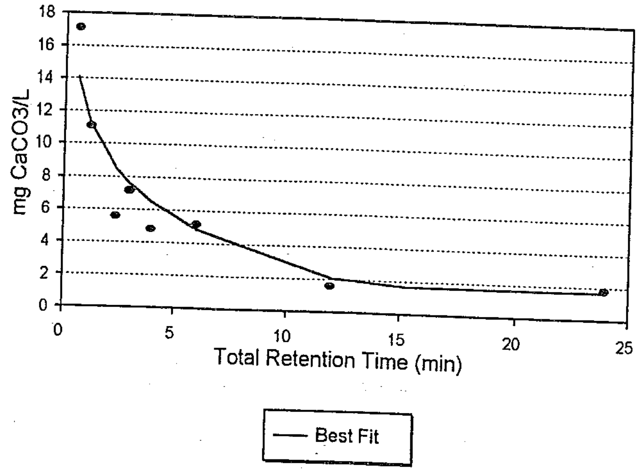


Figure 7-11: CCDP from Column 2

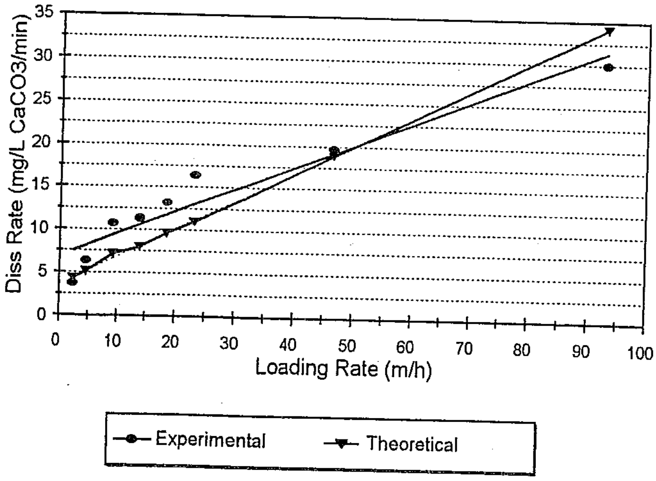


Figure 7-12: Calcium carbonate dissolution rate

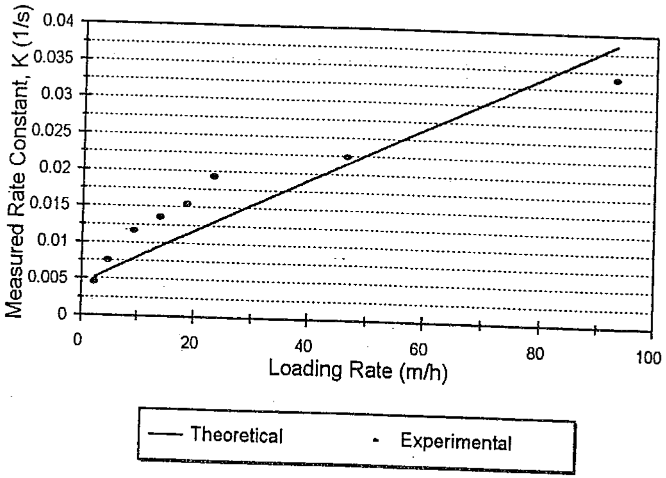


Figure 7-13: Compound rate constant

Simulated RO permeate: Batch #2

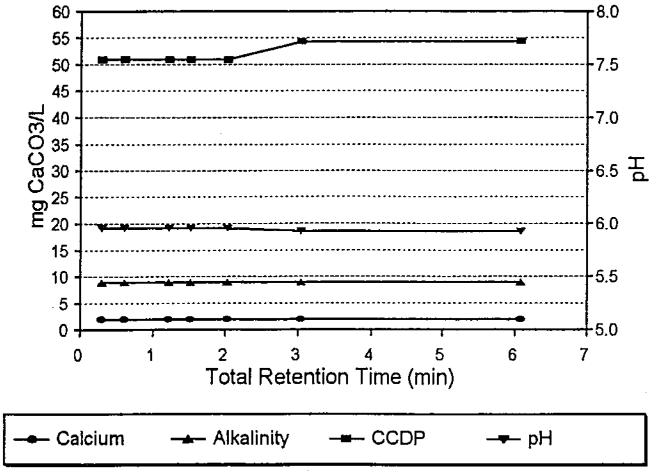


Figure 7-14: Raw feed quality

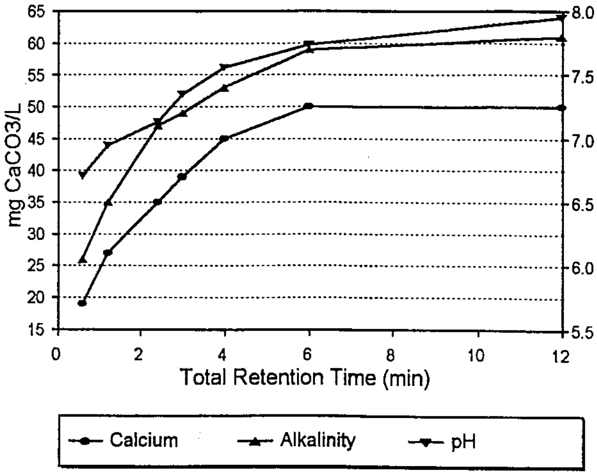


Figure 7-15: Final water quality

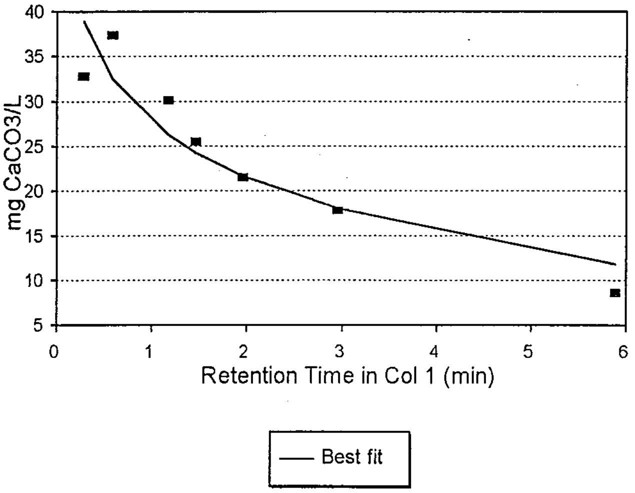


Figure 7-16: CCDP from Column 1

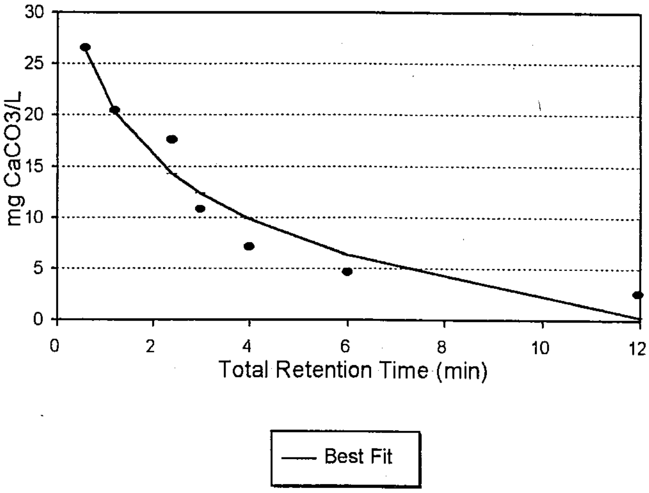


Figure 7-17: CCDP from Column 2

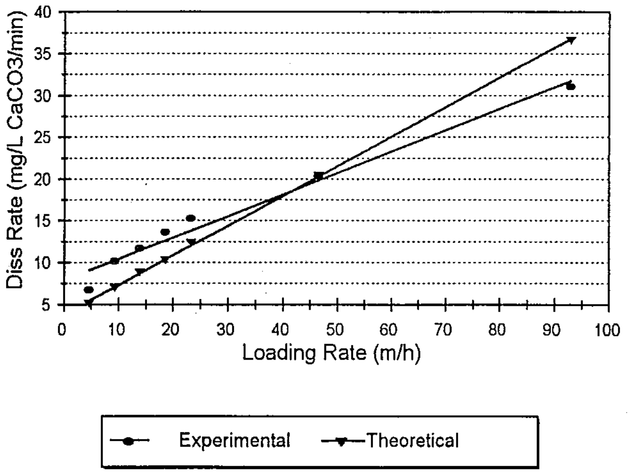


Figure 7-18: Calcium carbonate dissolution rate

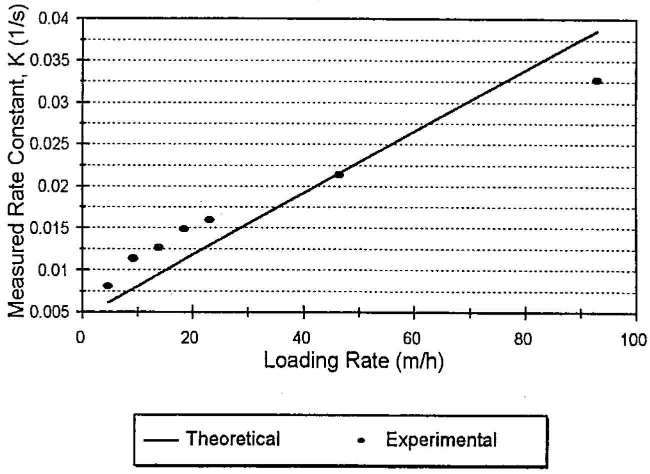


Figure 7-19: Compound rate constant

Dissolution rate in Column 2 - small particle sizes

