

**ASSESSMENT OF THE LIMESTONE MEDIATED
SIDESTREAM STABILISATION PROCESS, WITH
EMPHASIS ON USE THEREOF BY RAND
WATER FOR STABILISATION OF THE
LESOTHO HIGHLANDS SCHEME WATER**

GS Mackintosh • GJ du Plessis • PF de Souza

WRC Report No. 1027/1/02



Water Research Commission





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FINAL REPORT

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EXECUTIVE SUMMARY

BACKGROUND AND MOTIVATION



A significant proportion of the waters of South Africa and Lesotho are soft and acidic with characteristically low calcium, total alkalinity and carbonate species concentration. Distribution of such waters results in aggressive attack of cement concrete pipes and linings, and corrosive attack of metal pipes, valves etc. within the distribution network. The impact of such attack is usually significant, and usually includes the loss of water, the need for expensive repairs and deterioration in drinking-water quality.

Water conditioning to prevent aggression and/or corrosion (termed stabilisation) is conventionally achieved by the addition of lime ($\text{Ca}(\text{OH})_2$) and carbon dioxide (CO_2). Although this process is well documented and understood, it has a number of drawbacks which include the use of notoriously troublesome lime dosing equipment, high chemical operating costs, and the need for high quality white lime which is currently in short supply in South Africa. An alternative stabilisation process is stabilisation via contact with limestone (solid calcium carbonate), which has been shown to have many advantages over lime-mediated stabilisation. In light of the aforementioned lack of availability of white lime in South Africa, it should also be noted that sufficient quantities of limestone suitable for drinking water stabilisation purposes are available in South Africa. A geophysical survey of an existing limestone quarry near Bredasdorp revealed that sufficient quantities of suitable limestone were available to stabilise all the waters of Rand Water, Umgeni Water and Cape Metropolitan Council for approximately 100 years. However, the use of limestone mediated stabilisation has hitherto been limited to smaller water treatment works as a result of the large contact tanks required. Use of limestone for large water treatment works is made viable by the development by CSIR of the limestone mediated Sidestream Stabilisation Process (SSP).

The SSP consists of taking a sidestream of the unstabilised water, dosing high levels of gaseous carbon dioxide (CO_2), and then contacting the CO_2 -acidified stream with limestone. The acidified sidestream takes up considerable amounts of calcium carbonate (CaCO_3), increasing the alkalinity and the calcium concentration. Thereafter CO_2 is stripped, recovered and reused in the process.

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After CO₂ stripping, the sidestream is blended with the main stream in the correct proportions to allow for a fully stabilised main stream. Indications from preliminary pilot plant trials and theoretical assessments have shown that the SSP process potentially provides significant cost savings and other advantages over conventional stabilisation. SSP technology and its derivations are patented internationally.

AIMS AND OBJECTIVES

Rand Water is in the process of considering water transport and treatment requirements for the Lesotho Highlands Scheme Water. The waters of the Lesotho region are relatively soft and acidic, requiring conditioning to prevent attack of cement concrete and metal structures and conduits. It was with this in mind that Rand Water identified the SSP as a potentially attractive alternative to conventional stabilisation using lime and carbon dioxide. In particular, the SSP presents a potentially attractive and viable option for the Katze Dam water if it is piped directly, but may still be suitable if the water is fed by the Ash-Liebenberg-Wilge River system. As the envisaged pipe system is likely to cost around three billion Rand, protection thereof from aggressive and corrosive attack is a top priority.

The original aims of the project were to:

- Develop and calibrate a process model describing the aqueous, gaseous and solid phase chemistry of the carbonate weak acid/base system and influencing parameters using a commercially available process modelling package. The model would be used to, (i), identify the operational limitations of SSP, and (ii), identify means to improve the performance and optimise the operation of the process.
- Determine the desirability and suitability of the SSP for the Lesotho Highlands scheme, and assess the motivation for industrialisation and full-scale implementation of the process.

During the project, deviations from the original project objectives arose as a result of both limitations experienced with the commercially available process modelling package and specific requests from the Steering Committee. These are mentioned below:

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- Programming and software development. The original project objectives required the use of a commercially available process modelling package to model SSP (the use of an "off-the-shelf" package was regarded as advantageous to Rand Water and other future users). At an advanced stage in the project it became apparent that the chosen package had fatal limitations regarding modelling of aqueous-gaseous phase interactions, and that for this reason further use of the package was pointless. Accordingly, originally unenvisioned programming and software development was carried out.
- Consideration of a simplified sidestream stabilisation process. As a result of Steering Committee concerns regarding the practicalities of full-scale carbon dioxide stripping and recovery, the project team presented an alternate "simplified SSP" process for consideration.

SUMMARY OF RESULTS AND CONCLUSIONS

The Use of Process Modelling Packages for Predicting the Behaviour of the SSP

One of the major aims of the project was to use a commercially available process modelling package to develop and calibrate a process model describing the SSP. The model developed would be used to both identify the operational limitations of SSP, and identify means to improve the performance and optimise the operation of the process.

Of the many available process modelling packages two possible candidates for modelling the SSP were identified, namely: *ASPEN PLUS* and *PRO/II*. Following detailed investigation of the modelling packages, it was agreed by the Steering Committee and the project team that *PRO/II* would be used to model the SSP process.

Development of a model using *PRO/II* showed that:

- The model developed was able to accurately simulate the incoming feed stream conditions, the condition of the sidestream after CO₂ addition and dissolution, and the condition of the sidestream after CaCO₃ dissolution (if appropriate inputs are added).

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- The model was, however, unable to accurately simulate CO₂ stripping and recovery as what had been observed from SSP pilot plant operation. The developers of the software were unable to identify the source of the limitation and revealed that the package may have previously unidentified carbonate chemistry limitations. As the CO₂ stripping and recovery step is critical in the SSP process, the use of *PRO/II* was abandoned.

In light of the failure of the commercially available process modelling package, CSIR initiated development of its own model. Due to concerns of the practical limitations of CO₂ recovery and recycling, the project team first considered a "simplified SSP" process.

This simplified SSP process does not include CO₂ recovery and subsequent recycling (but does incorporate CO₂ stripping to waste). It was envisaged that by using *STASOFT 4* and *Watchem* to model this simplified SSP, the project team would develop the necessary background to be able to develop a model of the SSP process at a later stage. This represented a major deviation from the original aims of the project.

Consideration Of The Viability Of A Simplified SSP

In the simplified SSP process the raw water stream is split into a mainstream and a sidestream. Carbon dioxide is dosed to the sidestream, after which the sidestream is contacted with solid calcium carbonate in a contactor, to take up alkalinity and calcium. The sidestream is blended in with the mainstream again to form the final blend. Variations of the process include different sidestream: mainstream blending ratio's, stripping CO₂ to the atmosphere before or after blending or not at all, and the addition of various alkali's such as lime, sodium hydroxide or sodium carbonate.

The theoretical viability of the simplified SSP was considered by the development by the project team of a model that included the use of *JAVA* programming, *STASOFT 4* and *Watchem*. If model development was successful it would be used as the basis for the further development of a model describing SSP (regardless of the viability of the simplified SSP).

Findings included *inter alia*:

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- Stripping CO₂ to the atmosphere before blending the sidestream and mainstream was not financially attractive.
- Stripping CO₂ to the atmosphere after blending the sidestream and mainstream, was financially attractive. The financial attractiveness varied with the both the CO₂ stripping efficiency and the alkali's used for final pH adjustment. Use of sodium alkali's was found to provide little or no saving relative to the use of lime, as a result of the high cost of these chemicals.
- Where partial stripping of the mainstream was accompanied by lime dosing, an attractive chemical cost saving incurred.
- Importantly, where no stripping of CO₂ was practised and nominal lime dosing was employed, significant chemical savings relative to conventional lime and CO₂ mediated stabilisation were observed. For example,
 - ◆ Where a final total alkalinity of 50 mg/L and a CCPP of zero was required, use of a 20% sidestream would lead to a chemical cost saving of 2.63 c/kL. On a 100 ML/day treatment plant this would translate to a saving of R78 900 / month, and R959 950 / year.
 - ◆ Where a final total alkalinity of 30 mg/L and a CCPP of zero was required, a potential chemical cost saving of 1.25 c/kL is available at a 10% sidestream. On a 100 ML/day treatment plant this translates to a saving of R37 500 / month, and R456 250 / year.
- Considering the practical implications of CO₂ stripping from a main stream in a large water treatment works, it is of particular interest that the study showed that significant savings are potentially possible where no CO₂ stripping is required. It should, however, also be noted that the viability of the process is highly dependant on the costs of the required chemicals (CO₂/white lime vs. limestone). These costs need to be carefully considered at each particular application.

From this desktop investigation the project team gained a better understanding of the SSP process.

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Development Of "SSP-MOD" Program For Predicting The Behaviour Of The SSP

As a result of *PRO/II* not being suitable for modelling SSP, the project team undertook previously unenvisioned programming and development of a *JAVA* based process model to describe the SSP process.

The steady state *SSP-MOD* describes the various unit processes of the SSP process including CO_2 stripping, recovery and subsequent recycling. The model was compared with *STASOFT 4* and found to be accurate. Subsequently, the model was compared with actual data obtained from preliminary operation of the SSP pilot plant. This preliminary investigation had the following findings:

- For the particular operating conditions under which the pilot plant was tested, the model predicted a significantly lower CO_2 recovery than what had been observed calculated (using pH measurements and *STASOFT 4*) from pilot plant operation (~ 11% vs. 35 – 45%).
- The model predicts that increasing the amount of "fresh" CO_2 added to the sidestream increases the CO_2 recovered, to a maximum of ~ 70%.
- The model predicts that an increase in vacuum pressure (i.e. closer to absolute zero pressure – 0 kPa) within the recovery vessel increases the amount of CO_2 recovered (this relationship only holds at higher CO_2 doses).
- Contrary to expectations based on historical pilot plant operation, the model predicts that addition of air would assist CO_2 recovery, the addition of 5 L atmospheric air/L sidestream decreased the final water total alkalinity and the amount of CO_2 recovered. This result indicated that the addition of air may not always be beneficial and would have to be further investigated during pilot plant trials.

Pilot Plant Operation using an Eductor For CO_2 Recovery

In order to assess the accuracy of *SSP-MOD* developed in predicting the behaviour of the SSP process, the model needed to be verified and calibrated on data obtained from operation of the

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SSP pilot plant. In parallel with verification and calibration of the model, was the need to optimise SSP pilot plant operation. These two objectives were to be carried out in an iterative manner. Assessment of the SSP process had shown that the stripping and recovery of CO₂ is an essential step in the SSP and that maximizing CO₂ recovery at economical "fresh" CO₂ doses was of primary importance in an attempt to optimise the process. Previous pilot plant work had shown that CO₂ recovery using vacuum pumps is effective, yet potentially problematic in full-scale applications. Considering the potential benefits of eductors in full-scale applications, the use of an eductor was selected for this project. Eductors have the potential advantages over vacuum pumps of low cost, simplicity and reliability, ease of installation, non-electrical unit, corrosion and erosion resistant.

During the testing and operation of the SSP pilot plant using an eductor, the following important observations were made:

- The use of an eductor ensures that a steady vacuum can be obtained.
- For the successful operation of the SSP, the use of a correctly sized eductor is of critical importance.
- Unfortunately, during this project both eductors tested did not operate at the required design specifications. This was despite considerable effort being made by the project team to ensure that correctly sized eductor's were obtained.
- Investigation revealed that wrt the 1st eductor the South African distributors provided incorrect specifications for the eductor to the USA specialist eductor manufacturer. Wrt the 2nd eductor, although considerable efforts were made to ensure that a correctly sized eductor was obtained, the eductor could not meet the required design specifications. A meaningful reason could not be provided by either the South African distributors or the USA manufacturers. This poor service puts the use of eductors in a negative light.
- Three "Long Run" pilot plant experiments were conducted (pilot plant operates for ~74 hours per run). From these tests the following observations were made:
 - ◆ Data obtained from Long Run 1 (low vacuum – approximately 62 - 68 kPa, high "fresh" CO₂ dose – 788 mg/L) showed that even though pilot plant performance was not optimal (due to poor

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performance of the eductor) CO₂ recoveries of 30 – 40% were obtained.

- ♦ Data obtained from Long Run 2 and Long Run 3 (high vacuum – approximately 40 - 45 kPa, low “fresh” CO₂ dose – 302 mg/L and 319 mg/L respectively) showed that CO₂ recoveries of 20 – 40% were obtained.

Due to the non-performance of the eductor, a long run incorporating high vacuum and a high “fresh” CO₂ dose was not possible.

Assessment of the SSP-MOD Model by Comparison with Pilot Plant Results

At the end of the pilot plant trials, outputs from the SSP-MOD model were compared with data obtained from pilot plant operation. These investigations revealed that:

- The model accurately predicted the characteristics of the feed, CO₂ acidified sidestream and sidestream after CaCO₃ uptake.
- The model, however, predicted a significantly lower CO₂ recovery than what had been experienced during pilot plant operation (e.g. for Long Run 1 the model predicted a CO₂ recovery of ~ 8%, while a CO₂ recovery of 30 – 40% had been obtained from pilot plant operation).
- Subsequent extensive review and analysis of the model by the project team and specialist third parties yielded no significant errors in the model, and at the close of the project a meaningful explanation as to why such discrepancies had occurred had not been reached.
- Based on observations from historical pilot plant operation where it seemed that the introduction of small amounts of air improved CO₂ recovery, further modelling with the addition of air to the recovery vessels was investigated. The SSP-MOD model showed that the addition of small amounts of air (0.1 – 1 L air/L sidestream) could aid CO₂ recovery, and that, based on data from Long Run 1, CO₂

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recoveries as high as 70% could be achieved if a relatively high vacuum pressure (in the range 40 - 50 kPa) could be maintained within the recovery vessel. This result therefore confirms historical pilot plant observations.

- A significant limitation with regards to the use of eductors is the unit's non-capability of maintaining a vacuum with addition of even nominal levels of air to the recovery vessel. This result compromises the further use of eductors as the ability to introduce small amounts of air appears vital to high percentage CO₂ recovery.

Assessment of the Suitability of the SSP for the Lesotho Highlands Scheme

The second major aim of the project was to determine the desirability and suitability of the SSP process for the Lesotho Highlands scheme, and assess the motivation for industrialisation and full-scale implementation of the process.

Considering the inability of the CSIR project team to optimise operation of the SSP pilot plant at high percentage carbon dioxide recovery levels (i.e. carbon dioxide recovery greater than 50%), and the inability of Rand Water project team to finalise water treatment and stabilisation requirements, a number of conservative assumptions were made.

Both basic and more complex financial assessments were carried out. The basic financial assessment (encompassing chemical running costs only) identified that where treatment is via filtration assisted by ferric chloride dosing, an appropriate stabilisation scenario is "high % sidestream (10%) combined with low percentage CO₂ recovery and re-use (10%) where the assumption is that the treated but unstable water was not equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation. In addition an airstrip of the blended stream is required. The basic financial assessment showed a potential chemical cost saving of approximately R17.1 million/annum or 2.3 c/kL.

Both Rand Water process engineers and the CSIR project team considered this scenario appropriate in that it can be regarded as operationally and financially conservative with a relatively large percentage sidestream (increased capital cost) and low percentage CO₂ recovery (lower than that achieved in pilot plant operation and with associated high chemical cost).

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The detailed financial model considers the higher capital cost of SSP and the ongoing chemical savings of SSP and using these, and other running costs, to essentially assess the ability of the SSP process to pay for itself. The financial assessment showed that payback period corrected for inflation (7%) is 2.5 years, and payback period corrected for inflation and risk (37%) is 4.3 years. Both of these are very attractive.

Furthermore, the model calculates a Net Present Value (NPV) and an Internal Rate of Return (IRR) for the project lifespan. To infer financial feasibility, the NPV needs only to be greater than zero. The NPV was calculated to be R2,7 million with an associated IRR of 52%. These two figures indicate that the project, with the assumptions made, is financially viable and that a risk factor of up to 35% (52% - 7% (inflation) - 10% (required return)), could still be applied and give an NPV of zero.

The detailed financial assessment therefore showed that even with a number of conservative assumptions to the detriment of SSP (lifespan of 10 years, raised electricity costs for SSP, risk discount factor of 30% per annum, minimum required return of investment of 10% per annum, low percentage CO₂ recovery) the process potentially provides significant financial advantage over conventional lime/CO₂ stabilisation.

Final Thoughts

It must be noted that of obvious consideration for the financial assessments conducted (both simplified SSP vs. conventional lime-CO₂ stabilisation and SSP vs. conventional lime-CO₂ stabilisation) are the costs of the required chemicals (CO₂/white lime vs. limestone). The prices for both limestone and white lime vary geographically with transport costs. In recent years the price of high quality white lime has risen dramatically (depending on quality, the Rand exchange rate, and the region to which the product must be transported). Individual assessment of the relevant process therefore needs to be considered on a case-by-case basis. Due to these variations a direct comparison between the simplified SSP and the SSP cannot be made from the information presented in this report. The trend of chemical costs is that raw, graded limestone will always be significantly less expensive than use of beneficiated lime and CO₂ (with the latter two requiring considerable energy inputs). This cost difference is exaggerated by the present South African need to import high quality white lime. Hence,

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whilst use of the simplified SSP and SSP needs to be considered on a case-by-case basis, these processes should always offer significant chemical cost savings over the use of lime and CO₂ based stabilisation. A number of important conclusions can be made and these are summarised below.

In conclusion,

- The low risk simplified SSP was shown via desktop based equilibrium chemistry modelling to be a viable alternative for the full stabilisation of soft, acidic waters.
- The simplified SSP provides significant financial savings over conventional lime and carbon dioxide stabilisation. For example, on a 100 ML/day treatment plant treating a typical Stellenbosch raw water, and requiring a final Total alkalinity of 50 mg/L and a CCPP of zero, the use of a 20% sidestream would result in a saving of R78 900 / month, and R959 950 / year.
- Although optimisation of SSP pilot plant operation could not be achieved, results from operation with sub-standard eductors revealed that CO₂ recoveries of 20 – 40% were obtained. It can therefore be assumed that higher CO₂ recoveries could be obtained if pilot plant operation was optimal.
- Conservative financial assessment of SSP for use at Clarens (Lesotho Highlands Scheme), in which CO₂ recovery and re-use assumptions were well within pilot plant performance, indicates that SSP provides significant financial savings over conventional lime and CO₂ stabilisation with a project payback period of 4.3 years, NPV of R2,7 million and IRR of 52%.

The above results serve as strong motivation for further investigation and industrialisation of both the simplified SSP and SSP.

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

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Mr IR Morrison; water chemistry consultant
Prof WA Pretorius; University of Pretoria
Dr A Lewis; University of Cape Town
Mr SA Pieterse; Cape Metropolitan Council
Mr RG Batson; The Wren Group
Mr DJ Nozaic; Umgeni Water
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Mr OCE Hempel; Water Research Commission (Committee Secretary)

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CHAPTER 1

INTRODUCTION

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1.1 STABILISATION OF SOFT, ACIDIC WATERS

Approximately forty percent of the surface waters of South Africa, and the surface waters of Lesotho, are soft and acidic with low calcium, alkalinity and carbonate species concentration (1) (see Figure 1.1). Typically these waters have low conductivity (5-50 mS/m), low total alkalinity* (0-20 mg/L as CaCO_3), low calcium (0-20 mg/L as CaCO_3) and low pH (4.0 - 7.0). Furthermore, conventional water purification, using flocc agents such as ferric chloride, ferric sulphate and aluminium sulphate, further depresses pH and alkalinity.

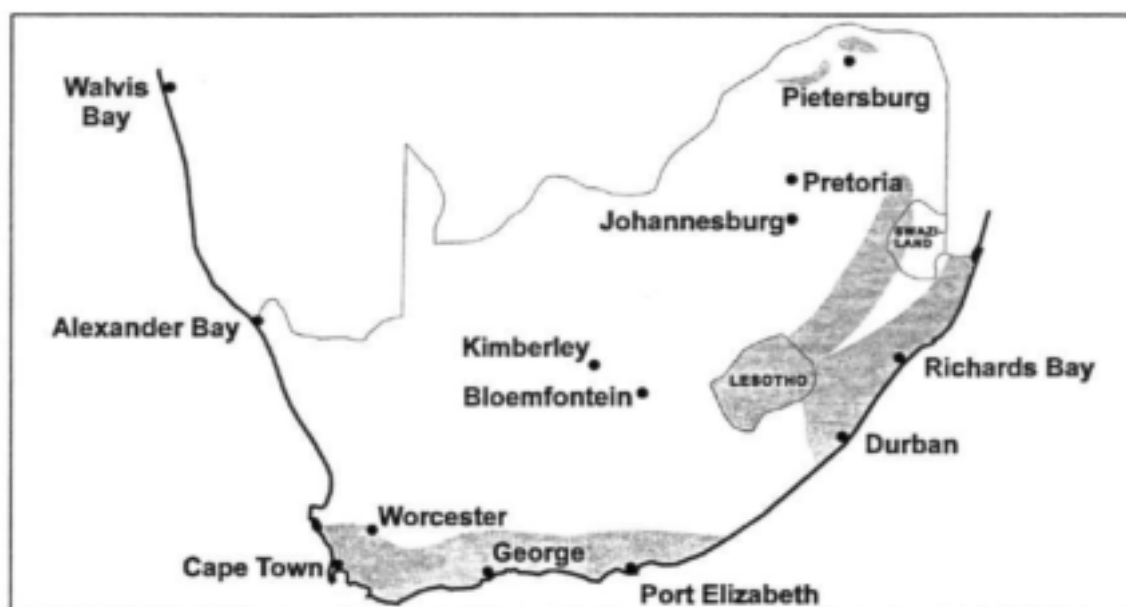


Figure 1.1: Approximate distribution of soft, acidic surface waters in South Africa.

The general problem arising from distribution of such waters is one of aggressive attack of cement concrete pipes and linings, and corrosive attack of metal pipes, valves, etc. within the distribution network. The impact of such attack is usually significant, and comprises the following:

Lost water

The magnitude and cost of water lost from compromised reservoirs and pipe systems as a result of aggressive and corrosive attack can be as high as 50% of treated water, and the associated cost can be substantial. For example: in the Durban townships of Kwamashu, Umlazi and Ntuzuma, total water losses from service reservoirs and the reticulation network was "found to be around 50% of the total bulk volume of water purchased from Umgeni Water" prior to rehabilitation. The annual cost of lost water amounted to about twelve million Rand in 1992 (2).

* For the purposes of this report alkalinity reflects the mass concentration of acid to be added to bring the pH to the H_2CO_3^* equivalence point. This form of alkalinity can either be referred to as H_2CO_3^* alkalinity, total alkalinity, methyl red alkalinity or Alkalinity (LOEWENTHAL et al, 1986). For the purposes of this report, hereinafter, total alkalinity is referred to.

Repairs

The cost of reservoir and pipe rehabilitation can be significant for water supply authorities. For example: in the Stellenbosch area, prior to the upgrading of stabilisation facilities, an average of 30 sections of cement concrete pipe were replaced per month at a cost of R4,000 to R7,000 per section (3). In Durban, Umgeni Water had to carry out expensive repairs to the Durban Heights Reservoir in 1990, to overcome a leak of 300 m³/day (4). At consumer level, corrosive attack can necessitate expensive replacement of pipes and geysers. For example: corrosive attack of internal plumbing in a six year old five star hotel in the Western Cape, necessitated close to one million Rand of repair (5).

Potability

Deterioration in both chemical and microbiological water quality as a result of raised levels of dissolved metals and pipe leakage can be significant; resulting in failure with regards to drinking water standards.

To overcome these problems effective stabilisation is required.

Water conditioning to prevent aggression and/or corrosion can be achieved through stabilisation. Stabilisation of soft, acidic waters comprises the chemical conditioning of water by increasing pH, calcium and total alkalinity concentrations to values satisfying established guidelines. Conventionally, such stabilisation is achieved by the addition of lime (Ca(OH)₂) and carbon dioxide (CO₂). Although this process is well documented and understood, it has a number of drawbacks (6) including:

- Lime dosing equipment is troublesome, and particularly so for small works who are constrained by equipment and staff.
- High quality white lime suitable for water treatment is in short supply in South Africa and the increasing shortfall has to be imported at growing cost. The use of an appropriate alternative to white lime is therefore of strategic importance as it will reduce dependency on imported lime.
- Lime and carbon dioxide stabilisation is expensive, comprising about 50% of the chemical treatment cost.
- The use of poor quality lime results in expensive maintenance shutdown periods.

1.2 SIDESTREAM STABILISATION PROCESS

An alternative stabilisation process is stabilisation via contact with limestone (solid calcium carbonate). Stabilisation via contact with an appropriate limestone in a fixed bed process has been shown to have a number of significant advantages over lime-mediated stabilisation (1).

The use of limestone-mediated stabilisation has, however, hitherto been limited to smaller water treatment works of up to, say, 20 ML/day, as a result of the large contact tanks required. Use of limestone based stabilisation for large city sized water treatment works is potentially made possible by the development by CSIR of a novel limestone mediated sidestream stabilisation process.

The Sidestream Stabilisation Process (SSP) is achieved by taking a sidestream (of a predetermined percentage) of the unstabilised water, dosing high levels of gaseous carbon dioxide (CO₂), and

then contacting the CO₂-acidified stream with limestone. The acidified sidestream takes up considerable amounts of calcium carbonate (CaCO₃), increasing both the total alkalinity and the calcium concentrations. Thereafter CO₂ is stripped, recovered and reused in the process. After CO₂ stripping, the sidestream is blended with the main stream in the correct proportions to allow for a fully stabilised main stream. SSP and its derivations are patented internationally.

Indications from preliminary pilot plant trials and theoretical assessments have shown that the SSP process potentially provides significant cost savings and other advantages over conventional stabilisation (6). These include:

- Chemical cost savings of around 50% resulting from both the use of inexpensive limestone and the recovery and recycling of CO₂ (thereby lowering the requirement for expensive "fresh" CO₂). *NOTE:* The cost of white lime has been seen to fluctuate considerably in the past four years, with recent significant increases in white lime prices. Typical costs for suitable quality limestone and white lime delivered in Cape Town, Western Cape, 2001 are SAR 225/t and SAR 1200/t respectively.
- Reduction in capital costs (as only a small sidestream is required to undergo extensive treatment prior to blending with the bulk stream, only a fraction of the total plant throughput requires retention and treatment).
- Simplicity of storage facilities (as the raw materials are not readily soluble).
- Non-problematic nature of the process (vs. notoriously difficult lime dosing).
- Reduction in plant shutdown (the lime process results in calcification deposits in works and reservoirs).
- The use of unburnt limestone in preference to process lime is energy efficient and environmentally friendly.
- In light of the aforementioned lack of availability of white lime in South Africa, it should also be noted that sufficient quantities of limestone suitable for drinking water stabilisation purposes are available in South Africa. A geophysical survey of the limestone quarry near Bredasdorp revealed that sufficient quantities of suitable were available to stabilise all the waters of Rand Water, Umgeni Water and Cape Metropolitan Council for approximately 100 years (7).

1.3PROJECT MOTIVATION

Rand Water is in the process of considering water transport and treatment requirements for the Lesotho Highlands Scheme Water. The waters of the Lesotho region are relatively soft and acidic, requiring conditioning to prevent attack of cement concrete and metal structures and conduits. It was with this in mind that Rand Water identified the SSP process as a potentially attractive alternative to conventional stabilisation using lime and carbon dioxide. In particular, the SSP presents a potentially attractive and viable option for the Katze Dam water if it is piped directly, but may still be suitable if the water is fed by the Ash-Liebenberg-Wilge River system. As the envisaged pipe system is likely to cost around three billion Rand, protection thereof from aggressive and corrosive attack is a priority consideration.

To ascertain the relative advantage of using the SSP, it is necessary to identify the operational limitations and optimised performance capabilities of SSP, and to consider the desirability and suitability of an optimised SSP for various Lesotho Highlands Scheme water treatment/transfer scenarios. In addition, the motivation for potential industrialisation and full-scale implementation of the process must be assessed.

1.4 WORK APPROACH

The original aims of the project were to:

- Develop and calibrate a process model describing the aqueous, gaseous and solid phase chemistry of the carbonate weak acid/base system and influencing parameters using a commercially available process modelling package. The model would be used to, (i), identify the operational limitations of SSP, and (ii), identify means to improve the performance and optimise the operation of the process.
- Determine the desirability and suitability of the SSP for the Lesotho Highlands Scheme, and assess the motivation for industrialisation and full-scale implementation of the process.

During the project, deviations from the original project objectives arose as a result of both limitations experienced with the commercially available process modelling package and specific requests from the Steering Committee. These are mentioned below:

- Programming and software development. The original project objectives required the use of a commercially available process modelling package to model SSP (the use of an "off-the-shelf" package was regarded as advantageous to Rand Water and other future users). Careful attention was given to choosing the best affordable commercially available process modelling package. At an advanced stage in the project it became apparent that the chosen package had fatal limitations regarding modelling of aqueous-gaseous phase interactions, and that for this reason further use of the package was pointless. Accordingly, originally envisaged programming and software development was carried out.
- Consideration of a simplified sidestream stabilisation process. As a result of Steering Committee concerns regarding the practicalities of full-scale carbon dioxide stripping and recovery, additional desktop development work was carried out into a "simplified SSP" concept. The project team presented the alternate "simplified SSP" process for consideration.

NOTE: Throughout the project consideration has been given to the financial attractiveness of using the SSP systems. During the project period (approximately 3 years) the price of water treatment chemicals has varied not insignificantly. Prices current at the time of the assessment were used throughout the project, and these prices are provided. As the motivation for use, and indeed the viability, of the SSP is largely based on chemical cost savings, updated costs applicable to a particular circumstance must be individually considered.

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2.1 STABILISATION

2.1.1 Aggressive and Corrosive Attack

Of the raw water types used for potable water supply purposes, many are soft and acidic, with low conductivity, alkalinity, calcium and pH. In addition, conventional water purification processes such as clarification and desalination, further depress pH and alkalinity prior to release of the purified water into the distribution network. These characteristics result in the water being **aggressive** (to cement concrete) and **corrosive** (to metals), attacking pipes, conduits and reservoirs.

In many municipal water distribution systems, approximately 90% of the pipes are either composed of a cement-type material, or are cement-lined iron pipes. Soft, acidic waters attack cementitious material by dissolving free lime, and calcium carbonates, -silicates and -aluminates from the cement matrix. This aggressive attack results principally in two adverse effects. Firstly, the integrity of both cement type pressure conduits and water containing structures is lost, resulting in leakage, bursts and structural failure. Secondly, for reinforced concrete structures, the concrete cover is removed, exposing the steel to a corrosive environment, resulting in spalling and eventual failure. Conventionally, the aggressive properties of a water are terminated by adjusting its chemical characteristics to a state where it is saturated or slightly supersaturated with respect to CaCO_3 .

The conduit material in municipal water reticulation systems when made of mild steel or cast iron will be subject to corrosion. Corrosion of 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 effect will be either limited to dissolution of metal ions into solution, or may also result in the formation of large tubercles over the cathodic areas. The latter affects flow characteristics and creates an environment harbouring iron oxidising bacteria. Adverse effects are loss of pipe function and eventual failure of the conduit.

Failure to prevent aggressive and corrosive attack can have significant financial impact in terms of increased network maintenance and lost water, and can impact deleteriously on water quality (1). Chemical conditioning of potable water to ameliorate such attack is referred to as stabilisation.

2.1.2 Stabilisation

Stabilisation of soft, acidic waters to prevent aggressive attack principally requires adjusting the chemical characteristics of the water such that the water is saturated with respect to CaCO_3 . However, to guard against the development of undersaturated conditions from carbon dioxide generation, a slight degree of supersaturation is desirable, and a calcium carbonate precipitation potential (CCPP) of 1 to 2 mg/L is recommended (2). (CCPP is a measure of the amount of solid CaCO_3

that will precipitate from a water to reach aqueous-solid phase equilibrium; whereas CaCO_3 dissolution potential (CCDP) describes the mass of CaCO_3 that will dissolve from a water to reach such equilibrium).

Where reticulation systems include cast iron or mild steel conduits, control of corrosion may take several forms including chemical addition and selection of materials resistant to corrosion. Corrosion prevention and minimisation approaches include use of protective films and pH adjustment, poly- and/or ortho-phosphate addition, addition of silica and suitable materials. The predominant corrosion control measure utilised by water utilities is pH adjustment for calcium carbonate saturation control.

Proposed guidelines pertinent to soft, acidic waters for minimising iron corrosion are that the water should be saturated, or slightly supersaturated, with respect to CaCO_3 , and that the calcium and total alkalinity values should not be less than 50 mg/L (as CaCO_3) (2). Additional criteria, which include minimum concentrations of oxygen, maximum concentrations of chloride and sulphate concentrations, and flow velocity also need to be specified.

With regards to minimising corrosion of copper and brass, passivation by the formation of a protective copper oxide layer is generally achievable by ensuring pH in the range 7.1 to 8.0, low carbon dioxide and ammonia concentrations, and velocity below 1.2 m/s (3).

Stabilisation is usually 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 to adjust pH. However, the use of lime to achieve the above is non-ideal. Firstly, it requires the addition of two expensive industrially produced products, namely lime and carbon dioxide, and secondly, lime dosing is troublesome and problematic. Furthermore, in South Africa, the availability of high quality white lime is poor.

2.1.3 Limestone Mediated Stabilisation

An alternative means of stabilising low pH, calcium and alkalinity deficient waters is by contact with naturally occurring solid calcium carbonate or limestone. In this process, the natural CaCO_3 dissolution driving force of the water - reflected by the CCDP - is used to take up calcium and carbonate species by exposing the water to graded particles of solid limestone. In this manner, alkalinity, calcium and pH are increased. Typically, a water with CCDP of 25 mg/L CaCO_3 will take up close to 25 mg/L CaCO_3 . By definition, this approach will never lead to a CaCO_3 supersaturated water. Nevertheless, such partial stabilisation significantly reduces the aggressive and corrosive characteristics of the water, making the water essentially non-aggressive to cement concrete, non-corrosive to copper, and significantly less corrosive to iron. Such "partial stabilisation" has significant advantages over the traditional use of powdered lime and carbon dioxide:

- The water treats itself, taking up calcium and alkalinity to satisfy equilibrium requirements.
- pH is controlled naturally at desirable upper limits.
- The process is robust and problem-free, with low supervision and maintenance requirements.
- Lime dosing equipment is notoriously troublesome, and impractical in small scale water treatment plants.
- Limestone is significantly cheaper than lime.
- Complicated dosing of expensive carbon dioxide is not required.
- Chemical cost of stabilisation is greatly reduced.

Internationally, use of limestone mediated stabilisation is rare and mostly limited to household size units. This is as a result of the high profile accorded to failures of limestone stabilisation systems. Nearly all failures result from a combination of poor hydraulic design, the use of inappropriate limestone and/or inadequate consideration of special requirements of groundwater. In South Africa, CSIR reinitiated research into limestone stabilisation in the early 1990's which has lead to the successful development and implementation of small and medium sized limestone stabilisation systems. This work is comprehensively reported in WRC Report No 613/1/98 entitled *Stabilisation of Soft, Acidic Waters with Limestone* and the final report of WRC Project No K5/1026 entitled *Consolidation and Transfer of Limestone Mediated Stabilisation Technology for Small to Medium Scale Users*. Furthermore, CSIR has carried out research and development of the SSP system for city size works.

2.1.4 Sidestream Stabilisation Process

The sidestream stabilisation process (SSP) is a limestone mediated stabilisation process for larger water purification installations and is shown conceptually in **Figure 2.1**.

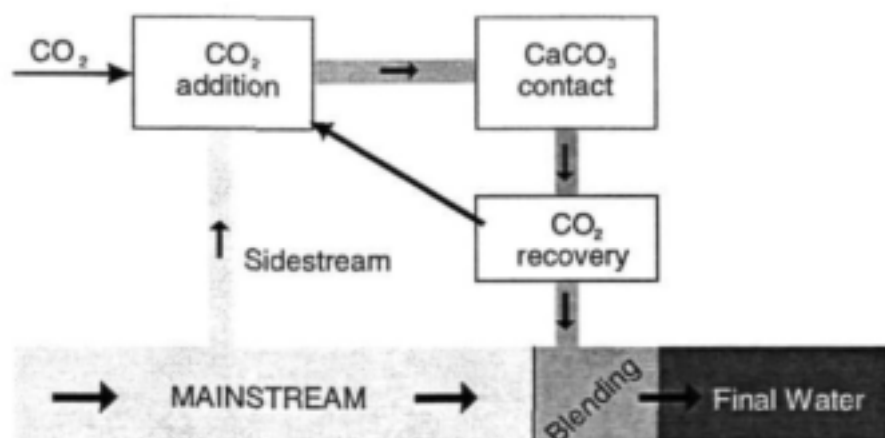


Figure 2.1: Conceptual description of SSP

The process involves taking a sidestream of un-stabilised water, dosing high levels of gaseous CO_2 and then contacting the CO_2 acidified stream with limestone. The acidified sidestream takes up considerable amounts of the solid CaCO_3 , thereby increasing both alkalinity and calcium. Thereafter, CO_2 is stripped and recovered, the CO_2 stripped sidestream then being blended with the main stream in the correct proportions to allow for a fully stabilised mainstream. CO_2 recovery and re-use can be such that the use of "fresh" CO_2 in the process is minimal.

2.2 THEORETICAL CONSIDERATIONS

Of interest to this process are the principles governing the carbonate system in the aqueous, gaseous and solid phases. In particular, dissolution of gaseous carbon dioxide into a liquid phase, dissolution of solid calcium carbonate into a liquid phase, and recovery of excess dissolved carbon dioxide from the liquid phase to the gaseous phase have to be considered. It is not the objective here to address these issues in detail; however, it is useful to note the following:

The kinetics of **carbon dioxide dissolution** into an aqueous media depend on a number of factors, *inter alia* the difference in CO_2 concentration in the two phases, the surface area at the gas/liquid interface, and the mixing of the aqueous phase. In addition, temperature, pressure and ionic strength are important considerations. However, by using a gas phase with a CO_2 partial pressure very much greater than that normally encountered by aqueous media, inordinately high concentrations of molecularly dissolved carbonate species can be attained. Such high concentrations of carbonate species and the dosing chemical type (CO_2) lead to a water with exceptionally high total acidity and calcium carbonate dissolution potential.

The **dissolution of calcium carbonates** can only occur if the solution is undersaturated with regard to solid carbonate. The solubility of CaCO_3 is influenced by temperature and pressure of the system, calcium and carbonate species distribution and the partial pressure of carbon dioxide. Within the normal pH range of natural waters, the dissolution rate of carbonate minerals is surface controlled; that is, the rate of dissolution is determined by a chemical reaction at the water-mineral interface. Whilst at very low pH, the rate of dissolution is so fast that the rate is limited by the transport of the reacting species between the bulk of the solution and the surface of the mineral. The rate can then be described in terms of transport of the reactants and products through a stagnant boundary layer (4). However, suffice to note that waters with high acidity and calcium carbonate dissolution potential brought into contact with solid calcium carbonate minerals will take up exceptionally high levels of calcium and carbonate species.