Figure 7-20 and **Figure 7-21** show the calcium carbonate dissolution rate and compound rate constant in Column 2 (small particles) against reactor loading rate, for the first batch of simulated RO permeate:

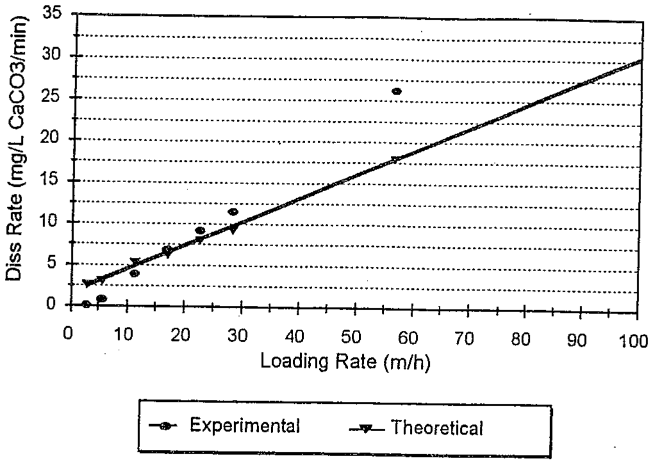


Figure 7-20: Batch #1 Simulated RO permeate: Dissolution Rate - Column 2

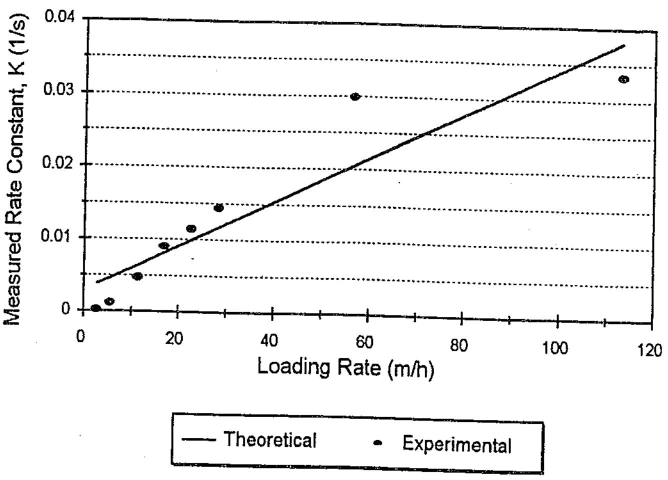


Figure 7-21: Batch #1 Simulated RO permeate: Compound Rate Constant - Column 2

7.5.5 Discussion of results

Stellenbosch water

Although the raw feed Alkalinity and calcium were consistently low, the pH varied considerably between 5 and 6. This resulted in considerable variation in raw feed CCDP, between 20 and 180 mg/ℓ as $CaCO_3$ (see **Figure 7-2**). Regardless of the variation in CCDP of the raw feed, a clear trend in CCDP reduction can be seen (**Figure 7-4** and **Figure 7-5**). An exponential curve was fitted through the CCDP vs retention time data.

A high reduction in CCDP was achieved at low retention times. A CCDP of ± 3 mg/ℓ as $CaCO_3$ was reached, from a feed CCDP of 52.6 mg/ℓ as $CaCO_3$, after a contact time of ± 1.5 minutes (**Figure 7-5**). The CCDP will eventually reduce to zero, after sufficient contact time. The slightly negative CCDPs (**Figure 7-4** and **Figure 7-5**) could be due to inaccuracy in the chemical results. It is evident that the minimum achievable CCDP will be reached after ± 10 minutes.

From **Figure 7-6** can be seen that the theoretical approach, developed in Chapter 5, gave a reasonable indication of reaction rates in Column 1. The experimentally determined dissolution rates were generally faster than the theoretically predicted ones. This would have lead to a conservative design if the theoretical considerations were used to determine the required retention time. The loading rate at which 95 % reduction of CCDP was achieved was between 25 and 50 m/h. In this range, the theoretically predicted reaction rate was approximately 27 % lower than the measured rate.

Simulated RO permeate

Two large batches of simulated RO permeate were prepared. The quality of the raw feed remained almost unchanged throughout the tests (**Figure 7-8** and **Figure 7-14**). The raw feed CCDP of Batch #1 varied between 60 and 70 mg/ℓ, both as $CaCO_3$, and that of Batch

#2 between 50 and 55 mg/ℓ, both as $CaCO_3$.

Column 1 managed to reduce the CCDP of both batches to below 8 mg/ℓ in 6 minutes (**Figure 7-10** and **Figure 7-16**). Column 2 further reduced the CCDP to ± 2 mg/ℓ as $CaCO_3$. The total contact time required to reduce the CCDP to 2 mg/ℓ as $CaCO_3$ was 12 minutes (**Figure 7-11** and **Figure 7-17**). Longer retention times were needed for stabilisation of the simulated RO permeate than for the Stellenbosch water, because the acidity of the simulated RO permeate was higher.

From **Figure 7-12** and **Figure 7-18** can be seen that the theoretical approach gave a reasonable indication of reaction rates in Column 1. As for the Stellenbosch water, the experimentally determined dissolution rates in Column 1 were generally faster than the theoretically predicted ones, especially at the lower loading rates (i.e. at longer retention times). The loading rate where 95 % reduction of CCDP was achieved, was approximately between 9 and 14 m/h. In this range, the theoretically predicted reaction rates were 25 to 33 % lower than the measured rates.

Figure 7-20 and **Figure 7-21** show the experimentally determined dissolution rate and compound rate constant in Column 2 (small particle sizes) for Batch #1 of the simulated RO permeate. Also shown are the theoretically predicted rates and rate constants, determined inter alia from **Equation 17**. When comparing the compound rate constants in Column 1 (**Figure 7-13**) to that in Column 2 (**Figure 7-21**), it is evident that the rate constants were somewhat lower in Column 2. This is contrary to the expected, because the larger total area of exposed surfaces in the case of the smaller particles would be expected to result in a faster dissolution rate. A possible explanation could be that "fresh" limestone particles were added into Column 1, whereas Column 2 contained particles flushed out of Column 1. The particles in Column 2 had therefore had longer contact times, and more of their insoluble particle surfaces had been exposed with time.

It is clear from **Figure 7-12**, **Figure 7-13**, **Figure 7-18**, **Figure 7-19**, **Figure 7-20** and **Figure 7-21** that the fluidised bed pilot plant performed at a high level of efficiency with regard to achieving the theoretical dissolution rate. Measured reaction rates and compound rate constants displayed broad similarities with those determined from theoretical considerations. The remaining discrepancies, however, between the simulated and experimentally determined reaction rates, indicate the importance of conducting pilot trial runs with a specific water before a larger scale fluidised bed plant is designed to stabilise the water.

7.5.6 Retention time design criteria

The exponential curves that were fitted through the CCDP versus total retention time data were used to determine the required total retention time (contact time in both columns). Regressions were also carried out on the percentage reduction in CCDP versus retention time.

The equations for the regression curves were of the form:

$$t_R = e^{\frac{k_1 - (CCDP)}{k_2}} \qquad \textbf{(7-17)}$$

and

$$t_R = e^{\frac{(\% Red) - k_3}{k_4}} \tag{7-18}$$

where:

t_R = Total retention time in both columns [minutes]

$\% Red$ = Required % reduction of CCDP

DP = CCDP [mg/ℓ as $CaCO_3$]

k_1, k_2, k_3, k_4 = Constants

The following table gives the regression coefficients for the different waters:

Table 7-6 Regression constants: CCDP vs total retention time

Water :	Stellenbosch Water	Simulated RO Permeate	
		Batch#1	Batch#2
k_1 :	2.955	12.543	21.864
k_2 :	1.593	4.839	8.674
r^2 :	0.83	0.9	0.94
k_3 :	92.522	80.777	57.018
k_4 :	5.772	6.228	17.19
r^2 :	0.7	0.84	0.94

r^2 : Correlation coefficient ($r^2 = 1$ for a perfect fit)

The total retention time required to achieve ± 95 % reduction in CCDP was determined for each of the waters. For the Stellenbosch water, a retention time of ± 1.5 minutes was sufficient. For the two batches of simulated RO permeate, retention times of 9.8 and 9.1 minutes were required for 95 % reduction. These retention times were not feasible, because it would require very large units for the 10 Mℓ/d plant. It was therefore decided to choose slightly shorter retention times for the two batches of aggressive water. The required final CCDP for the simulated RO permeate was therefore adjusted. The new requirement was a final CCDP of ± 5 mg/ℓ.

The characteristics of the stabilised waters, as well as the retention times required to achieve the stabilisation, are given in **Table 7-7**.

Table 7-7 Characteristics of water stabilised by fluidised bed process

Determinant	Stellenbosch Water	Simulated RO Permeate	
		Batch #1	Batch #2
pH	9	7.74	7.7
Alkalinity (mg/ℓ as $CaCO_3$)	15	47	56
Calcium (mg/ℓ as $CaCO_3$)	14	42	47.5
Temperature (°C)	15	14	13
Conductivity (mS/m)	6.5	25	32
CCDP (mg/ℓ as $CaCO_3$)	2.81	4.73	5.55
% CCDP Reduction	95	92	90
Total Retention Time Required (minutes)	1.54	5	5

7.6 Design of 10 Mℓ/d Units

7.6.1 Introduction

Using design data and equations established in the previous section, a hypothetical 10 Mℓ/d stabilisation plant was designed to stabilise, (i), Stellenbosch water and (ii), the simulated RO permeate. Similar to the pilot plant, this unit would consist of two vertical columns.