The kinetics of **carbon dioxide stripping** from an aqueous media depend on a number of factors, *inter alia* the difference in CO_2 concentration in the aqueous and gaseous phases, the surface area at the gas/liquid interface, and pressure. Importantly, by increasing the free surface area and substantially reducing the pressure, transfer to

the gaseous phase by gas-water contact represents a convenient and possibly cost-effective treatment method for removing excess dissolved carbon dioxide.

2.3 DESCRIPTION OF EXISTING CSIR PILOT PLANT

The basic laboratory pilot plant and the conceptual configuration of the pilot plant are shown in **Figure 2.2**. The raw water feed is split, with a predetermined percentage sidestream being abstracted from a constant header tank and fed by a centrifugal pump into the pilot plant; the sidestream flow rate is controlled at 300 L/h using a rotameter, thereby treating a total stream of 6000 L/h. The water passes in a downward direction through the three carbon dioxide dissolution vessels in series. DV1 and DV2 are of dimension: height = 1810 mm, diameter = 200 mm, and DV3: height = 2050 mm, diameter = 150 mm. The first two carbon dioxide dissolution vessels receive pumped recovered carbon dioxide, and the last receives "fresh" carbon dioxide from a commercial gas cylinder. The carbon dioxide is added via diffusers located near the base of the dissolution vessels, and is therefore added counter flow. A constant pressure of about 300 kPa¹ is maintained in the dissolution vessels. Any excess undissolved carbon dioxide in DV3 and DV2 is reintroduced to DV2 and DV1 respectively by liquid level control solenoid valves. Excess gas build-up in DV1 is vented to atmosphere.

Having passed through the dissolution vessels, the acidified water enters the up-flow, flooded, packed-column limestone contactors. The limestone contactors are of dimension: total height = 2410 mm, limestone bed depth = 1615 mm, diameter = 300 mm. The limestone pebbles rest on perforated support plates situated 100 mm from the bottom. A constant pressure of 300 kPa is maintained in the limestone contactors. The water flows through the two contactors in series, taking up calcium carbonate. Thereafter the calcium carbonate enriched water enters the carbon dioxide recovery vessels.

The water passes through the carbon dioxide recovery vessels in series. RV1 and RV2 are of dimension: total height = 2050 mm, diameter = 200 mm. Water is sprayed into the top via spray nozzles and percolates downwards over a packing of Pall rings, and collects at the bottom, with a water level maintained at 200 mm depth. The recovery vessels are operated at a pressure of about 50 kPa; the required vacuum being created by vacuum pumps that pump recovered CO₂ from RV1 to DV2 and from RV2 to DV1 respectively. The sidestream is blended with the balance of the feed.

¹ Pressure is reported in absolute pressure terms throughout this report. Therefore, to determine gauge pressure it is necessary to subtract atmospheric pressure (101.325 kPa at sea level) from the absolute pressure measurement given. For example, an absolute pressure of 300 kPa would have an approximate gauge pressure of 200 kPaG, and a absolute pressure of 20 kPa (vacuum) would have an approximate gauge pressure of -80 kPaG.

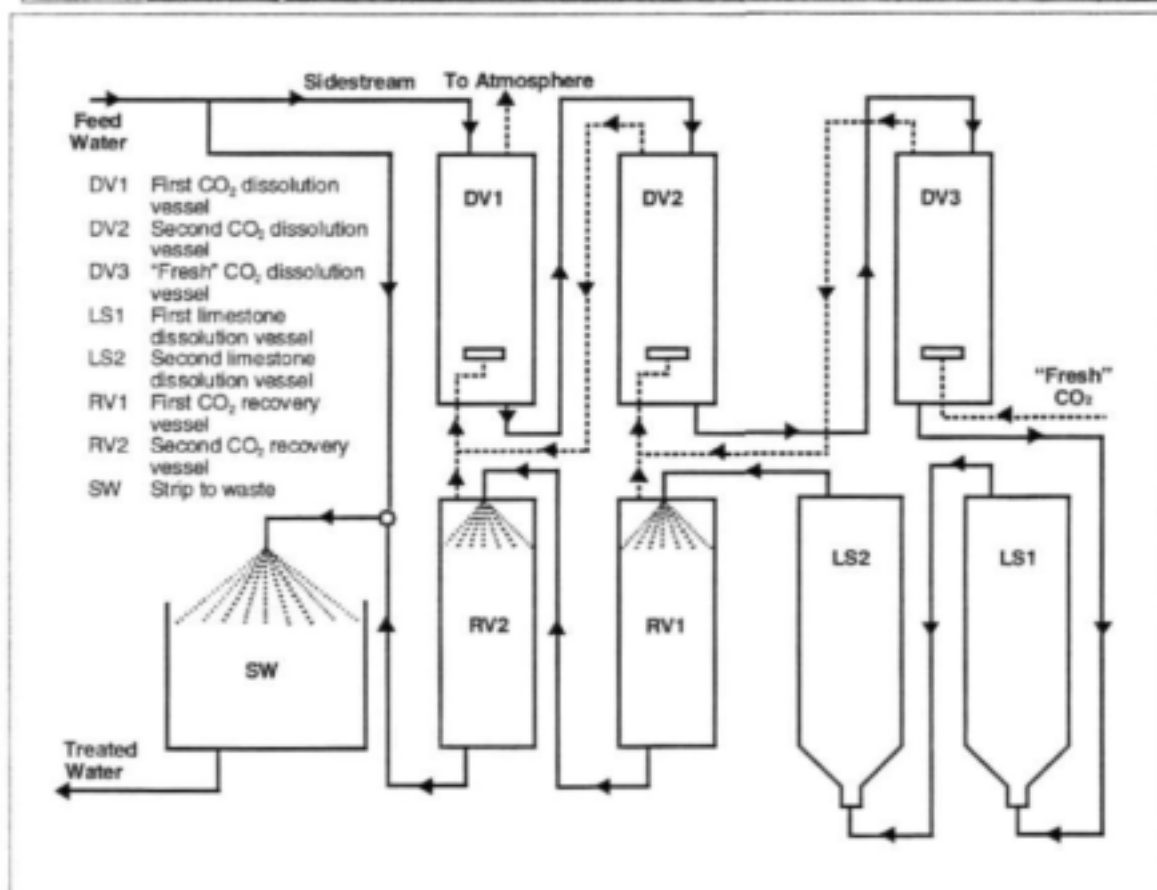


Figure 2.2: Pilot plant and process diagram for the SSP

The blended water then undergoes a final stripping of any excess carbon dioxide, by spraying the water through nozzles into a container. An air stream passes through the container, stripping excess CO_2 from the water, and is then vented to the atmosphere. Eight on-line pH probes provide pH measurement of raw water, final blended water, and after each CO_2 dissolution vessel, limestone contactor, and CO_2 recovery vessel.

The limestone used on the pilot plant is the commercially available limestone pebbles, termed "Aquastab", from P&B Limeworks, Bredasdorp, Western Cape, South Africa. The Bredasdorp deposit is a sedimentary deposit of a porous, friable nature. The cation content of this limestone is (by mass): 96% calcium, 1.7% silica and 1.3% magnesium. Iron and manganese are present at less than 0.1%. Thus, the Bredasdorp limestone deposit can be classified as a high calcium (and low magnesium) limestone. The raw limestone used in the pilot plant had a grading of +12 mm - 15 mm.

2.4 HISTORICAL PILOT PLANT OPERATION AND RESULTS

Preliminary investigation was carried out to confirm desktop predictions as to critical stages in the process, and to develop empirically determined operating parameters (6). A brief description of these stages and findings related thereto are given below:

2.4.1 Acidification via CO_2 Addition

This stage entails the addition of gaseous CO_2 into the aqueous phase sidestream. Desktop calculations indicated that in order to satisfactorily stabilise the main stream with a sidestream of about 5% of the total plant throughput, the required characteristics of the acidified water were: pH of about 3.5, total acidity of about 3000 mg/L (as CaCO_3) and a CO_2 dosage rate of about 1.2 g/L. It was found that at the normal range of temperatures experienced (15 to 25 °C) and a dissolution vessel pressure of 300 kPa this was readily achieved. Accurate measurement of CO_2 addition was not possible via either total acidity calculations (using STASOFT (5) and based on in-line pH measurement), and/or total acidity titrations. (The pH meters were calibrated with pH 4 and pH 7 buffers.) The most accurate means of measuring this parameter to date was via mass loss of the CO_2 cylinder as measured by electronic scale.

2.4.2 Limestone Dissolution

This stage entails the dissolution of CaCO_3 from the solid phase into the aqueous phase. Desktop calculations indicated that in order to introduce sufficient calcium and alkalinity into the main stream via a 5% sidestream, dissolution of about 550 mg/L of CaCO_3 was required. It was shown that this was readily achievable with a CO_2 dosage rate of about 1.2 g/L with vessel pressure of 300 kPa. Total alkalinity was measured via strong acid titration and calcium was measured by atomic absorption spectrophotometry.

2.4.3 Calcium and Alkalinity Dosing Prediction

A relationship between CO₂ dose and the mass of CaCO₃ dissolved was determined experimentally under actual pilot plant operating conditions. This relationship, presented in a so-called "Bones" curve, was found to be reasonably accurate in predicting CaCO₃ dissolution at different CO₂ dosages. The empirically derived relationship was used for the prediction of calcium carbonate uptake, and for the interpretation of CO₂ recovery results.

2.4.4 Determination of Percentage CO₂ Recovery

Probably the most critical stages in the process are the recovery of CO₂ after limestone contact, and reintroduction of the recovered CO₂ into the aqueous phase at the head of the sidestream. Desktop calculations indicated that it is theoretically possible to recover more than 80% of the CO₂ dosage requirement. Initial investigations utilised a single stage CO₂ recovery and re-use system, i.e. referring to **Figure 2.2**, DV1 and RV2 were not operational. The following historical results presented pertain only to single stage recovery. The empirically derived relationship described in Section 2.4.3 was used to determine the total CO₂ dissolved in the water entering the limestone contact columns.

2.4.5 Single Stage Pilot Plant Results

Results of pilot trials using single-stage CO₂ recovery are shown in **Figure 2.3** below. In this particular run, a sidestream of 4.5% of the feed was treated before re-blending with the balance of the feed. The total CO₂ dissolved (880 mg/L) was determined by measuring the amount of CaCO₃ dissolved in the water leaving the limestone contactors and by using the empirically determined relationship described in Section 2.4.3. The amount of CO₂ recovered (547 mg/L) was then calculated by subtracting the amount of CO₂ added (333 mg/L) from the total amount of CO₂ dissolved (880 mg/L). This amounted to a CO₂ recovery of 62%.

After CO₂ stripping and re-blending of the sidestream with the balance of the feed, a considerable amount of CO₂ was still dissolved in the water, which resulted in a pH that was still relatively low at 6.46, and a negative calcium carbonate precipitation potential of 36.9 mg/L as CaCO₃. Using theoretical calculations, air stripping to atmosphere was employed to remove the excess CO₂, which raised the pH to 7.87, and reduced the negative precipitation potential to -4.7 mg/L as CaCO₃. Thereafter, nominal lime dosage was required to obtain a product with a slightly positive precipitation potential.

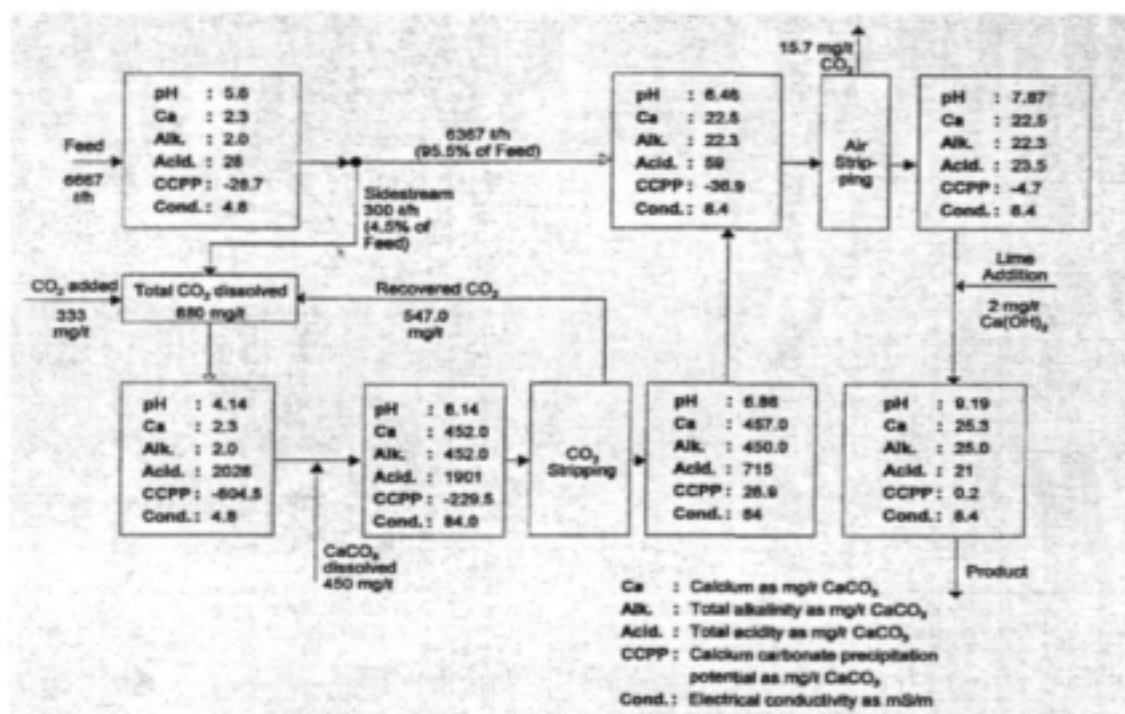


Figure 2.3: Single stage pilot plant results

2.4.6 Financial Considerations

The motivation for an alternate process for stabilization is twofold: (i), circumventing problematic aspects associated with lime mediated stabilisation, such as unavailability of high quality (white) lime in South Africa and difficulties associated with both dry lime dosing equipment and lime saturators, and (ii), the potential cost savings afforded by this alternate process. Potential savings were calculated in a comparison of lime/CO₂ mediated stabilisation versus the sidestream stabilisation process, for a conventional water treatment works processing 225 ML/day of typical soft, acidic, coloured, Cape water as utilised by Cape Town. Both a simple chemical running cost comparison, and a more detailed project finance evaluation were carried out.

In considering the simple chemical running cost comparison, the saving afforded is governed by both the price differential between lime and limestone, and the percentage CO₂ recovered for re-use. Basic comparison of stabilisation chemical running costs for a typical Cape water using chemical costs as current in 1997, shows the importance of maximising CO₂ recovery (**Figure 2.4**). As is clearly illustrated, running cost savings are strongly influenced by percentage CO₂ recovery. At a recovery of 60% (as obtained during the preliminary investigation), reasonable savings accrue. However, at the then envisaged recovery of 80%, the chemical costs of stabilization would be halved from approximately 2.6 cents/m³ to about 1.3 cents/m³, resulting in associated annual savings of about R1.06 million per annum for

the 225 ML/day water purification plant (using 1997 prices, Western Cape). Such a saving is significant as stabilisation costs make up approximately half of water treatment costs of Cape waters.

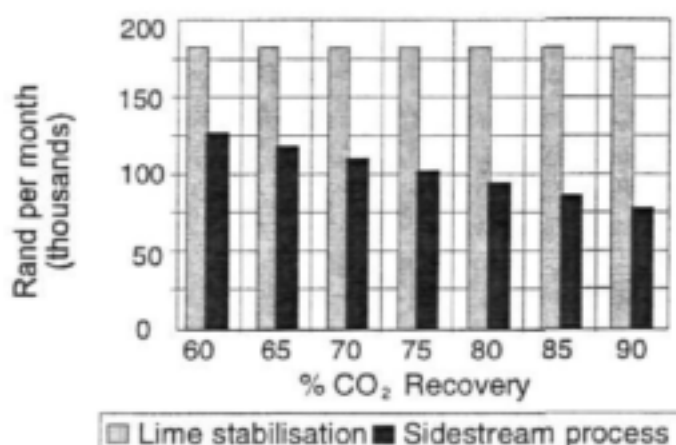


Figure 2.4: Basic comparison of chemical running costs of conventional lime stabilisation and sidestream stabilisation processes

In a more complex evaluation, cognisance was taken of the fact that the potential operating cost savings afforded by replacing the conventional process with the new sidestream stabilisation process would need to pay for the capital expenditure to install the new process (i.e. not a green field project). Therefore, in the comparison, the operating and capital cost of the alternate sidestream stabilisation process was offset against the operating costs of the existing lime stabilisation process. The financial model used for the comparison took into account chemical costs, labour costs, maintenance shutdowns, capital cost recovery, inflation, required return on investment and risk in the Western Cape in 1997. A presumed CO₂ recovery level of 80% was presumed, and a project life span of 10 years, and a discount rate of 50% (10% for inflation, 10% for return above inflation, and 30% for risk) were assumed as reasonable. The potential benefit of replacing the existing process with the sidestream stabilisation process is clearly illustrated in **Figure 2.5**, which shows a payback period of two years, and **Figure 2.6**, which show a projected project Net Present Value of R 964,000. The Internal Rate of Return was calculated to be 65%. These financial indicators illustrate the potentially very attractive financial benefits of the sidestream stabilisation over conventional lime/CO₂ stabilisation.

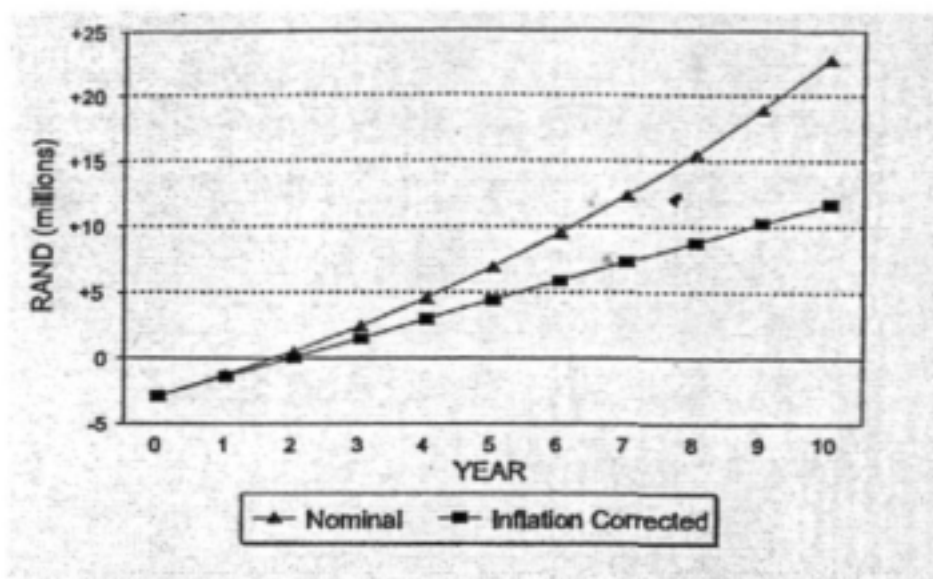


Figure 2.5: Nominal and inflation corrected savings afforded by replacement of existing lime stabilisation process with the sidestream stabilisation process

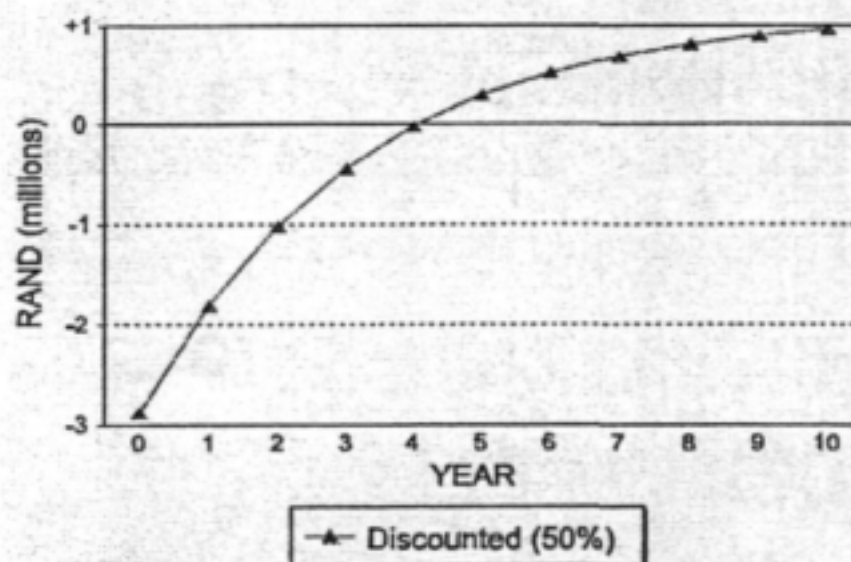


Figure 2.6: Discounted savings afforded by replacement of existing lime stabilisation process with the sidestream stabilisation process

This preliminary investigation showed that the SSP process was potentially very attractive and provided the basis of motivation for continued research.

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CHAPTER 3

THE USE OF PROCESS MODELLING PACKAGES FOR PREDICTING THE BEHAVIOUR OF THE SIDESTREAM STABILISATION PROCESS

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3.1 INTRODUCTION

The aim of this investigation was to accurately predict the behaviour and to develop models describing the aqueous, gaseous and solid phase chemistry of the Sidestream Stabilisation Process (SSP), using commercially available process modelling packages. This would then allow for the further consideration and optimisation of the SSP process, and understanding of its limitations, prior to any industrial scale construction.

The process models developed using the simulation packages would be largely based on the configuration of the pilot plant. The ability of the process modelling package to predict the operation of the SSP would be based on obtaining similar results for the process simulations as experienced during pilot plant operation and from known aquatic chemistry software.

Many process modelling packages are commercially available. The first step in the investigation was to short list packages that seemed viable for modelling the SSP. Thereafter, a preliminary assessment of at most two potential packages would be carried from which a single process modelling package would be chosen with inputs from the Steering Committee. Finally, the chosen package would be used for the development of a process to model SSP.

In order to short list suitable packages inputs from industry, the Departments of Chemical and Civil Engineering of University of Cape Town, the Departments of Chemical Engineering at the University of Stellenbosch and Cape Technikon were sought. After some deliberation, the packages selected for further consideration were:

- *ASPEN PLUS*, manufactured and distributed by *Aspen Technology Inc.*
- *PRO/II*, manufactured and distributed by *Simulation Sciences Inc. (SIMSCI)*.

3.2 PRELIMINARY ASSESSMENT OF ASPEN PLUS AND PRO/II AS PROCESS SIMULATION PACKAGES

A literature review of the two process modelling packages indicated that they are generally very similar (1, 2, 3). Both packages are widely used in industry for process development and optimisation, and have the ability to perform rigorous mass and energy balances. Therefore in order to assist decision-making an initial hands-on preliminary assessment was conducted. The aim of this preliminary investigation was to try and simulate the conditions and results as obtained from prior operation of the SSP pilot plant within a limited time frame, and in doing so ascertain the suitability of the relevant package for extended modelling of SSP.

3.2.1 Preliminary Assessment - ASPEN PLUS

ASPEN PLUS is a process simulation package that is popular in the chemical process engineering industry. The package performs rigorous mass and energy balances and enables the operator to run many cases, conduct "what-if" analyses, perform sensitivity studies and optimisation runs.

Simulation Model Generation

A process is translated into a process simulation model in *ASPEN PLUS* by the following steps:

- Define the process flowsheet configuration. The unit operations and process streams must be defined, and appropriate unit operation models must be selected from the *ASPEN PLUS* library.
- Specify the chemical components in the process. Components can be defined or selected from the *ASPEN PLUS* databanks.
- Choose appropriate thermodynamic models to represent the physical properties of the components and mixtures in the process.
- Specify the component flow rates and the thermodynamic conditions (temperature, pressure, etc.) of feed streams to the process.
- Specify the operating conditions for the unit operations in the flowsheet.
- Run the simulation.

The simulation results are then saved in an output file, where one is able to analyse data obtained for both product streams and unit operations. Unit operations found in *ASPEN PLUS* are listed below:

- Mixers and splitters
- Flashes, heaters and heat exchangers
- Shortcut and rigorous distillation
- Reactors, including stoichiometric, yield, equilibrium, Gibbs energy minimization, CSTR, PFR and batch reactors.
- Pumps and compressors
- Stream manipulators
- Pipes and valves
- Crushers and screens
- Gas-solid separators
- Liquid-solid separators
- Solids Washers

ASPEN PLUS also has a Design Specification (*Design-Spec*) feature that can be employed to meet a specific process design target by manipulating any simulation input variable. This feature is useful for process control and optimisation.

Preliminary *ASPEN PLUS* Process Model

The aim of the preliminary investigation was to try and simulate the conditions and results as obtained from operation of the SSP pilot plant. The initial model generated would be simplistic and would attempt to identify the capabilities and limitations of the *ASPEN PLUS* modelling package.

The model was generated with the following assumptions:

- Steady state pilot plant operation.
- Reactions reach thermodynamic equilibrium.
- Reaction kinetics can be ignored.

The flowsheet model generated in *ASPEN PLUS* is shown below.

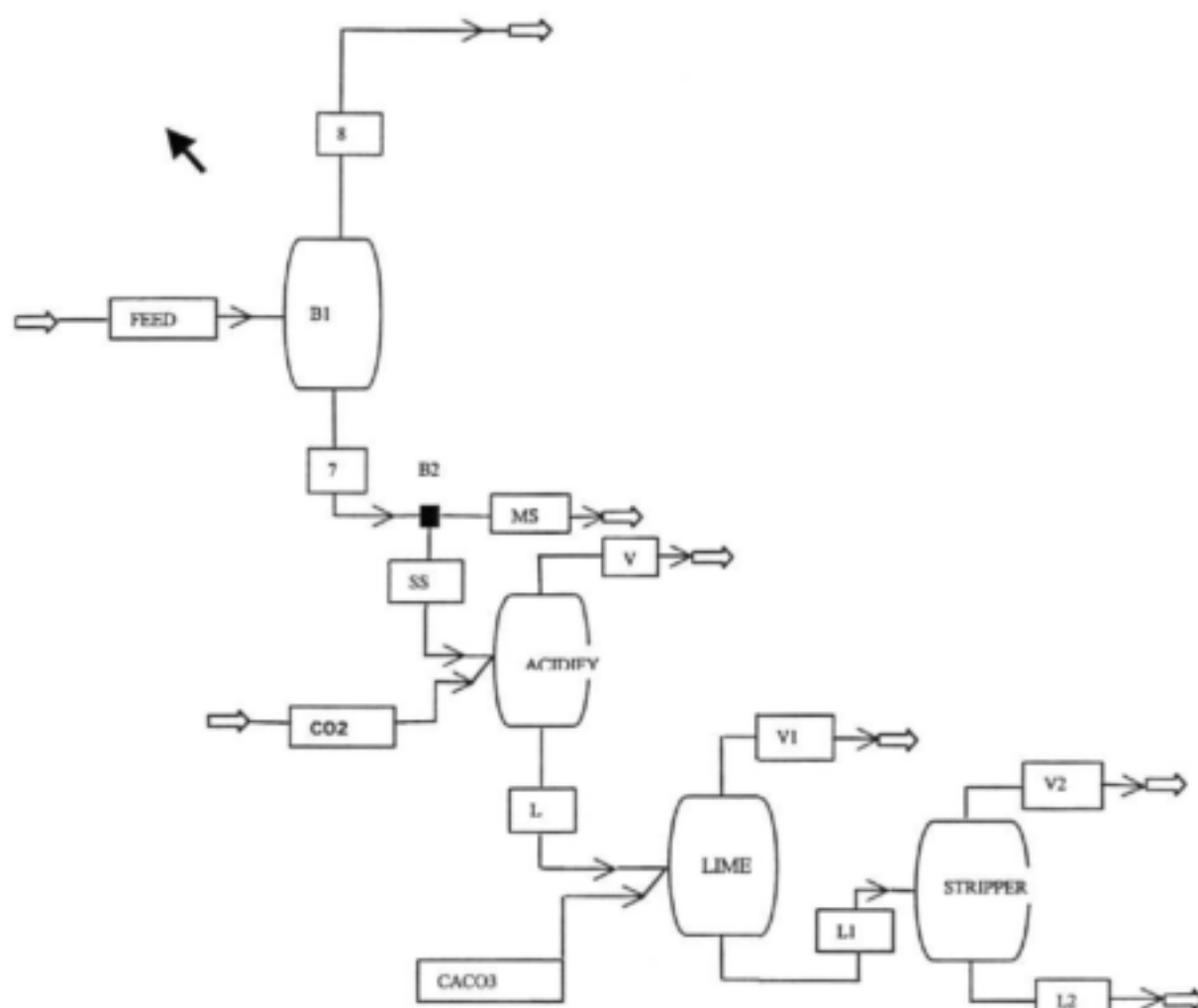


Figure 3.1: Sidestream Stabilisation simulation model generated in *ASPEN PLUS*

The model generated encompassed the following critical steps of the SSP:

- Addition of CO₂ gas to the sidestream.
- Addition of limestone to the acidified stream.
- Stripping of CO₂ from the stabilised stream.

From the above simulation the following results were generated:

Table 3.1: Comparison between pilot plant and *ASPEN PLUS* model results for the feed stream

FEED	SIDESTREAM PILOT PLANT	ASPEN PLUS MODEL
pH	5.6	5.6

Calcium as CaCO ₃ (mg/L)	2.3	2.3
Total alkalinity as CaCO ₃ (mg/L)	2.0	2.0
Total acidity as CaCO ₃ (mg/L)	28	27
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-28.7	-27.1
Electrical Conductivity (mS/m)	4.8	4.8

Table 3.2: Comparison between pilot plant and ASPEN PLUS model results for the acidified sidestream

CO ₂ ADDITION	SIDESTREAM PILOT PLANT	ASPEN PLUS MODEL
pH	4.14	4.11
Calcium as CaCO ₃ (mg/L)	2.3	2.3
Total alkalinity as CaCO ₃ (mg/L)	2.0	2.0
Total acidity as CaCO ₃ (mg/L)	2028	2187
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-604.5	-552.0
Electrical Conductivity (mS/m)	4.8	4.8

Table 3.3: Comparison between pilot plant and ASPEN PLUS model results for the stabilised sidestream

LIMESTONE ADDITION	SIDESTREAM PILOT PLANT	ASPEN PLUS MODEL
pH	6.14	6.10
Calcium as CaCO ₃ (mg/L)	452.0	502.3
Total alkalinity as CaCO ₃ (mg/L)	452.0	502.0
Total acidity as CaCO ₃ (mg/L)	1901	2181.8
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-229.5	-135.0
Electrical Conductivity (mS/m)	84.0	84

Table 3.4: Comparison between pilot plant and ASPEN PLUS model results for the stabilised sidestream after CO₂ stripping

CO ₂ STRIPPING	SIDESTREAM PILOT PLANT	ASPEN PLUS MODEL
pH	6.88	6.10
Calcium as CaCO ₃ (mg/L)	457.0	502.3
Total alkalinity as CaCO ₃ (mg/L)	450.0	502.0
Total acidity as CaCO ₃ (mg/L)	715	2181.8
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	28.9	-135.0
Electrical Conductivity (mS/m)	84	84

From the tables it is clear that when using *ASPEN PLUS* it was possible to accurately simulate feed conditions as used during SSP pilot plant operation. Both the results of the CO₂ acidified

sidestream, and the stabilised (via limestone addition) sidestream show that the model in *ASPEN PLUS* could accurately predict the conditions in these streams on the SSP pilot plant.

However, the apparent accuracy of the process model is undermined by the fact that:

- The total amount of CO₂ added was greater than that in the pilot plant operation (i.e. addition of 966.45 mg/L of CO₂ instead of 880 mg/L as found in the pilot plant operation).
- The amount of limestone (CaCO₃) added was also greater than that in the pilot plant operation (i.e. addition of 500 mg/L of CaCO₃ instead of 450 mg/L as found in the pilot plant operation).

If the correct inputs had been entered, the results would not be as accurate as would appear.

The preliminary investigation encountered a problem when CO₂ was required to be stripped from the limestone stabilised stream. In practice, water containing CO₂ is sprayed into the top of the CO₂ recovery vessels (RV1 and RV2) via spray nozzles, thus stripping the water of CO₂. The water percolates downwards over a packing of Pall rings, and collects at the bottom, after which it blends with the untreated feed stream. The recovery vessels operate at a pressure of about 50 kPa; the required vacuum being created by vacuum pumps. These pumps transport the recovered CO₂ to the CO₂ dissolution vessels (DV1 and DV2) where the CO₂ is added counter flow, via diffusers (located at the base of the dissolution vessels) to the incoming sidestream.

The above operation can be modelled using the flash drum unit operation in *ASPEN PLUS*. This operation was, however, unable to separate CO₂ from the liquid mixture at the required vacuum conditions (50 kPa). A further model revealed that at pressures lower than 40 kPa, a small quantity of CO₂ was recovered. Despite repeated attempts over a period of about four weeks to receive comment/assistance from the *ASPEN Helpdesk* to address this problem, no reply was received prior to the end-date of this preliminary assessment.

Conclusions: Preliminary Assessment of *ASPEN PLUS*

The initial investigation using *ASPEN PLUS* indicated that the modelling package was able to accurately simulate certain key steps of the SSP.

However, problems were encountered when developing the model for the CO₂ stripping and recovery step. It became apparent that this step required careful consideration and the *ASPEN Helpdesk* was therefore contacted. Unfortunately, despite repeated attempts over a period of about four weeks to receive comment/assistance from the *ASPEN Helpdesk* to address this problem, no reply was received prior to the end-date of this preliminary assessment.

3.2.2 Preliminary Assessment - *PRO/II*

The *PRO/II* modelling package is similar to *ASPEN PLUS*. The *PRO/II* process simulation package performs rigorous mass and energy balances for a wide range of chemical processes, and

has been successfully used in industry for designing new processes, evaluating alternative plant configurations and optimising existing plants.

Simulation Model Generation

A process can be translated into a process simulation model in *PRO/II* by the following steps:

- Draw your flowsheet. Select the appropriate unit operations from the *PROVISION* suite of process icons and define the streams (feed and product).
- Define your components selected from the *PRO/II* database.
- Select your thermodynamic calculation methods. Choose from the list of commonly used methods, generalized correlations, equations-of-state methods, liquid-activity methods, and special data packages.
- Define your feed streams. Enter in required information such as flowrates, compositions, temperature and pressure.
- Provide your process conditions.
- Run your simulation.

The simulation results are then outputted into a file, where one is able to analyse data obtained for both product streams and unit operations. The following unit operations and models are available for use in *PRO/II*:

- Mixers and splitters
- Flashes, heaters and heat exchangers
- Distillation
- Reactors, including stoichiometric, conversion, equilibrium, Gibbs energy minimization, CSTR, PFR batch and in-line *FORTRAN* reaction kinetics reactors.
- Pumps, compressors and expander
- Pipes and valves
- Solids models
- Polymer models

PRO/II also contains various functions that employ control (feedback, feedforward, etc.) and optimisation techniques. These operations perform similar functions to the Design Specification feature found in *ASPEN PLUS*.

PRO/II offers optional add-on modules that allow the user to simulate refinery reactors with batch distillation, batch reactors, electrolyte systems, Honeywell HiSpec Solutions Profimatics models, and polymer processes. For the purpose of modelling the SSP, the electrolyte add-on module was required.

***PRO/II* Electrolytes**

The electrolyte add-on module of *PRO/II* allows the user to model the behaviour of systems containing electrolytes. At present, the following unit operations can be used in the current version of the electrolyte module:

- Flash
- Pump
- Valve
- Mixer, Splitter
- Pipe
- Simple heat exchanger, LNG heat exchangers
- Conversion reactor, equilibrium reactor
- Stream calculator
- Heating/cooling curve
- Calculator
- Controller, Optimiser
- Column

As can be seen from the above list, several unit operations normally available for use in *PRO/II* are still unavailable for use with electrolytes. The main reasons for this are that electrolyte models may not be used for calculating non-aqueous electrolyte systems, free water decant, water dew points, entropy and heat capacity. The units not available are discussed below:

Compressor/Expander

These units both require entropy and are therefore not available with *PRO/II* Electrolytes.

Reactors

When using reactors it should be remembered that in *PRO/II* Electrolytes, a reactor is not always necessary in order to get a "reaction". For reactions in aqueous solution that involve a "rearrangement" of ions, the reactor model is not necessary.

- *Gibbs Reactor*
This unit requires entropy, and can therefore not be used with electrolyte thermodynamic methods.
- *PFR/CSTR*
These units are currently not available with electrolyte thermodynamic methods as they are unable to handle liquid-solid phase type components, which electrolyte models usually contain.

Dissolver

This unit may be successfully used with *PRO/II* Electrolytes if care is taken in setting up the problem. If the only purpose of the unit is to dissolve solids to the equilibrium concentration, a flash drum should be used instead. The dissolver should only be used when the process does not reach equilibrium, or when it is important to know the particle size distribution of the product.

Eight built-in electrolyte thermodynamic models are provided, which can be used to simulate aqueous systems in a wide range of industrial application. The models apply to fixed component lists with a pre-defined set of thermodynamic methods for K-values, enthalpies and densities. The following electrolyte models are available in this release:

- Amine systems

- Acid systems
- Mixed salt systems
- Sour water systems
- Caustic systems
- Benfield systems
- Scrubber systems
- LLE and Hydrate systems

The user can create additional models if the optional *Electrolyte Utility Package (EUP)* is employed.

From the above electrolyte thermodynamic models, the most appropriate system for modelling the SSP had to be selected. For this, the model employed would need to contain all the components present in the SSP. Of the available models, the *SCRU* function of the Scrubber systems model was selected.

Preliminary *PRO/II* Process Model

The aim of the preliminary investigation was to try and simulate the conditions and results as obtained from prior operation of the SSP pilot plant, and in doing so ascertain the suitability of the package for extended modelling of SSP. The initial model generated would be simplistic and would attempt to identify the capabilities and limitations of *PRO/II*. The preliminary investigation using *PRO/II* was to include:

- Process simulation package familiarisation.
- Creating a basic model of the SSP.
- Preliminary investigation and review of the simulation package, to test the capabilities and limitations with regards to:
 - CO₂ addition
 - CaCO₃ dissolution
 - CO₂ stripping
 - CO₂ recovery and recycle

The model was generated with the following assumptions:

- Steady state pilot plant operation.
- Reactions reach thermodynamic equilibrium.
- Reaction kinetics can be ignored.
- As the pilot plant was tested at sea-level conditions, atmospheric pressure within the simulation is 101.325 kPa.
- The operating temperature of the process, and thus the simulation, is 20°C.

From the process description and diagram the following *PRO/II* process flowsheet was generated.