The design of a fully optimised full-scale unit will depend on a number of considerations other than just the required retention time of the water in the reactor, including practical considerations. Nevertheless, for the purpose of obtaining an indication of whether the fluidised bed stabilisation process would be a viable treatment option, as opposed to more conventional processes, a full-scale unit that was based on the pilot plant, was designed.

7.6.2 Assumptions

Particle sizes

The 10 Mℓ/d units were designed to use the same limestone as used for the pilot trials. The first column was designed to be fed with +6.7 mm -4.75 mm crushed Bredasdorp limestone pebbles. The fluidising and flushing velocities were the same as for the pilot units. The column diameters were chosen in such a way that the bed approaching velocities in the two columns would be the same as on the pilot plant. Similar to the pilot plant, the full-scale unit was designed to expand its limestone beds optimally.

Recirculation rates

In order to select the appropriate column diameters, the recirculation rates of water through the two columns had to be considered. Recirculation would require two extra pumps in addition to the raw feed pump. In order to maintain the required bed approaching velocity for optimum bed expansion, a large diameter column will need a high recirculation rate, whereas a smaller diameter column will need a lower recirculation rate. The required CCDP reduction determines the required volume of the reactors. Depending on the choice of recirculation rates, the shape of the units could range from tall, narrow columns, on the one side of the range, to short, wide columns on the other. The tall, narrow columns will require recirculation pumps that can deliver a large head. In contrast, the short, wide columns will require recirculation pumps that can deliver a high flow. Theoretically, the choice of recirculation rate is not critical in terms of determining the pumping energy requirements, because the theoretical power requirement for recirculation equals the product of the volumetric flow rate and required pressure head. Pump characteristics, e.g. the power efficiency, have to be considered to minimise the pumping energy requirement, and hence the running costs. Design criteria for the selection of optimal recirculation rates for the 10 Mℓ/d units should also take cognisance of fluidisation hydraulics in large diameter cylinders, as well as characteristics of available pumps. Hydraulic considerations include obtaining a proper flow distribution over the cross-sectional area, which is required to achieve fluidisation.

It was decided to design the columns with no recirculation. The raw feed pump will therefore be the only pump that will pump the feed through Column 1, from where it will gravity feed through Column 2. No recirculation pumps are therefore required in this design. The column diameters were chosen such that the required bed approaching velocities for optimum expansion were maintained. It is possible that this design will not be feasible due to practical considerations, but, for the purpose of this study, it was considered to be adequate.

Hydraulic characteristics

During pilot trial tests it was concluded that the pilot units acted like completely-mixed reactors, rather than plug-flow reactors. The assumption was made that the hydraulic characteristics in a 10 Mℓ/d unit would also be that of a completely mixed reactor.

7.6.3 Design parameters for 10 Mℓ/d plant

Two 10 Mℓ/d fluidised bed plants were designed to stabilise, (i), Stellenbosch water and (ii), the simulated RO permeate. The dimensions and operating characteristics of the full-scale plants are given in **Table 7-8**.

Table 7-8 10 Mℓ/d stabilisation plant - dimensions and operating characteristics

Parameter			Stellenbosch Water		Simulated RO Permeate	
			Column 1	Column 2	Column 1	Column 2
Plant Capacity		Mℓ/d	10		10	
Total Retention Time		minutes	1.536		5	
Retention Time in Column		minutes	0.755	0.781	2.459	2.541
Fixed Bed Height	ℓ	m	3.68	1.8	12	5.8
Expanded Bed Height	ℓ_e	m	4.78	2.52	15.6	8.12
Bed Expansion %			30	40	30	40
Flow Rate through Bed	F	m^3/h	417.5	414.8	416.8	419
Velocity at expansion	v_e	m/s	0.0743	0.0346	0.0743	0.0346
Column Diameter	D	m	1.41	2.058	1.409	2.069
Limestone Grade		mm	-6.7+4.75	-1.7+1.0	-6.7+4.75	-1.7+1.0
Fixed Bed Porosity	p_0		0.613	0.505	0.613	0.505
Expanded Bed Porosity	p_e		0.702	0.646	0.702	0.646
Frictional Pressure Loss over Beds	$\Delta P_{f,bed}$	m H_2O	2.65	1.44	8.64	4.65

7.6.4 Energy requirements

Frictional pressure losses over beds

In order to determine the required fluidisation energy, the expected frictional pressure losses over the two limestone beds had to be determined. The pressure losses over the pilot units were measured. Measured pressure losses per metre bed height were:

Unit	Pressure loss (m H_2O/m)
Column 1	0.48
Column 2	0.535

The measured pressure losses were multiplied by a factor of 1.5 for the design of the 10 Mℓ/d units, to allow for additional unknown pressure losses, e.g. due to pipes and fittings.

Required hydrostatic head

The required hydrostatic head of the raw feed pump depended on the height difference between the pump outlet and the outlet of Column 1. The columns were designed with outlets positioned at half the expanded bed heights above the expanded beds. This was to allow for flexibility in degree of bed expansion.

Feed pump requirement

The total required dynamic head of the raw water feed pump, which will pump water into the bottom of Column 1, was calculated. The required head of the feed pump is the sum of the required hydrostatic head and frictional pressure loss over Column 1:

$$\Delta H = \Delta P_{f,Col\ 1} + 1.5\ell_{e,Col\ 1} \tag{7-19}$$

	Required Head of Feed Pump (m H_2O)
Stellenbosch Water	9.8
Simulated RO permeate	32.04

Centrifugal pumps, suitable to deliver the required flows and heads, were selected. The characteristics of the selected pumps, operating at the required flow rates, are:

Table 7-9 **Pump characteristics**

Parameter	Units	Stellenbosch Water	Simulated RO Permeate
Head	m H_2O	12.5	31
Flow Rate	m^3/h	420	420
Efficiency (η)	%	69	78
Power Consumption	kW	20	45
Outlet Diameter	mm	260	320

Required head for Column 2

The height difference between the outlets of Column 1 and Column 2 , ΔH, provides enough hydrostatic head to overcome the frictional pressure loss over Column 2, and was calculated using:

$$\Delta H = (1.5\ \ell_{e,Col\ 1}) - (1.5\ \ell_{e,Col\ 2}) \tag{7-20}$$

where:

ΔH	=	Available hydrostatic head of water leaving Column 1	[m H_2O]
ℓ_e	=	Expanded bed height	[m]

Using the expanded bed heights (ℓ_e) from **Table 7-9**, ΔH was calculated as 3.39 m and 11.22 m for the Stellenbosch water and simulated RO permeate respectively. These available heads were enough to overcome the frictional pressure losses ($\Delta P_{f,bed}$) over Column 2, namely 1.44 and 4.65 m H_2O, for the two waters respectively.