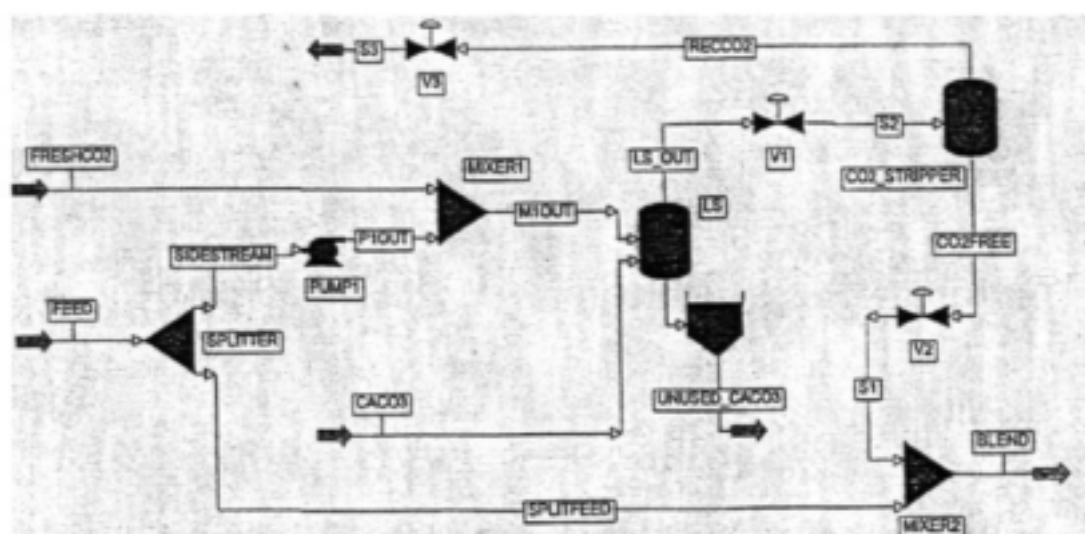


Figure 3.2: Process Flowsheet for the Sidestream Stabilisation Process as modelled in PRO/II

The model generated encompassed the following critical steps of the SSP:

- Addition of CO₂ gas to the sidestream.
- Addition of limestone to the acidified stream.
- Stripping of CO₂ from the stabilised stream.
- Recovery and recycle of CO₂ from the stabilised stream.
- Addition of stabilised sidestream to the balance of the feed to form a blended stream.

Initially, the model was kept as simple as possible as this would aid in understanding what occurs within each unit operation of the process. Attempts to employ the same unit operation in series (as is the case on the pilot plant) showed that their use was redundant.

In the above process model, raw water is fed into a splitter, with a 4.5% sidestream being abstracted and fed into the SSP pilot plant. The total feed flowrate is 6667 L/hr with a sidestream flow of 300 L/hr. The splitter unit is generally used to split a single feed, or mixture of feeds, into two or more products of identical composition and phase condition. The outlet stream pressure

may be specified, if desired, and an adiabatic flash is used to determine the outlet temperature and phase.

A pump was employed to raise the pressure of the sidestream to those conditions experienced on the pilot plant (300 kPa). The pump unit operation is generally used to compute the energy required to increase the pressure of a process stream. In the calculations carried out, only one liquid phase is allowed (i.e. no solids in the stream - as a default *PRO/II* sets the solids flow to zero). The default pump efficiency is 100%. A compressor was not employed as this unit operation is currently not supported in the Electrolytes module.

The sidestream then enters three CO₂ dissolution vessels in series (DV1, DV2 and DV3), which were modelled as a single mixer. The mixer unit combines two or more streams into a single product stream. The default pressure drop across the unit is zero, and the outlet temperature and phase condition are determined with an adiabatic flash from the feed conditions. Fresh CO₂, at 300 kPa, is added, together with the sidestream, to the mixer and the blended CO₂-water stream then enters the limestones columns.

The limestone columns (LS1, LS2) were modelled using the "Flash with Solids" unit operation operating at 300 kPa. Solid limestone is added to the flash unit, together with the CO₂-acidified stream. Any unused CaCO₃ will report to the stream provided. The stabilised water then enters the CO₂ recovery columns (RV1, RV2), which strips and recovers CO₂ for further use. The recovery of CO₂ was modelled as follows. The stabilised stream passes through a valve which generates the required vacuum conditions for CO₂ recovery, and then enters a flash drum which recovers CO₂ in the overhead product. The recovered CO₂ is then recycled for re-use in the process. A valve increases the pressure of the recovered stream from the vacuum conditions to the operating pressure of the CO₂ dissolution columns (i.e. 300 kPa).

The CO₂-free water also passes through a valve that increases the pressure of the stream from vacuum conditions to atmospheric pressure. This water is then mixed with the balance of the feed water to form a blended stabilised stream. This stream can then be sent, if necessary, for stripping of any excess CO₂ and for the addition of lime.

Review of Preliminary *PRO/II* Model Generated

This section gives critical comment with regards to the preliminary model generated in *PRO/II*. The review highlights the methodology used to determine the required unit operation for the process simulation, problems encountered while modelling the SSP, and the results generated for the simulation are discussed.

Feed

The initial objective was to try and simulate the feed as used in the SSP pilot plant tests as closely as possible. If the feed conditions could be accurately simulated, it would provide a basis for comparing the results for the other streams in the simulated model. When simulating the feed conditions, the following assumptions were made:

- Acidity only originates from the quantity of CO₂ present in the water (i.e. no other acid (e.g. hydrochloric acid) is present).

- Calcium present in the feed is only as a result of the dissolution of CaCO_3 (and not calcium hydroxide (Ca(OH)_2) or calcium chloride (CaCl_2)).

Using these assumptions, and the conditions of the feed water used in the pilot plant, the following results were generated.

Table 3.5: Comparison between pilot plant and PRO/II model results for the feed stream

FEED	SIDESTREAM PILOT PLANT	PRO/II MODEL
pH	5.6	5.68
Calcium as CaCO_3 (mg/L)	2.3	2.1
Total alkalinity as CaCO_3 (mg/L)	2.0	2.1
Total acidity as CaCO_3 (mg/L)	28	24
Calcium carbonate precipitation potential as CaCO_3 (mg/L)	-28.7	-24.0
Electrical Conductivity (mS/m)	4.8	3.8

The results indicate that the quality of the feed water produced closely resembles that used in the pilot plant.

CO₂ Addition

After the feed is split, the sidestream enters three CO_2 dissolution vessels in series (DV1, DV2 and DV3). These dissolution vessels were modelled as a single mixer. Modelling the dissolution vessels as a mixer seems viable, as the task the mixer performs is essentially the function of the dissolution vessels (i.e. contacting CO_2 and water in cross-flow in order to obtain a water mixture saturated with CO_2). The mixer unit combines the incoming CO_2 stream with the sidestream to form a single product stream. Using this configuration in the process flowsheet, the following results were generated.

Table 3.6: Comparison between pilot plant and PRO/II model results for the acidified sidestream

CO ₂ ADDITION	SIDESTREAM PILOT PLANT	PRO/II MODEL
pH	4.14	4.14
Calcium as CaCO_3 (mg/L)	2.3	2.1
Total alkalinity as CaCO_3 (mg/L)	2.0	2.1
Total acidity as CaCO_3 (mg/L)	2028	1998
Calcium carbonate precipitation potential as CaCO_3 (mg/L)	-604.5	-514
Electrical Conductivity (mS/m)	4.8	0.6

The results indicate that the water quality of the sidestream after CO_2 addition closely resembles that found when operating the pilot plant.

CaCO₃ Dissolution

After the addition of CO₂, the acidified water is contacted with two limestone packed beds. In practice, the limestone columns are essentially plug flow reactors (PFR's). Water is fed at the bottom of the column, passes upwards through a limestone bed and exits via the top. Unfortunately it is not currently possible to use a PFR model in *PRO/II* Electrolytes and an alternative unit operation was thus required. The alternatives considered included:

- Conversion/equilibrium reactor
- Dissolver
- Flash drum with solid separator/Flash with Solids

Conversion/Equilibrium Reactor

When using a reactor model, a reaction set must be generated. This reaction data set is generated from the list of components, by supplying the stoichiometric coefficients for the selected reactants and products. Ions, however, cannot be entered into this field, and therefore these units were not used (products are limited to those components available in the thermodynamic model; ions can not be entered as final products). The following inputs are also required for the reactions within the limestone contactor: heats of reaction, equilibrium data (equilibrium coefficients) and kinetic data (pre-exponential factor, activation energy, temperature exponent, reaction order and activity basis). This makes the use of these reactors a very tedious exercise.

In addition, as stated previously, it is not always necessary to use a reactor model when using electrolytes as the reactions usually involve a rearrangement of ions.

Dissolver

The dissolver unit operation models the dissolution of solids into liquid solutions, by transforming crystals in solution, from the solid to the liquid phase. *PRO/II* models the most common type of dissolver; the stirred tank dissolver, but this operation does not occur in the SSP (i.e. the limestone columns of the SSP act on a plug flow basis). When using the dissolver unit operation, both the overhead and the bottoms product must be specified. The bottoms contains the liquid product along with any remaining crystals, while the overhead contains any vapour generated in the unit.

An attempt was made to model the limestone dissolution columns using the dissolver function. The two limestone columns were modelled as a single dissolver (with volume equal to the sum of the two limestone columns). The limestone particle size distribution was specified as +12 - 15 mm (same as that used in the pilot plant operation) and the dissolution rate was calculated from diffusivity using *Treybal's Correlation* (system default). The results, however, indicated that the *Wilke-Chang* diffusivity calculations failed, and that a new thermodynamic method set was required. As the thermodynamic set used (*SCRU*) was the only method from the *PRO/II* Electrolyte database that contained all the components required to model the SSP, the use of the dissolver function was abandoned.

In addition, as stated previously, if the only purpose of the dissolver is to dissolve solids to the equilibrium concentration (as occurs in the SSP), a flash drum should be used.

Flash Drum with Solid Separator/Flash with Solids

A flash unit may be used to model any equilibrium calculations where two of the conditions are defined (e.g. temperature and pressure). The phase equilibrium is determined, and the product

stream is separated into product streams corresponding to the phases. The overhead product contains any vapour generated, while the bottoms product would contain any liquid/solid product. This liquid/solid product could then be sent to a solid separator. This unit models the separation of solid phase material from a mixture of feed streams.

However, in *PRO/II*, a unit operation termed "Flash with Solids" is recommended for flash calculations where a solids product stream is present. The unit essentially models a flash drum with four product streams:

- A vapour phase overhead stream from the flash drum section.
- A liquid phase stream from the flash drum section.
- A decanted liquid stream from the solids separator section.
- A solid phase bottom stream from the separator section. The system default is complete separation of the solid from the liquid stream.

From the available models, the "Flash with Solids" unit was deemed most appropriate for modelling the behaviour of the limestone columns. The incoming water, and a solid stream of calcium carbonate (CaCO_3) with a rate of 450 mg/L is fed into the flash with solids unit operation at 20°C and 300 kPa. The CaCO_3 enriched water then enters the CO_2 recovery vessels. A stream for any unused solid CaCO_3 is also provided. Using these criteria, the following results were generated.

Table 3.7: Comparison between pilot plant and *PRO/II* model results for the stabilised sidestream

LIMESTONE ADDITION	SIDESTREAM PILOT PLANT	<i>PRO/II</i> MODEL
pH	6.14	6.08
Calcium as CaCO_3 (mg/L)	452.0	452.7
Total alkalinity as CaCO_3 (mg/L)	452.0	433.5
Total acidity as CaCO_3 (mg/L)	1901	1983
Calcium carbonate precipitation potential as CaCO_3 (mg/L)	-229.5	-178.0
Electrical Conductivity (mS/m)	84.0	80.0

The results indicate that the flash with solids unit operation accurately modelled the behaviour of the limestone columns in the pilot plant operation. It should also be noted that the stream created for any unused CaCO_3 had no flow (i.e. did not contain any components). This is expected, as the rate of CaCO_3 dissolution was determined experimentally on the pilot plant, and used as the input of solid CaCO_3 for the model. The result indicates that all of the available CaCO_3 is consumed.

CO₂ Stripping and Recovery

After the sidestream is stabilised, CO_2 is stripped and recovered for further use in the SSP. On the SSP pilot plant the CO_2 recovery vessels operate at a vacuum of 50 kPa, drawing off CO_2 , and allowing aerated water to trickle through a packed bed of Pall Rings for further treatment. This vacuum generation was modelled using the valve unit operation, as this function is able to model a pressure drop within a line. (The pump unit operation can only be used when an increase in

pressure is required, while the expander unit operation cannot be employed, as it is not currently supported in the Electrolytes module.) The required vacuum generated by the valve was 50 kPa.

On the SSP pilot plant, CO₂ recovery is affected via two vessels in series. Initially, these recovery columns were modelled as a single flash unit, with CO₂ gas being recovered as the overhead product from the mixed solution. The flash drum, however, did not yield any overhead vapour product at the specified conditions of 20°C and 50 kPa, and thus an alternative to perform this separation was considered. The stream calculator unit operation was then employed, as this function is able to split a feed stream into two product streams with defined compositions. This would enable the user to specify the amount of CO₂ required for recovery. Unfortunately, this unit operation did not operate satisfactorily, as it requires the output specifications for all the components in the product streams, which is unknown.

The CO₂ recovery columns were then modelled as a single splitter. The splitter unit operation can be used to attach a specification to a particular component (in our case the desired specification would be on the quantity of CO₂ recovered in the overhead product). The unit operation was able to recover the desired quantity of CO₂, but due to the operating principal of the splitter, the stream contained a large quantity of water. (The splitter unit operation generally splits a single feed, or mixture of feeds, into two or more products of *identical composition* and phase condition. This implies that if the recovered CO₂ stream contained 70% of the total CO₂ available in the incoming feed stream to the splitter, the same stream would contain 70% of the total water in the feed stream. The balance of the components would report to the other product stream/s.)

At this stage it appeared as though separating CO₂ from a liquid mixture could be problematic in PRO/II at 20°C and 50 kPa. Using a flash drum once again, it was found that as the vacuum pressure increased, the quantity of CO₂ recovered also increased. The following table briefly indicates the relationship between the vacuum pressure and the amount of CO₂ recovered.

Table 3.8: Amount of CO₂ recovered as a function of vacuum pressure

VACUUM PRESSURE (KPA)	AMOUNT OF CO ₂ RECOVERED (MG/L)
40	36.0
30	227.3
20	425.3
10	637.7

The table indicates that when modelling the SSP in PRO/II significant CO₂ recovery can only be obtained at very low pressures (high vacuums), which does not correspond to SSP pilot plant studies.

The following results were generated for the stripping and recovery of CO₂ from the mixed solution at a vacuum pressure of 14.14 kPa.

Table 3.9: Comparison between pilot plant and PRO/II model results for the stabilised sidestream after CO₂ stripping

CO ₂ STRIPPING	SIDESTREAM PILOT PLANT	PRO/II MODEL
pH	6.88	6.51
Calcium as CaCO ₃ (mg/L)	457.0	452.7
Total alkalinity as CaCO ₃ (mg/L)	450.0	327.0
Total acidity as CaCO ₃ (mg/L)	715	767
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	28.9	-35.8
Electrical Conductivity (mS/m)	84	61

From the previous table it is clear that the results generated in *PRO/II*, although relatively similar, are not the same as those found while operating the pilot plant. The results indicate a lowered total alkalinity and pH of the stream. When further analysing the results of this stream, it was evident that at a vacuum pressure of 14.14 kPa, *PRO/II* reports that a relatively large quantity of solid CaCO₃ precipitate is formed (37% of the total CaCO₃ available in the stream). This was not taken into account when calculating the total alkalinity and therefore a discrepancy existed.

A further study revealed that even at a vacuum pressure of 50 kPa (operating vacuum pressure in the pilot plant), a small quantity (0.2% of the total CaCO₃ available in the stream) of solid CaCO₃ is present. This vacuum pressure, however, could not be used in the simulation, as no CO₂ could be recovered in *PRO/II* at this pressure (see above).

CO₂ Recycle

In the pilot plant operation, CO₂ is stripped, recovered and then re-used in the process. This minimizes the required input of fresh CO₂ into the SSP, which in turn lowers the operating cost of the process.

From theoretical considerations and pilot plant operation, 333 mg/L of fresh CO₂ and 547 mg/L of recovered CO₂ are added to the incoming sidestream. Initially, when constructing the process model, the total quantity of CO₂ added to the sidestream (880 mg/L), was added as fresh CO₂ into the dissolution vessels. It would therefore be possible to accurately construct the remaining unit operations of the recycle loop (i.e. limestone columns and recovery columns), such that the results obtained from these unit operations would resemble the results obtained from the pilot plant operation. Once this had been achieved, CO₂ could be recycled, and the quantity of fresh CO₂ lowered to the amount added on the pilot plant.

However, due to the problems experienced with CO₂ stripping and recovery in this preliminary investigation, CO₂ recycle was not thoroughly investigated. The recovered CO₂, at a pressure of 14.14 kPa was allowed to pass through a valve, thereby increasing the pressure of the recovered CO₂ stream to that of the dissolution vessels (300 kPa). This resulted in an increase in the temperature of the stream from 20°C to 74.5°C. In practice, however, CO₂ entering the dissolution columns from the recovery vessels does not undergo an increase in temperature.

Blend

After the CO₂ is stripped, the stabilised stream is blended with the balance of the feed stream. The following results were generated for the combination of these two streams.

Table 3.10: Comparison between pilot plant and PRO/II model results for the blended stabilised stream

BLEND	SIDESTREAM PILOT PLANT	PRO/II MODEL
pH	6.46	6.46
Calcium as CaCO ₃ (mg/L)	22.5	22.4
Total alkalinity as CaCO ₃ (mg/L)	22.3	22.3
Total acidity as CaCO ₃ (mg/L)	59	58
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-36.9	-35.3
Electrical Conductivity (mS/m)	8.4	4.4

The table indicates that although the water quality obtained after CO₂ stripping for the simulation was not exactly the same as that obtained from the pilot plant, it was still possible to obtain a blended stream with a water quality that closely resembles that used in the pilot plant.

In addition to the results of the streams discussed above, the following other aspects of the SSP were briefly investigated:

- Air stripping of excess CO₂ from the blend stream.
- Lime addition to yield a fully stabilised stream.

When air stripping of excess CO₂ from the blended stream was modelled, similar problems as experienced when modelling CO₂ stripping from the sidestream occurred. The addition of lime to the blended stream to form a blended stream was easily modelled and yielded accurate results.

Conclusions: Preliminary Assessment of PRO/II

The preliminary assessment showed that it was possible to readily model most of the critical steps of SSP in PRO/II. As in the process model developed using ASPEN PLUS, difficulties were encountered when CO₂ was to be stripped and recovered from a mixed liquid stream. Nevertheless, interactions with the SIMSCI Helpdesk showed that problems identified could be readily addressed and as this was only a limited intensity preliminary investigation this apparent shortcoming was not regarded as problematic.

3.3 CHOICE OF PROCESS MODELLING PACKAGE

Based on information received from manufacturers, and from the preliminary assessment of the two packages, a summary assessment of the capabilities and shortcomings/limitations of the two packages tools was conducted. The following table summarises the findings from the preliminary review of the two packages.

Table 3.11: Pro's and Con's of ASPEN PLUS and PRO/II

ASPEN PLUS	PRO/II
- Interface is very user friendly - All functions are available in one complete package <i>Design Spec</i> feature may prove troublesome	- Interface is very user-friendly - Comes as a standard package Additional modules must be purchased at extra cost - Controllers, Optimiser and stream calculator are simple to use
- Balanced reactions easily entered into the available reactor models - Extent of kinetic modelling unknown	- Only reactor models available are for equilibrium and conversion reactors, requiring extensive inputs - Calculator unit operation with <i>Fortran</i> programming makes the input and calculation of kinetic rate equations possible
Can enter your own components and products (in compound or ionic form)	Products are limited to those available in the selected thermodynamic model (non-ionic form) i.e. cannot enter your own products
Flowsheet construction is a simple, stepwise process	Flowsheet construction is a simple, stepwise process
High cost	Relatively low cost
Very slow and inadequate response from help-desk	Rapid response time from very helpful and friendly help-desk.

The preliminary investigation revealed that both modelling packages appear capable of modelling the various unit processes of the SSP. However, due to the high cost and a lack of extensive knowledge of the kinetic modelling capabilities of the *ASPEN PLUS* package, the project team proposed that *PRO/II* be selected as the simulation package to model the SSP. This proposal was supported by the Steering Committee.

3.4 FURTHER DEVELOPMENT OF PRO/II MODEL

The initial model developed showed that the modelling package was capable of accurately simulating a number of steps in the SSP including CO₂ and CaCO₃ addition. However, problems

were encountered when modelling the stripping and recovery of CO_2 . The objectives of this secondary investigation were therefore to further develop the SSP model, paying particular attention to the stripping and recovery of CO_2 . Ultimately, once the predictive capability of the model was found to be reasonably consistent with the results obtained from operation of the pilot plant (and to what is predicted by *STASOFT 4*), the model would be calibrated against the pilot plant and used to both:

- Identify the operational limitations of the SSP, and
- Identify means of optimising the performance of the process.

3.4.1 Assumptions and Model Development

The model was developed using the same assumptions as used during generation of the preliminary model, namely:

- Steady state pilot plant operation.
- Reactions reach thermodynamic equilibrium.
- Reaction kinetics can initially be ignored.
- As the pilot plant was tested at sea-level conditions, atmospheric pressure within the simulation is 101.325 kPa.
- The operating temperature of the process, and thus the simulation, is 20°C.

With respect to CaCO_3 dissolution reaction kinetics, although equilibrium conditions are not readily achieved during pilot plant operation (resulting in a smaller uptake of CaCO_3 than what is evident from process simulations), the initial model developed would assume steady state/equilibrium operation.

The model generated encompassed the following critical steps of the SSP:

- Generation of a feed water.
- Splitting the feed into a sidestream and a mainstream (balance of feed).
- Addition of CO_2 gas to the sidestream.
- Addition of CaCO_3 to the acidified stream.
- Stripping and recovery of CO_2 from the stabilised stream.
- Recycle of CO_2 from the stabilised stream.
- Addition of stabilised sidestream to the balance of the feed to form a blended stream, with nominal alkali addition (if required).

The following unit operations in *PRO/II* were used to model the required steps of the SSP:

- **Splitting the feed into a sidestream and a mainstream (balance of feed)**

Unit operation: *Splitter*

The splitter unit is generally used to split a single feed, or mixture of feeds, into two or more products of identical composition and phase condition. The outlet stream pressure may be specified, if desired, and an adiabatic flash is used to determine the outlet temperature and phase.

- **Addition of CO₂ gas to the sidestream**

Unit operation: *Mixer*

The three CO₂ dissolution vessels on the pilot plant (DV1, DV2 and DV3) were modelled as a single mixer. The mixer unit combines two or more streams into a single product stream. The default pressure drop across the unit is zero, and the outlet temperature and phase condition are determined with an adiabatic flash from the feed conditions.

- **Addition of limestone to the acidified stream**

Unit operation: *Flash with Solids*

The two limestone columns (LS1, LS2) were modelled using a single "Flash with Solids" unit operation. This unit operation is recommended for flash (equilibrium) calculations where a solids product stream is present. Solid limestone is added to the flash unit together with the CO₂-acidified stream. If reaction kinetics are to be included the calculator unit operation should be employed.

- **Stripping, recovery and recycle of CO₂ from the stabilised stream**

This step was not accurately modelled during the previous investigation and would have to be thoroughly investigated.

- **Formation of a blended stream, with nominal alkali addition**

Unit operation: *Mixer*

The addition of the stabilized sidestream to the balance of the feed to form a blended stream can be modelled using a single mixer. The required alkali can also be directly added to the mixer.

3.4.2 Critical Review of Process Model

This section describes the process model generated, and provides a critical comparison of the results obtained with what is predicted using *STASOFT 4* (a well established aquatic chemistry model). In this manner, the ability or limitations of the process modelling package to accurately model the SSP will be highlighted. In particular, attention will be paid to problems encountered while modelling the SSP.

From the SSP process description the following basic *PRO/II* process flowsheet was generated.

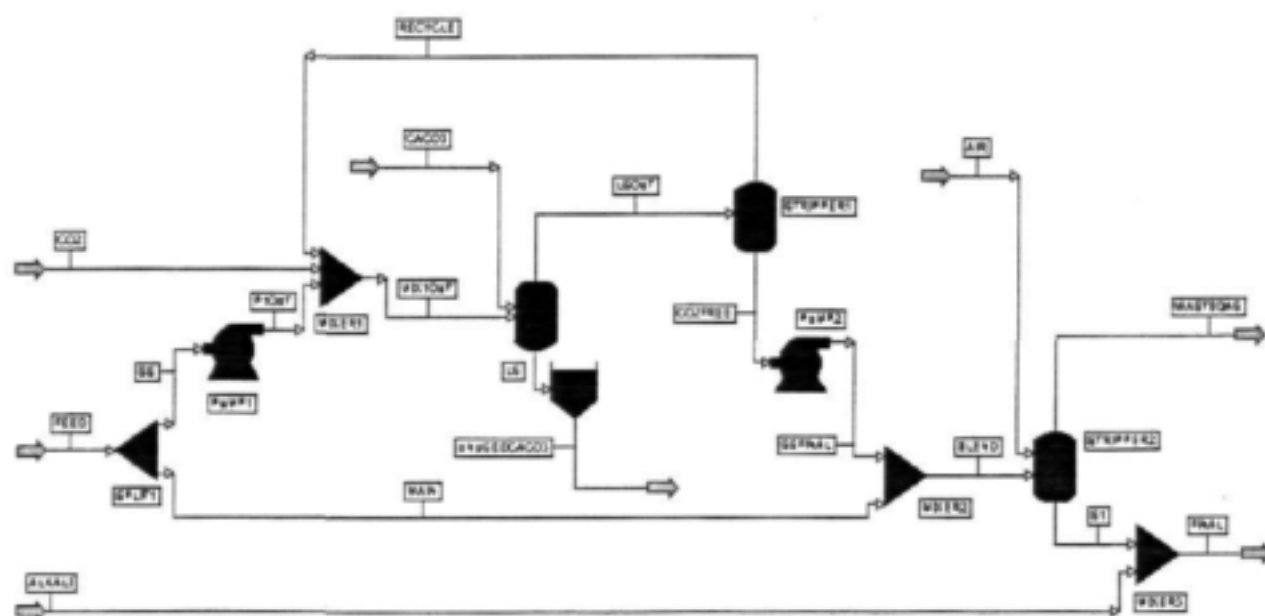


Figure 3.3: Process Flowsheet for the Sidestream Stabilisation Process as modelled in PRO/II

Raw water is fed into a splitter, with a decided percentage sidestream being abstracted and fed into the SSP pilot plant. A pump was then employed to raise the pressure of the sidestream to those conditions experienced on the pilot plant (300 kPa). The sidestream then enters three CO₂ dissolution vessels in series (DV1, DV2 and DV3), which were modelled as a mixer. Fresh CO₂ is added together with the sidestream, to the mixer and the blended CO₂-water stream then enters the limestones columns. The limestone columns (LS1, LS2) were modelled using the "Flash with Solids" unit operation operating at 300 kPa. Solid limestone is added to the flash unit, together with the CO₂-acidified stream. Any unused CaCO₃ will report to the stream provided. The stabilised water then enters the CO₂ recovery columns (RV1, RV2), which strips and recovers CO₂ for further use.

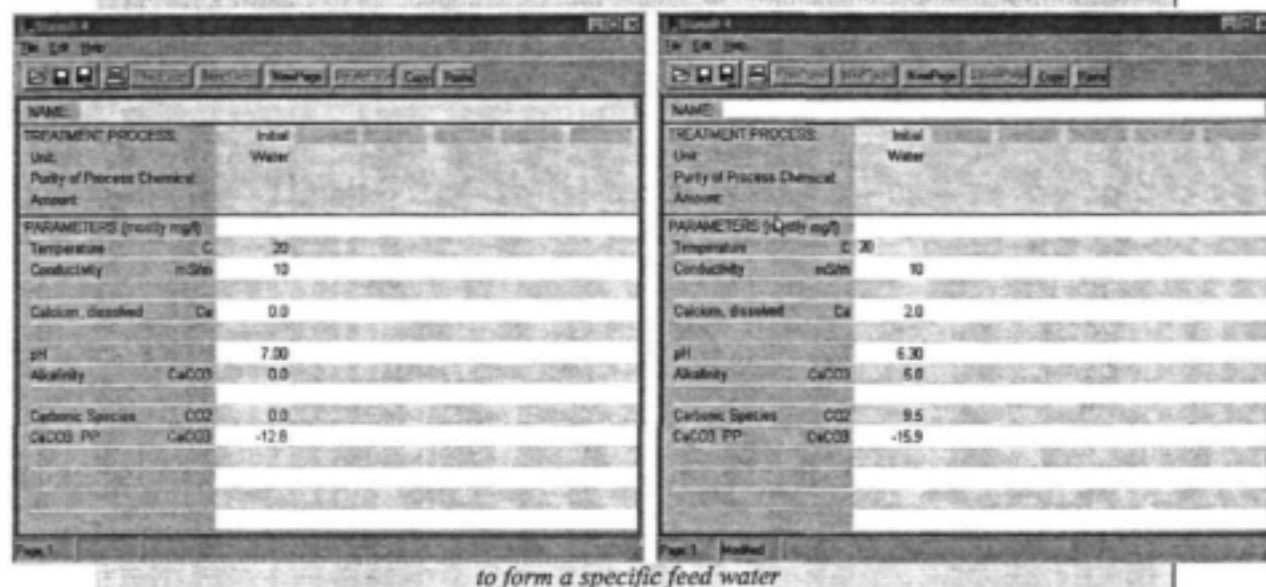
Various unit operations were assessed to test the suitability of these units for modelling the CO₂ stripping step. This will be discussed in greater detail at a later stage. The above figure shows the use of the flash drum unit operation (gas-liquid equilibrium vessel). The CO₂-free water is then mixed with the balance of the feed water to form a blended stabilized stream. If required, nominal alkali (lime) addition can then occur.

The following section describes the various procedures followed and problems encountered to model the various steps of the SSP in PRO/II. Results obtained from the model are compared to what is obtained using STASOFT 4.

Feed Generation: STASOFT 4

The start of the model entailed simulating a typical Cape soft, acidic surface water (as recorded from analysis of Stellenbosch raw water) to serve as the feed for the model. In *STASOFT 4*, the generation of a particular required feed is a simple process. The desired pH, temperature, electrical conductivity, calcium and total alkalinity are added to the initial distilled water to produce the desired feed. The following example shows how the initial distilled water can be easily manipulated to obtain a desired feed water quality.

Figure 3.4: Manipulation of distilled water in STASOFT 4



The process is, however, much more complicated in *PRO/II*, and a water with the above conditions can only be obtained after much effort. In *PRO/II*, guessed concentrations of compounds that may occur in a typical surface water need to be added to the distilled water stream. The results obtained in the output file then need to be analysed, and manual calculations are performed for calcium, total alkalinity and carbonic species. (It is not possible to extract concentrations of ionic species directly from the simulation at run-time and therefore water quality parameters such as total alkalinity, etc. cannot be displayed to the flowsheet.) Due to the iterative (trial & error) manner of the process, this task is time consuming, and mistakes can easily occur if incorrect ionic and compound concentrations are used in the calculations.

In addition, the assumptions made with respect to species present in a typical surface water may be incorrect.

Due to the time consuming trial & error method to obtain a specific required feed, it was decided to first simulate a typical surface water in *STASOFT 4*, and then to use the inputs obtained in the *PRO/II* model. The following feed simulated in *STASOFT 4*, and subsequently in *PRO/II*, serves as an example of the process required to generate a specific feed in the two software packages. (It should be noted that *STASOFT 4* makes no allowance for the presence of humic acids and assumes that the total alkalinity and pH are the result of the presence of a particular combination of hydroxide ions and carbon dioxide.)

Lime ($\text{Ca}(\text{OH})_2$) is dosed to distilled water until the desired amount of calcium is present in the feed water. This water stream is then equilibrated with air (where the CO_2 partial pressure is 0.00035 atm). The feed water generated is illustrated below:

STASOFT 4				
File Edit Help				
Print PrintPage NewPage DeletePage Copy Paste				
NAME:				
TREATMENT PROCESS:				
Unit:	Initial Water	$\text{Ca}(\text{OH})_2$ mg/l	Eqm Air pp Atm	
Purity of Process Chemical:		100.0%		
Amount:		3.7	0.00035	
PARAMETERS (mostly mg/l)				
Temperature C	20	20	20	
Conductivity mS/m	10	11	11	
Calcium, dissolved Ca	0.0	2.0	2.0	
pH	7.00	10.15	7.22	
Alkalinity CaCO_3	0.0	5.0	5.0	
Carbonic Species CO_2	0.0	0.0	5.0	
CaCO_3 PP CaCO_3	-12.8	-8.7	-9.3	
Page 1 Modified				

Figure 3.5: Simulation of a typical soft, acidic surface water in STASOFT 4

Feed Generation: PRO/II

For the simulation in PRO/II, a distilled water specific flowrate (L/hr) was assumed. The $\text{Ca}(\text{OH})_2$ input of 3.7 mg/L from STASOFT 4, is then translated into a mass flow (kg/hr) for input into PRO/II. This solid $\text{Ca}(\text{OH})_2$ stream is added to the distilled water and then together with a "large" air stream, is fed into an equilibrium flash vessel. The feed simulation follows:

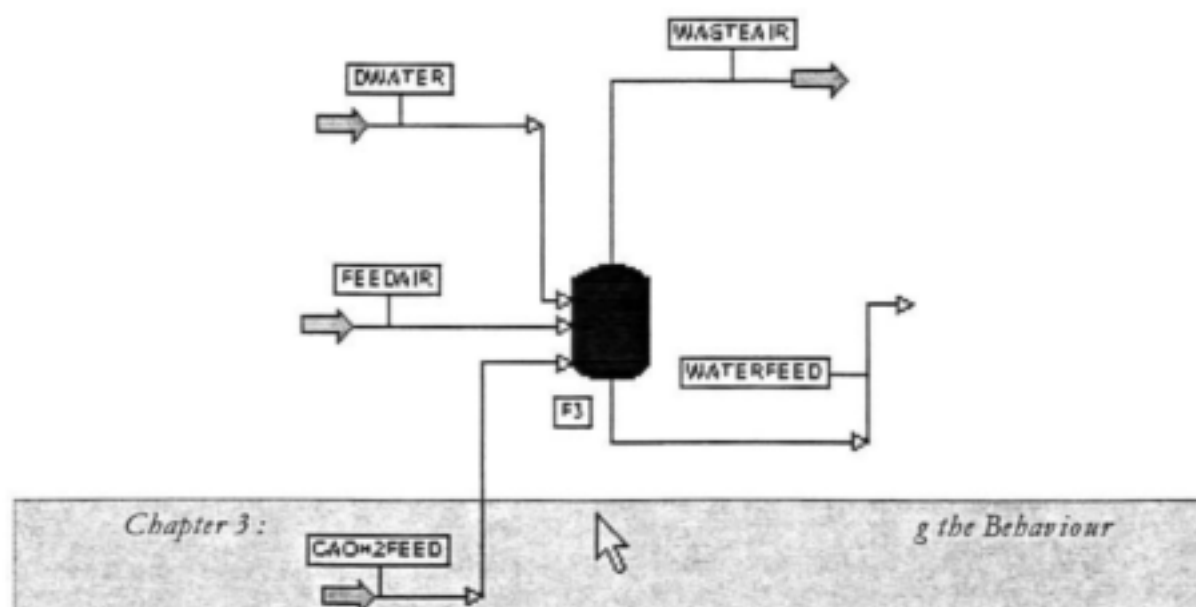


Figure 3.6: Flow diagram of model generated for feed in PRO/II

The results obtained from the simulation are stored in an output file. An extract from the output file follows. The results on the far right are for the feed water generated in *PRO/II* using the *STASOFT 4* inputs, and will be compared to the results obtained in *STASOFT 4*.

SIMULATION SCIENCES INC.		R		PAGE P-17	
PROJECT		PRO/11	VERSION 5.1 ELEC US.4	386/EM	
PROBLEM		OUTPUT			
STREAM WEIGHT COMPONENT RATES				18/05/00	

STREAM ID		UNUSED/CAC03	VENT	WASTE/AIR	WATER/FEED
NAME					
PHASE		SOLID	VAPOR	VAPOR	LIQUID
FLUID RATES, KG/HR					
1	CO2	0.0000	0.5395	0.7799	0.0180
2	N2	0.0000	663.6449	13272.8012	0.0949
3	O2	0.0000	203.3488	4066.9209	0.0536
4	H2O	0.0000	4.2592	259.2236	6390.8253
5	HCL	0.0000	0.0000	0.0000	0.0000
6	HCN	0.0000	0.0000	0.0000	0.0000
7	HCOOH	0.0000	0.0000	0.0000	0.0000
8	SO2	0.0000	0.0000	0.0000	0.0000
9	NaOH	0.0000	0.0000	0.0000	0.0000
10	CaCO3	0.0000	0.0000	0.0000	0.0332
11	CaCl2	0.0000	0.0000	0.0000	0.0000
12	NaCl	0.0000	0.0000	0.0000	0.0000
13	Na2CO3	0.0000	0.0000	0.0000	0.0000
14	NaHCO3	0.0000	0.0000	0.0000	0.0000
15	NaCOOH	0.0000	0.0000	0.0000	0.0000
16	CaOH2	0.0000	0.0000	0.0000	0.0000
TOTAL FLUID, KG/HR		0.0000	871.7923	17607.7255	6391.0250
MW SOLID RATES, KG/HR					
1	CO2	0.0000	0.0000	0.0000	0.0000
2	N2	0.0000	0.0000	0.0000	0.0000
3	O2	0.0000	0.0000	0.0000	0.0000
4	H2O	0.0000	0.0000	0.0000	0.0000
5	HCL	0.0000	0.0000	0.0000	0.0000
6	HCN	0.0000	0.0000	0.0000	0.0000
7	HCOOH	0.0000	0.0000	0.0000	0.0000
8	SO2	0.0000	0.0000	0.0000	0.0000
9	NaOH	0.0000	0.0000	0.0000	0.0000
10	CaCO3	0.1325	0.0000	0.0000	0.0000
11	CaCl2	0.0000	0.0000	0.0000	0.0000
12	NaCl	0.0000	0.0000	0.0000	0.0000
13	Na2CO3	0.0000	0.0000	0.0000	0.0000
14	NaHCO3	0.0000	0.0000	0.0000	0.0000
15	NaCOOH	0.0000	0.0000	0.0000	0.0000
16	CaOH2	0.0000	0.0000	0.0000	0.0000
TOTAL MW SOLID, KG/HR		0.1325	0.0000	0.0000	0.0000
TOTAL RATE, KG/HR		0.1325	871.7923	17607.7255	6391.0250

STREAM ID		UNUSED/CAC03	VENT	WASTE/AIR	WATER/FEED
NAME					
PHASE		SOLID	VAPOR	VAPOR	LIQUID
AQUEOUS RATES, KG/HR					
	H2O	N/A	N/A	N/A	6390.8628
	CO2	N/A	N/A	N/A	3.4356E-03
	N2	N/A	N/A	N/A	0.0949
	O2	N/A	N/A	N/A	0.0536
	OH-1	N/A	N/A	N/A	1.4976E-05
	CAHCO3+1	N/A	N/A	N/A	5.5388E-05
	CA+2	N/A	N/A	N/A	0.0133
	CAOH+1	N/A	N/A	N/A	4.0047E-08
	CO3-2	N/A	N/A	N/A	5.0884E-05
	HCO3-1	N/A	N/A	N/A	0.0403
	H+1	N/A	N/A	N/A	3.1981E-07
TOTAL AQUEOUS, KG/HR		N/A	N/A	N/A	6391.0685
TEMPERATURE, C					
		20.0000	20.0000	20.0000	20.0000
PRESSURE, BAR					
		3.0000	3.0000	1.0000	1.0000
ENTHALPY, H=KW-HR/HR					
		-4.4459E-07	-1.8633E-05	-1.0148E-03	-0.0282
MOLECULAR WEIGHT					
		100.0872	28.7779	28.0079	18.0155
WEIGHT FRAC VAPOR					
		0.0000	1.0000	1.0000	0.0000
WEIGHT FRAC LIQUID					
		0.0000	0.0000	0.0000	1.0000
WEIGHT FRAC MW SOLID					
		1.0000	0.0000	0.0000	0.0000
PH					
		N/A	N/A	N/A	7.31035
IONIC STRENGTH					
		N/A	N/A	N/A	1.55874E-04
MOLECULAR WEIGHT (AQUEOUS)					
		N/A	N/A	N/A	18.0157

Figure 3.7: PRO/II output file for simulation of a typical soft, acidic surface water

The above extract of the *PRO/II* output file shows that the outputs are not in normal aqueous/carbonate chemistry terms of calcium, total alkalinity, carbonic species, etc. These need to be calculated from the given fluid, solid and aqueous (ionic) species outputs. An *MSEExcel* spreadsheet was employed in this regard.