7.7 Limestone vs Lime Stabilisation: Economic Considerations

7.7.1 Introduction

The objective of this evaluation was to compare the more readily determinable components of operating costs, namely chemical and energy operating costs, of the fluidised bed stabilisation process, with that of the lime stabilisation processes. Whilst other operating costs, such as labour, and capital costs will be of importance, these are less readily determinable at this stage. Comparison of chemical and energy costs will give a good indication as to the financial attractiveness of the fluidised bed process, and as to whether the process warrants further development.

7.7.2 Basis for chemical and energy comparisons

Chemical and energy operating costs of the following three stabilisation methods were estimated:

- fluidised limestone bed stabilisation,
- lime dosing, and
- lime and carbon dioxide dosing.

This comparison was complicated by the fact that, due to the differing nature of the various processes:

(i) the quality of the final water that would be produced by the different processes would differ. That is, it is not possible to achieve the same final chemical water quality.

(ii) it is not always possible to meet the post-stabilisation water quality guidelines. i.e. calcium and Alkalinity $\geq$ 50 mg/ℓ as $CaCO_3$, 6.5 < pH <9.5 and CCPP of + 4 mg/ℓ as $CaCO_3$.

Hence, the different processes would impart different levels of stabilisation, and therefore different benefits, which complicated the cost-benefit analysis. Bearing in mind this limitation, the following scenario's were regarded as reasonable for comparative purposes:

<u>Fluidised limestone bed</u>

Chemical uptake in the fluidised limestone process is dominated by the aqueous-solid phase equilibrium of water and $CaCO_3$. Accordingly, a water stabilised in this manner will reach a condition whereafter pH, calcium and Alkalinity can not be further increased without other chemical addition. Furthermore, a positive CCPP, normally specified to ensure complete stabilisation, cannot be achieved with this process. **Table 7-10** shows the experimentally determined final water quality for both Stellenbosch water and Batch's #1 and #2 of the simulated RO permeate, in which the significant variation in final stabilised water pH, calcium and Alkalinity is evident.

Table 7-10 Comparison of three stabilisation methods

		Raw Water	Post Fluidised Bed	Post Lime Process	Post Lime & CO_2 Process
		Stellenbosch Water			
pH		5.13	9	9	8.4
Calcium	mg/ℓ as $CaCO_3$	1	14	28.8	26.3
Alkalinity	mg/ℓ as $CaCO_3$	1	15	28.8	26.3
Acidity	mg/ℓ as $CaCO_3$	54	13.4	40.1	26.1
Conductivity	mS/m	4.02	6.5	4.02	4.02
Temperature	°C	15	15	15	15
CCPP	mg/ℓ as $CaCO_3$	-52.6	-2.8	-12	-2.7
Limestone Dosage	mg/ℓ as $CaCO_3$	-	13	-	-
Lime Dosage	mg/ℓ as $Ca(OH)_2$	-	-	20.56	18.7
CO_2 Dosage	mg/ℓ as CO_2	-	-	-	0.1
		Simulated RO Permeate: Batch #1			
pH		5.61	7.74	9	9.0
Calcium	mg/ℓ as $CaCO_3$	2	42	35.7	42
Alkalinity	mg/ℓ as $CaCO_3$	5	47	38.7	45
Acidity	mg/ℓ as $CaCO_3$	69	51	52.14	41.3
Conductivity	mS/m	16	25	16	16
Temperature	°C	14	14	14	14
CCPP	mg/ℓ as $CaCO_3$	-62.8	-4.7	-13.8	+2.5
Limestone Dosage	mg/ℓ as $CaCO_3$	-	40	-	-
Lime Dosage	mg/ℓ as $Ca(OH)_2$	-	-	24.93	29.6
CO_2 Dosage	mg/ℓ as CO_2	-	-	-	5.41
		Simulated RO Permeate: Batch #2			
pH		5.96	7.7	9	9.0
Calcium	mg/ℓ as $CaCO_3$	2	47.5	29	47.5
Alkalinity	mg/ℓ as $CaCO_3$	9	56	36	54.5
Acidity	mg/ℓ as $CaCO_3$	60	61.4	46.4	49.6
Conductivity	mS/m	23	32	23	23
Temperature	°C	13	13	13	13
CCPP	mg/ℓ as $CaCO_3$	-50.9	-5.6	-11.5	+4.0
Limestone Dosage	mg/ℓ as $CaCO_3$	-	45.5	-	-
Lime Dosage	mg/ℓ as $Ca(OH)_2$	-	-	19.99	33.7
CO_2 Dosage	mg/ℓ as CO_2	-	-	-	15.5

Note:

- For the STASOFT simulations of the lime and lime/carbon dioxide processes the temperatures of the different raw waters were assumed to be the same as the temperatures measured during the fluidised bed trials on the different raw waters.
- Chemical dosages are based on the assumption of 100 % purity of the different chemicals.

Lime dosing to a pH of 9

When stabilising soft, acidic water by dosing lime only, the final pH is a limiting factor. For the purpose of this comparison, lime dosing was carried out to a pH of 9.0, which coincides with the SABS 241-1984 Specification for Water for Domestic Supplies recommended upper pH limit of 9.0. Lime dosing to a pH of 9.0 will raise the Alkalinity and calcium of the raw waters to values between about 30 and 40 mg/ℓ as $CaCO_3$. However, for all three raw waters, lime dosage to a pH of 9.0 will not reduce the CCDP to <10 mg/ℓ $CaCO_3$, therefore still resulting in a fairly aggressive final water.

Lime and carbon dioxide dosing

When stabilising using lime and CO_2, it is possible to meet all of the stabilisation guidelines and a pH of 9.0. However, in a running cost comparison this would unfairly penalise lime and CO_2 mediated stabilisation. For the purpose of this comparison, stabilisation was carried out as follows:

- For comparison for the Stellenbosch water, dosing was such that a similar CCDP as attained by the fluidised bed process was attained with a minimum of lime and CO_2 addition.
- For the simulated RO permeate waters, dosing was such that a similar calcium and Alkalinity as attained by the fluidised bed process was attained, and a CCDP satisfying stabilisation guidelines.

Note: In the case of the fluidised limestone bed process, chemical dosages used in this cost comparison were based on data obtained from the pilot trials; for the lime dosing and lime/carbon dioxide dosing processes, the STASOFT package was used to estimate required dosages for the three different raw waters.