The following results were generated from the model and are compared to *STASOFT 4*.

Table 3.12: Comparison between *STASOFT 4* and *PRO/II* model results for the feed stream

FEED	<i>STASOFT 4</i>	<i>PRO/II</i> MODEL
pH	7.22	7.31
Calcium as CaCO ₃ (mg/L)	2.0	2.0
Total alkalinity as CaCO ₃ (mg/L)	5.0	5.0
Carbonic species as CO ₂ (mg/L)	5.0	5.0
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-9.3	-7.97
Electrical Conductivity (mS/m)	11.0	1.25

The results indicate that the quality of the feed water produced closely resembles that found in the *STASOFT 4* simulation. Discrepancies in pH are as a result of differences in pH for distilled water in the two packages (*STASOFT 4* pH = 7.00 vs. *PRO/II* pH = 7.09).

Concluding Remarks: Feed

- In general, comparison with *STASOFT 4* shows that *PRO/II* is able to accurately simulate a feed water (this is shown in the above example).
- However, the generation of a specified feed is not an easy process when modelling in *PRO/II*, due to the fact that *PRO/II* is not primarily an aquatic chemistry/water treatment process modelling package (and therefore does not contain inputs for aquatic chemistry parameters such as calcium, total alkalinity, etc). Therefore, in order to simulate a specific feed water numerous iterative (trial & error) steps are needed to arrive at a water with the desired aquatic chemistry parameters.
- In order to quickly simulate a specified feed (and avoid the iterative procedure), inputs from *STASOFT 4* are required. This highlights the interdependence of *PRO/II* with *STASOFT 4* to effectively model the required feed water, and makes modelling a feed water with ever changing conditions difficult if only *PRO/II* is employed.

CO₂ Addition/Dissolution: *STASOFT 4*

In *STASOFT 4*, when a certain dose of CO₂ is added to a particular water, the results are displayed immediately. This allows for easy process optimisation. The following example shows how CO₂ can be added to distilled water to obtain a desired acidified water.

The screenshot shows the STASOFT 4 software window. It has a menu bar (File, Edit, Help) and a toolbar with icons for file operations and simulation controls. The main area is a table for defining the treatment process and parameters.

NAME			
TREATMENT PROCESS:		Initial	CO2
Unit:		Water	mg/l
Purity of Process Chemical:			100.0%
Amount:			100.0
PARAMETERS (mostly mg/l)			
Temperature	C	20	20
Conductivity	mS/m	10	10
Calcium, dissolved	Ca	0.0	0.0
pH		7.00	4.52
Alkalinity	CaCO3	0.0	0.0
Carbonic Species	CO2	0.0	100.0
CaCO3 PP	CaCO3	-12.8	-187.1

At the bottom, there are buttons for 'Page 1', 'Modified', and 'Select a parameter'.

Figure 3.8: STASOFT 4 simulation for the addition of CO₂ to a distilled water stream

CO₂ Addition/Dissolution: PRO/II

The addition/dissolution of CO₂ in PRO/II is modelled using the mixer unit operation. This operation proved accurate and results obtained from PRO/II closely resembled results obtained with the same inputs in STASOFT 4. The simulation for the addition and dissolution of CO₂ follows:

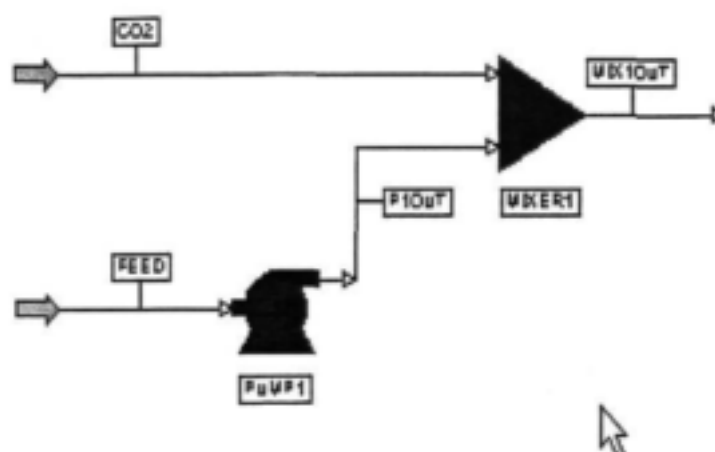


Figure 3.9: Flow diagram of model generated for CO₂ addition in PRO/II

However, as previously mentioned the generation of a specified final water quality after the addition of CO₂ is time consuming (iterative/trial & error process) due to the data output format in PRO/II.

By way of example, for the addition of 100 mg/L CO₂ to distilled water, the following results were generated.

Table 3.13: Comparison between STASOFT 4 and PRO/II model results for the acidified sidestream

CO ₂ ADDITION	STASOFT 4	PRO/II MODEL
pH	4.52	4.52
Calcium as CaCO ₃ (mg/L)	0.0	0.0
Total alkalinity as CaCO ₃ (mg/L)	0.0	0.0
Total carbonic species as CO ₂ (mg/L)	100.0	100.0
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-187.1	-231.0
Electrical Conductivity (mS/m)	10	0.6

The results indicate that the water quality of the stream after CO₂ addition closely resembles that found when modelling the process in STASOFT 4.

Concluding Remarks: CO₂ Addition/Dissolution

- In general, comparison with STASOFT 4 shows that PRO/II is able to accurately simulate the acidified water (i.e. after the addition of CO₂) using the mixer unit operation.
- However, as previously mentioned the generation of a specified acidified stream water quality is time consuming, and STASOFT 4 is normally employed to speed up the process.

- This makes optimisation (to determine optimal CO₂ dosing) difficult for ever changing raw water quality, if only *PRO/II* is employed.

CaCO₃ Addition/Dissolution: *STASOFT 4*

The addition of CaCO₃ to the acidified stream in *STASOFT 4* can take either of the following two forms:

- A certain dose of CaCO₃ is added to a particular water, or
- CaCO₃ is added to reach equilibrium.

The results obtained are displayed immediately which allows for easy process optimisation. The following example shows how CaCO₃ can be added to an acidified water. In this example CaCO₃ is added to equilibrium.

The screenshot shows the STASOFT 4 software window. It has a menu bar (File, Edit, Help) and a toolbar with icons for file operations and calculation. Below the toolbar is a 'NAME' field. The main area contains a table with the following data:

TREATMENT PROCESS:		Initial	CO ₂	EqmCaMg
Unit:		Water	mg/l	
Purity of Process Chemical:			100.0%	
Amount:			100.0	
PARAMETERS (mostly mg/l)				
Temperature	C	20	20	20
Conductivity	mS/m	10	10	43
Calcium, dissolved	Ca	0.0	0.0	74.9
pH		7.00	4.52	7.29
Alkalinity	CaCO ₃	0.0	0.0	187.1
Carbonic Species	CO ₂	0.0	100.0	182.3
CaCO ₃ PP	CaCO ₃	-12.8	-187.1	0.0
Calcium, precipitate	Ca	1000.0	1000.0	925.1

At the bottom of the window, it says 'Page: 1' and 'Modified'.

Figure 3.10: STASOFT 4 simulation for the addition of CO₂ to a distilled water stream

CaCO₃ Addition/Dissolution: *PRO/II*

In practice, the limestone columns are essentially plug flow reactors (PFR's). Water is fed at the bottom of the column, passes upwards through the limestone bed and exits via the top.

Unfortunately it is not currently possible to use a PFR model in *PRO/II* with the Electrolytes add-on module, and an alternative unit operation was thus required. The alternatives considered included:

- Conversion/equilibrium reactor
- Dissolver
- Flash drum with solid separator/Flash with Solids.

Investigation revealed that the Flash drum with solid separator/Flash with Solids unit operation was the most appropriate unit operation for modelling the limestone columns.

Flash Drum with Solid Separator/Flash with Solids

A flash unit may be used to model any equilibrium calculations where two of the conditions are defined (e.g. temperature and pressure). The phase equilibrium is determined, and the product stream is separated into product streams corresponding to the phases. The overhead product contains any vapour generated, while the bottoms product would contain any liquid/solid product. This liquid/solid product could then be sent to a solid separator. This unit models the separation of solid phase material from a mixture of feed streams.

However, in *PRO/II*, a unit operation termed "Flash with Solids" is recommended for flash calculations where a solids product stream is present. The unit essentially models a flash drum with four product streams:

- A vapour phase overhead stream from the flash drum section.
- A liquid phase stream from the flash drum section.
- A decanted liquid stream from the solids separator section.
- A solid phase bottom stream from the separator section. The system default is complete separation of the solid from the liquid stream.

This unit operation therefore models the addition of CaCO_3 to equilibrium (as *STASOFT 4* does). If an excess of CaCO_3 has been specified, the remaining CaCO_3 will report to the stream provided for any unused solid CaCO_3 , which is recorded in the output data.

The simulation for the addition and dissolution of CaCO_3 follows:

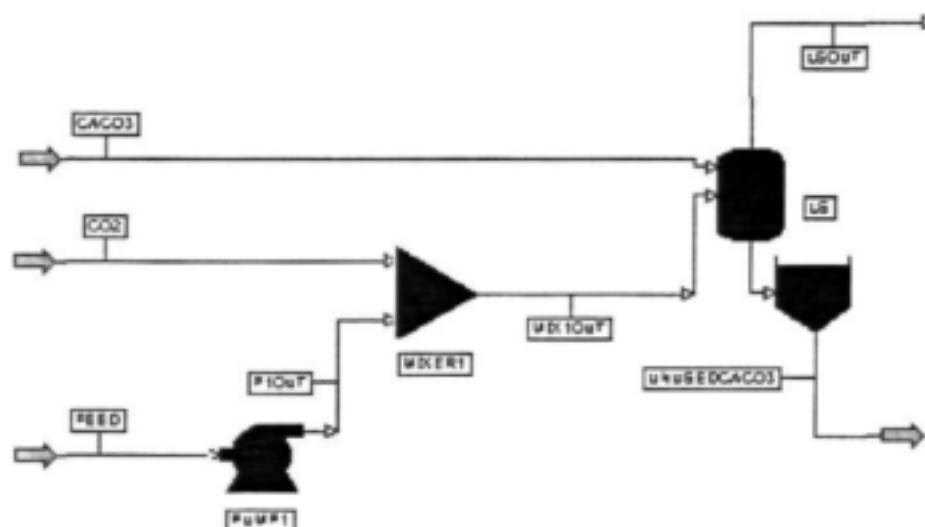


Figure 3.11: Flow diagram of model generated for CaCO_3 addition in PRO/II

By way of example, for the addition of CaCO_3 to equilibrium in STASOFT 4 and adding in an excess amount of CaCO_3 in PRO/II (the addition of CaCO_3 to equilibrium with the unused CaCO_3 reporting to the stream provided), the following results were generated.

Table 3.14: Comparison between STASOFT 4 and PRO/II model results for the stabilized sidestream (CaCO_3 addition to equilibrium)

LIMESTONE ADDITION	STASOFT 4	PRO/II MODEL
pH	7.29	7.06
Calcium as CaCO_3 (mg/L)	187.25	164.4
Total alkalinity as CaCO_3 (mg/L)	187.1	161.24
Total carbonic species as CO_2 (mg/L)	182.3	172.3
Calcium carbonate precipitation potential as CaCO_3 (mg/L)	0	-18.9
Electrical Conductivity (mS/m)	43	30

The results indicate that CaCO_3 equilibrium using the flash with solids unit operation in PRO/II differs to STASOFT 4. This may be as a result of the use of different equilibrium relationships within the two programs. However, if the same CaCO_3 inputs are used (For example: the addition of 100 mg/L CaCO_3 to a previously acidified stream) the final results obtained for both PRO/II and STASOFT 4 correlate. This is shown in the following table:

Table 3.15: Comparison between STASOFT 4 and PRO/II model results for the stabilized sidestream

LIMESTONE ADDITION	STASOFT 4	PRO/II MODEL
pH	6.54	6.55
Calcium as CaCO ₃ (mg/L)	40	40
Total alkalinity as CaCO ₃ (mg/L)	100	99
Total carbonic species as CO ₂ (mg/L)	144	144
Calcium carbonate precipitation potential as CaCO ₃ (mg/L)	-87.1	-80.3
Electrical Conductivity (mS/m)	28	19

Concluding Remarks: CaCO₃ Addition/Dissolution

- In general, comparison with *STASOFT 4* shows that *PRO/II* is able to accurately simulate the stabilised water (i.e. after the addition of CaCO₃) using the flash with solids unit operation. However, CaCO₃ equilibrium in *PRO/II* differs to results obtained using *STASOFT 4*, which may be as a result of the use of different equilibrium relationships within the two programs.
- In addition, as mentioned earlier, the nature of the *PRO/II* data output makes the generation of a specified stabilised stream time consuming.

CO₂ Stripping and Recovery

CO₂ stripping and recovery on the SSP pilot plant is dependant on a number of factors including:

- CO₂ fraction in the gas/liquid stream, which can be altered via addition of air that acts as a carrier gas.
- Vacuum pressure within the stripping/recovery vessel.

The initial objectives were to create a model based on a specific feed water quality, with a set CO₂ and CaCO₃ addition, which could accurately predict the final water quality and CO₂ recovered at specified conditions of air flow (to aid CO₂ stripping), and CO₂ recovery vessel vacuum pressure. Once a basic model had been created investigation into the effect of varying the feed water quality, percentage sidestream, fresh CO₂ input, etc. could be undertaken. This would allow optimisation and highlight the practical limitations of the CO₂ stripping process.

Initial Investigation

In practice CO₂ is stripped from the water stream at pressures of ~50 kPa. This is achieved by spraying the water containing the entrained CO₂ through a series of spray nozzles into a column, containing a packing of Pall Rings, and under vacuum conditions. These CO₂ stripping vessels operate in "cascade" mode (not flooded). The gas released by the spray nozzles is then sucked off leaving a water with considerable less dissolved CO₂.

It was believed, and subsequently shown during preliminary pilot trials that the stripping of CO₂ from the water may be further enhanced by introducing an air stream into the stripping vessel, thus reducing the equilibrium partial CO₂ pressure in the vessel. In addition, preliminary pilot trials have also shown that the addition of a carrier gas such as air is not necessary to strip CO₂. The initial model developed therefore did not include an air stream to aid CO₂ stripping.

From the previous modelling exercise, it was evident that the stripping and recovery of CO₂ was not occurring in *PRO/II* as expected from SSP pilot plant operation, and would therefore require thorough investigation. Initially, the two recovery columns on the SSP pilot plant were modelled as a single flash unit (with no air input), with CO₂ gas being recovered as the overhead product from the mixed solution. The flash drum, however, did not yield any overhead vapour product at the specified conditions of 20°C and 50 kPa (typical operating conditions of the SSP pilot plant). The preliminary *PRO/II* findings further showed that without the introduction of an air stream to act as a carrier gas, very little/no CO₂ stripping was occurring even at very low operating pressures (approaching absolute zero pressure, 0 kPa). The *SIMSCI Helpdesk* was therefore contacted to advise on how to model such a gas strip using *PRO/II*.

The *SIMSCI Helpdesk* confirmed that when simulating the stripping and recovery of CO₂ in *PRO/II* a flash vessel should be used. However, as the initial investigation using this approach did not yield accurate results, a different approach that involved the use of the stream calculator function was suggested by the *SIMSCI Helpdesk*.

CO₂ Stripping and Recovery using the Stream Calculator in PRO/II

The stream calculator unit operation was then employed, as this function is able to split a stream into two product streams with defined compositions. This would enable the user to specify the amount of CO₂ required for recovery. Using this unit operation we were able to, for example, specify the amount of CO₂ to be recovered. The stream calculator then splits the stream such that the specified quantity of CO₂ reports to the overhead stream. (For example, for an 80% recovery of CO₂, one would specify that 80% of the CO₂ report to the overhead product.) The input screens for the stream calculator unit operation and its representation in the *PRO/II* flowsheet follows.

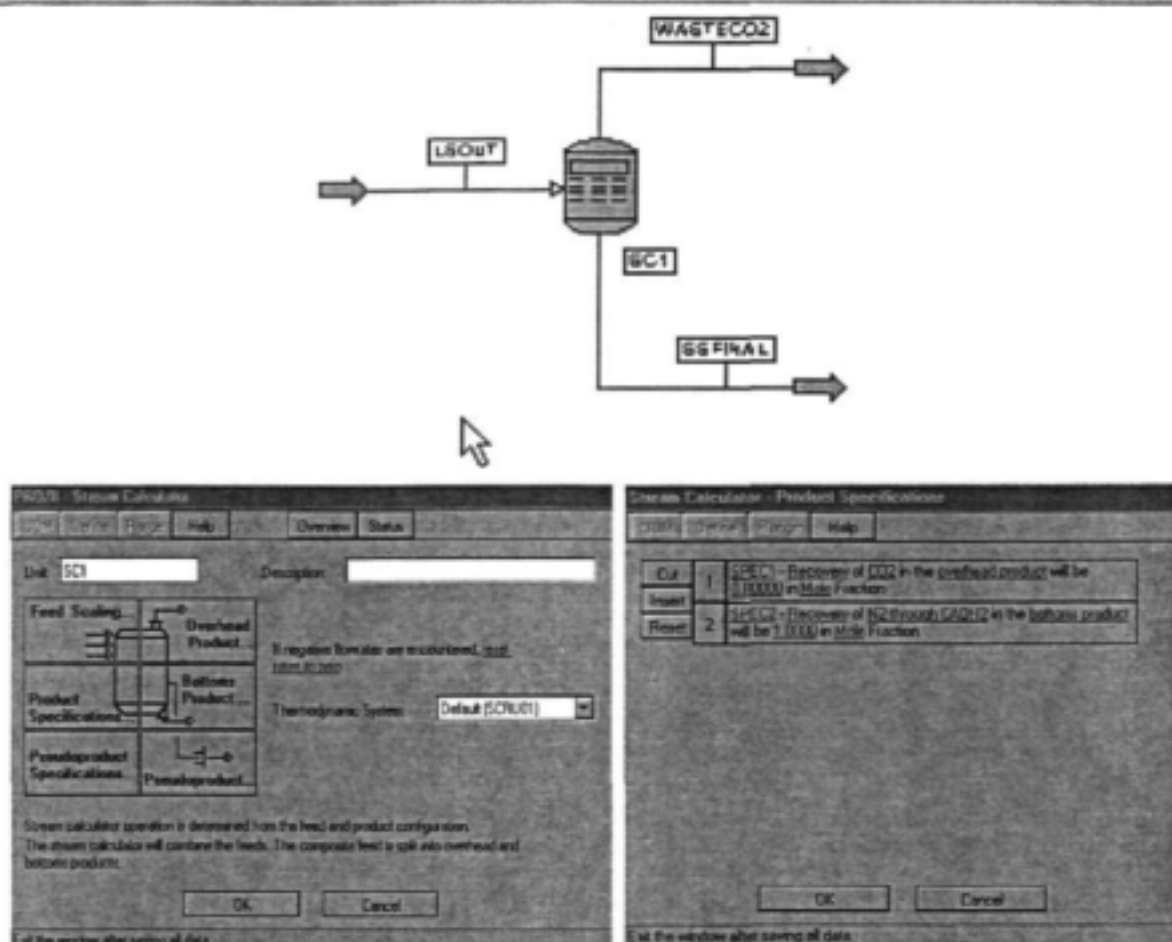


Figure 3.12: Flow diagram of model generated and input screens for stream calculator function in PRO/II

In the product specifications window the different specifications for the stream components are selected. In this example, it shows that 80% of the CO₂ will report to the overhead product (on a mole basis). The other components will report to the bottoms product, along with the remaining (20%) CO₂. Although this unit operation is able to strip any desired quantity of CO₂, it is not practical as the amount of gas recovered is calculated according to the specified inputs. The model is therefore unable to tell you if the process specified is practically possible. Essentially the stream calculator requires the output specifications for all the components in the product streams, which would be unknown in practical applications. In addition, when the gas is to be recycled, the percentage removal/accumulation of N₂, O₂ and CO₂ within the recycle loop will be unknown. The use of this function was therefore abandoned.

The *SIMSCI Helpdesk* was therefore once again contacted. During these discussions it was conveyed that we were comparing results obtained using *PRO/II* with *STASOFT 4*, a well recognized and widely accepted carbonate chemistry/water treatment software package, and that prior to commencing with further pilot plant trials, we wanted to compare results obtained from *PRO/II* with results predicted by *STASOFT 4*.

The various methodologies, functions, limitations, etc of the *STASOFT 4* package were then conveyed to the *SIMSCI Helpdesk*. In addition, a detailed breakdown of the modelling and analysis

methodology to date was presented. During these numerous and extensive interactions it was conveyed that:

- CO₂ addition/dissolution, and
- CaCO₃ addition/dissolution (equilibrium conditions)

generally showed good agreement/correlation when compared to the same processes in *STASOFT 4*, but that:

- CO₂ stripping from the resultant water stream

showed poor agreement/correlation between the two software packages. The following section highlights the main discussion points conveyed to the *SIMSCI Helpdesk* with regards to CO₂ stripping and recovery in *STASOFT 4* and *PRO/II*.

CO₂ Stripping and Recovery: *STASOFT 4*

In *STASOFT 4*, the effect of CO₂ stripping on a water can be determined via a process called "equilibrium with air". This process essentially models the process whereby an air stream passes through a water body, simulating the conditions at equilibrium of a surface water stream after contact with the atmosphere. The air acts as a carrier gas thus stripping CO₂ from the water stream.

In the *STASOFT 4* package one is required to specify the final partial CO₂ pressure of the air stream in equilibrium with the water. By varying this partial CO₂ pressure, one can strip various quantities of CO₂ from the water stream. In practice, one can reduce the partial pressure in the stripping vessel by introducing a gas stream into the stripper. The larger the air stream, the lower the partial CO₂ pressure of the equilibrated gas stream. If the size of the air stream is increased, the equilibrium partial CO₂ pressure of the air in contact with the water is expected to decrease, asymptotically approaching 0.00035 atm for relatively large air streams (that being the partial pressure of CO₂ in the normal atmosphere). At this point, an increase in air flow at atmospheric pressure (i.e. an even larger air stream at ~1 bar) will not strip off any more CO₂. We therefore expect the pH and Ct values to "level out" at relatively large air flows (i.e. stay constant for all practical purposes).

In the following *STASOFT 4* example, 100 mg/L CO₂ and 100 mg/L CaCO₃ are added to a distilled water after which the water stream is equilibrated with air, where the CO₂ partial pressure = 0.00035 atm (the partial CO₂ pressure was specified as 0.00035 atm, to determine the amount of CO₂ that can theoretically be stripped off from a water if it is contacted with a large air-stream at 1 atmosphere pressure). The *STASOFT 4* flowsheet is shown in the following figure:

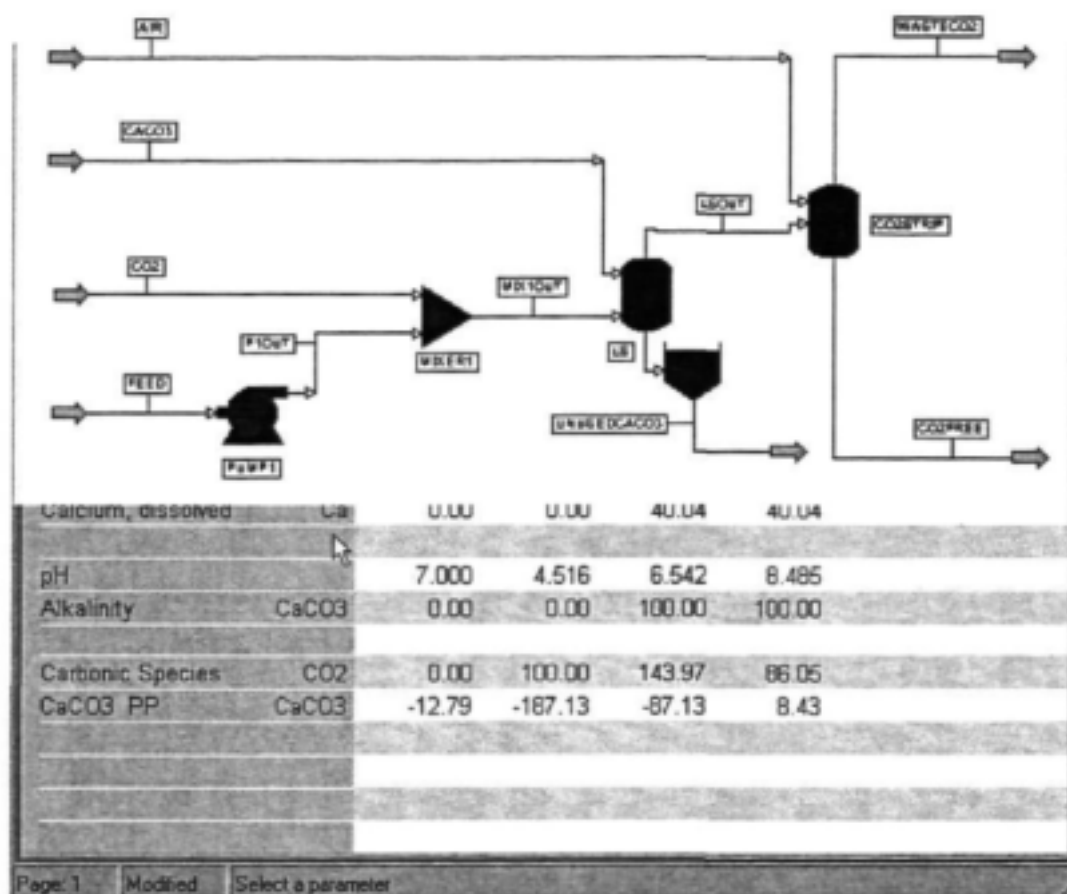


Figure 3.13: STASOFT 4 simulation for the addition of CO_2 and CaCO_3 to a distilled water stream followed by CO_2 stripping via "equilibrium with air"

CO_2 Stripping and Recovery: PRO/II

Following the aforementioned interactions with the *SIMSCI Helpdesk* it was decided to simulate the operation as occurring in *STASOFT 4*, with the introduction of an air stream into the equilibrium flash vessel. The following figure shows the flowsheet developed in *PRO/II* to simulate the previously mentioned process steps.

Figure 3.14: Flow diagram of model generated and input screens for stream calculator function in *PRO/II*

With the addition of an air stream into the equilibrium flash vessel we were able to strip CO_2 from the water stream. Numerous runs were performed where the stripping pressure (vacuum) within

the flash vessel was varied with the air flow into the flash vessel. From the data collected graphs describing the variation in final water pH, calcium, total alkalinity and CO₂ recovered were constructed. (It must be noted that analysis/interpretation of the data collected and construction of the appropriate graphs is a time consuming process. Initially graphs were constructed based on a specific feed water quality, percentage sidestream, and a set CO₂ and CaCO₃ dosage.) These preliminary graphs could then be employed for pilot plant optimisation. However, analysis of the data compared to STASOFT 4 predictions showed clear discrepancies in the results.

When running the simulation in PRO/II using the equilibrium flash vessel with a relatively "large" air stream for CO₂ stripping (the molar fraction CO₂ in the air stream into the flash vessel was specified as 0.00035), the model predicts that all the carbonate species (except that added in the form of calcium carbonate) can be stripped from the water. This is in strong contrast to what STASOFT 4 predicts. In addition, final water pH conditions are not the same as obtained in STASOFT 4. The results obtained are shown in the following table and compared to that obtained in STASOFT 4.

Table 3.16: Comparison between STASOFT 4 and PRO/II model results after CO₂ stripping

STASOFT 4

DETERMINANT	
Calcium as Ca (mg/L)	40
pH	8.485
Total alkalinity as CaCO ₃ (mg/L)	100
Carbonic Species, Ct as CO ₂ (mg/L)	86.05

PRO/II

DETERMINANT	AIR FLOW (m ³ /hr)						
	10	20	50	100	150	153.5	154
Calcium as Ca (mg/L)	40	40	40	40	40	40	-
pH	8.173	8.178	8.182	8.183	8.183	8.183	Error
Total alkalinity as CaCO ₃ (mg/L)	100	100	100	100	100	100	-
Carbonic Species, Ct as CO ₂ (mg/L)	61.15	59.85	56.25	50.35	44.46	44.05	-

When simulating the process in PRO/II, we had to pass a relatively large air stream through the water before the pH of the outgoing water was raised to more than 8.0. We then increased the air flow until the pH was steady, at which conditions we assumed that the partial pressure of CO₂ in the equilibrium gas stream approached 0.00035 atm. The resulting water was expected to be similar to the final water in the STASOFT 4 run.

However, analysis of the data presented above, shows that the *PRO/II* model predicts that it is possible to strip off all the carbonic species present in the H_2CO_3 and HCO_3^- form. According to *STASOFT 4*, there should still be ~86 mg/L (as CO_2) carbonic species left in the water after stripping it with a large air stream, and not only ~44 mg/L (as CO_2) of carbonic species (which was introduced via CaCO_3 addition). In addition, the pH of the final water is also lower than what *STASOFT 4* predicts (having removed more acidity from the *PRO/II* water in the form of CO_2 , one would have expected a higher pH in *PRO/II* than in *STASOFT 4*). At an air flow of $154 \text{ m}^3/\text{hr}$ an error was reported (at this stage all the CO_2 in the stream is stripped).

Therefore, although the final calcium and total alkalinity values obtained in *PRO/II* correspond to what is obtained in *STASOFT 4*, the carbonic species and pH results do not.

pH Inversion in *PRO/II*

A further investigation was then conducted with respect to variation in pH with air input for CO_2 stripping. This was due to the fact that in various previous *PRO/II* simulations an unexpected pH inversion occurred in the final water stream (after CO_2 stripping), with an increase in air flow. As stated earlier, one would not expect such an inversion, as more air is expected to remove more acidity from the water in the form of CO_2 , therefore only an increase in pH is expected with an increase in air flow (until the maximum amount of CO_2 is removed, after which the pH should "level off". The following table shows a typical result compared to the *STASOFT 4* output after "equilibrium with air" (with CO_2 partial pressure = 0.00035 atm).

Table 3.17: Comparison between *STASOFT 4* and *PRO/II* model results after CO_2 stripping highlighting pH inversion

	pH		AIR FLOW (m^3/hr)	pH
<i>STASOFT 4</i>	8.485	<i>PRO/II</i>	10	8.150
			20	8.159
			30	8.162
			40	8.164
			50	8.165
			100	8.167
			175	7.484
			200	7.153
			203	7.120
			204	7.110
			205	Error

Further Investigations: CO_2 Stripping and Recovery in *PRO/II*

At this stage the project team were concerned with regards to the discrepancies between the models insofar as CO₂ stripping is concerned. The *SIMSCI Helpdesk* was therefore once again approached and the following questions were posed:

- Is the flash vessel appropriate to model the CO₂ stripper as described in the pilot plant operation?
- Would the flash vessel with an air stream be appropriate to simulate a packed column in "cascade" mode with water entering the top, flowing downwards with an air stream being introduced at the bottom and flowing out the top?
- Why is pH inversion sometimes occurring with an increase of airflow at high airflows?
- According to the aquatic chemistry equilibria used in *STASOFT 4*, it is not theoretically possible to strip off more than ~58 mg/L of CO₂ from the water stream as described in the above example. This would seem to be possible, however, considering the *PRO/II* output we obtained.

From these interactions the *SIMSCI Helpdesk* once again confirmed that the flash vessel was indeed the appropriate unit operation to model CO₂ stripping as on the pilot plant. In addition, they suggested the use of the controller and calculator unit operations to accurately predict the air input required to model the "equilibrium with air" process step in *STASOFT 4*. The use of these unit operations would "stabilise" the simulation, thereby limiting possible convergence errors, which may be causing pH inversion. Using the controller and calculator, CO₂ is removed from the liquid with CO₂ having a partial pressure of 0.00035 atm in the stripped gas. However, as the air (modelled as N₂, O₂ and CO₂) input already had this quantity of CO₂, it was eliminated from the air input, and the controller was used to vary the air (N₂ and O₂) inlet rate to yield the required CO₂ partial pressure in the CO₂ "rich" stripped gas.

The stripping process using the controller, where the incoming air flow is varied in order to obtain a waste gas stream with a CO₂ partial press = 0.00035 atm, for all practical purposes models exactly the same process as *STASOFT 4* does (and therefore one would expect similar results to that obtained in *STASOFT 4*). However, the results for pH and total inorganic carbonic species are still different to that obtained in *STASOFT 4*. This is shown in the table below:

Table 3.18: Comparison of *STASOFT 4* and *PRO/II* after the introduction of the controller/calculator unit operations

SPECIES	DETERMINANT	STASOFT 4	PRO/II
After addition of CaCO ₃	Calcium as Ca (mg/L)	40	40
	Total alkalinity as CaCO ₃ (mg/L)	100	98.73
	pH	6.54	6.55
	Carbonic species as CO ₂ (mg/L)	144	144
After CO ₂ stripping	Calcium as Ca (mg/L)	40	40
	Total alkalinity as CaCO ₃ (mg/L)	100	99.75
	pH	8.48	8.16
	Carbonic species as CO ₂ (mg/L)	86.1	62.5

In addition to the above discrepancies, it is also clear that the controller cannot be used when the recycle loop is to be employed, as the characteristics of the gases in the recycle loop are unknown and cannot be specified.

Following this result, literature was consulted on the methods used by the *STASOFT 4* package to calculate the various parameters (4, 5, 6). *STASOFT 4* determines equilibrium ratios between the three inorganic carbonic species CO_3^{2-} , HCO_3^- , and H_2CO_3^* according to the thermodynamic equilibrium constants and the total carbonic species concentration, temperature and ionic strength. $[\text{H}_2\text{CO}_3^*]$ is the total amount of dissolved CO_2 and aqueous H_2CO_3 in the water, which is reported as CO_2 -aqueous in *PRO/II*. *STASOFT 4* then determines the ratio between dissolved CO_2 in water and CO_2 in a gas in equilibrium contact with that water by Henry's Law:

$$[\text{H}_2\text{CO}_3^*] = K_{\text{CO}_2} \cdot P_{\text{CO}_2}$$

where p is the partial pressure of CO_2 in the equilibrium-gas, $[\text{H}_2\text{CO}_3^*]$ is molar concentration, and K is the Henry's Law constant, which is temperature dependent. $\text{p}K_{\text{CO}_2}$ is calculated in *STASOFT 4* from $\text{p}K_{\text{CO}_2} = (-1760.0/T) + 9.619 - 0.00753 \cdot T$ (T in Kelvin).

The *SIMSCI Helpdesk* was asked to comment on the *STASOFT 4* approach, and whether *PRO/II* incorporates the same equations. In addition, it was also requested if they could provide any comments as to where the possible discrepancy could lie between *STASOFT 4* and *PRO/II*'s determinations of the amount of CO_2 that is expelled by the water into a gas stream of which the partial CO_2 pressure is specified. The *SIMSCI Helpdesk* forwarded these requests to the *PRO/II* developers in the United States of America for clarification. In response, the developers replied that the *PRO/II* package may have hitherto unidentified carbonate chemistry limitations and that, considering the project team's Academic License, they would not take this matter further. This result jeopardised the further use of *PRO/II*.

Concluding Remarks: CO_2 Stripping and Recovery

- The stripping and recovery of CO_2 is a critical step in the SSP. It is therefore vital that the process simulation package is able to accurately predict all facets relating to this gas strip.
- Investigation into various models/methods in *PRO/II* for carrying out gas stripping has shown that poor correlation exists between the results produced by *STASOFT 4* and *PRO/II*.
- Interactions with the developers of *PRO/II* revealed that the package may have hitherto unidentified carbonate chemistry limitations, which jeopardised further use thereof.

Completion of the *PRO/II* Model

The *PRO/II* model was also to contain the following steps of the SSP:

- CO_2 recycle
- Blending of the stabilised sidestream and main stream
- Excess CO_2 stripping and lime addition (if required)

Due to the problems previously discussed (with regards to stripping and recovery of CO_2), these processes were not thoroughly investigated. The following section highlights the main points from preliminary investigations conducted.

CO_2 Recycle

In the pilot plant operation, CO_2 is stripped, recovered and then re-used in the process. This minimizes the required input of fresh CO_2 into the process, which in turn lowers the operating cost of the process.

In the normal operation of the pilot plant, fresh CO_2 and recovered CO_2 are added to the incoming sidestream. In the *PRO/II* process model the Wegstein Acceleration method was used to determine what could be expected to occur in the recycle loop. The preliminary investigation showed that an accumulation of N_2 , O_2 and CO_2 would occur within the recycle loop if venting of these gases did not occur at the dissolution vessels. However, due to the problems associated with the equilibrium flash vessel, the results obtained are not of quantitative significance.

Blending

After the CO_2 is stripped, the stabilized stream is blended with the balance of the feed stream. Analysis of numerous simulation runs show that if the water quality obtained after CO_2 stripping for the *PRO/II* simulation is the same as what *STASOFT 4* predicts, it is possible to obtain a blended stream in *PRO/II* with a water quality that closely resembles the results obtained using *STASOFT 4*.

Excess CO_2 Stripping and Nominal Alkali Addition (if required)

In the pilot plant operation, the stripping of excess CO_2 is achieved using a set of spray nozzles, which aerates the incoming blend stream at atmospheric pressure and the addition of an air stream. Similar problems to what was experienced with CO_2 stripping from the sidestream occurred at this stage and was therefore not thoroughly investigated.

With regards to the addition of alkali to the final blended stream, investigation showed that *PRO/II* closely followed *STASOFT 4* results for the addition of lime, but that the iterative procedure required to obtain results in *PRO/II* was longer, more cumbersome and more prone to error than the immediate results output format in *STASOFT 4*.

Conclusions: Process Model generated in *PRO/II*

The investigation has shown that it is possible to accurately model certain steps of the SSP in a process simulation package such as *PRO/II*. In general:

- Feed generation (if correct inputs are added)
- CO_2 addition and dissolution, and
- CaCO_3 addition and dissolution (appropriate amount of CaCO_3 to be added calculated using *STASOFT 4*)

showed good agreement/correlation when compared to the same processes in *STASOFT 4* (under equilibrium conditions), but:

- CO₂ stripping from the resultant water stream

showed poor agreement/correlation between the two software packages. Of further importance is that the generation of a specified feed water quality, acidified stream or stabilized stream is time consuming (due to the iterative/trial & error process required), and *STASOFT 4* is normally employed to speed up the process (interdependence on *STASOFT 4* for "quick" results). This would make optimisation (to determine optimal dosing) difficult for an ever changing feed water quality, if only *PRO/II* is employed.

Problems were encountered when CO₂ was required to be stripped and recovered from a mixed liquid stream. The separation of CO₂ from the stream was impossible at the operating conditions of the pilot plant (50 kPa). The *SIMSCI Helpdesk* were consulted with regards to the aforementioned problem. Various process options/unit operations were assessed in *PRO/II*, but results from the models generated showed poor correlation to what is expected from simulations in *STASOFT 4*. The developers of *PRO/II* in the United States of America were contacted, in an attempt to understand why such discrepancies exist. These interactions revealed that the package may have hitherto unidentified carbonate chemistry limitations. This significant development led to the abandonment of using *PRO/II*.

3.5 DISCUSSION AND CONCLUSIONS: ASSESSMENT OF PROCESS MODELLING PACKAGES FOR MODELLING THE SSP

The aim of this section of the project was to develop a process modelling capability that could accurately predict the behaviour of SSP. This would allow for both optimisation of the process, and allow a better understanding of the limitations thereof, prior to industrial scale construction. The accuracy of the process models developed would be based on comparison with results obtained during pilot plant operation and from known aquatic chemistry software.

Review of current literature found that many process modelling packages are commercially available. Initially the investigation attempted to identify possible packages that seemed capable of modelling the SSP. From this investigation two packages were selected namely, *ASPEN PLUS*, manufactured and distributed by *Aspen Technology Inc.* and *PRO/II*, manufactured and distributed by *Simulation Sciences Inc. (SIMSCI)*.

A preliminary assessment of the capabilities and shortcomings/limitations of the two modelling packages was conducted. This investigation revealed that although problems were experienced during the preliminary assessment, both modelling packages appeared capable of modelling the various unit processes of the SSP. However, due to the high cost, apparent lack of kinetic modelling capabilities of the *ASPEN PLUS* package and the poor support of the *ASPEN Helpdesk*, the project team proposed that *PRO/II* be selected as the simulation package to model the SSP. This proposal was supported by the Steering Committee.

A thorough investigation using *PRO/II* to model the SSP was conducted. The investigation showed that it was possible to accurately model certain steps of the SSP, namely: feed generation, CO₂

addition and dissolution, and CaCO_3 addition and dissolution (equilibrium conditions). However, difficulties were encountered when it was required that CO_2 be stripped from the sidestream. The *SIMSCI Helpdesk* were consulted with regards the aforementioned problem. Various process options/unit operations were assessed in *PRO/II*, but results from the models generated showed poor correlation to what is expected from simulations in *STASOFT 4*. The developers of *PRO/II* in the United States of America were contacted, in an attempt to understand why such discrepancies exist. These interactions revealed that the package may have hitherto unidentified carbonate chemistry limitations. This significant development led to the abandonment of using *PRO/II*.

During a period of growing concern as to the limitations of *PRO/II*, the project team initiated efforts to develop their own model. This effort was combined with a request from the Steering Committee that the project team try to avoid the complexities of CO_2 recovery and recycling. Accordingly, preliminary modelling considered a "simplified SSP" process. This simplified SSP process does not include CO_2 recovery and subsequent recycling (but does in some instances incorporate CO_2 stripping to waste). It was envisaged that by using *STASOFT 4* and *Watchem* to model this simplified SSP, the project team would develop the necessary background to be able to model the SSP process at a later stage. The development and assessment of this model to describe a "simplified SSP" will be discussed in the following chapter.

3.6 REFERENCES – CHAPTER 3

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CHAPTER 4

**CONSIDERATION OF THE VIABILITY
OF A “SIMPLIFIED SSP”**

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4.1 INTRODUCTION

As described in the Chapter Three, it was found that use of the PRO II package was accurate for prediction of carbon dioxide dosing and calcium carbonate uptake. However, during the course of the project it became of concern that possibly severe and fatal limitations existed with regards to the capability of PRO II package to model carbon dioxide stripping and recovery. As the ability to model the carbon dioxide stripping and recovery steps is crucial to consideration of SSP, it was necessary to consider an alternative modelling approach to the PRO/II package. This requirement coincided with the suggestion by the Steering Committee that SSP be simplified further where possible, and in particular with regards to carbon dioxide stripping and recovery.

Accordingly, a "simplified" version of SSP was considered in which no carbon dioxide recovery is practiced. The theoretical viability of the so-called "simplified SSP" was considered by the development by the project team of a model. The model included JAVA programming and the use of STASOFT 4 and Watchem. (At the time, STASOFT 4 development was in its final stages, and a preliminary test-version of the software was kindly made available by Mr Ian Morrison for the purpose of modelling the simplified SSP. The Watchem program is a command line and input file driven program supplied together with STASOFT 4). Regardless of the viability of the simplified SSP, if the model developed was successful it would be used as the basis for the further development of a model describing SSP.

4.2 THE SIMPLIFIED SSP

The simplified SSP consists of the following steps:

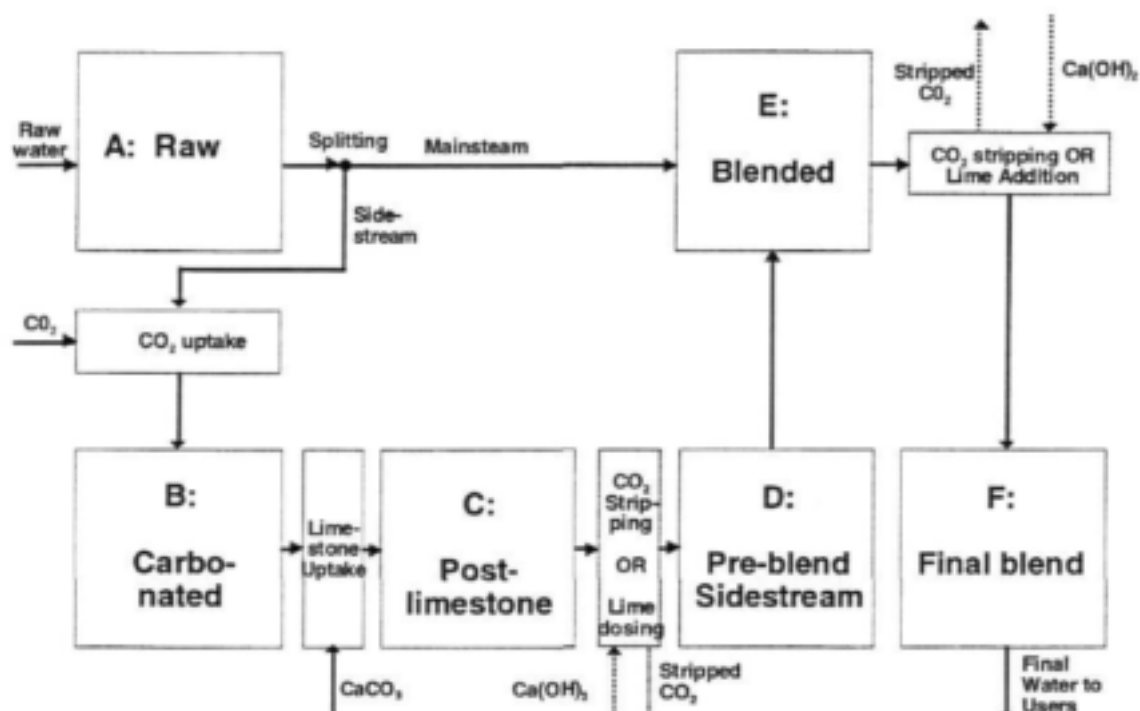


Figure 4.1: Possible steps in simplified SSP configuration

The raw water stream is split into a mainstream and a sidestream. Carbon dioxide is dosed to the sidestream, after which the sidestream is contacted with solid calcium carbonate in a contactor, to take up alkalinity and calcium. The sidestream is blended in with the mainstream again to form the final blend. The boxes between C and D and E and F indicate possible unit processes that may be employed to ensure that the final blend at F meets the user's set requirement. The various alternatives (of which probably only one will be used in a specific configuration) are:

- Stripping CO_2 to the atmosphere (i.e. to waste) **before** blending back the sidestream into the mainstream (process located between C and D on above diagram).
- Stripping CO_2 to the atmosphere (i.e. to waste) **after** the sidestream has been blended back into the mainstream (process located between E and F).
- Adding lime to the sidestream **before** blending back the sidestream into the mainstream (process located between C and D).
- Adding lime to the sidestream **after** the sidestream has been blended back into the mainstream (process located between E and F).

After a configuration has been chosen for consideration, a number of parameters can be varied, to either test whether the configuration will be able to attain the required

final water quality, or to optimise the system in terms of running costs and/or capital costs. The following parameters may be varied:

- The **raw water quality**, namely pH, calcium, total alkalinity and electrical conductivity values.
- The **final water quality**, in terms of the same determinants as the ones given above. These determinants are used to evaluate whether the stabilisation requirements are met in the final water. Stabilisation requirements are normally expressed in terms of minimum calcium and alkalinity levels, and/or a minimum Calcium Carbonate Dissolution Potential (CCDP).
- the **percentage sidestream** separated from the mainstream for treatment (this percentage will determine the size of equipment required, and hence the capital cost), and
- the **CO₂ consumption** as a result of CO₂ dosed to the sidestream (between A and B), expressed as mg CO₂ per litre of raw water.

The following assumptions are made:

- Calculations are based on chemical equilibrium conditions (liquid/solid/gaseous) for the carbonate system being attained in each of the processes.
- CO₂ is stripped to the atmosphere, i.e. CO₂ is wasted to the atmosphere. An excess volume of air can therefore be used in stripping, because recovery of CO₂ from the air stream will not be attempted. Because an excess air volume is used, the CO₂ concentration in the air inside the stripping vessel will only be raised slightly above the normal atmospheric concentration. The assumption is therefore made that the air in contact with water will have a CO₂ concentration of 0.00035 atm, unless stated otherwise.
- The CO₂ dosed in all the systems will dissolve completely, even if the system is only at atmospheric pressure (1 atm). This is a reasonable assumption, since at a partial CO₂ pressure of 1 atm, the equilibrium CO₂ concentration in a soft, acidic water in contact with the CO₂ atmosphere is approximately 1700 mg/L CO₂.
- It is assumed in all cases that chemical saturation with calcium carbonate will be attained in the calcium carbonate contactor.

A method of computation has been developed for testing premises regarding a specific choice of design, to compare different possible designs, and to optimise a chosen design.

4.3 COMPUTATIONAL METHOD TO TEST/OPTIMISE USE OF A SIMPLIFIED SSP

4.3.1 STASOFT 4

STASOFT 4 is an aquatic chemistry calculation package, the development of which was funded by the Water Research Commission of South Africa. *STASOFT 4* shows significant improvements since the previous release in terms of flexibility and user-friendliness of the program, as well as in the unit processes it simulates, making the program significantly more suitable for the purpose of modelling the simplified SSP.

At the time, *STASOFT 4* development was in its final stages, and a preliminary test-version of the software was kindly made available for the purpose of modelling the simplified SSP. For this reason the developer of *STASOFT 4*, Mr Ian Morrison, provided assistance during the simplified SSP evaluation. The *STASOFT 4* package consists of two programs, namely one with a user friendly Graphical User Interface (called here Standard *STASOFT 4*), and a DOS version which is used together with data input and output files, (called here *Watchem*).

Since there is no gas recycling stream in the simplified SSP, *STASOFT 4* can model the whole process. However, when it came to the repetition of a large number of runs (used to investigate the influence of varying CO₂ dosage and percentage sidestream), the use of *STASOFT 4* became impractical. The *Watchem* program (a command line and input file driven program) was used to overcome this limitation. This program is supplied together with *STASOFT 4*. It uses exactly the same aquatic chemistry routines as *STASOFT 4*, but its user interface is via input-files, which makes it possible to specify the variance of input parameters over a range, and the output is made in output-files that the user can customize and import into *MSEXCEL*, to obtain graphical representation of the output.

STASOFT 4 and *Watchem* were used to model the following equilibrium steps in the simplified SSP:

- CO₂ dosage
- Saturation with CaCO₃
- An optional step: stripping of the sidestream to waste
- Blending of the sidestream with the remainder of the feed stream
- An optional step: stripping of the blended stream to waste
- Addition of an alkali, such as lime, NaCO₃ or NaOH

Required chemical dosages given as output from these runs were used for running cost calculations, and running costs at different percentage sidestreams were represented in graphical format.

4.3.2 Example of the Use of Standard STASOFT 4

Standard *STASOFT 4* may be used to simulate any configuration of the simplified SSP. As an example, consider the simplified SSP process with air stripping after blending being applied to a typical Stellenbosch raw water. The raw water used in this test case is as follows:

Temperature = 20 °C, Electrical conductivity = 6 mS/m, Dissolved calcium = 2 mg/L as Ca, pH = 6.3 and total alkalinity = 5 mg/L as CaCO₃. Use of this set of determinants is sufficient to fully characterise the carbonate species chemistry of the water.

The raw water is to be split into a 30% SSP and 70% mainstream, and 100 mg/L CO₂ is to be dosed to the sidestream. Three of the four variable parameters (as described in 4.1) are thus fixed. The remaining parameter "final water quality" can now be determined and evaluated to ascertain whether it meets stabilisation requirements. As an example, a slightly positive Calcium Carbonate Dissolution Potential (CCDP) is required.

The water in the example undergoes the following processes:

- Separation into a sidestream and a mainstream.
CO₂ addition.
- Limestone contact (equilibrium with calcium carbonate).
- Blending of the sidestream and mainstream.
- Air stripping of the blend to the atmosphere.

When *STASOFT 4* is started, an initial page appears, as in **Figure 4.2**. The initial page is blank, except for a number of default initial water quality determinants. New initial water determinants can be added, and unwanted ones can be deleted. Once the initial water has been specified, the user can specify various water treatment processes across the page in the top row. Addition of a determinant or a process is done by clicking in the area where the next parameter/process is to be added. A menu appears, from which the correct parameter/process is selected.

PARAMETERS (mostly mg/l)		
Temperature	C	20
Conductivity	mS/m	10
Calcium, dissolved	Ca	0.0
pH		7.00
Alkalinity	CaCO ₃	0.0
Carbonic Species	CO ₂	0.0
CaCO ₃ PP	CaCO ₃	-14.4

Page 1

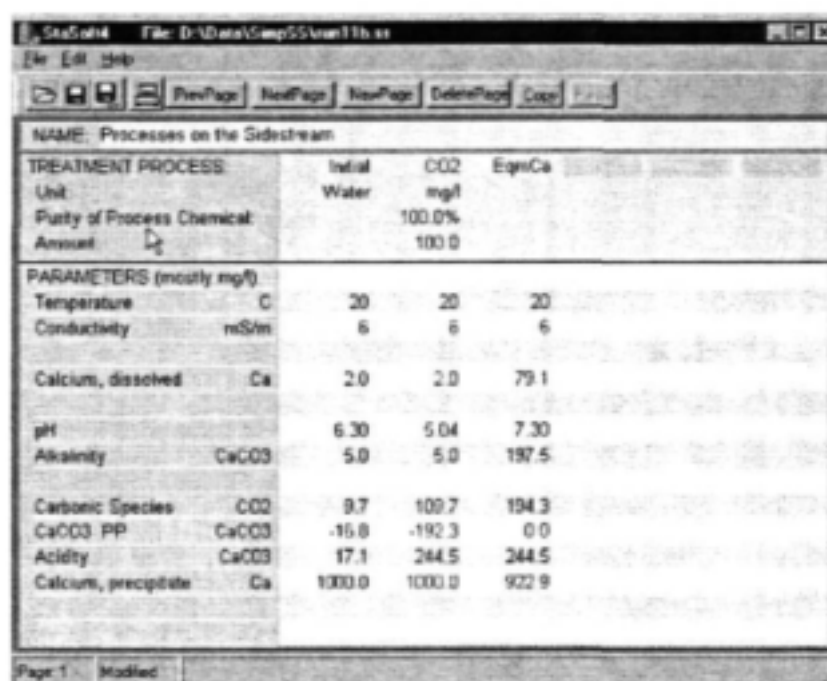
Figure 4.2: Initial screen in standard *STASOFT 4*

Standard *STASOFT 4* allows the user to specify various initial waters on different pages, and a different train of processes for each initial water. One of the processes the user can specify is "blending". This entails blending in a specified fraction of the **final water on page 1** into the stream at the specific point in the treatment train.

The processes undergone by the sidestream are specified on page 1 of *STASOFT 4* (the initial quality of the sidestream water being identical to the raw water quality). On page 2 of *STASOFT 4*, the mainstream (before and after blending with the sidestream) is simulated. The initial quality of the mainstream is also identical to the raw water, therefore, under initial water on page 2 of *STASOFT 4*, the raw water quality is added. The first process on page 2 of *STASOFT 4* is blending the sidestream into the mainstream - the final water from page 1 of *STASOFT 4* (i.e. the sidestream after treatment) is blended into the mainstream, the sidestream forming 30% of the blend. The rest of the processes undergone by the blended stream are then specified on page 2 of *STASOFT 4*, to ascertain the final water quality (shown in the last column).

Figure 4.3 shows page 1 of *STASOFT 4*, which is the processes undergone by the sidestream. The initial water is specified by clicking in the appropriate areas, and selecting the appropriate parameter to add from a pop-up list. The parameters that are needed to fully characterise the water mentioned should be made editable by ticking off "editable" in a tick-box appearing below the pop-up list. Editable parameters must be supplied by the user, whereas uneditable parameters are

calculated automatically by the system. On this page (as well as on page 2 of STASOFT 4) the editable parameters are: temperature, conductivity, calcium, pH, total alkalinity and precipitated calcium (at the bottom). Precipitated calcium refers to an amount of solid calcium carbonate available for dissolution if the water is allowed to equilibrate with CaCO_3 . If an excess of calcium carbonate is available (as in this case) a sufficiently large value is entered here. Carbonic species, calcium carbonate precipitation potential and total acidity are additional, non-editable parameters, which the system will calculate for the user. The initial water's editable parameters are added by clicking on the appropriate spaces and typing in the values. Calculations are carried out automatically when ENTER is pressed, or when the user clicks somewhere else on the screen.



The screenshot shows the STASOFT 4 software window. The title bar reads 'STASOFT4 File: D:\Data\SimpSSUser11b.st'. Below the title bar is a menu bar with 'File', 'Edit', and 'Help'. A toolbar contains icons for file operations and buttons for 'PrevPage', 'NextPage', 'NewPage', 'DeletePage', 'Copy', and 'Paste'. The main area is titled 'NAME: Processes on the Sidestream'. It contains a table with columns for 'TREATMENT PROCESS', 'Unit', 'Initial Water', 'CO2 mg/l', and 'Eqn/Ca'. The table lists several parameters and their values after treatment.

TREATMENT PROCESS	Unit	Initial Water	CO2 mg/l	Eqn/Ca
Purity of Process Chemical:			100.0%	
Amount			100.0	
PARAMETERS (mostly mg/l)				
Temperature	C	20	20	20
Conductivity	mS/m	6	6	6
Calcium, dissolved	Ca	2.0	2.0	79.1
pH		6.30	5.04	7.30
Alkalinity	CaCO_3	5.0	5.0	197.5
Carbonic Species	CO_2	9.7	109.7	194.3
CaCO_3 PP	CaCO_3	-16.8	-192.3	0.0
Acidity	CaCO_3	17.1	244.5	244.5
Calcium, precipitate	Ca	1000.0	1000.0	922.9

At the bottom of the window, it says 'Page 1' and 'Modified'.

Figure 4.3: Example of a Standard STASOFT 4 screen – Page 1

The sidestream undergoes two treatment processes, namely addition of 100 mg/L CO_2 , and equilibration with calcium carbonate. The processes are added by clicking in the appropriate areas and selecting the process from a pop-up list. If the process entails addition of a substance, the amount of the substance to add must be specified in a field appearing below the name of the process. After a process has been added, the resultant quality of the water appears automatically in the column below the process name. In this case it can be seen that after CO_2 has been dosed to the initial water, and the water was contacted (equilibrated) with calcium carbonate, it should have a pH of 7.3, and calcium carbonate precipitation potential of 0.

Figure 4.4 shows page 2 of STASOFT 4. The initial water here is the mainstream before blending. The mainstream is then blended in a 70:30 ratio with the treated sidestream water (the water from the last column on page 1 of STASOFT 4), and the resultant water is equilibrated with the atmosphere, which has a partial CO₂ pressure of 0.00035 atm.

It can be seen in the last column that the final water will have a pH of 8.33, total alkalinity of 62.7 mg/L as CaCO₃ and a CaCO₃ precipitation potential of 0. It should therefore meet most users' stabilisation requirements. In this example, three of the four variable parameters were specified, namely the raw water quality, the percentage sidestream and CO₂ dosage. The fourth parameter, the final water quality, was calculated by the system. Any three of the four variable parameters may be specified to obtain the fourth. However, a trial-and-error iterative approach must be followed to determine the unknown variable parameter if the user wants to specify final water requirements upfront.

NAME: Process on Mainstream and Blended Stream		Initial Water	Blend:Pp1 % Page1	EqmCO2 sp Atm
TREATMENT PROCESS				
Unit:				
Purity of Process Chemical				
Amount			30.0	0.00035
PARAMETERS (mostly mg/l)				
Temperature	C	20	20	20
Conductivity	mS/m	6	6	6
Calcium, dissolved	Ca	2.0	25.1	25.1
pH		6.30	7.12	8.33
Alkalinity	CaCO ₃	5.0	62.7	62.7
Carbonic Species	CO ₂	9.7	65.1	65.2
CaCO ₃ PP	CaCO ₃	-16.6	-20.1	0.1
Acidity	CaCO ₃	17.1	65.3	62.8

Figure 4.4: Example of Standard STASOFT 4 screen – Page 2

4.3.3 Watchem

Watchem is a command line version of STASOFT 4, deriving information about initial water quality and processes from an instruction file, compatible with STASOFT 4 data files. The reason why Watchem (which is less user-friendly than STASOFT 4) was used in this investigation was that it allows multiple process doses to be specified on a single process line in the instruction file. This means that a range of dosages, for example a range of CO₂ dosages to the sidestream, can be tested with a

single run of *Watchem*. Output is generated in the form of a text file, or a comma separated text file, which can easily be imported into a spreadsheet program for further data analysis and graphical representation.

4.3.4 Example of the use of *Watchem*

Watchem can be used, for instance, to determine the effect of varying CO₂ dosage on the final quality of the sidestream, before blending the treated sidestream with the mainstream.

To use *Watchem*, the user has to create an instruction file in which the initial water is specified, as well as the processes that the water undergoes. In this case, the raw water is the typical soft Stellenbosch raw water that was also used in the previous example. In the following example only treatment of the sidestream is investigated, with the sidestream undergoing two treatment processes, namely the addition of CO₂ and equilibration with CaCO₃ (contact with solid CaCO₃). The following instruction file is created to specify the raw water and treatment processes that the water undergoes:

Table 4.1: Example of *Watchem* instruction file, named "run 1"

```
# Typical Stellenbosch raw water
# A range of CO2 dosages to raw water
# For each CO2 dosage, equilibrate resultant water with CO2
RW: Temp=20 EC=6 Ca=2 pH=6.3 Alk=5 CPP Acy Ct pCa=1000
PR: CO2 step 1 0 1500
PR:p EqmCa
```

The program reads the instructions line-by-line. If a line is started with "#", the rest of the line is ignored (the user can therefore enter comments after a "#"). A line anywhere in the file may start with "#", not only at the beginning of the file.

The first line not starting with a "#" must be the specification of the raw water. The raw water is indicated by starting the line with "RW:". The rest of the line contains values for parameters that the user specifies. As explained in the *STASOFT 4* example above, the user must specify enough parameters to fully characterise the water. In this example, the water is characterised by specifying its temperature ("Temp") in °C, electrical conductivity ("EC") in mS/m, dissolved calcium ("Ca") in mg/L Ca, pH, total alkalinity ("Alk") in mg/L as CaCO₃, and solid calcium carbonate available for dissolution (pCa) in mg/L as Ca. Parameters additional to these ones that characterise the water may be added, without specifying their values. Their values will be calculated by the system and could be printed to an output file. In the example instruction file above, the following extra parameters were added, without

specifying their values: calcium carbonate precipitation potential ("CPP") in mg/L as CaCO_3 , total acidity ("Acy") in mg/L as CaCO_3 and total carbonic species ("Ct") in mg/L as CO_2 .

In the lines following the raw water line the treatment processes that the water undergoes are specified. A line in which a process is specified is started by "PR:", followed by a symbol for the process, e.g. "CO2" for CO_2 addition, and "EqmCa" for equilibrium with CaCO_3 . The process may also require an additional quantity, such as the amount of a chemical that is added, or the partial pressure for equilibration with CO_2 . Addition of 100 mg/L CO_2 will be specified by "PR: CO2 100". Precision of calculation may be specified by adding the required number of decimal places after the process symbol, e.g. "CO2:6". Instead of one dosage, a range of dosage values may be specified, either by typing a series of dosage values, or by specifying an automatically calculated dosage range, as in the example: "PR: CO2 step 1 0 1500" means: calculate CO_2 dosage from 0 to 1500 mg/L in steps of 1. The last line in the example specifies equilibration of the water with solid calcium carbonate: "PR:p EqmCa". The system will calculate the resultant quality after equilibration for every dosage of CO_2 . Similarly, "PR:p EqmCO2 0.00035" would mean: calculate the quality of resultant water if the water is equilibrated with an atmosphere with partial CO_2 pressure of 0.00035 atm. The "p" instructs the program to print the quality of the resultant water. The water quality after the treatment indicated by "p" will be printed in a single line. The user is advised to only print the quality of the final water; otherwise the output data would become too confusing.

Detailed instructions and a list of all the raw water parameters and treatment processes that may be specified in the instruction file are given in a help-file accompanying the *Watchem* program, named "Watchem.wpd".

Command line usage is as follows:

Watchem: [-s] [-p] [--] filename

where:

-s	Means: Output results in form suitable for use with spreadsheets i.e. with comma separated values. If -s is not specified, values are separated by blank characters only
-p	Means: Output data for all lines, even if not so marked.
--	Means: Display this message
filename:	Instruction file name

Output goes to the screen but can be redirected to a file, e.g.

Watchem run1 > run1.dat

Watchem -s run1 > run1.csv

Output is redirected to the file specified after >. In this case, the second command line was used, to obtain the output in a comma separated value file named "run1.csv". The first part of the file is shown below.

Table 4.2: Example of a Watchem output file with comma separated values, named "run1.csv"

HD.Temp.	EC.	Ca.	pH.	Alk.	CPP.	Acy.	Ct.	pCa.	CO2.	EqmCa
PR. 20.	6.	8.7.	9.3.	21.8.	0.0.	17.1.	17.1.	993.3.	0.0.	0
PR. 20.	6.	9.4.	9.22.	23.6.	0.0.	19.4.	18.9.	992.6.	1.0.	0
PR. 20.	6.	10.2.	9.14.	25.4.	0.0.	21.7.	20.7.	991.8.	2.0.	0
PR. 20.	6.	10.9.	9.07.	27.3.	0.0.	23.9.	22.5.	991.1.	3.0.	0
PR. 20.	6.	11.7.	9.00.	29.3.	0.0.	26.2.	24.4.	990.3.	4.0.	0
PR. 20.	6.	12.5.	8.94.	31.2.	0.0.	28.5.	26.3.	989.5.	5.0.	0
PR. 20.	6.	13.3.	8.88.	33.3.	0.0.	30.8.	28.1.	988.7.	6.0.	0
PR. 20.	6.	14.1.	8.82.	35.3.	0.0.	33.0.	30.0.	987.9.	7.0.	0
PR. 20.	6.	15.0.	8.77.	37.4.	0.0.	35.3.	31.9.	987.0.	8.0.	0
PR. 20.	6.	15.8.	8.72.	39.4.	0.0.	37.6.	33.9.	986.2.	9.0.	0

Values for the parameters specified in the raw water line are displayed. Each line shows the quality of the water after a different CO₂ dosage.

This file can be opened with a spreadsheet program for further analysis and graphical representation. In *Corel Quattro 8*, "run1.csv" is simply opened as one would open any "*.wb3" file. In *MSE Excel 2000*, open the file like a normal file. The Text Import Wizard will be activated to assist the user to import the comma delimited data file. Under "Original Data Type", select "Delimited", then click on the "Next" button at the bottom. In the next window that appears, under "Delimiters", select "Comma" - leave the rest of the options with their defaults unchanged. Click on the "Next" button, and on the "Finish" button in the final window. The data will now be available in spreadsheet format for further manipulation.

As an example of a graphical representation of the data, the total alkalinity of the treated sidestream water is plotted against CO₂ dosage - see **Figure 4.5**.

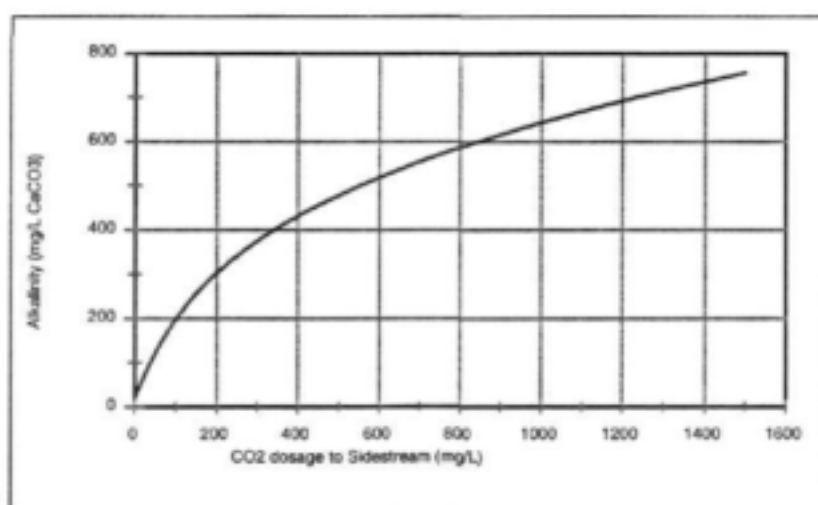


Figure 4.5: Total alkalinity of treated sidestream water vs. CO₂ dosage

As shown by the example above, *Watchem* may be used for any type of investigation where the characteristics of the SSP need to be investigated over a large range of different dosages.

4.3.5 Prices Used for Cost Assessments

The following prices for chemicals were used in the cost assessments. (NOTE: The prices for chemicals used vary considerably with both the quality of the product and the region to which the product must be transported. The cost of white lime has in particular fluctuated considerably. The costs presented below were valid in Stellenbosch, South Africa in November 1999.)

CaCO ₃	Calcium carbonate is dosed in the form of limestone (Aquastab Pebbles, Bredasdorp): Price: R140/ton limestone Purity: 95.0%
Lime	Local lime with available CaO of 65% was used: Price: R750/ton Purity: 85.9%
CO ₂	Price: R730/ton Purity: 100%
Sodium Hydroxide	In flake form in bags. Price: R2500/ton Purity: 100%
Soda Ash	Dense soda ash was used: Price: R1700/ton Purity: 95%

Electricity cost

A very rough estimate of electricity cost was made, namely
1 c/kL of the treated water (i.e., per kL of the sidestream).

4.4 IDENTIFICATION AND ASSESSMENT OF CRITICAL PARAMETERS

In section 4.2 the basic configuration of the SSP is set out. Alternative ways could be used to ensure that final water meets the requirements, namely stripping CO₂ to waste, either before or after blending, or, alternatively, adding relatively small dosages of lime, either before or after blending. Each of the alternatives are analysed and critical parameters identified in the following section.

4.4.1 CO₂ Stripping After Blending - 100% Efficiency Stripping of CO₂ to Waste - Aiming for a Final CCPP of Zero, Regardless of Final Total Alkalinity Required

In this configuration of the simplified SSP, the raw water undergoes the following treatment steps:

- Separation into a sidestream and a mainstream.
- CO₂ addition.
- Limestone contact (equilibrium with calcium carbonate).
- Blending of the sidestream and mainstream.
- Air stripping of the blend to the atmosphere, with 100% efficiency in removal of excess CO₂

In this system there are four basic parameters that are potentially variable, namely:

- Raw water quality
- Final water quality
- The percentage sidestream
- CO₂ consumption

Raw water quality is normally a given (i.e., not variable). In this case we assume it is a typical Stellenbosch soft raw water, with temperature = 20 °C, conductivity = 6 mS/m, dissolved calcium = 2 mg/L as Ca, pH = 6.3 and total alkalinity = 5 mg/L as CaCO₃. We also fix the final water quality by specifying that it should have a calcium carbonate precipitation potential of 0. In the *STASOFT 4* example above we saw that a precipitation potential of 0 in the final water was attainable by using a 30% sidestream and dosing 100 mg/L CO₂ to the sidestream, blending the sidestream back into the mainstream, and equilibrating the blended stream with the atmosphere. The final water quality may be fully characterised by specifying its total alkalinity, total acidity and dissolved calcium. (Temperature and conductivity play lesser roles, they are therefore not taken into account here). The final water's dissolved calcium

depends only the raw water's dissolved calcium, and alkalinity uptake via limestone contact, therefore, in this case alkalinity and dissolved calcium are not independent from each other. This leaves only acidity and alkalinity. The final water is in equilibrium with air - under this constraint its acidity is a function of its alkalinity. There is therefore only one variable parameter in this case, namely alkalinity. By slightly adjusting the *STASOFT 4* example above we see that a final water with a CaCO_3 precipitation potential of 0 has a total alkalinity of 61.8 mg/L. Air stripping the blended stream does not affect its total alkalinity (it only reduces its total acidity). The blended stream (before air stripping) should therefore have the same total alkalinity as the final water, namely 61.8 mg/L.

The quality of the final blend (after stripping) is therefore fixed as shown in the following table.

Table 4.3: Quality of final blend (after stripping)

Determinant	Value
pH	8.32
Total alkalinity (mg/L as CaCO_3)	61.8
Calcium (mg/L as Ca)	24.7
Electrical conductivity (mS/m)	6.0
Temperature ($^{\circ}\text{C}$)	20.0
Calcium carbonate dissolution potential (mg/L as CaCO_3)	0.0

The sidestream and mainstream can be blended in any ratio to result in a blended water with total alkalinity of 61.8 mg/L by varying the alkalinity uptake in the sidestream via CO_2 dosage. The percentage sidestream can be varied between 0% and 100%, and by a simple mass balance calculation, the required total alkalinity in the sidestream that would result in a total alkalinity of 61.8 mg/L after blending can be determined.

Table 4.4: Percentage sidestream vs. required total alkalinity in treated sidestream for a CaCO_3 precipitation potential of 0 in final blend, for a raw water with pH 6.3, 2 mg/L calcium, 5 mg/L total alkalinity

% Sidestream	Total alkalinity in Treated Sidestream
10	573.00
20	289.00
30	194.33
40	147.00
50	118.60
60	99.67
70	86.14
80	76.00
90	68.11
95	64.79
100	61.80

In the *Watchem* example, the total alkalinity in the treated sidestream is given as a function of the CO_2 dosage to the sidestream. The CO_2 dosage required to obtain a zero CaCO_3 precipitation potential in the final treated water can therefore be determined for each different sidestream percentage. This dosage is expressed per litre of blended stream in **Figure 4.6**.

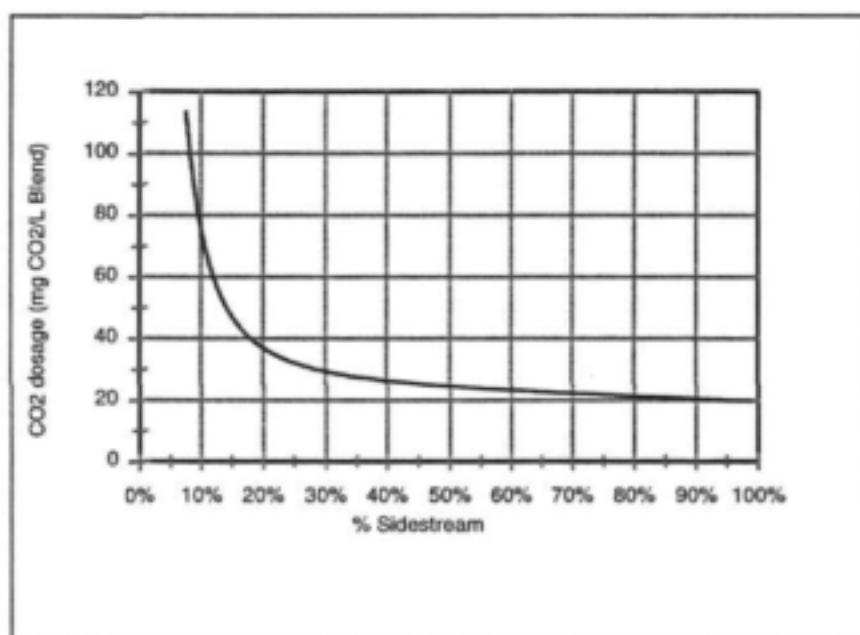


Figure 4.6: CO_2 dosage required (per L blended stream) at various sidestream percentages, to obtain a CaCO_3 precipitation potential of 0 in final water

It can be seen from the plot that the required CO_2 dosage reduces exponentially as the percentage sidestream is increased. This is in part due to the shape of the plot of alkalinity uptake by the sidestream vs. CO_2 dosage (**Figure 4.5**).

Procedure followed to determine dosages

The following is a summary of the procedure followed to determine the required CO₂ dosages (and the amount of calcium carbonate taken up in the limestone fixed bed), if the simplified SSP is implemented with complete stripping of CO₂ to waste after blending.