A comparison of the three alternative stabilisation methods in terms of dosing requirements and final water quality is given in(see next page).

7.7.3 Operating cost comparison

Using the data from **Tables 7-9** and **7-10**, the dosing chemical and energy costs for the stabilisation of the three waters were estimated (**Table 7-11**). Labour and maintenance costs were not included in the comparisons, due to the fact that these would be difficult to estimate accurately. The energy requirements of the two lime processes were not included, because these were expected to be very small in comparison to the pumping energy requirement for fluidisation.

Table 7-11 Running Cost Comparison

		Stellenbosch Water	Simulated RO Permeate	
			Batch #1	Batch #2
Fluidised Limestone Bed				
Limestone Consumption	mg/ℓ as $CaCO_3$	13.0	40.0	45.5
Limestone Cost[1]	R / Mℓ Treated Water	1.5	4.6	5.2
Power Requirement	kW	20.0	45.0	
Energy Cost [2]	R / Mℓ Treated Water	7.9	17.7	17.7
Final pH		9.0	7.7	7.7
Final CCPP	mg/ℓ as $CaCO_3$	-2.8	-4.7	-5.6
TOTAL COST	R/Mℓ	**9.4**	**22.3**	**22.9**
Lime Process				
Lime Consumption	mg/ℓ as $Ca(OH)_2$	20.6	24.9	20.0
Lime Cost[3]	R / Mℓ Treated Water	18.1	22.0	17.6
Final pH		9.0	9.0	9.0
Final CCPP	mg/ℓ as $CaCO_3$	-12	-13.8	-11.5
TOTAL COST	R/Mℓ	**18.1**	**22.0**	**17.6**
Lime & CO_2 Process				
Lime Consumption	mg/ℓ as $Ca(OH)_2$	18.7	29.6	33.7
Lime Cost[3]	R / Mℓ Treated Water	16.5	26.1	29.7
CO_2 Consumption	mg/ℓ as CO_2	0.1	5.4	15.5
CO_2 Cost[4]	R / Mℓ Treated Water	0.07	3.8	10.9
Final pH		8.4	9.0	9.0
Final CCPP	mg/ℓ as $CaCO_3$	- 2.7	+2.5	+ 4
TOTAL COST	R/Mℓ	**16.6**	**29.9**	**40.6**

Assumptions:

(1) **Limestone Cost:** R105/tonne, 91.25 mg available $CaCO_3$/100 mg limestone
(2) **Electricity Cost:**
Demand Charge: R40.89/Max kVA in half an hour intervals in a specific month (Maximum demand assumed to be 1.1 times the average demand)
Consumption Charge: 10.21c/kWh
(Prices are for the Stellenbosch Region which should be comparable to other regions in the country)
(3) **Lime Cost:** R 750/tonne (Imported (high purity) lime's cost was used)
Slightly cheaper lime is available locally at ± R680/tonne, but is of lower quality
Assumed purity: 65 kg available CaO per 100 kg lime (min required by Cape Region)
Assumed lime wastage: 1 %
(4) **Carbon dioxide price:** R700/tonne

7.7.4 *Discussion of operating cost comparison*

The method of lime dosing alone, to a pH of 9.0, will raise Alkalinities and calciums of the various raw waters to between 29 to 39 mg/ℓ as $CaCO_3$, but will still result in final waters with CCDPs ranging from 11 to 14 mg/ℓ as $CaCO_3$. Lime dosing will therefore not adequately protect a reticulation network against aggression and corrosion, if pH is limited to 9.0, which is the recommended limit in the SABS 241-1984 specification for water for domestic supplies. Therefore, the final conclusions of the fluidised bed feasibility study were based on an operating cost comparison between the fluidised limestone bed process and the lime and CO_2 process.

Stellenbosch water

The fluidised bed process attained a treated water quality with pH of 9, CCDP of + 2.8 mg/ℓ, and Alkalinity and calcium of ± 15 mg/ℓ (all as $CaCO_3$). The conventional lime and CO_2 process will attain Alkalinity and calcium levels of ± 26 mg/ℓ as $CaCO_3$, pH of 8.4 and CCDP of + 2.7 mg/ℓ as $CaCO_3$ (i.e. a similar CCDP to that attained by the fluidised bed process). Such partial stabilisation would significantly reduce rate of aggressive attack of cementitious material, and reduce iron corrosivity; however, the calcium and Alkalinity levels do not satisfy guidelines levels for negation of iron corrosion, namely 50 mg/ℓ as $CaCO_3$ for both calcium and Alkalinity.

Comparing the fluidised bed process to the conventional lime and CO_2 dosage process, the conclusion is made that the fluidised bed can partially stabilise Stellenbosch water at 43 % lower overall chemical and energy operating cost. On a 10 Mℓ/d fluidised bed plant, this annual operating cost saving would amount to ± R26 000. The lime and CO_2 dosing process will, on the other hand, achieve almost twice the final Alkalinity and calcium levels, which will provide improved protection against aggression and corrosion.

Simulated RO permeate

The simulated RO permeate batches had higher Acidities than the Stellenbosch water, therefore the fluidised bed process attained higher Alkalinity and calcium levels in stabilising the simulated RO permeate. Final pH's of 7.7, Alkalinities of 47 and 56 mg/ℓ as $CaCO_3$, and calciums of 42 and 47.5 mg/ℓ as $CaCO_3$ were achieved. The CCDPs of the RO permeate batches were reduced from 63 and 51 mg/ℓ respectively, both as $CaCO_3$, to ± 5 mg/ℓ as $CaCO_3$, which left the final waters significantly less aggressive than the raw waters. Such partial stabilisation would significantly reduce rate of aggressive attack of cementitious material, and reduce iron corrosivity; however, the calcium and Alkalinity levels do not satisfy the guideline levels for negation of iron corrosion, namely 50 mg/ℓ as $CaCO_3$ for both calcium and Alkalinity. The conventional lime and CO_2 process attained pH 9.0, Alkalinity and calcium levels ranging between 39 and 46 mg/ℓ as $CaCO_3$, and positive CCPPs of 4 mg/ℓ as $CaCO_3$, thereby almost satisfying stabilisation guidelines.