- First it must be determined what total alkalinity is needed to ensure that the final blended stream reaches a CCPP of zero after equilibration with the atmosphere. This can be determined using *STASOFT 4*. Set up the following treatment steps in *STASOFT 4*: Initial water, calcium carbonate addition, equilibration with air (partial CO₂ pressure=0.00035 atm). Adjust the amount of calcium carbonate addition until a CCPP of zero after equilibration with the air is reached. Read off the characteristics of the water after equilibration (especially note the total alkalinity - this is the final total alkalinity the must be aimed for in order to ensure a CCPP of zero, regardless of the percentage sidestream that will be used).
- Obtain a series of CO₂/total alkalinity pairs for the initial water under consideration (i.e., the total alkalinity reached by the water after x amount of CO₂ has been dosed to it and it has been equilibrated in contact with solid calcium carbonate.) This can be done using *STASOFT 4*, or a large number of data-pairs for CO₂ dosages ranging between 5 and 500 mg/L may be obtained using the Watchem program, and importing the output data to a spreadsheet.
- For each different CO₂ dosage, calculate the percentage sidestream needed to obtain the required total alkalinity (see above) in the blended stream. The following formula is used:

$$X = (\text{Required final total alkalinity} - \text{Initial "raw" water total alkalinity}) / (\text{Total alkalinity in sidestream after equilibration with CaCO}_3 - \text{initial "raw" water total alkalinity})$$

Where:

X = the sidestream fraction.

- From all the data obtained above, calculate for a range of CO₂ dosage values the amount of calcium carbonate used per litre of the blended stream, as well as the CO₂ dosage per litre of the blended stream. This is done by multiplying the dosages to the sidestream by the sidestream fraction.

The total usage of CO₂ and CaCO₃ per L of the blended stream was determined for the various sidestream percentages (CaCO₃ dosage is fixed at different sidestream percentages). The total chemical costs were calculated as a function of sidestream percentage. Whereas the total chemical costs decrease exponentially with increase in

sidestream percentage, the electricity cost should increase linearly with increase in sidestream percentage, due the larger stream that need to be pumped.

Figure 4.7 shows how chemical and electricity costs vary with percentage sidestream. A very rough estimate of electricity cost has been made, namely 1 c/kL of sidestream. The plot shows that running costs are significantly reduced when the percentage sidestream is increased from 8% to $\pm 30\%$. The running cost of a plant such as this one does not seem to be sensitive to variations in sidestream percentage between 30% and 100%. (NOTE: In most cases the lowest treatment cost occurs at a sidestream of 100%. Such a situation, however, implies that the entire raw water stream undergoes stabilisation, which would result in large capital costs, negating the benefit of the SSP process. Smaller sidestreams are therefore usually investigated to quantify the relevant benefit of the SSP process.)

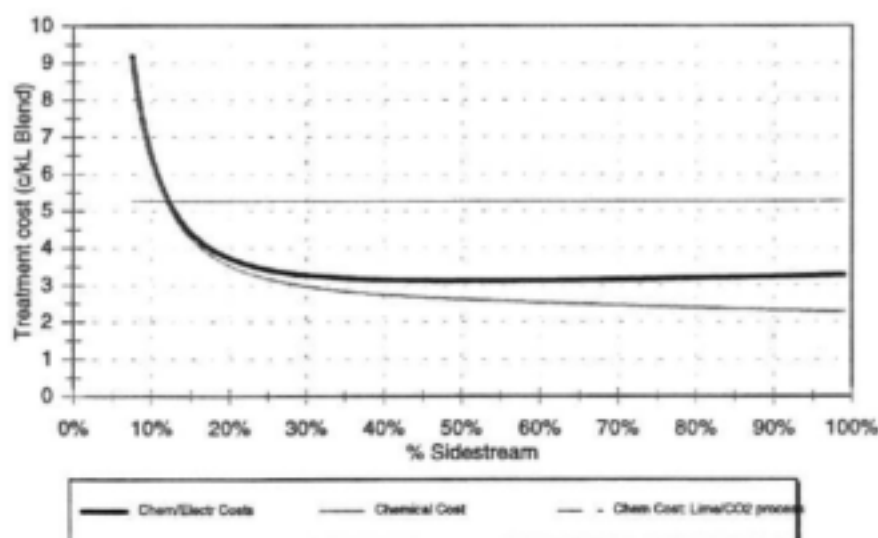


Figure 4.7: Running costs per kL blend, to obtain a final CaCO_3 dissolution potential of 0, stripping CO_2 to waste after blending

4.4.2 CO_2 Stripping Before Blending - 100 % Efficiency Stripping Of CO_2 . Aiming For A Final CCPP Of Zero, Regardless Of Final Total Alkalinity Required

In this configuration of the simplified SSP, the raw water undergoes the following treatment steps:

- Separation into a sidestream and a mainstream.
- CO_2 addition.
- Limestone contact (equilibrium with calcium carbonate).

- Air stripping the sidestream - wasting CO_2 to the atmosphere.
- Blending of the sidestream and mainstream.

In this system there are four basic parameters that are potentially variable, namely:

- Raw water quality
- Final water quality
- The percentage sidestream
- CO_2 consumption

As previously, the quality of a typical Stellenbosch soft water is used for the raw water quality, therefore the raw water quality is fixed. Again, we will specify that the final water should have a CaCO_3 precipitation potential of 0 mg/L, therefore we fix the final water quality. The remaining two parameters, namely percentage sidestream and CO_2 dosage can therefore be varied when trying to optimise other factors such as running costs.

It was found that, unlike in the previous case, none of the water quality determinants in the final treated stayed fixed when the % sidestream was varied to obtain a zero precipitation potential at a specific CO_2 dosage. Also, unlike previously, a calculation function could not be formulated for the determination of the required sidestream total alkalinity at each different sidestream percentage. Failure to formulate such a function does not mean that such a function does not exist, however, a different, trial-and-error, method was followed to determine for each sidestream percentage the required CO_2 dosage that will result in a final blend with a precipitation potential of zero. The simplified SSP was modelled using *STASOFT 4*. The CO_2 dosage was varied for a range between 5 and 500 mg/L, and, for each CO_2 dosage, the sidestream percentage was varied until the final blend precipitation potential was zero.

Procedure followed to determine dosages

The following procedure was followed to determine the required CO_2 and CaCO_3 dosages for various sidestream percentages, in the case where complete CO_2 stripping to waste occurs before blending of the mainstream and sidestream.

- Set up the following treatment steps in *STASOFT 4*:
 - On Page One: Initial water, CO_2 addition, equilibration with CaCO_3 , lime addition, equilibration with air.
 - On Page Two: Initial water, blending with final water on Page One.
- Choose a CO_2 addition value and enter this on Page One (any value between 5 and 500 mg/L).
- On Page Two, vary the sidestream blend-ratio until the CCPP after blending is zero. Note the final water's characteristics, especially the total alkalinity required for a CCPP of zero.
- Repeat the above steps for various CO_2 dosages in the range between 5 and 500 mg/L.

The required CO_2 and CaCO_3 usage rates that were determined for the different sidestream percentages are shown in Figure 4.8.

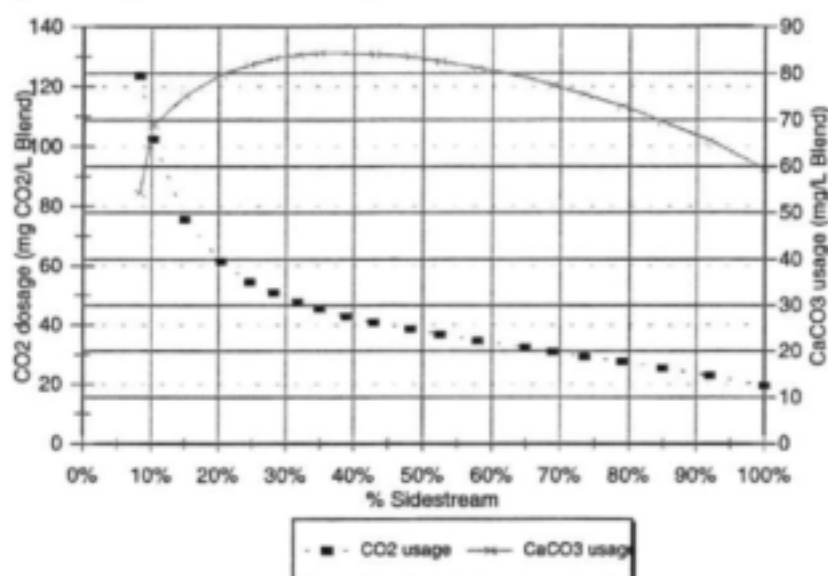


Figure 4.8: Stripping to waste before blending: CO_2 and CaCO_3 usage per litre blend

Final water quality

The pH of the final blended water ranges between 8.03 and 8.32, depending on the percentage sidestream. Total alkalinity ranges between 61.4 and 85.2 mg/L as CaCO_3 , and calcium between 24.6 and 34.1 mg/L as Ca. The calcium carbonate precipitation potential of the final water is 0. The final water is also fairly balanced in terms of gaseous equilibrium with the air. This is to be expected, because the sidestream has been equilibrated with the atmosphere, and the raw and mainstream water should not be significantly super-saturated with CO_2 . If the final water is equilibrated with the atmosphere, less than 2 mg/L CO_2 will escape. The pH will increase slightly, causing the final water pH range to fall between 8.32 and 8.46. The precipitation potential of the equilibrated waters will vary between 0 and 3.4 mg/L as calcium carbonate.

Conventional lime/ CO_2 method - dosages required

Direct comparison between the above method of stabilisation and the conventional lime/ CO_2 dosage method is not possible, because the final water quality will differ for the two cases. However, the following case for the conventional stabilisation was considered for the purpose of this comparison: dosage of 33.3 mg/L lime (assuming available lime of 62% as CaO), followed by dosage of 31.9 mg/L CO_2 . The lime dosage is enough to obtain a final water with a total alkalinity of 50 mg/L (recommended by iron corrosion guidelines), and the CO_2 dosage is enough to bring the pH down to 9, and the CCPP to 4 mg/L. The final water obtained by this method has the following characteristics: pH = 9.05, total alkalinity = 50 mg/L, calcium = 20 mg/L as Ca, CCPP = 4 mg/L.

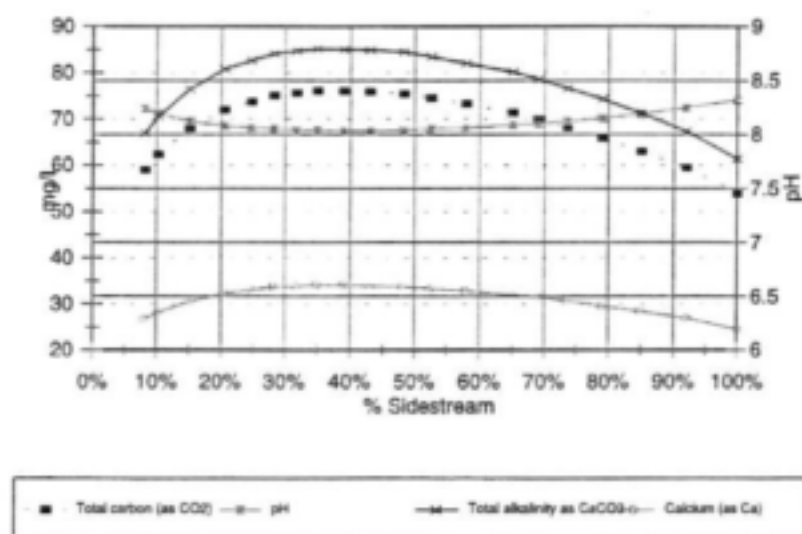


Figure 4.9: Strip to waste before blending: quality of the final blended water

The chemical and running costs for this SSP configuration are shown in **Figure 4.10**. The chemical cost for the conventional lime/CO₂ dosage method is also shown in this plot. Unlike the previous case, the percentage of sidestream has a significant effect on chemical costs throughout the range of possible percentages. Running cost is also significantly higher as in the previous case where the blend was stripped.

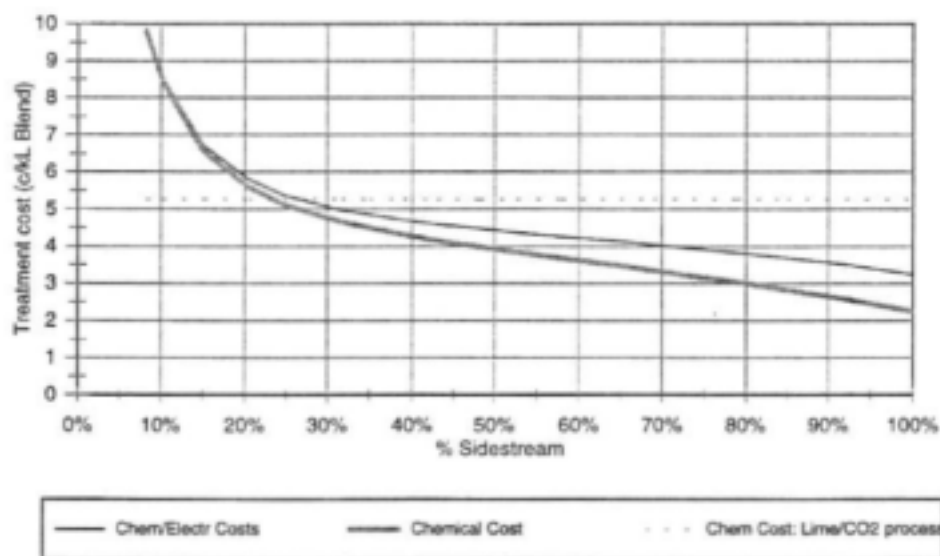


Figure 4.10: Running costs per kL Blend, to obtain a final CaCO₃ dissolution potential of 0, stripping to waste before blending

4.4.3 No CO₂ Stripping Before Blending + Lime Dosing To A Predetermined Total Alkalinity And Final CCPP Of Zero

In this configuration of the simplified SSP, the raw water undergoes the following treatment steps:

- Separation into a sidestream and a mainstream.
- CO₂ addition.
- Limestone contact (equilibrium with calcium carbonate).
- Blending of the sidestream and mainstream.
- Addition of lime.

In this system there are five parameters that are potentially variable, namely:

- Raw water quality
- Final water quality
- The percentage sidestream
- CO₂ consumption
- Amount of lime added

The requirement for a final total alkalinity is decided on before determining the chemical dosages and the percentage sidestream. Two worked examples are presented. In the first example, a total alkalinity of 50 mg/L was chosen. In the second example, a total alkalinity of 30 mg/L was chosen.

Example One: Final total alkalinity of 50 mg/L

As previously, the raw water quality is fixed. The final water can be characterised fully by its alkalinity, acidity and dissolved calcium. In this case, we want the final water to have a total alkalinity of 50 mg/L, and a precipitation potential of zero. Three parameters are needed to characterise a water. The total alkalinity and precipitation potential are specified, leaving the final water quality with one degree of freedom. If any two of three parameters that may be used to characterise the final water are shown to be interdependent, though, we will know that there is only one final water that could meet the requirements.

The final water's calcium is a function of the raw water calcium and amount of calcium added by lime and calcium carbonate addition. The final water's total acidity is a function of the raw water total acidity, CO₂ addition, and lime addition. CO₂ addition can be related to calcium carbonate addition, therefore, both the final water total acidity and final water calcium can be written as a function of raw water quality, CO₂ addition and lime addition. The final water's calcium and total acidity are therefore not independent variables. Three parameters may be used to characterise the final water: calcium, total alkalinity and total acidity. Calcium is fixed as 50 mg/L, and the remaining two, total alkalinity and total acidity, are

dependent on each other. Specifying that the precipitation potential must be zero therefore fixes the remaining two dependent parameters (total alkalinity and total acidity). Therefore, only one final water will meet the required criteria (total alkalinity of 50 mg/L, and calcium carbonate dissolution potential of 0).

Procedure to determine required calcium carbonate, CO₂ and lime dosages

Two formulae (given below) can be used to determine the required lime/CO₂ dosages at various percentage sidestreams. However, these formulae require the final total acidity, which has to be determined first by using *STASOFT 4*. For the given initial water and set of treatment steps, there would be a specific final water total acidity that would ensure a final water CCPP of zero, regardless of what the sidestream percentage is. The first step is therefore to ascertain the required final water quality needed for a CCPP of zero, and, when that is known, the final water's total acidity may be substituted in the formulae, to determine the lime dosage required at various sidestream percentages.

- Set up *STASOFT 4*, with the following treatment steps:
Page One: Initial water, CO₂ dosage, equilibrium with calcium carbonate.
Page Two: Initial water, blending, lime addition, equilibrium with air (the last treatment step is strictly not part of the process).
- On page Two, set the lime dosage to zero.
- Set the CO₂ dosage on Page One - choose any CO₂ dosage between 5 and 500 mg/L to initialise the process.
- Adjust the percentage of the blend until you obtain the required final total alkalinity (50 mg/L in this example).
- It will be noticed that after blending the CCPP is negative. The lime dosage must therefore be adjusted until a CCPP of zero is obtained. However, when lime is dosed, the alkalinity increases. The percentage blend therefore has to be adjusted as well at the same time, in such a way that the total alkalinity after lime dosage stays at the required level (50 mg/L in this case) all the time. Therefore gradually increase the lime dosage from zero, whilst adjusting the percentage sidestream so as to maintain the total alkalinity at the required value. After each adjustment of the lime addition and associated change to the percentage sidestream, check the CCPP. Repeat the procedure until a CCPP of zero after lime addition is obtained.

NB: Note that the objective is to find the minimum lime dosage for which a CCPP of zero can be obtained. Therefore, check that you cannot obtain a CCPP of zero with a lower lime dosage, before terminating this step.

- Record the water quality after lime addition, including the acidity.

- Repeat the process for a range of CO₂ additions, from 5 mg/L to 500 mg/L. This can also be done automatically, using the formulae for X (sidestream percentage) and lime dosage given below. On a spreadsheet that contains pairs of calcium and total acidity values for the initial water after different CO₂ dosages and equilibration with calcium carbonate, you can enter the above formulae to automatically calculate the required sidestream percentages and lime dosages at the various CO₂ dosages.

The final water with the required total alkalinity and CCPP of zero is shown in the following table.

Table 4.5: Final water with required total alkalinity and CCPP of zero

Determinant	Value
pH	8.53
Total alkalinity (mg/L as CaCO ₃)	50.0
Total acidity (mg/L as CaCO ₃)	49.0
Calcium (mg/L as Ca)	20.0
Electrical conductivity (mS/m)	6.0
Temperature (°C)	20.0
Calcium carbonate dissolution potential (mg/L as CaCO ₃)	0.1

After equilibration with the atmosphere, the above water would have a dissolution potential of 1.3 mg/L, pH of 8.23 and total acidity of 50.5 mg/L.

In the *Watchem* example, various dosages of CO₂ to the sidestream were considered, noting the calcium and total alkalinity of the treated sidestream as a result of the various CO₂ dosages. For a specific raw water, the same *Watchem* results may be used to establish a relationship between dissolved calcium and total acidity of the treated sidestream.

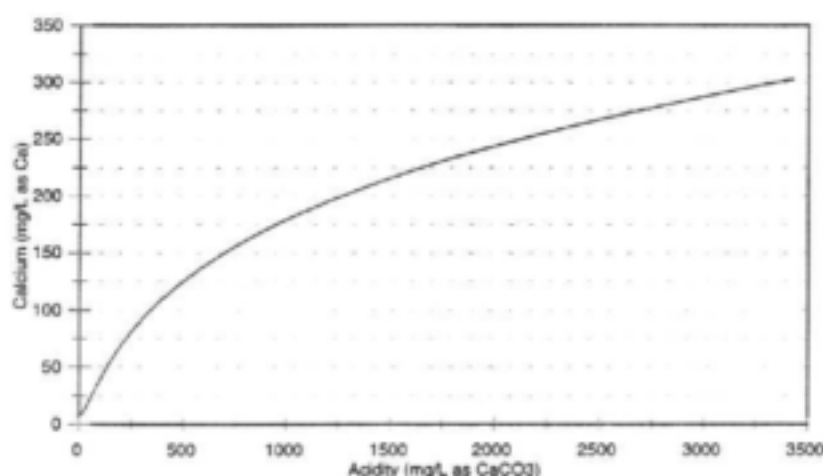


Figure 4.11: Relationship between dissolved calcium and total acidity in treated sidestream for a raw water with pH 6.3, and calcium and final total alkalinity of 5 mg/L as CaCO₃.

The percentage sidestream and lime addition required at different CO₂ dosages were determined by doing two mass balances before and after blending, one for calcium, and one for total acidity.

Calcium mass balance

$$(\text{Raw Ca}) * (1 - X) + (\text{Treated SS Ca}) * X = (\text{Required Ca in final blend}) - (\text{lime added}) / 74 * 100$$

Total acidity mass balance

$$(\text{Raw Ac}) * (1 - X) + (\text{Treated SS Ac}) * X = (\text{Required Ac in final blend}) + (\text{lime added}) / 74 * 100$$

Where:

Treated SS Ca: Dissolved calcium in the treated sidestream, in mg/L as CaCO₃

Treated SS Ac: Total acidity in the treated sidestream, in mg/L as CaCO₃

Matching values for the above may be read from the plot in **Figure 4.11**. Each pair would correspond to a CO₂ dosage value that can be calculated as the difference between the total acidity of the treated sidestream and the raw water total acidity. The above two mass balances were used to obtain a formula to calculate percentage sidestream (X) for different Treated SS Ca/Treated SS Ac pairs:

$$X = (\text{Required Ca in final blend} + \text{Required Ac in final blend} - \text{Raw Ca} - \text{Raw Ac}) / (\text{Treated SS Ca} + \text{Treated SS Ac} - \text{Raw Ca} - \text{Raw Ac})$$

When the sidestream percentage (X) for a specific CO₂ dosage has been established, the corresponding lime dosage may be determined by re-arranging the above calcium mass-balance equation:

Lime dosage (mg/L as $\text{Ca}(\text{OH})_2$) = (Required Ca in final blend - Raw Ca * (1 - X) - Treated SS Ca * X) * 74 / 100

The above information was used to determine required chemical dosages at various sidestream percentages:

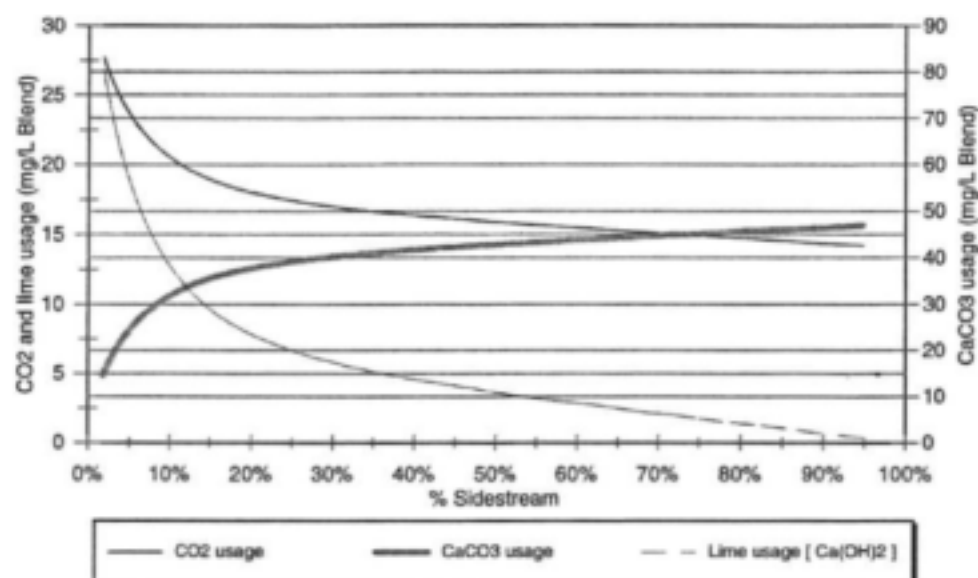


Figure 4.12: Required dosages at various sidestream percentages for the configuration with lime dosage after blending, for final total alkalinity of 50 mg/L

Conventional lime/CO₂ addition method

The following "conventional" case was considered for a cost comparison between the method described above and the conventional lime/CO₂ method. An amount of 33.3 mg/L lime is added, (assuming available lime of 62% as CaO), followed by dosage of 31.9 mg/L CO₂. The lime dosage is enough to obtain final water with a total alkalinity of 50 mg/L (recommended by iron corrosion guidelines), and the CO₂ dosage is enough to bring the pH down to 9, and the CCPP to 4 mg/L. The final water obtained by this method has the following characteristics: pH = 9.05, total alkalinity = 50 mg/L, calcium = 20 mg/L as Ca, CCPP = 4 mg/L. The chemical costs for both methods are shown in Figure 4.13. This shows that if this option was chosen (no stripping with lime dosage after blending), use of a 20% sidestream would lead to a chemical cost saving of 2.63 c/kL. On a 100 ML/day treatment plant this would translate to a saving of R78 900 / month, and R959 950 / year.

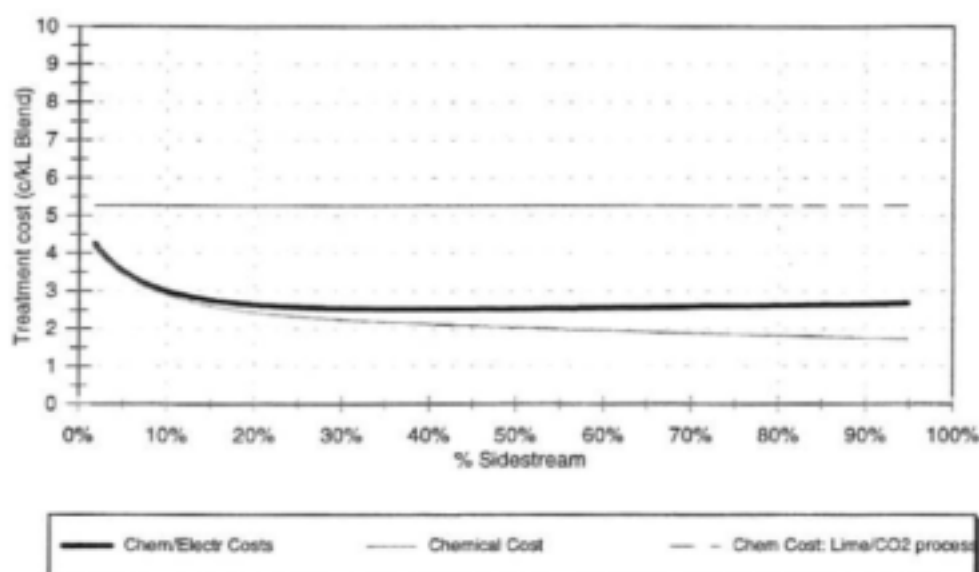


Figure 4.13: Chemical and running costs for simplified sidestream configuration with lime dosage after blending, for a final total alkalinity of 50 mg/L

Example Two: Final total alkalinity of 30 mg/L

The case where a final total alkalinity of 30 mg/L is required was also considered. Here, the quality of the final water would be as shown in the following table.

Table 4.6: Quality of final water

Determinant	Value
pH	8.98
Total alkalinity (mg/L as CaCO ₃)	30.0
Total acidity (mg/L as CaCO ₃)	27.0
Calcium (mg/L as Ca)	12.0
Electrical conductivity (mS/m)	6.0
Temperature (°C)	20.0
Calcium carbonate dissolution potential (mg/L as CaCO ₃)	0.0

For comparison purposes, the amount of lime/CO₂ that would need to be dosed if the conventional stabilisation method was used were determined using STASOFT 4, namely 18.5 mg/L lime as Ca(OH)₂ (assuming 62% available lime as CaO), and 15.3 mg/L CO₂. The final water has the following characteristics: pH = 8.98, total alkalinity = 30 mg/L, calcium = 12 mg/L as Ca, and CCPP = 0 mg/L.

Figures 4.14 and 4.15 shows the dosages and estimated costs of lime addition in the case where the final total alkalinity is 30 mg/L. This shows that if this option was

chosen (no stripping with lime dosage after blending), a potential chemical cost saving of 1.25 c/kL is available at a 10% sidestream. On a 100 ML/day treatment plant this translates to a saving of R37 500 / month, and R456 250 / year.

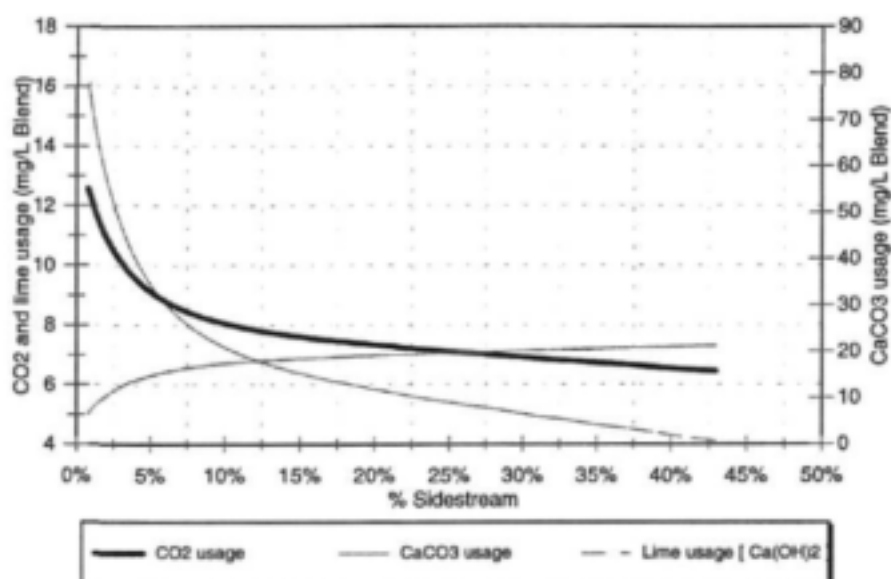


Figure 4.14: Required dosages at various sidestream percentages for the configuration with lime dosage after blending, for final total alkalinity of 30 mg/L

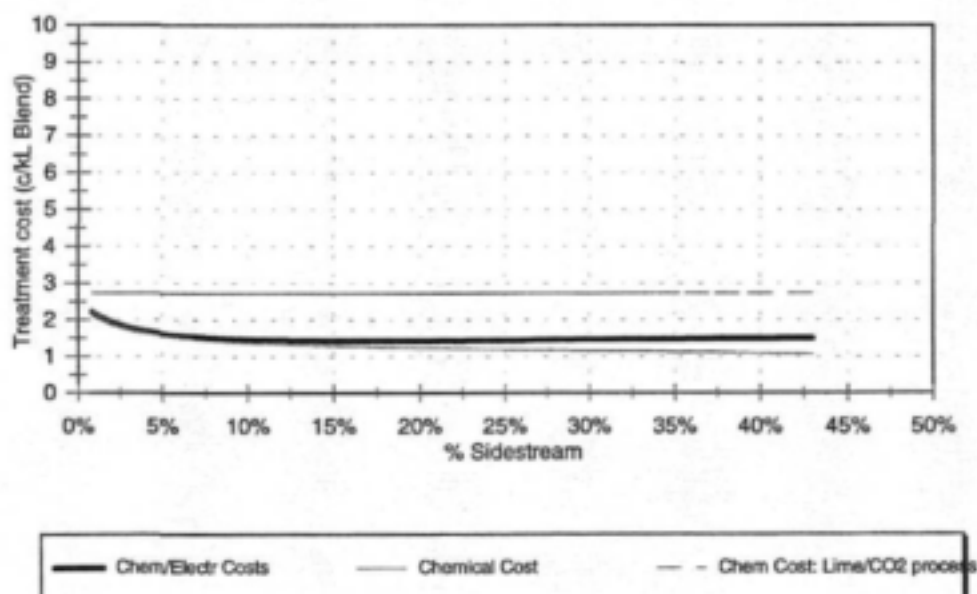


Figure 4.15: Chemical and electricity costs for lime addition at various sidestream percentages, for a final total alkalinity of 30 mg/L

Dosing lime before blending

Lime may be dosed to the sidestream (before blending) instead of to the mainstream (after blending). This will have no effect on the lime dosage required to obtain a final blend with total alkalinity = 50 mg/L and CaCO_3 precipitation potential of zero. The same amount of lime per litre of the blended stream will be required in both cases, therefore, the choice of where to dose the lime will not depend on chemical cost factors. Figures 4.12 to 4.15 therefore also apply to the costs of the simplified SSP where lime is dosed before blending as apposed to after.

4.4.4 Partial CO_2 Stripping After Blending + Sodium Hydroxide Addition For A Final CCPP Of Zero, Regardless Of Final Total Alkalinity Required

In this configuration stripping to waste occurs after blending the sidestream and mainstream. However, in this case incomplete stripping occurs, i.e. complete two-phase equilibrium between the blended stream and the atmosphere cannot be attained. Sodium hydroxide is dosed to the partially stripped water to ensure a precipitation potential of zero in the final water.

In determining the required chemical dosages and costs at various sidestream percentages using this method of stabilisation, the same approach was followed as previously (where the final total alkalinity was chosen as to obtain a final CCPP of zero for the specific initial "raw" water). The CO_2 dosages and sidestream percentages, as well as final total alkalinity (62 mg/L in this case), were applied for this case as well. However, in this case, the stripping of the blend does not remove the theoretical maximum possible amount of CO_2 , but only a fraction (e.g. 80%, or 50%) of the CO_2 . Therefore, after partial stripping the calcium carbonate precipitation potential is still slightly negative. To obtain a CCPP of zero, an alkali - sodium hydroxide in this case - is dosed. This results in a final water that will be slightly supersaturated with respect to calcium carbonate if it is equilibrated with the atmosphere.

Similar to the strip to waste case earlier described (100% CO_2 removal), the amount of total alkalinity added to the sidestream is dictated by the total alkalinity required in final water to obtain a CCPP of zero in a water that is in equilibrium with the atmosphere. This alkalinity is dependent on the calcium concentration, (calcium and alkalinity can only increase in equal amounts), but independent of sidestream ratio. A total alkalinity of 61.8 mg/L is required in the final water. This ensures a completely balanced final water, with CCPP = 0, and which will not become under- or supersaturated when left in contact with the atmosphere. The incomplete removal of CO_2 during the stripping stage is compensated for by dosing of an alkali. Because the bulk of CO_2 has been removed, and enough alkali has been dosed to obtain a near-balanced water, only small quantities of alkali should be necessary, and the final water will only be slightly supersaturated when left in contact with the atmosphere. STASOFT 4 was used to simulate this configuration. Two worked examples are presented. In the first example, removal of 80% of possible maximum amount of CO_2

was chosen. In the second example, removal of 50% of possible maximum amount of CO_2 was chosen.

Example One: Removing 80% of possible maximum amount of CO_2

Similar CO_2 doses are used as in 4.4.1 at the various sidestream percentages. The amount of NaOH needed after the partial CO_2 stripping depends on the percentage of the maximum possible CO_2 that was stripped away. It is assumed here that approximately 80% of the possible maximum CO_2 is removed. For this specific example this corresponds to attaining equilibrium at a partial CO_2 pressure of 0.00265 atmospheres, which yields a water with pH = 7.45, total alkalinity = 61.4, dissolved calcium = 24.6 mg/L as Ca, total acidity = 71.7 and precipitation potential = -9.3 mg/L as CaCO_3 . If this water eventually reaches equilibrium after extended contact with the atmosphere, it will resemble the final water of 4.4.1, namely pH = 8.32 and calcium carbonate dissolution potential = 0 mg/L. However, if the partially equilibrated water (pH = 7.45) needs to be changed to a water with precipitation potential = 0, only a relatively small amount of NaOH can be dosed. For our example, where 80% of the possible maximum amount of CO_2 has been stripped away, dosage of 4.0 mg/L NaOH would result in a water with pH = 8.29, total alkalinity = 66.5 mg/L, total acidity = 66.7 mg/L as CaCO_3 and CaCO_3 precipitation potential = 0. If this water eventually reaches equilibrium with the atmosphere it will only be slightly super-saturated with respect to CaCO_3 , namely with a precipitation potential of 0.4 mg/L, pH = 8.35 and total acidity = 66.3 mg/L. The efficiency of CO_2 stripping for the water in our example determines the required NaOH dosage for a precipitation potential of zero. The required NaOH dosage is plotted against the percentage stripping efficiency (i.e. CO_2 stripped as a percentage of possible maximum at atmospheric partial CO_2 pressure) in Figure 4.16.

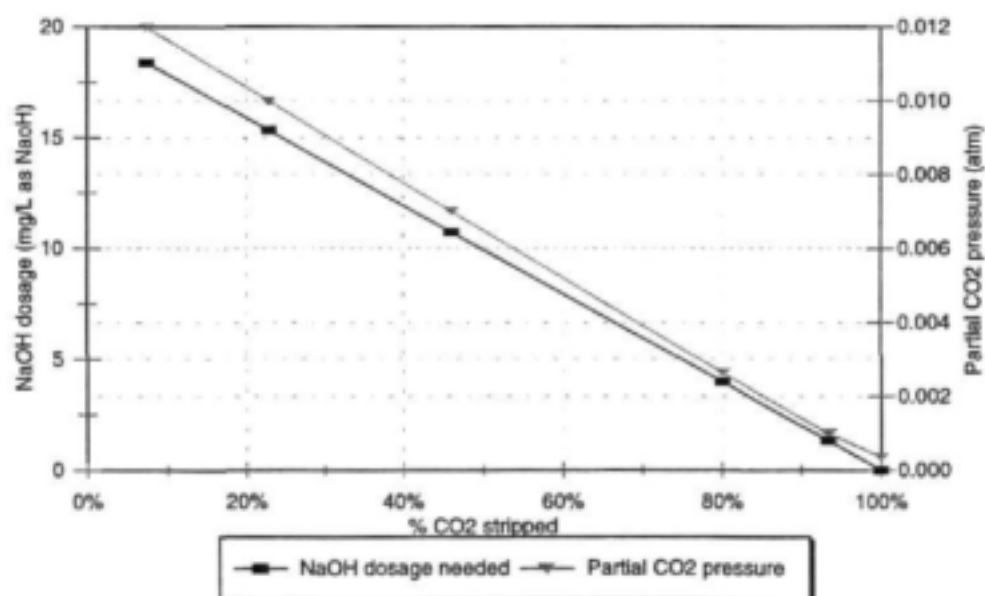


Figure 4.16: Partial strip to waste after blending - NaOH dosage needed at various stripping efficiencies to obtain final dissolution potential of zero

The required CO_2 dosages at the different sidestream percentages are identical to those in **Figure 4.6** (section 4.4.1). CaCO_3 dosage per litre blended stream is also identical to that in section 4.4.1. NaOH dosage (for our example) remains constant with sidestream percentage at 4.0 mg/L. The costs of chemicals and electricity is estimated in **Figure 4.17**. Electricity cost per kL is estimated as slightly lower than before (0.7 c/kL vs. 1 c/kL before), due to an assumed saving resulting from only partial stripping, instead of full stripping.