Comparing the fluidised bed process to the conventional lime and CO_2 dosage process, the conclusion is made that the fluidised bed can partially stabilise the simulated RO permeate at 25 % and 44 % lower overall chemical and energy operating costs, for the two batches of simulated RO permeate respectively. On a 10 Mℓ/d fluidised bed plant, these annual operating cost savings would amount to ± R28 000 and ± R64 000 for the two batches respectively. The lime and CO_2 dosing process will, on the other hand, achieve slightly positive CCPPs, compared to slightly negative CCPPs in the case of the fluidised bed; hence lime and CO_2 dosing will provide better protection against aggression and corrosion.

7.8 Conclusions

The following conclusions were made:

- Experimental trials with different types of aggressive water showed that the fluidised limestone bed reactor can significantly reduce the CCDP of an aggressive water, almost eliminating aggressiveness to cement, within reasonably short retention times.

For example, in the simulated RO permeate Batch #1 test, the CCDP of 63 mg/ℓ as $CaCO_3$ was reduced by 92 % to 5 mg/ℓ as $CaCO_3$ with a 5 minute retention time.

- In the fluidised limestone bed process, the characteristics of the raw water determine both the rate of calcium carbonate dissolution (and hence the retention time required for stabilisation) and the chemical characteristics of the final water. The latter is problematic in that it is not possible to ensure that the final stabilised water will have chemical characteristics that satisfy the guideline levels for negation of corrosion. For example, the process was shown to reduce the CCDP of Stellenbosch water from 53 mg/ℓ to 2.8 mg/ℓ as $CaCO_3$, with associated final Alkalinity and calcium levels of about 15 mg/ℓ as $CaCO_3$. The latter are considerably lower than the guideline levels of $\geq$ 50 mg/ℓ as $CaCO_3$.

- The fluidised limestone bed process was shown to be able to reduce the CCDP of the test waters at reasonable overall chemical and energy savings relative to the conventional lime and CO_2 dosing process. Such savings ranged between 25 % (simulated RO permeate: Batch #1) and ± 44 % (Stellenbosch water and simulated RO permeate: Batch #2), and are influenced significantly by the raw water characteristics.

- It appears that whilst the fluidised limestone bed process is able to effectively reduce the driving force of aggressive attack (namely, the CCDP), the potential fullscale application for medium to large water treatment works is unattractive, because:

  (i) the fluidised bed process alone is unable to meet water quality stabilisation guidelines for all aggressive and corrosive waters, and

  (ii) whilst the capital costs of the various processes were not assessed, the capital cost of the fluidised bed process is likely to be an order of magnitude larger than that of the alternate conventional lime and CO_2 process. Hence, the apparently attractive annual overall chemical and energy savings of between ± 25 % (± R26 000) and ± 44 % (± R64 000), are relatively insignificant and unlikely to redeem the increased capital cost.

REFERENCES - CHAPTER 7

Fluidised bed studies

AMIRTHARAJAH A (1972) Predicting expansion of filters during backwash. *Journal of American Waterworks Association,* Vol 64, pp 52-59.

CAIRNS EJ and PRAUSNITZ JM (1960) Macroscopic Mixing in Fluidization. *American Institute of Chemical Engineers Journal*, Vol 6, pp 554-560.

FRIEND JFC and LOEWENTHAL RE (1992) Chemical conditioning of low- and medium-salinity waters, STASOFT Version 3.0. Water Research Commission, Pta.

HOWARD JR (1989) *Fluidized bed technology*. New York: Adam Hilger.

KUNII D and LEVENSPIEL O (1969) *Fluidization engineering*. New York: Wiley & Sons.

MACKINTOSH GS and DE VILLIERS HA (1995) Stabilization of Water. CSIR RSA Patent No.: 94/5602, Acceptance date 6/3/1995. Correspponding foreign patents: Lesotho: LS/P/94/00005, Malawi: MW 31/94, Namibia: 94/0054, Zimbabwe: 95/94, Botswana: P956, Swaziland RP/46/1995.

SCHARFETTER O and FREHSE C (1993) Stabilisation of aggressive waters with limestone, using fluidized bed technology. B.Eng thesis, Dept Civil Eng, University of Stellenbosch.

SCHUTTE R (1994) Fluidized bed expansion: stabilization of aggressive water with limestone. B.Eng thesis, Dept Civil Eng, University of Stellenbosch.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The need for the stabilisation of soft, acidic waters, to prevent the costly and irksome impact of corrosive and/or aggressive attack on distribution systems, household plumbing and deterioration of water quality, is clear and convincing. This need is felt equally in large scale distribution networks, and smaller community user systems, albeit not always for the same reasons. Conventionally, stabilisation is achieved via the addition of lime and carbon dioxide. However, whilst such stabilisation is well documented and understood, it requires well trained staff and reliable equipment; both which are seldom available in the many towns and communities receiving such waters. Hence, in many cases only lime mediated pH adjustment to more desirable pH levels of, say, 8.0, is practised, thereby providing only a partially stabilised water. Even so, for the smaller municipal installation, dosing of lime (with or without carbon dioxide) remains problematic and difficult to control. Furthermore, stabilisation with lime is expensive, often comprising about half of the chemical cost of treating water. For small volume water users, e.g. rural communities and farmers, stabilisation is not possible and the consequent costs of corrosion can be significant. An alternative approach is the use of limestone. Limestone mediated stabilisation would appear to be an attractive alternative for both small scale and large scale systems, principally because of potential ease and simplicity of operation, and reduced chemical costs.

The first objective of this study was to identify suitable limestone sources. Five limestone deposits were assessed for suitability, with emphasis on deposits in the Western Cape. Mineral composition analysis and laboratory scale tests showed that both the Bredasdorp deposit, as well as a deposit in the Northwest Province were suitable for further consideration. Of these, the Bredasdorp deposit was found to be the most suitable for use in pilot plant trials, in terms of geographical proximity to the study area, dissolution rates, mineral structure and mineral composition.

The second objective of this study was to develop a kinetic model describing limestone dissolution. This was carried out to provide an understanding and quantification of the driving forces in the chemical treatment process, and thereby to ensure correct focus in the development of operational units. Suitable calcium carbonate dissolution kinetic models were identified for consideration. Experimental observation indicated that the compound rate constant of the diffusion controlled model of Plummer, Parkhurst and Wigley of 1979 varied with mixing energy (i.e. with hydrodynamic conditions) - an observation that identified this model as the most appropriate model, as opposed to an alternate surface controlled model. Thereafter, the diffusion controlled model was calibrated for the Bredasdorp limestone under varying hydrodynamic conditions. The dependence of the compound rate constant (for Bredasdorp limestone) on granule size and reactor loading rate was investigated, and led to the formulation of an empirical relationship describing the compound rate constant as a function of loading rate and nominal mean granule size. Accordingly, a methodology was developed for the calibration of the model for other limestones and waters.

The third objective of the study was the development and assessment of limestone stabilisation units for both small users (about 50 m^3/day) and large users (greater than 1000 m^3/day). Small user systems were designed and operated. Separate systems were developed for, (i), groundwater, and (ii), surface water, as a result of the presence of dissolved iron, manganese and dissolved carbon dioxide in groundwater, and the critical role that dissolved carbon dioxide plays in groundwater.

The groundwater stabilisation unit called "Spraystab", after the treatment configuration, was found to be highly effective at treating soft, acidic groundwater with no iron or manganese present. It was shown that a limestone bed retention time of about 3 minutes was sufficient to significantly reduce the calcium carbonate dissolution potential (CCDP) and increase pH, calcium and Alkalinity to desirable levels. The "Spraystab" system was shown also to be effective at treating soft, acidic groundwater with low levels of iron present (about 2 mg/ℓ). The system was shown to stabilise the water satisfactorily and to remove the dissolved iron present with a limestone bed retention time of about 5 minutes. The process was also shown to be compact and robust, requiring minimal operator attention and/or maintenance. The "Spraystab" system has shown itself to be an effective and attractive water treatment system in a market niche area for which there are no other viable alternatives.

The surface water stabilisation unit, called "Presstab", after the configuration thereof, was found to be effective for the stabilisation of a range of surface waters. Waters tested varied from "white" water, to strongly coloured "brown" water, whilst dissolved iron levels varied between 0 and 2 mg/ℓ. The process was found to be effective, provided that, (i), turbid waters containing suspended matter are filtered prior to stabilisation, and (ii), it is accepted that when treating highly coloured waters there will be a reduction in efficiency owing to the "coating" of the limestone pebbles with time. It was shown that the "Presstab" process operates effectively at a limestone bed retention time of around ten minutes, for a range of waters. The process was also shown to be compact and robust, requiring minimal operator attention and/or maintenance. The "Presstab" system has shown itself to be an attractive water treatment system in a market niche area for which there are no other viable alternatives.

The large user limestone stabilisation technology investigated was a fluidised limestone bed process. An understanding of fluidised bed theory was attained, in order to design the fluidised bed plant. Thereafter, a pilot plant was constructed and operated. Trials were carried out on two types of aggressive, corrosive water, namely Stellenbosch mountain catchment water, and a simulated RO permeate. The experimental trials showed that the fluidised limestone bed reactor can significantly reduce the CCDP of an aggressive water, almost eliminating aggressiveness to cement, within reasonably short retention times. However, the characteristics of the raw water determine both the rate of calcium carbonate dissolution (and hence the retention time required for stabilisation) and the chemical characteristics of the final water. The latter is problematic in that it is not possible to ensure that the final stabilised water will have chemical characteristics which satisfy the guideline levels for negation of corrosion in distribution networks. For example, the process was shown to reduce the CCDP of Stellenbosch water from 53 mg/ℓ to 2.8 mg/ℓ as $CaCO_3$, with associated final Alkalinity and calcium levels of about 15 mg/ℓ as $CaCO_3$. The calcium and Alkalinity values are considerably lower than the guideline levels of $\geq$ 50 mg/ℓ as $CaCO_3$.

The final project objective was to consider the cost benefit of limestone versus alternate processes. With regards to the small user systems, no alternate competing technologies exist for comparison. With regards to the fluidised bed system, the results of the pilot plant development were used to derive design parameters for a 10 Mℓ/d unit, for which an operating chemical and energy cost comparison was carried out against conventional stabilisation processes. The fluidised limestone bed process was shown to be able to reduce the CCDP of the test waters at reasonable savings relative to the conventional lime and CO_2 dosing process. Such savings ranged between 25 % (simulated RO permeate) and ± 44 % (Stellenbosch water), and are influenced significantly by the raw water characteristics. However, the potential of full-scale application of the fluidised limestone bed process for medium to large water treatment works is unattractive because, (i), the fluidised bed process alone is unable to meet water quality stabilisation guidelines for all aggressive and corrosive waters, and (ii), the capital cost of the fluidised bed process is likely to be an order of magnitude larger than that of the alternate conventional lime and

CO_2 process. Hence, the apparently attractive chemical and energy savings of between about 25 % (± R26 000/annum) and 44 % (± R64 000/annum), are relatively insignificant and unlikely to redeem the increased capital cost.

Recommendations for further research were determined by the project team and the Steering Committee as follows:

(i) With regards the small user systems, further research and development is required regarding:

- assessment of the "Spraystab" system for waters containing a wider range of iron and manganese levels and identification of the upper limit in terms of removal thereof,
- scaling up of the "Spraystab" to treat greater volumes of water, say up to 1 000 m^3/day, such that it is suitable for small town purposes,
- identification of the colour level in surface waters at which the NOM coating of the limestone becomes problematic, and
- the information available be collated into a practically oriented guideline for the use of small user limestone mediated stabilisation systems.

(ii) With regards to medium sized stabilisation units (1 000 to 20 000 m^3/day), CSIR has carried out its own research, development and implementation work into fixed bed limestone contactors. To date, 9 full scale units have been installed in the Western Cape and have shown the process to be an effective means of partial stabilisation. The process has been shown to provide a significant total running cost saving of about 70 % versus lime and carbon dioxide, and is robust and simple in operation. This technology could be very useful at conditioning acidic waters created by treatment processes, such as desalination, or clarification using ferric salts. It is recommended that:

- pilot scale tests be implemented to assess the suitability of fixed bed limestone contactors for different types of product water, including reverse osmosis permeate,
- a study be undertaken into the relative degree of protection afforded to common conduit materials (copper, cement concrete, iron) by limestone mediated "partial stabilisation" versus "complete stabilisation", and consideration of the relative cost implications thereof,
- the kinetic model be developed further to provide a computer based design package for fixed bed limestone contactors,
- the information available be collated into a guideline for the stabilisation of medium to large user systems with limestone.

(iii) It is recommended that:

- following the completion of (i) and (ii) above, a **Manual for the Stabilisation of Waters with Limestone** be collated, published and distributed,
- an Expert Systems based package be developed to go with the Manual, covering in particular the design/construction of both the small scale and medium to large scale systems,
- a technology transfer programme be implemented, including two regional seminars (Western Cape and Natal), technical papers, and profiling through WISA and the relevant groupings in SAICE and IMESA.