Conventional lime/ CO_2 addition

For comparison to this case, the following lime and CO_2 dosages were considered, using the conventional lime/ CO_2 dosage method: 33.3 mg/L lime is added, (assuming available lime of 62% as CaO), followed by dosage of 31.9 mg/L CO_2 . The lime dosage is enough to obtain a final water with a total alkalinity of 50 mg/L (recommended by iron corrosion guidelines), and the CO_2 dosage is enough to bring the pH down to 9, and the CCPP to 4 mg/L. The final water obtained by this method has the following characteristics: pH = 9.05, total alkalinity = 50 mg/L, calcium = 20 mg/L as Ca, CCPP = 4 mg/L.

The chemical costs calculated for the two methods of stabilisation were used to chemical running costs - see **Figure 4.17** below:

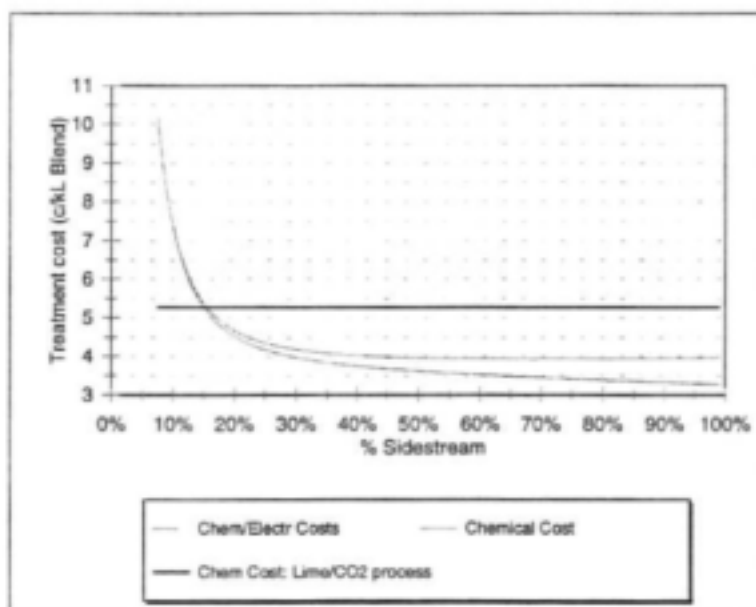


Figure 4.17: Running costs (Partial strip to waste after blending + NaOH dosage) 80% of possible maximum CO_2 is removed, to obtain a final total alkalinity of 66.5 mg/L

Example Two: Removing 50% of possible maximum amount of CO₂

The partial stripping of the blended stream may not be as efficient as assumed in the paragraph above. If only 50% of the possible maximum amount of CO₂ can be removed a higher dosage of NaOH will be required, namely 9.9 mg/L. For this specific example this corresponds to attaining equilibrium at a partial CO₂ pressure of 0.0065 atmospheres, which yields a water with pH = 7.06, total alkalinity = 61.4 mg/L, dissolved calcium = 24.6 mg/L as Ca, total acidity = 87.1 mg/L and precipitation potential = -22.9 mg/L as CaCO₃. If this water eventually reaches equilibrium after extended contact with the atmosphere, it will resemble the final water of section 4.4.1, namely pH = 8.32 and calcium carbonate dissolution potential = 0 mg/L. If the partially equilibrated water (pH = 7.06) needs to be changed to a water with precipitation potential = 0 by dosing NaOH, 9.9 mg/L NaOH will be required, resulting in a water with pH 8.24, total alkalinity = 73.9 mg/L, total acidity = 74.6 mg/L as CaCO₃ and CaCO₃ precipitation potential = 0 mg/L. If this water eventually reaches equilibrium with the atmosphere it will only be slightly supersaturated with respect to CaCO₃, namely with a precipitation potential of 1.1 mg/L, pH = 8.40 and total acidity = 73.4 mg/L. **Figure 4.18** shows the estimated running costs for the case where 50% stripping occurs.

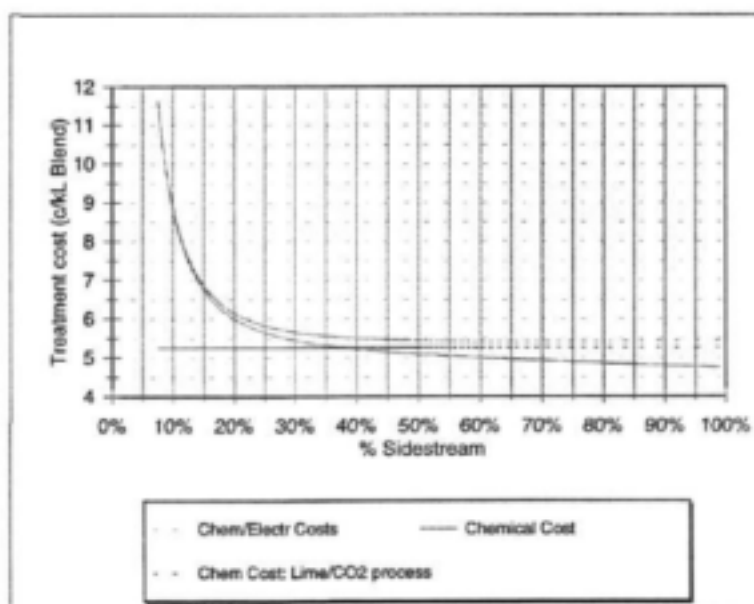


Figure 4.18: Running costs (Partial strip to waste after blending + NaOH dosage) 50% of the possible maximum CO₂ is removed, to obtain a final total alkalinity of 74 mg/L

It's clear that at the relatively high price of NaOH (estimated at R2500/ton) this is not a viable alternative to the conventional process.

4.4.5 Partial CO₂ Stripping After Blending + Sodium Carbonate Or Lime Addition For A Final CCPP Of Zero, Regardless Of Final Total Alkalinity Required

In this configuration stripping to waste occurs after blending the sidestream and mainstream. Incomplete stripping occurs, i.e. complete two-phase equilibrium between the blended stream and the atmosphere cannot be attained. Here, we consider stripping 50% of the theoretical maximum amount of CO₂. An alkali is dosed to the partially stripped water to ensure a precipitation potential of zero in the final water. Here, sodium carbonate and lime are considered respectively, as possible alkali's.

In determining the required chemical dosages and costs at various sidestream percentages using this method of stabilisation, the same approach was followed as in section 4.4.1 (where the final total alkalinity was chosen as to obtain a final CCPP of zero for the specific initial "raw" water). The CO₂ dosages and sidestream percentages, as well as final total alkalinity (62 mg/L in this case), were applied here as well. However, the stripping of the blend does not remove the theoretical possible amount of CO₂, as in section 4.4.1, but only 50%. Therefore, after partial stripping the calcium carbonate precipitation potential is still slightly negative. To obtain a CCPP of zero, an alkali is dosed. This results in a final water that will be slightly supersaturated with respect to calcium carbonate if it is equilibrated with the atmosphere.

It was clear from the previous graphs that if only 50% of the maximum amount of CO₂ is stripped away after blending, sodium hydroxide as a final dosing chemical is not feasible. Hence, consideration of alternative dosing chemicals, namely sodium carbonate and lime.

Sodium carbonate

If 25.6 mg/L sodium carbonate is dosed to the partially stripped stream, a final water with pH = 8.17, total alkalinity = 85.6 mg/L, total acidity = 87.1 mg/L and precipitation potential of 0 mg/L will be obtained. If this water eventually reaches equilibrium with the atmosphere a water with pH = 8.46, precipitation potential = 2.2 mg/L and total acidity = 84.6 mg/L will result.

Figure 4.19 shows the estimated running costs for this case.

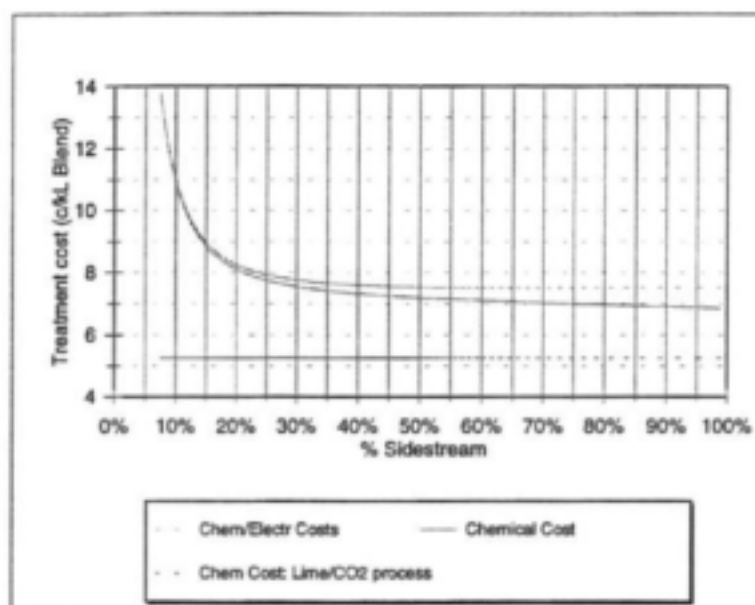


Figure 4.19: Running costs (partial strip to waste after blending + sodium carbonate dosage) 50% of possible maximum CO_2 was removed, to obtain a final total alkalinity of 86 mg/L

Lime

If 9 mg/L lime ($\text{Ca}(\text{OH})_2$) is dosed to the partially stripped stream, a final water with pH = 8.16, total alkalinity = 73.6 mg/L, total acidity = 74.9 mg/L and precipitation potential of 0 mg/L will be obtained. If this water eventually reaches equilibrium with the atmosphere a water with pH = 8.40, precipitation potential = 1.6 mg/L and total acidity = 73.1 mg/L will result. **Figure 4.20** shows the estimated running costs.

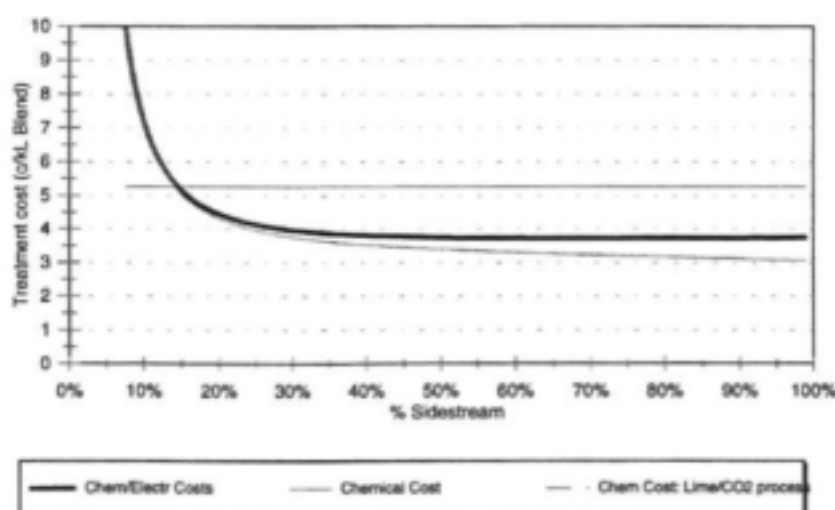


Figure 4.20: Running costs (partial strip to waste after blending + lime dosage) 50% of possible maximum amount of CO_2 was removed, to obtain a final total alkalinity of 74 mg/L.

If the last option was chosen (partial stripping of the blended stream, followed by lime dosage), use of a 30% sidestream would lead to a chemical cost saving of 1.51 c/kL. For a 100 ML/day treatment plant this would amount to a saving of R45 300 / month, and R551 150 / year.

4.4.6 Partial CO₂ Stripping After Blending (80% CO₂ Removal) + Lime Dosing For A Final Total Alkalinity Of 30 Mg/L And CCDP Of Zero

The guideline requirement of a final total alkalinity of at least 50 mg/L may be regarded as too stringent, requiring too high dosages of alkali and CO₂. The question may be asked how the simplified SSP would compare in terms of chemical dosage requirements if one aims for a lower total alkalinity in the final water, namely 30 mg/L. The method to determine the dosage requirements for this case differs slightly from the one used in sections 4.4.4 and 4.4.5, because the controlling parameter is a final total alkalinity of 30 mg/L and CCPP of zero, whereas in the previous case the total alkalinity was not specified, but the final water was slightly supersaturated when brought to equilibrium with the atmosphere. A water with total alkalinity and calcium of ± 30 mg/L will be slightly undersaturated with respect to calcium carbonate when in equilibrium with the atmosphere.

In this configuration of the simplified SSP, the raw water undergoes the following treatment steps:

- Separation into a sidestream and a mainstream.
- CO₂ addition.
- Limestone contact (equilibrium with calcium carbonate).
- Blending of the sidestream and mainstream
- Partial stripping to waste of the blended stream (80% removal of the maximum removable CO₂ takes place in this example)
- Addition of lime to the blended stream, to obtain a final water with CCPP of zero.

Assumption - 80% CO₂ removal

It is assumed in this case that 80% of the theoretical maximum amount of removable CO₂ will be removed from the blended stream.

Method of determination

These steps were followed to estimate the required dosages of CO₂ and lime at various percentage sidestreams, to obtain a final total alkalinity of not less than 30 mg/L, and a CCPP of zero:

- Set up the processes in *STASOFT 4*:

On page one the following treatment steps are: Initial water, CO₂, EqmCa.

On page two: Initial water, Blend%, Eqm Air, Lime addition, Eqm Air.

- If total acidity is not listed under the default PARAMETERS, add it to page two.

- On page one, enter the initial water quality parameter values, and a CO₂ dosage rate (choose a rate).
- On page two, vary the % blend, to obtain a total alkalinity of 30 mg/L.
- Ensure that the partial pressure in the equilibrium treatment step is the default, namely 0.00035 atm.
- Calculate the difference in total acidity between the post-blend stream and post-equilibration stream.
- Work out what the total acidity would be after 80% of the CO₂ has been removed from the post-blend stream - it is the total acidity of the post-blend stream minus 80% of the difference calculated in the previous step.
- Adjust the CO₂ partial pressure until the total acidity calculated above is obtained.
- Adjust the lime dosage, until a CCPP of zero is obtained.
- Note the calcium, total alkalinity and pH after lime addition, and after the last equilibration with atmospheric air.
- Repeat the above steps for CO₂ dosages ranging between 5 mg/L to 500 mg/L.

Final water characteristics

The final water (after lime addition) for a 10% sidestream and 150 mg/L CO₂ will have the following characteristics (approximately the same for any sidestream percentage):

pH = 8.9, total alkalinity = 33.8 mg/L, calcium = 13.5 mg/L as Ca, CCPP = 0 mg/L.

Lime addition is nominal, ranging between 1.38 mg/L as Ca(OH)₂ for a 77.4% sidestream to 4.6 mg/L for a 5.28% sidestream.

Equilibration with air of final water

As stated earlier, a water with total alkalinity and calcium of ± 30 mg/L will be slightly undersaturated when equilibrated with the atmosphere. When equilibrated, the final water will have a pH of ± 8.1 , and CCPP of -3 mg/L.

Conventional lime/CO₂ method

If the conventional lime/CO₂ addition is used to obtain more or less a similar water (total alkalinity of 30 mg/L and CCPP of 0 mg/L), dosages required are: lime: 18.5 mg/L as Ca(OH)₂, and CO₂: 15.3 mg/L. The final water will have the following characteristics: pH = 9.00, CCPP = 0 mg/L, total alkalinity = 30 mg/L. If the final water reaches equilibrium with the atmosphere, its pH will change to 8.01, and its CCPP will reduce to -3.5 mg/L.

Figure 4.21 shows the required CaCO₃, CO₂, and lime dosages required for the simplified SSP (partial aeration, then lime addition). **Figure 4.22** shows the chemical and electricity costs for the various possible sidestream percentages, comparing it to the cost of the equivalent conventional lime/CO₂ dosage process.

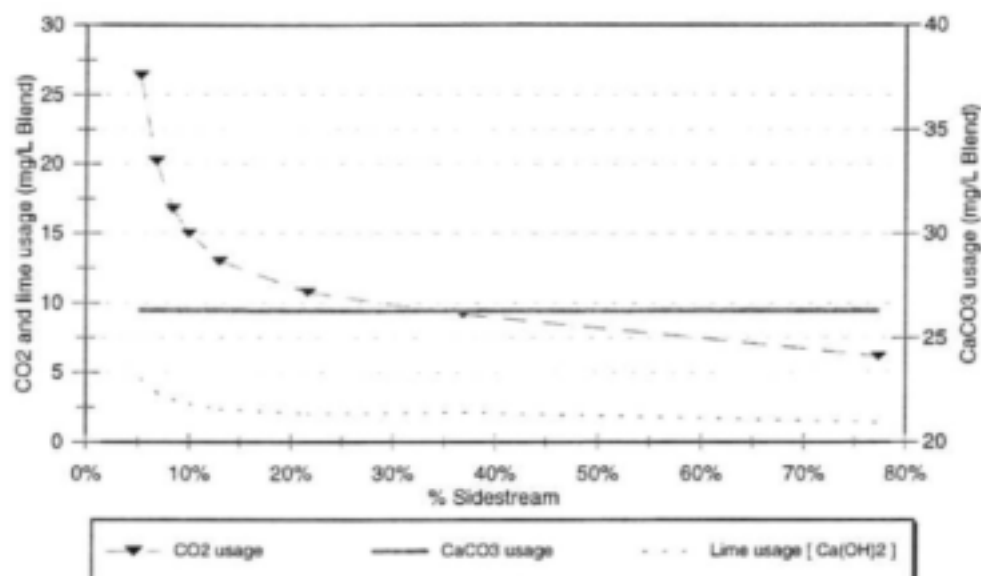


Figure 4.21: Required dosages - blending sidestream to obtain total alkalinity of 30 mg/L, removing 80% of theoretical maximum CO₂ after blend, adding lime to obtain CCPP = 0.

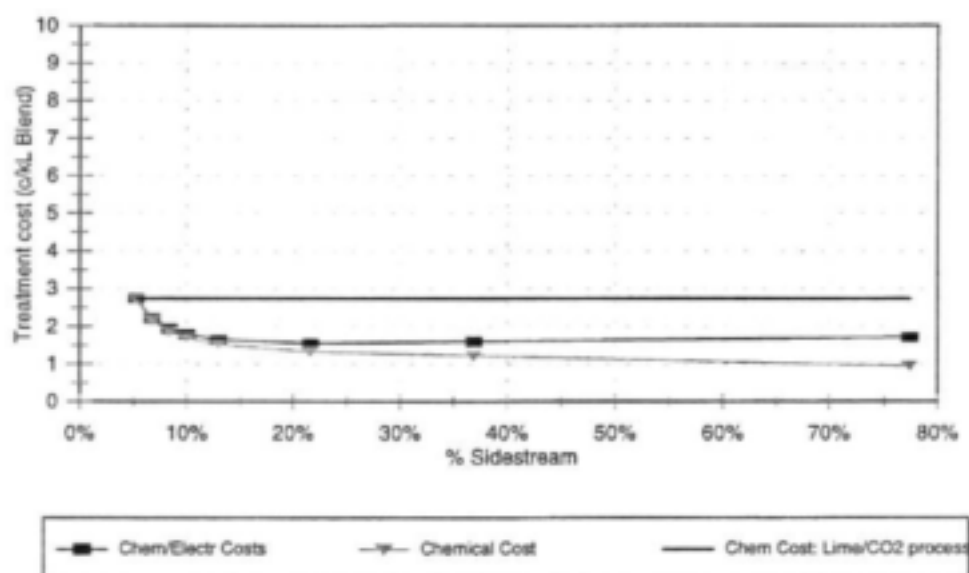


Figure 4.22: Costs of stabilisation - blending in sidestream to obtain total alkalinity of 30 mg/L, 80% removal of CO₂ and addition of lime to obtain CCPP = 0 mg/L.

If this option was chosen (80% effective partial stripping of the blended stream, followed by lime dosage), use of a 22% sidestream would lead to a chemical cost saving of 1.39 c/kL. On a 100 ML/day plant this would amount to a saving of R41 700 / month, and R507 350 / year.

4.5 DISCUSSION AND CONCLUSIONS

In light of the possible practical full-scale limitations of the SSP process with regards to CO₂ stripping and recovery, the project team undertook a theoretical desktop analysis of a simplified SSP process. This entailed an investigation of the influence of:

- The presence and placement of stripping and alkali addition steps.
- The CO₂ dosage to the sidestream.
- The percentage sidestream.

The viability of the so-called "simplified SSP" was considered by the development by the project team of a model. The model included *JAVA* programming and the use of *STASOFT 4* and *Watchem*. (At the time, *STASOFT 4* development was in its final stages, and a preliminary test-version of the software was kindly made available by Mr Ian Morrison for the purpose of modelling the simplified SSP. The *Watchem* program is a command line and input file driven program supplied together with *STASOFT 4*). Since there is no gas recycling stream in the simplified SSP, *STASOFT 4* can model the whole process.

The model modelled the following equilibrium steps in the simplified SSP:

- CO₂ dosage
- Saturation with CaCO₃
- An optional step: stripping of the sidestream to waste
- Blending of the sidestream with the remainder of the feed stream
- An optional step: stripping of the blended stream to waste
- Addition of an alkali, such as lime, NaCO₃ or NaOH

Required chemical dosages given as output from these runs were used for running cost calculations, and running costs at different percentage sidestreams were represented in graphical format.

These desktop assessments showed that under specific circumstance a simplified SSP might well be financially more attractive than using conventional lime and carbon dioxide dosing. Findings included inter alia:

- Stripping CO₂ to the atmosphere before blending the sidestream and mainstream was not financially attractive.

- Stripping CO₂ to the atmosphere after blending the sidestream and mainstream, was financially attractive. The financial attractiveness varied with the both the CO₂ stripping efficiency and the alkali's used for final pH adjustment. Use of sodium alkali's was found to provide little or no saving relative to the use of lime, as a result of the high cost of these chemicals.
- Where partial stripping of the mainstream was accompanied by lime dosing, an attractive chemical cost saving incurred.
- Importantly, where no stripping of CO₂ was practised and lime dosing was employed, significant chemical savings relative to conventional lime and CO₂ mediated stabilisation were observed. For example,
 - Where a final total alkalinity of 50 mg/L and a CCPP of zero was required, use of a 20% sidestream would lead to a chemical cost saving of 2.63 c/kL. On a 100 ML/day treatment plant this would translate to a saving of R78 900 / month, and R959 950 / year.
 - Where a final total alkalinity of 30 mg/L and a CCPP of zero was required, a potential chemical cost saving of 1.25 c/kL is available at a 10% sidestream. On a 100 ML/day treatment plant this translates to a saving of R37 500 / month, and R456 250 / year.
- Considering the practical implications of CO₂ stripping from a main stream in a large water treatment works, it is of particular interest that the study showed that significant savings are potentially possible where no CO₂ stripping is required.

Considering the above, it is clear that under certain circumstances, the simplified SSP process without CO₂ recovery may be an attractive option. Further investigation including both modelling and pilot plant studies should, however, be conducted to confirm these findings.

From this desktop model based investigation of the simplified SSP, the project team gained a better understanding of the modelling requirements for the SSP process. Bearing this in mind, and the fact that the commercially process modelling package was not suitable for modelling the SSP, the project team undertook the development of a JAVA based process model to describe the SSP process. The aim of the development of this process model was to accurately predict the operation of the SSP process whilst overcoming the problems experienced with the commercially available packages. The development of the JAVA based model, termed "SSP-MOD" is described in the following chapter.

4.6 REFERENCES – CHAPTER 4

- (1) MORRISON IR and LOEWENTHAL RE (2000) Manual for STASOFT 4, Report to the Water Research Commission, Pretoria.

CHAPTER 5

DEVELOPMENT OF “*SPP-MOD*” PROGRAM FOR PREDICTING THE BEHAVIOUR OF THE SIDESTREAM STABILISATION PROCESS

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5.1 INTRODUCTION

In trying to address the problems with *PRO/II*, the project team developed modelling routines for crosscheck purposes. As a result of the difficulties/complexity of addressing the *PRO/II* limitations, these routines became progressively more complex and complete. Eventually, as a response to growing concern that *PRO/II* would prove to be fatally flawed for use in modelling SSP, and despite considerable effort and time having been invested into *PRO/II*, the project team felt it prudent to develop a *JAVA* program that models the SSP process. The model developed was termed "*SSP-MOD*".

5.2 HISTORY OF DEVELOPMENT OF *SSP-MOD* MODEL

The following section describes the development of the *SSP-MOD* modules:

- A spreadsheet was developed to model the dissolution of calcium carbonate in a limestone column. This required the following routines:
 - Calculation of total acidity from pH, calcium, total alkalinity and electrical conductivity
 - Calculation of $[\text{CO}_3^{2-}]$
 - Calculation of pH after calcium and total alkalinity have been increased due to CaCO_3 dissolution (iterative calculation)
- These formulas were used as part of a *JAVA* program that formed part of a limestone expert system, which calculated the CCDP of a water, before and after equilibration with atmospheric air. New modules were developed to determine:
 - CCDP
 - Determining pH of a water after equilibration with CO_2 at 0.00035 atm
- The above routines formed the basis of the aquatic chemistry modules that were developed for the *SSP-MOD* program.

The next step was to consider the SSP with a gas-recovery stream. *STASOFT 4/Watchem* could not be used for these simulations, since it does not provide a mechanism to take the feedback gas stream into account. The only way in which this process could be simulated was through the use of existing chemical engineering process modelling packages, such as *PRO/II*, or through programming. It was shown in CHAPTER 3 that *PRO/II* does not contain adequate routines to model the CO_2 stripping step. Since this step is crucial in the modelling of the SSP, a computer program had to be written to model the whole process. *JAVA* was used as a programming language, due to its relatively user friendly object oriented style. Modules were developed to model the following:

- Acidity increase of a water through CO_2 addition.
- CaCO_3 saturation of a water.
- CO_2 loss from a water as a result of contact with an atmosphere with a specified CO_2 composition.
- Blending of two different water streams.
- Dissolution of air into water.

- Equilibrium carbonate chemistry (as applied in STASOFT 4).

The following simplifications were applied to keep the complexity manageable:

- Ideal gas law.
- The solution/dissolution of the inert gases (N_2/O_2) were modelled using a single Henry's law constant, namely that for air.
- Assuming dissolution of CO_2 is at equilibrium level (i.e. kinetic limitations not taken into account).
- Assuming stripping of CO_2 is at equilibrium level (i.e. kinetic limitations not taken into account) – stripping was initially assumed to be a single-phase equilibrium flash. This was later refined to a multi-stage counter-flow stripping model.

Comments on validity of simplifications:

- The ideal gas law is a reasonable assumption as total pressures are not exceeding 300 kPa in the SSP.
- The second assumption is reasonable, because air consists mainly of nitrogen and the composition of the inert gas fraction should reflect this in both the dissolution and stripping vessels in the SSP as well.
- Visual observation of the dissolution column showed that CO_2 bubbles disappear quickly, indicating fast reaction kinetics.
- The last simplification is likely to affect the ability of the model to accurately simulate the "real-life" process.

5.4 SUB-ROUTINES USED TO MODEL THE SIDESTREAM

First, sub-routines were developed to simulate a number of aquatic chemistry processes.

5.4.1 Aquatic Chemistry Sub-routines

- **CO_2 dosage to a water:**
The pH, total alkalinity, dissolved calcium, electrical conductivity (EC) and temperature of the initial water is specified, together with the CO_2 dosage. The procedure uses chemical equilibrium relationships to calculate the quality of the water after CO_2 addition.
- **Saturation of a water with $CaCO_3$:**
The initial water quality is specified. The procedure determines the quality of the water after saturation with $CaCO_3$.
- **Lime addition to a water:**
The initial water quality is specified, together with a lime dosage amount. The procedure determines the quality of the water after lime addition.
- **Bringing a water into two-phase equilibrium with an atmosphere with a specified CO_2 partial pressure:**
The initial water quality is specified, together with the partial pressure of CO_2 in the equilibrium gas-stream. The procedure calculates the quality of the equilibrated water stream and the amount of CO_2 expelled from (or taken up by) the water stream.
- **Blending two waters:**

Quality of the two waters is specified, together with the ratio in which to blend the waters. The procedure calculates the quality of the blended water.

5.4.2 Sub-routine to Simulate a Two-phase Equilibrium Flash Vessel

Next, a sub-routine was developed to determine the composition of gas and liquid product streams in equilibrium with each other, leaving a flash vessel, given the flow rate and composition of a feed liquid and gas stream. This is necessary to simulate the dissolution and the air stripping-for- CO_2 -recovery stages.

The two-phase equilibrium procedure described above needs as input the partial CO_2 pressure in the equilibrium gas stream, as in the similar *STASOFT 4* treatment step. The partial CO_2 pressure, however, depends on the composition of the equilibrated gas stream, which is part of the output that is required from the sub-routine. An algorithm was therefore developed to solve this in an iterative fashion. The algorithm (described below) is based on the following:

- A molar mass-balance around the flash vessel for air.
- A molar mass-balance around the flash vessel for CO_2 .
- Henry's Law for the dissolution of air in water.
- Dalton's Law for determination of the partial pressures of air and CO_2 .
- The two-phase equilibrium procedure above, determining the amount of CO_2 dissolved/expelled from a specified water stream at a specified partial CO_2 pressure.

The air stripper in the sidestream diagram (**Figure 5.1**) has been used as an example of a flash vessel, and has been used for the air and CO_2 mass balances (see "mass balance over stripper" **Figure 5.1**). The air and CO_2 flows (in moles per litre sidestream water) are named by alphabetic letters in the figure.

Basis for mass-balances:

1s, where the flowrate of the sidestream (after separation from the mainstream) is 1 L/s.

1 L of water = 1000g.

W is defined as the number of moles of water in 1 L water, where:

$$W = 1000/18 = 55,556 \text{ moles/s}$$

$$\begin{array}{lcl} \text{Air In} & = & \text{Air Out} \\ z + e & = & a + g \end{array} \quad -1$$

$$\text{CO}_2 \text{ expelled by water stream} = b - f \quad -2$$

Dalton's Law for air:

$$\begin{array}{lcl} y \pi & = & p_{\text{air}} \\ \text{where:} & & \end{array} \quad -3$$

- y : molar fraction of air in the gas stream,
 π : total pressure over the air stripper, and
 p_{air} : partial pressure of air in the gas stream, in atmospheres

Henry's law for dissolution of air in water:

$$p_{air} = X_{air} H_{air} \quad - 4$$

where:

- X_{air} : Molar fraction dissolved air in water
 H_{air} : Henry's Law Constant for air, taken as $7,2 \times 10^4$ atm/mole fraction (Perry, 6th edition) @ 25°C. The constant given by Perry was calculated from the absorption coefficients of O₂ and N₂, taking into consideration the correction for constant argon content. It is assumed that the initial water's temperature will be approximately 20°C. However, the temperature of the water in the dissolution and air stripping vessels would probably be a few degrees higher than that, due to the heat generated by the sidestream pumps, therefore the constant given for 25°C is used. (At 20°C, $H = 6,64 \times 10^4$ atm/mole fraction).

The molar amount of air dissolved in the water stream is very small when compared to the molar amount of water ($1,4 \times 10^{-5}$ moles air vs. 55,556 moles water at a total air pressure of 1 atm), therefore the total molar amount of dissolved air/water is

assumed to be equal to the molar amount of water, giving this equation for X_{air} :

$$X_{air} = \frac{g}{W} \quad - 5$$

where:

g : Molar amount of dissolved air in the water stream leaving the air stripper, and,

W : Moles water leaving the air stripper (55,556 moles/s)

Substituting 5 in 4, and equalizing 3 and 4:

$$\frac{a}{a+b} \pi = \frac{g}{W} H_{air} \quad - 6$$

From 1:

$$g = z + e - a$$

Substituting 1 in 6:

$$\frac{a}{a+b} \pi = \frac{z+e-a}{W} H_{air} \quad - 7$$

7 can be rewritten to form a quadratic equation, from which ' a ' (the molar amount of air in the gas stream leaving the stripper) can be determined. To avoid confusion, ' a ' will be indicated in bold from here on:

$$0 = -\mathbf{a}^2 + \left(z+e - \frac{\pi}{H_{air}} W - b\right) \mathbf{a} + (z+e) b \quad - 8$$

a may be determined using:

$$\mathbf{a} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad - 9$$

where:

$$a = -1$$

$$b = z + e - \frac{\pi}{H_{air}} W - b$$

$$c = (z+e) b$$

Since a in 9 is negative, the denominator of 9 is negative, therefore the numerator must be negative if a meaningful (positive) value is to be determined for a (the molar amount of air leaving the stripper in the gas stream). It follows then that the value of the square-root will either have to be subtracted from $-b$, or, if it is added to $-b$, the

following condition have to be met:

$$\sqrt{b^2 - 4ac} \leq b$$

If the above substitutions for a , b and c are carried out, it is clear that the above condition can never be met, therefore the only meaningful solution for a will be obtained if the square-root's value is subtracted from $-b$, thus giving:

$$a = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \quad -10$$

This equation is used in the algorithm for calculation of two-phase equilibrium flash streams, set out below.

5.4.3 Algorithm for Two-phase Equilibrium Flash Vessel

The algorithm requires the following as **input**:

- e: The molar amount air in the gas stream entering the flash vessel.
- f: The molar amount CO₂ in the gas stream entering the flash vessel.
- z: The molar amount dissolved air in the water stream entering the flash vessel, and the quality (pH, total alkalinity, EC and temperature) of the water entering the flash vessel.

The values of e and f can be calculated from the volume, temperature, pressure and specified molar fractions of air and CO₂ in the gas stream entering the vessel, assuming that the ideal gas law applies. The ideal gas law is a reasonable assumption, since the temperatures and pressures used during the operation of the sidestream process should be relatively close to normal temperature and pressure.

The algorithm gives the following as **output**:

- a: Molar amount of air in the gas stream that leaves the vessel.
- b: Molar amount of air in the gas stream that leaves the vessel.
- g: Molar amount of dissolved air in the water stream that leaves the vessel.
The pH of the water that leaves the vessel. (The total alkalinity remains unchanged, and temperature and EC are also assumed to remain constant, which is reasonable, since dissolution energy is negligible, and no large change in ionic content of the water is expected.)

An iterative procedure is used: the partial pressure of CO₂ in the gas stream leaving the stripper is guessed and checked during a number of iterations. The "guess-range" is progressively narrowed down during iteration.

Iterative routine:

- (i) p_0 , the partial pressure of CO₂ in the gas stream leaving the vessel is guessed:

$$p_{b,guess} = \frac{p_{b, upper limit} - p_{b, lower limit}}{2}$$

The initial upper and lower limits for p_b are π and 0, respectively.

- (ii) The molar amount of CO_2 expelled by the water stream at partial pressure $p_{b,guess}$ is calculated, using the two-phase aquatic chemistry equilibrium procedure. A negative answer indicates that CO_2 is taken up by the water, as apposed to being expelled.
- (iii) b (the molar amount CO_2 in the gas stream leaving the flash vessel) is calculated from equation 2.
- (iv) a (the molar amount air in the gas stream leaving the flash vessel) is calculated using equation 9 (subtracting the square-root from $-b$).
- (v) The partial pressure of CO_2 in the gas stream leaving the flash vessel is determined from Dalton's Law:

$$p_b = \frac{b}{a + b} \pi$$
- (vi) The value for p_b calculated in (v) is compared with $p_{b,guess}$, from step (i), and the upper and lower limits adjusted accordingly. If $p_{b,guess}$ is higher than p_b , $p_{b,guess}$ becomes the new upper limit for p_b . If it is lower than p_b , $p_{b,guess}$ becomes the new lower limit for p_b .
- (vii) The process from steps (i) to (vi) is repeated, using the new upper and lower limits for p_b . Iteration is continued until the difference between $p_{b,guess}$ and p_b is smaller than a pre-specified "error" (chosen as 1×10^{-9} atm).
- (viii) When the process terminates, the composition of the gas stream leaving the flash vessel is known (i.e., a and b are known). Similarly, the pH of the water stream from the vessel is known. The amount of air in the water stream leaving the vessel (g) is calculated using equation 6.

5.4.4 Sub-routine to Solve CO_2 -recycle Part of the SSP Process

A critical aspect of the modelling of the SSP process is to determine the composition of the gas and water streams between the CO_2 dissolution and air stripping stages. The output from the air stripping stage forms part of the input to the CO_2 dissolution stage, therefore the section demarcated as "mass balance over sidestream" has to be solved by an iterative algorithm. This algorithm (described below) is based on the following:

- A molar mass-balance for air around the demarcated section.
- Molar mass-balances (for air and CO_2) before and after separation and blending of gas streams (gas separation and blending points indicated by dots in Figure 5.1).
- The algorithm for a two-phase equilibrium flash vessel, to simulate the CO_2 dissolution and air stripping-for- CO_2 -recovery stages.

- The aquatic chemistry sub-routine for limestone saturation, described under *Sub-routines used to model the Sidestream*.

Basis for mass-balances:

As previously, the basis for the molar mass-balance is 1s, where the flowrate of the sidestream (after separation from the mainstream) is 1 L/s.

Molar mass balance for air over the demarcated section "mass balance over sidestream":

$$i + x = k + g$$

Solving for k, it becomes:

$$k = i + x - g \quad - 11$$

A simple molar-mass balance around the gas mixing point before the air stripper (indicated in Figure 5.1 by a dot) gives:

$$e = v + x \quad - 12$$

Air from the atmosphere may or may not be used to increase the gas flow rate through the air stripper. Such potential stream is indicated in Figure 5.1 by $x + y$. An air stream from the atmosphere (if used in the configuration chosen by the user) would contain a certain amount of CO_2 (the y part), which must be specified by the user.

The product gas-stream from the CO_2 dissolution vessel will contain some undissolved air originating from the feed water and possibly from the optional atmospheric air stream introduced to the air stripper. This undissolved air must be purged from the system. It is unavoidable, however, that undissolved CO_2 from the dissolution vessel will also be purged together with the undissolved air. The purge stream is indicated in Figure 5.1 as k (purged air) and l (purged CO_2).

Provision has been made for the reintroduction of the product gas from the dissolution vessel – which may contain some undissolved CO_2 – into the gas feed to the air stripping stage, since it was felt that such reintroduction could possibly lead to higher CO_2 utilization rates in some cases. The user is required to specify B , the fraction of the product gas stream from the dissolution stage to be reintroduced into the air stripper. If B is specified as 1, the entire gas stream from the dissolution stage is purged. If so required, the user may give B a very small value, but not zero, because there must be provision for excess air in the gas recycle loop to be purged from the system.

The molar amount of air from the dissolution vessel that gets reintroduced to the stripping stage – v – can be calculated by:

$$v = (1 - B) t \quad - 13$$

The air in dissolution vessel product gas (t) is separated into k and v :

$$t = k + v \quad - 14$$

Substituting t in 13 with the above gives:

$$v = (1 - B)(k + v) \quad - 15$$

Solving the above for v:

$$v = \frac{k(1 - B)}{B} \quad - 16$$

Substituting v above in 12:

$$e = \frac{k(1 - B)}{B} + x \quad - 17$$

From 1:

$$a = e - g + z$$

All the air in the product gas stream from the stripper (a) is reintroduced to the CO₂ dissolution stage, therefore the air in the dissolution feed gas stream (s) equals a:

$$s = a \quad - 18$$

Therefore:

$$s = e - g + z$$

Substituting e above with 17 gives:

$$s = \frac{k(1 - B)}{B} + x - g + z$$

Substituting k above, using 11:

$$s = \frac{(i + x - g)(1 - B)}{B} + x + z - g \quad - 19$$

The values for all parameters above must be specified by the user, except for two parameters, namely z, the moles of air in the product water leaving the CO₂ dissolution stage, and g, the moles of air in the product water leaving the air stripping stage. These parameters cannot be calculated directly; therefore, an iterative solution is required to determine s.

Upper and lower limits need to be established for s, to make it possible to search iteratively for values for s, g and z that will satisfy the equation. To establish upper and lower bounds for s, upper and lower bounds need to be established for g and z.

An upper limit for g can be established by considering equation 6:

$$\frac{a}{a+b} \pi_{AS} = \frac{g}{W} H_{air} \quad - 6$$

where:

π_{DV} : Total pressure over the CO₂ dissolution vessel.

At this stage the values of a and b are unknown, but it is possible to establish the upper limit of

$\frac{a}{a+b}$ as 1, and hence the upper limit for g as follows:

$$g_{max} = \frac{\pi_{AS} W}{H_{air}} \quad - 20$$

Similarly, the upper limit for z can be established:

$$z_{max} = \frac{\pi_{DV} W}{H_{air}} \quad - 21$$

The lower limit for $\frac{a}{a+b}$ is 0, therefore the lower limit for g can be established as:

$$g_{min} = 0$$

and similarly for z:

$$z_{min} = 0$$

To establish the upper limit for s, the lower limit for g, and upper limit for z - g must be substitutes in equation 19. The upper limit for z - g can be calculated as follows:

$$\begin{aligned} (z - g)_{max} &= z_{max} - g_{min} \\ &= z_{max} \end{aligned}$$

Substituting g with g_{min} and (z - g) with $(z - g)_{max}$ in 19, to obtain s_{max} :

$$s_{max} = \frac{(i + x)(1 - B)}{B} + x + z_{max} \quad - 22$$

Substituting g with g_{max} and (z - g) with $(z - g)_{min}$ in 19, to obtain s_{min} :

$$s_{min} = \frac{(i + x - g_{max})(1 - B)}{B} + x - g_{max} \quad - 23$$

Since s is the molar amount of air in the dissolution vessel's feed, its value cannot be less than 0. Therefore, if s_{min} is calculated by 23 to be less than 0, it should be changed to 0.

The algorithm formulated to solve the CO₂-recycle part of the SSP process (demarcated section "mass balance over sidestream" in Figure 5.1) needs an initial value for s to initiate its calculations. It also requires an initial molar amount of CO₂ entering the CO₂ dissolution vessel. The latter amount also depends on the output from the air stripping stage, therefore it also needs to be calculated by an iterative loop. The algorithm therefore employs two iteration loops – the inner loop is used to calculate the CO₂ fed into the dissolution vessel, and the outer loop to calculate the amount of air fed to the dissolution vessel. In the outer loop, the value of s is "guessed" and adjusted iteratively, and in the inner loop, the value of R is "guessed" and adjusted. R is defined as the fraction of the CO₂ in the feed gas to the dissolution vessel that originates from the air stripper product gas:

$$R = \frac{b}{b + j} \quad - 24$$

where:

- b : Amount of CO₂ in the recycled product gas from the stripper
- j : Pure CO₂ introduced to the process.

The value of b can be calculated if R is known:

$$b = \frac{jR}{1 - R} \quad - 25$$

5.4.5 Algorithm for CO₂ Recycle Section

The algorithm requires the following as **input**:

- The quality of the feed water, including the molar amount dissolved air in the water.
- The amount of CO₂ dosed to the sidestream.
- π_{ov} , the total pressure in the CO₂ dissolution vessel.
- π_{kv} , the total pressure in the air stripping vessel.
- The flow and composition (in terms of percentage air and CO₂) of an atmospheric air stream introduced to the stripper – the flow can be zero, and x and y are determined from this data.
- B , the fraction of the product gas from the dissolution stage that is purged.

The algorithm determines the following as **output**:

The flows and composition of all air and gas streams inside, into and out of the demarcated area "mass balance over sidestream" in Figure 5.1.

Iterative routine:

- (i) s , the molar amount of air entering the CO_2 dissolution stage via the feed gas stream is guessed:

$$s_{\text{guess}} = \frac{s_{\text{upper limit}} - s_{\text{lower limit}}}{2}$$

The initial upper and lower limits for s are given in 22 and 23, respectively.

- (ii) R , the fraction CO_2 in the dissolution vessel feed ($b + j$) that originates from the air stripper product gas is guessed:

$$R_{\text{guess}} = \frac{R_{\text{upper limit}} - R_{\text{lower limit}}}{2}$$

The initial upper and lower limits for R are taken as 0,9999 and 0 respectively.

- (iii) The value of b is calculated, using R_{guess} in equation 25.
- (iv) The composition of the output streams from the CO_2 dissolution vessel (i.e. values of t , u and z) and the quality of the product water stream from the dissolution vessel is determined, using the algorithm for a two-phase equilibrium vessel (described earlier).
- (v) The flow and composition of the purged gas and recycled dissolution vessel product gas are calculated:

$$\begin{aligned} k &= B t \\ l &= B u \\ v &= (1 - B) t \\ w &= (1 - B) u \end{aligned}$$

- (vi) The recycled dissolution vessel product gas and atmospheric air stream are blended to form the air stripper's feed gas. The flow and composition of the feed gas is calculated:

$$\begin{aligned} e &= v + x \\ f &= w + y \end{aligned}$$

- (vii) The composition of the water after limestone contact is determined, using the CaCO_3 saturation sub-routine (see *Aquatic Chemistry Sub-routines*).
- (viii) The flows and composition of the water and gas streams leaving the air stripping vessel are determined, using the two-phase equilibrium flash procedure described earlier (i.e. the values of a , b and g are determined).
- (ix) The values of s and R are now determined from equations 18 and 24.
- (x) The value for R determined in (ix) is compared with R_{guess} , from step (ii), and the upper and lower limits for R adjusted accordingly. If R_{guess} is higher than R , R_{guess}

becomes the new upper limit; if it is lower than R , R_{guess} becomes the new lower limit.

- (xi) The process from steps (ii) to (x) is repeated, using the new upper and lower limits for R . Iteration of this "inner loop" is continued until the difference between R_{guess} and R is smaller than a pre-specified "error" (chosen as 1×10^{-8}).
- (xii) When one search sequence for R has been completed, the value of s determined in (ix) is compared to the value for s guessed in step (i), s_{guess} . If s_{guess} is higher than s , s_{guess} becomes the new upper limit; if it is lower than s , s_{guess} becomes the new lower limit.
- (xiii) The process from steps (i) to (xii) is repeated, using the new upper and lower limits for s . Iteration of this "outer loop" is continued until the difference between s_{guess} and s is smaller than a pre-specified "error" (chosen as 1×10^{-8} moles/L).
- (xiv) When both iterative loops have terminated, the flows and composition of all the water and gas streams inside, into and out of the "mass balance over sidestream" section in **Figure 5.1** are known.

5.4.6 Summary of SSP-MOD Input/Output

The previous section described in some detail the algorithm that was developed to model the CO_2 recycling part of SSP, since this was the most complicated part of the process to model. The simulation of the rest of the process is self evident from the process diagram in **Figure 5.1**.

The model requires the following as input:

Input:

- Calcium, total alkalinity (both as mg/L CaCO_3), pH, electrical conductivity (mS/m) and temperature ($^{\circ}\text{C}$) of the feed water.
- (It assumes that the feed water is saturated with air – Henry's Law constant for air at a temperature of 25°C was used to calculate the amount of dissolved air in the feed water, namely $8,297 \times 10^{-4}$ moles/L).
- (A flow for the feed water need not be specified – the model is based on a timescale of 1 second and a sidestream flow of 1 L/s).
- The pure CO_2 dosage (mg/L).
- The total pressure in the CO_2 dissolution vessel (atmospheres absolute pressure).
- The amount of CaCO_3 (in mg/L) taken up in the limestone contactor (optional) – if 0 is specified, the water is equilibrated with CaCO_3 .
- The total pressure in the air stripping vessel (atmospheres absolute pressure).
- Flow of an air stream into the air stripping vessel (in litres air per litre "sidestream" water) – this could be 0, if no air from the atmosphere is fed into the air stripping vessel.
- The molar fraction of CO_2 and temperature and pressure of the above mentioned air stream.
- The fraction of the product gas from the CO_2 dissolution vessel that is purged to the atmosphere – it could range between 0,1 and 1, but should not be 0, because excess

dissolved air in the feed water (made up of dissolved nitrogen and oxygen) has to be purged at some point in order to complete the mass balance of the system.

- The percentage sidestream.
- Specification of whether a pre-blend strip-to-waste step is carried out.
- The lime dosage to the blended stream.
- The user also specifies the output streams (gas and water streams) to be printed to the output text file.

Output:

Water streams

The following parameters for all the water streams in the process are given as output:

- Calcium (mg/L as CaCO_3)
- Total alkalinity (mg/L as CaCO_3)
- pH
- Electrical conductivity (mS/m)
- Temperature ($^{\circ}\text{C}$)
- Total inorganic carbon content (as mg/L CO_2) – calculated from the total acidity and total alkalinity
- CaCO_3 precipitation potential (CCPP) as mg/L CaCO_3
- Dissolved air concentration (mole air/L)

The above parameters are given for the following water streams (also see Figure 5.1):

- Initial feed
- Product water from the CO_2 dissolution stage
- Product water from the CaCO_3 contactor
- Product water from the air stripping stage
- Product water from the pre-blend strip-to-waste stage (only if such a step was specified in the input file)
- Water after blending of the "sidestream" and "mainstream"
- Water after lime addition
- The post-lime water after equilibration with atmospheric air

Gas streams

The model treats the combination of oxygen and nitrogen as a single gas, namely air, and assumes that all the gas streams are combinations of air and CO_2 . The following parameters are given for all the gas streams in the process:

- Flow (in litre gas per litre "sidestream" water)
- Molar fraction air (assuming air is mainly nitrogen and oxygen)
- Molar fraction CO_2
- Temperature ($^{\circ}\text{C}$)
- Total pressure (atmospheres absolute pressure)
- Total molar flow (moles per litre "sidestream" water)
- Molar flow air (moles per litre "sidestream" water)

- Molar flow CO_2 (moles per litre "sidestream" water)

The above parameters are given for the following gas streams:

- Feed gas to the CO_2 dissolution vessel
- Product gas from the CO_2 dissolution vessel
- Gas off-bleed (i.e. the purged gas stream)
- The "gas-recycle" (i.e. the portion of the dissolution vessel product gas that is recycled to the air stripping vessel)
- The air feed (i.e. the air stream fed from the atmosphere into the air stripping vessel)
- The air stripper feed gas (i.e. the combination of the atmospheric air stream and the recycled gas from the dissolution vessel)
- The air stripper product gas

The following additional output values are given in a column labelled "DOSAGE":

- The amount of CO_2 taken up by the water in the dissolution vessel
- The amount of CaCO_3 taken up by the water in the limestone contactor
- The amount of CO_2 stripped from the water in the air stripper

Finally, the following information is also given:

- The partial CO_2 pressures in the dissolution and air stripping vessels
- The percentage recycled CO_2 in the dissolution vessel feed (i.e. the percentage of the CO_2 in the feed to the dissolution vessel which originates from the air stripping stage)
- The fraction of CO_2 that is taken up by the water in the dissolution vessel that originates from the gas recycle from the stripper (this quantity is termed CO_2 recovery).

5.5 SSP-MOD MODEL VERIFICATION USING STASOFT 4

Once the *SSP-MOD* model had been developed, it was necessary to verify the operation thereof. Therefore, in order to assess the performance of the *SSP-MOD* model, it was compared with a known aquatic chemistry software package, namely *STASOFT 4*. Such a comparison would provide a basis for assessing the accuracy of the *SSP-MOD* model.

The following example was conducted to assess the accuracy of the *SSP-MOD* model. In this example, 800 mg/L CO_2 was dosed to an 8% sidestream of distilled water. Operating conditions were as what occurs during pilot plant operation. The equilibrium amount of CaCO_3 was added to the CO_2 acidified stream and the vacuum in the recovery vessels were assumed to be 30 kPa. In addition, no air was added into the recovery vessels and all air entering with the sidestream was bled off after the dissolution vessels. Furthermore, a nominal amount of lime was added to the blended stream that was subsequently stripped with air to waste.

These sequential operations can be seen in the "input data" section in the following figure, which also indicates the output data obtained from the model.


```

RUN: Distilled water, dose 800 mg/L CO2, for STASOFT comparison

INPUT DATA:
-----

SIDESTREAM WITH CO2 RECOVERY
FEED CHARACTERISTICS: CA(mg/L as CaCO3), ALK(mg/L as CaCO3), pH, EC(mS/m) T
0, 0, 7, 5, 20
CO2 DOSE TO SS: (mg/L) (at least 10 mg/L)
800
TOTAL PRESSURE IN DISSOLUTION VESSEL (Atm):
3
CACO3 DOSE TO SS (if made 0, eqbrn amount is dosed): (mg/L)
0
TOTAL PRESS IN RECOVERY VESSEL: (atm)
0.3
AIR FEED: Flow (L gas/L water)
0
AIR FEED CHARACTERISTICS: MoleFraction air, MoleFraction CO2, Press (atm), Temp:
0.99965, 0.00035, 1, 20
FRACTION GAS OFF-BLEED: (0.1 to 1)
1
PERCENTAGE SS:
8
STRIP SS TO WASTE BEFORE BLENDING: 1 for yes, 0 for no, if yes, specify CO2 partial press (atm)
0, 0.00035
LIME DOSAGE TO FINAL WATER: (mg/L as Ca(OH)2)
2
PRINT WAT STRMS? Feed, Post D/V, Post L/S, Post A/S, Post STW, Post Blend, Post Lime, Post
EqAir
1, 1, 1, 1, 1, 1, 1, 1
PRINT GAS STRMS? D/V Feed, D/V Prod, Purge, D/V Recycle, Air Feed, A/S Feed, A/S Prod
0, 0, 0, 0, 0, 0, 0

OUTPUT DATA:
-----

PROC:  DOSAGE    Ca    Alk    pH    EC    T    Ct    Ac    CAPP    Air
FEED:           0.0    0.0    7.0    5.0    20.0  -0.0  -0.0  -14.2  8.297E-4
CO2   1222.77    0.0    0.0    3.97   5.0    20.0  1222.8  2779.0  -669.2  0.001771
EQCA:   792.4  792.4  792.4  6.23  95.0    20.0  1571.4  2779.0  -0.0    0.001771
CO2    -433.51  792.4  792.4  6.53  95.0    20.0  1137.9  1793.8  134.6  3.47E-5
% STRM:    8.0   63.4   63.4   6.56  12.0    20.0   91.0  143.5  -66.8  3.47E-5
LIME:     2.0   66.1   66.1   6.61  12.0    20.0   91.0  140.8  -62.1  3.47E-5
EQAIR   3.5E-4   66.1   66.1   8.34  12.0    20.0   58.1   65.9    0.7  3.47E-5

          Vol  mfAir  mfCO2    T    Pres  nMole    moleAir    moleCO2
DV Feed-gas  0.24  0.05832  0.94168  20.0    3.0  0.02977  0.001736323  0.028034284
DV Prod-gas  0.01  0.76508  0.23492  20.0    3.0  0.00104  7.95009E-4  2.44113E-4
Gas Off-bleed 0.01  0.76508  0.23492  20.0    3.0  0.00104  7.95009E-4  2.44113E-4
Gas-recycle   0.0  0.76508  0.23492  20.0    3.0    0.0    0.0    0.0
Air feed      0.0  0.99965  3.5E-4  20.0    1.0    0.0    0.0    0.0
AS Feed-gas   0.0    0.0    0.0    20.0    3.0    0.0    0.0    0.0
AS Prod-gas   0.93  0.14983  0.85017  20.0    0.3  0.01159  0.001736331  0.009852466

CO2 dosage to SS :    800.0
Partial CO2 pressures (atm) DV: 0.704766 AS: 0.255051
Percentage recycled CO2 in DV feed 35.144

```

Figure 5.2: Example of a SSP-MOD run with distilled water, dosing 800 mg/L pure CO₂, without pre-blend strip-to-waste step

In the fifth line from the bottom, the partial CO₂ pressures in the dissolution and air stripping vessels are given. A STASOFT 4 simulation was done to compare the aquatic chemistry outputs of the SSP-MOD model with that of STASOFT 4. The mentioned partial CO₂ pressures were used as

input in *STASOFT 4* for this comparison. The *STASOFT 4* output is shown in the following figures.

TREATMENT PROCESS:		Initial	EqmAir	EqmCaMg	EqmAir
Unit:		Water	pp	Atm	pp
Purity of Process Chemical:					Atm
Amount:			0.70477		0.25505
PARAMETERS (mostly mg/l)					
Temperature	C	20	20	20	20
Conductivity	mS/m	5	6	139	138
Calcium, dissolved	Ca	0.0	0.0	318.1	318.1
pH		7.00	3.97	6.20	6.49
Alkalinity	CaCO ₃	0.0	0.0	794.5	794.5
Carbonic Species	CO ₂	0.0	1220.6	1569.9	1140.3
CaCO ₃ PP	CaCO ₃	-12.4	-794.3	0.0	150.9
Acidity	CaCO ₃	0.0	2775.8	2775.8	1798.8
Calcium, precipitate	Ca	1000.0	1000.0	681.9	681.9

TREATMENT PROCESS:		Initial	BlendPg1	Ca(OH) ₂	EqmAir
Unit:		Water	% Page1	mg/l	pp
Purity of Process Chemical:				100.0%	Atm
Amount:		8.0		2.0	0.00035
PARAMETERS (mostly mg/l)					
Temperature	C	20	20	20	20
Conductivity	mS/m	5	16	17	17
Calcium, dissolved	Ca	0.0	25.4	26.5	26.5
pH		7.00	6.55	6.60	8.32
Alkalinity	CaCO ₃	0.0	63.5	66.2	66.2
Carbonic Species	CO ₂	0.0	91.2	91.2	57.8
CaCO ₃ PP	CaCO ₃	-12.4	-66.2	-61.5	1.5
Acidity	CaCO ₃	0.0	143.9	141.2	65.3

Figure 5.3: STASOFT 4 simulation of a process simulated with SSP-MOD

Following this simulation, the output of the model was checked and found to be accurate by:

- Manual materials mass-balances for the inert gases ("air") and carbonic species.
- Manually checking Henry/Dalton equations in the dissolution and stripping vessels.

- Verifying carbonate chemistry calculations in dissolution, stripping and limestone vessels with *STASOFT 4* determinations. The model's calculations were very similar to those of *STASOFT 4*. The only noticeable deviation in some cases from *STASOFT 4* was in the determination of the saturation calcium carbonate concentration. The reason for this is that *STASOFT 4* uses a more sophisticated method to determine the effect of limestone dissolution on the ionic strength of the water, and the effect that this has on the calcium carbonate saturation calculation. The model's simplified method of taking ionic strength into account may lead to inaccuracy in saturation calcium uptake in the order of 10%.

The results obtained from analysis between *SSP-MOD* and *STASOFT 4* are shown in the following table.

Table 5.1: Comparison between output from *SSP-MOD* simulation (A) and *STASOFT 4* simulation (B)

DETERMINANT	FEED		POST-CO ₂ DISSLN (1223,8 mg/L CO ₂ DISS.)		POST L/S CONTACT (792,4 mg/L CaCO ₃ DISS.)		POST AIR STRIPPING (433,5 mg/L CO ₂ REMOVED)		POST-BLENDING (8% SSTREAM)		POST LIME DOSAGE (2 mg/L LIME DOSED)		EQUIL. WITH THE ATMOSPHERE	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
pH	7.00	7.00	3.97	3.97	6.23	6.20	6.53	6.49	6.56	6.55	6.61	6.60	8.34	8.32
Ca as Ca	0	0	0	0	317	318	317	318	25.4	25.4	26.4	26.5	26.4	26.5
Tot. alk	0	0	0	0	792	795	792	795	63.4	63.5	66.1	66.2	66.1	66.2
EC	5	5	5	6	95	139	95	138	12	16	12	17	12	17
Ct	0	0	1223	1221	1571	1570	1138	1140	91	91	91	91	58	57.8
Tot. acid	0	0	2779	2276	2779	2776	1794		143.5	143.9	140.8	141.2	65.9	65.3
CCDP	14.2	12.4	792	794	0	0	-135		66.8	66.2	62.1	61.5	0.7	1.5
Temp	20	20	20	20	20	20	20	20	20	20	20	20	20	20

The above table clearly shows that similar results were obtained with *STASOFT 4* and *SSP-MOD*, indicating that the aquatic chemistry determinations of *SSP-MOD* are reliable.

5.6 PRELIMINARY ASSESSMENT AND VERIFICATION OF THE ABILITY OF *SSP-MOD* TO SIMULATE DATA OBTAINED FROM SSP PILOT PLANT OPERATION

Following the successful comparison of *SSP-MOD* with *STASOFT 4*, it was decided that *SSP-MOD* would be compared to data obtained from operation of the SSP pilot plant.

The results of a preliminary weeklong (Monday to Friday) pilot plant run of the SSP process (termed Long Run) were used as a basis for these comparative purposes (this Long Run is discussed in detail in CHAPTER 6). Only the "sidestream" part of the process was simulated during operation of the pilot plant in the Long Run. On the pilot plant, water passes through three "CO₂ dissolution" vessels connected in series. In the first dissolution vessel, DV1, recovered CO₂ is contacted with the water. The water then only passes through DV2, and in DV3, pure CO₂ is added from a gas cylinder. From there, the water passes through two limestone columns, and then through two CO₂ stripping/recovery vessels, RV1 and RV2. The two recovery vessels are connected in parallel to the suction side of an eductor (a vacuum generating venturi device – see CHAPTER 6 for further details). Gas containing CO₂ is blended with the feed by the eductor, and the gas/water mixture is fed into the first dissolution vessel, DV1.

The following set of results is generally representative of the results obtained during the entire Long Run. (The particular sample collected was coded M66, and was collected 8 hours before the end of the run.)

Table 5.2: Pilot plant results – long run

	FEED	DV1	DV2	DV3	POST L/S	RV1	RV2
pH	8,14	4,75	4,91	4,14	5,80	5,79	6,17
Calcium (as mg/L Ca)	6	-	-	-	157	-	(157)
Total alkalinity (as mg/L CaCO ₃)	15	-	-	-	387	-	(387)
Electrical Conductivity (mS/m)	8	-	-	-	(67)	-	-
Carbonic species (as mg/L CO ₂)	13,3	-	-	-	1472,2	-	822

The absolute pressure within the dissolution vessels was 260 kPa throughout the run and a vacuum of approximately 35 kPa was maintained within the recovery vessels. Pure CO₂ was fed into DV3 at a measured rate of 570 mg/L (the amount of CO₂ added was measured based on mass loss from a CO₂ cylinder). No air was fed to the recovery vessels, and undissolved gas that accumulated at the top of the dissolution vessels were bled off from time to time.

A SSP-MOD run was carried out using the above input values. The SSP-MOD program has the option of allowing the water to reach CaCO₃ saturation in the limestone contact vessel, or to specify a CaCO₃ dosage. In this case, the CaCO₃ dosage was specified to reflect the actual amount of CO₂ taken up by the water. The SSP-MOD output is summarized in the following table.

Table 5.3: Run A, Output of SSP-MOD run, simulating a long pilot plant run

	FEED	POST CO ₂ DISSOLUTION	POST L/STONE	POST STRIPPING
		640 mg/L CO ₂ in total diss.	372 mg/L CaCO ₃ diss	
pH	8,14	4,71	6,19	6,31
Calcium (as mg/L Ca)	6	6	154,8	154,8
Total alkalinity (as mg/L CaCO ₃)	15	15	387,0	387,0

Electrical Conductivity (mS/m)	8	8	58	58
Carbonic species (as mg/L CO ₂)	13,3	652,9	816,6	707,2
CCPP (as mg/L CaCO ₃)	-5,5	-506,2	-190,7	-143,5

The *SSP-MOD* simulation predicts that 70 mg/L of recovered CO₂ can be re-dissolved in the dissolution vessels, which results in a total CO₂ dosage of 570 + 70 = 640 mg/L. However, correlation between the post-CO₂ dissolution pH (*SSP-MOD*) and DV3 pH (pilot plant run), and between the post-limestone pH (*SSP-MOD*) and post-limestone pH (pilot plant run) are poor. The *SSP-MOD* model therefore indicated that much less CO₂ was recovered than what had been calculated on the pilot plant (using pH values and *STASOFT 4*). Therefore, in order to assess the discrepancy between pH values measured at the dissolution vessels (which gives an indication of the CO₂ recovered), the pure CO₂ dosage was varied in *SSP-MOD* model in order to match the observed pH values (from the pilot plant run) with the model's output. It was found that when the CO₂ dosage is specified as 820 mg/L, the pH values after limestone contact and CO₂ stripping were similar. This result indicates that more CO₂ dissolved (and therefore more CO₂ was recovered) than what was predicted using the *SSP-MOD* model. (The amount of "fresh" CO₂ dosed was measured via mass loss and therefore decreases in pH measured in the dissolution vessels were as a result of recovered CO₂.) However, during subsequent analysis of both the *SSP-MOD* model and the pilot plant, it became evident that some of the in-line pH meters on the pilot plant were faulty, yielding inaccurate pH results, which may have resulted in the observed discrepancies in the pH values of the *SSP-MOD* model and the SSP pilot plant. The *SSP-MOD* model would therefore only be further verified and calibrated once new pH probes had been installed (see CHAPTER 6 for further details).

5.7 MULTIPLE *SSP-MOD* RUNS

From the above preliminary comparison with both *STASOFT 4* and Long Run data from the SSP pilot plant, it was shown that the *SSP-MOD* model could be used to optimise the SSP process. In light of these findings a series of multiple runs were carried out where various model input parameters were varied. The influence of the following parameters were assessed:

- Effect of CO₂ dosage
- Effect of pressure in the stripping/recovery vessel
- Effect of atmospheric air flow into the air stripper/recovery vessel.

The results from these model outputs are discussed in the following sections.

5.7.1 *Effect of CO₂ Dosage*

A *SSP-MOD* model run was carried out whereby the "fresh" CO₂ dosage was varied between 100 and 1500 mg/L. Distilled water was used as feed water. A 5% sidestream was assumed, with no stripping-to-waste before blending. A pressure of 300 kPa was assumed in the dissolution vessels while a vacuum pressure of 30 kPa was assumed in the recovery vessels. No air from the atmosphere was bled into the stripper. Undissolved gas from the dissolution vessel was bled to waste.

The following figure (Figure 5.4) shows the total alkalinity of the blended stream, and the percentage CO₂ recovery (percentage recovered CO₂ divided by the total CO₂ dosage, i.e. the pure plus the recovered CO₂). It can be seen that for this set of dissolution/stripping pressures the percentage CO₂ recovery increases to a maximum of ~ 70% (at a CO₂ dose of 1300 mg/L), after which it starts to decrease.

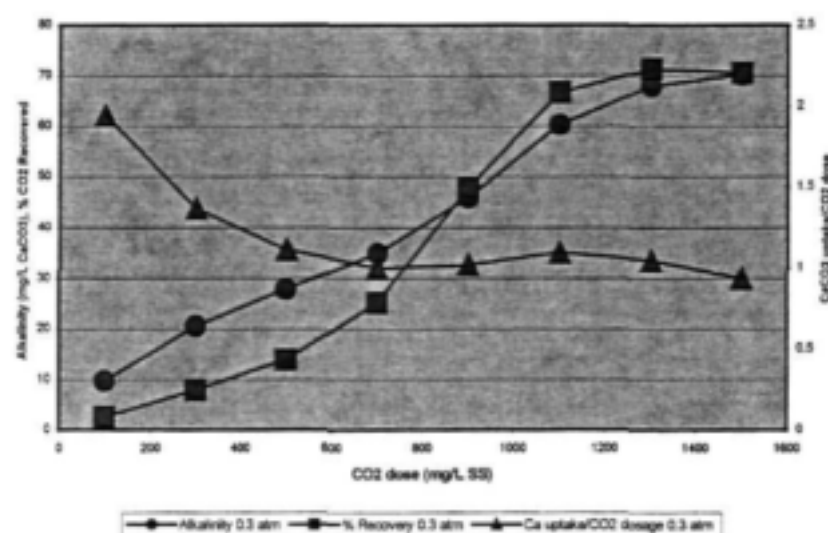


Figure 5.4: Output from a multiple SSP-MOD run, varying pure CO₂ dose between 100 and 1500 mg/L, i.e. showing total alkalinity after blending

5.7.2 Effect of Pressure in Recovery Vessel

It was believed by the project team that the vacuum pressure in the recovery vessel influences the amount of CO₂ that is recovered which would therefore influence the total amount of CaCO₃ taken up (if more CO₂ is available, more CaCO₃ will dissolve). This concept was verified by the SSP-MOD model, which showed that an increase in vacuum pressure resulted in a greater CaCO₃ uptake, indicating that more CO₂ is being recovered. Furthermore, it was found that CO₂ recoveries only increased with increased vacuum at higher "fresh" CO₂ doses. These results are shown in Figure 5.5.

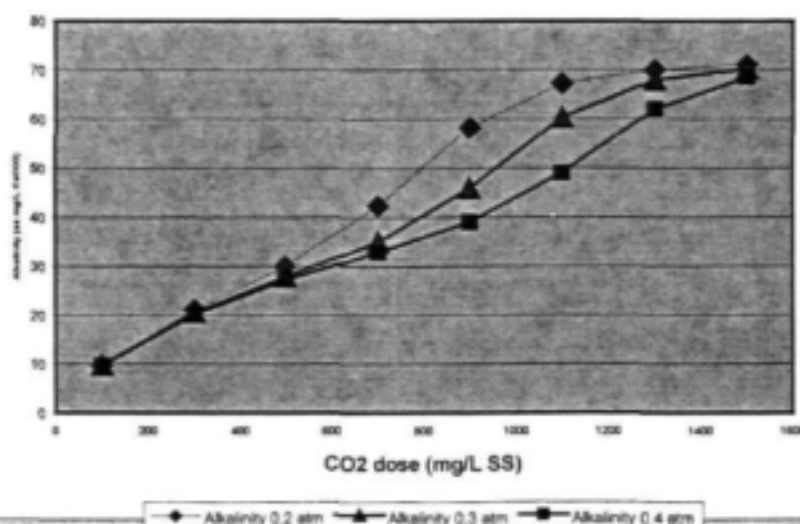


Figure 5.5: *Total alkalinity in the sidestream (after limestone contact at different recovery rates CO₂ doses, and for different pressures in the air stripping/recovery vessel)*

5.7.3 Effect of Atmospheric Air Flow into the Air Stripper/Recovery Vessel

It was believed by the project team that the addition of atmospheric air into the recovery vessel would improve CO₂ recovery, as the addition of air into the recovery vessel reduces the partial CO₂ pressure in the recovery vessel, thus allowing more CO₂ to be stripped from the water. This had been verified during previous pilot plant tests, which showed that the addition of air aided CO₂ stripping and recovery. Figure 5.6 shows the total alkalinities and percentage CO₂ recoveries at different CO₂ dosages, if no air flows into the recovery vessel, and if 5 L air/L sidestream flows into the recovery vessel (the total alkalinities shown are after blending a 5% sidestream with the mainstream).

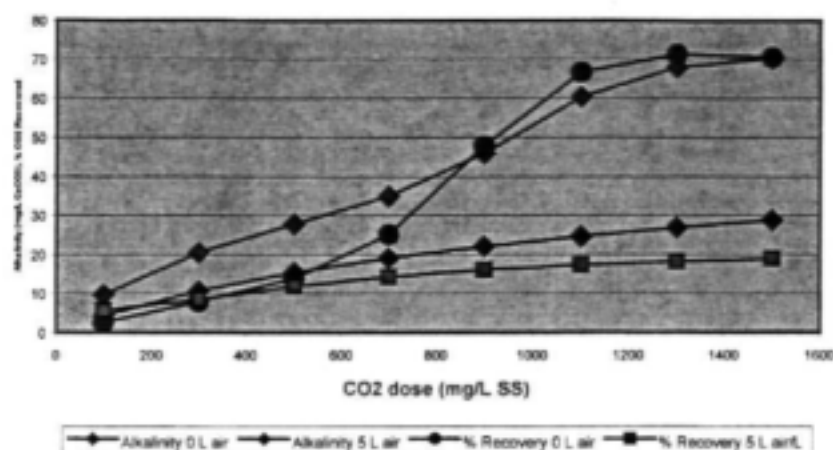


Figure 5.6: Total alkalinity and percentage CO₂ recovery in a 5% sidestream in the blended stream, at different CO₂ doses, with and without air flow into the stripper

The above graph indicates that the addition of 5 L air/L sidestream reduces the final total alkalinity and therefore the amount of CO₂ that is recovered. This result shows that the addition of air is not always beneficial and would need to be further investigated during subsequent pilot plant trials and optimisation.

5.8 DISCUSSION AND CONCLUSIONS: DEVELOPMENT OF SSP-MOD PROGRAM

In light of the poor correlation between the commercially available process modelling packages and the recognized STASOFT 4 aquatic chemistry software package, the project team undertook previously unenvisioned programming to create a model to describe the SSP process.

The SSP-MOD model developed requires the following as input:

- Calcium, total alkalinity, pH, electrical conductivity and temperature of the feed water.
- The “fresh” CO₂ dosage.
- The total pressure in the CO₂ dissolution vessel.
- The amount of CaCO₃ taken up in the limestone contactor (or if this is unknown the water is equilibrated with CaCO₃).
- The total pressure in the recovery vessel.
- Flow of an air stream into the air stripping vessel.
- The molar fraction of CO₂ and temperature and pressure of the above mentioned air stream.
- The fraction of the product gas from the CO₂ dissolution vessel that is purged to the atmosphere.
- The percentage sidestream.
- Specification of whether a pre-blend strip-to-waste step is carried out.
- The lime dosage to the blended stream.

The SSP-MOD model then generates an output file that describes the state of both the water and gas streams after undergoing the specified unit operations.

Following development, the model generated was compared with *STASOFT 4* and found to be accurate. Subsequent to this the model was compared with actual data obtained from preliminary operation of the SSP pilot plant. This investigation revealed that the model predicted that the amount of CO₂ recovered from the recovery vessels (and subsequently dissolved into the dissolution vessels) was less than what had been calculated (using pH measurements and *STASOFT 4*) from pilot plant operation. The investigation, however, further revealed that some of the pH probes used on the pilot plant were faulty and would need to be replaced. It was therefore decided that further comparison of outputs from the *SSP-MOD* model and the pilot plant would only continue after the faulty pH probes had been replaced.

From the above preliminary comparison with both *STASOFT 4* and data obtained from operation of the SSP pilot plant, it was shown that the *SSP-MOD* model could be used to optimise the SSP process. It was with this in mind that the project team undertook a series of multiple runs where the model input parameters were varied. These investigations showed that:

- Increasing the "fresh" CO₂ added to the sidestream increases the CO₂ recovered to a maximum of ~ 70% (at a "fresh" CO₂ dose of 1300 mg/L). At this stage an increase in fresh CO₂ dosed does not improve CO₂ recovery.
- An increase in vacuum pressure (i.e. closer to absolute zero pressure – 0 kPa) within the recovery vessel increases the amount of CO₂ recovered. This relationship was seen to only hold at higher CO₂ doses.
- Previous pilot plant trials had showed that the addition of air aided CO₂ stripping and recovery. The *SSP-MOD* model, however, showed that the addition of 5 L atmospheric air/L sidestream decreased the final water total alkalinity and therefore decreased the amount of CO₂ that could be recovered. This result indicated that the addition of air may not always be beneficial and would have to be further investigated during pilot plant trials.

This preliminary investigation using the *SSP-MOD* model showed that it could prove useful for optimising the SSP process. The model would, however, still need to be verified in subsequent pilot plant trials.

CHAPTER 6

PILOT PLANT OPERATION USING AN EDUCTOR FOR CO₂ RECOVERY AND ASSESSMENT OF THE *SSP- MOD* PROGRAM

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6.1 INTRODUCTION

The *SSP-MOD* model was developed to describe the SSP process. However, in order to assess the accuracy of the model for predicting the behaviour of the SSP process, it needed to be verified and calibrated on data obtained from operation of the SSP pilot plant. In parallel with verification and calibration of the model is the need to optimise the operation of the SSP pilot plant. Assessment of the SSP process has shown that the stripping and recovery of CO_2 is an essential step in the SSP, as the running costs of the SSP are strongly influenced by the amount of "fresh" CO_2 dosed. Maximizing the CO_2 recovery whilst using economical "fresh" CO_2 dosing rates is therefore of primary importance to optimise the process. Previous pilot plant work had shown that this step was potentially problematic, and therefore improved ways of recovering the maximum amount of CO_2 were to be investigated.

This chapter therefore describes work undertaken to both improve operation of the SSP pilot plant to achieve improved/optimised performance, and verification of the accuracy and calibration of the *SSP-MOD* model.

6.2 HISTORICAL STRIPPING AND RECOVERY OF CO_2

On the original SSP pilot plant, CO_2 stripping and recovery was achieved using vacuum pumps connected to the CO_2 recovery vessels (RV). Various mechanical problems arose with the use of these pumps generally resulting in decreased vacuum pressure over time. The decreased vacuum pressure resulted in lower CO_2 recoveries, which lowered the cost effectiveness of the process. Moisture (water vapour) was also found to be present in the recovered CO_2 , thus limiting the effectiveness of the vacuum pumps. Due to these operational problems alternative methods for recovering CO_2 were considered. Investigation revealed that venturi devices may be suitable for use on the SSP pilot plant as their use provides a means of overcoming moisture related problems, without compromising vacuum generation efficiency.

6.3 VENTURI THEORY

A venturi is a device that uses the basic Bernoulli principle to relate fluid velocity to pressure. In this regard, a venturi has the ability to create a vacuum that can be used to draw off a liquid or gas, and then mix it with the incoming fluid stream, to create a blended discharge stream.

Venturis, ejectors, jet pumps and eductors all fall into the same broad category as they operate under the same principle, and are highly efficient, differential pressure systems. In general, a pressure difference between the inlet and the outlet ports of the venturi device creates a vacuum inside the venturi body, which then initiates suction through the suction port. When a pressurized motive (operating) fluid enters

the venturi inlet, it is constricted toward the converging nozzle and changes into a high velocity jet stream. The increase in velocity through the nozzle results in decrease in pressure, thereby enabling an additive material to be drawn through the suction port and be entrained into the motive stream. As the jet stream is diffused toward the venturi outlet its velocity is reduced and is re-converted into pressure energy (but at a pressure lower than the venturi inlet pressure). **Figure 6.1** shows the basic configuration of a venturi device.

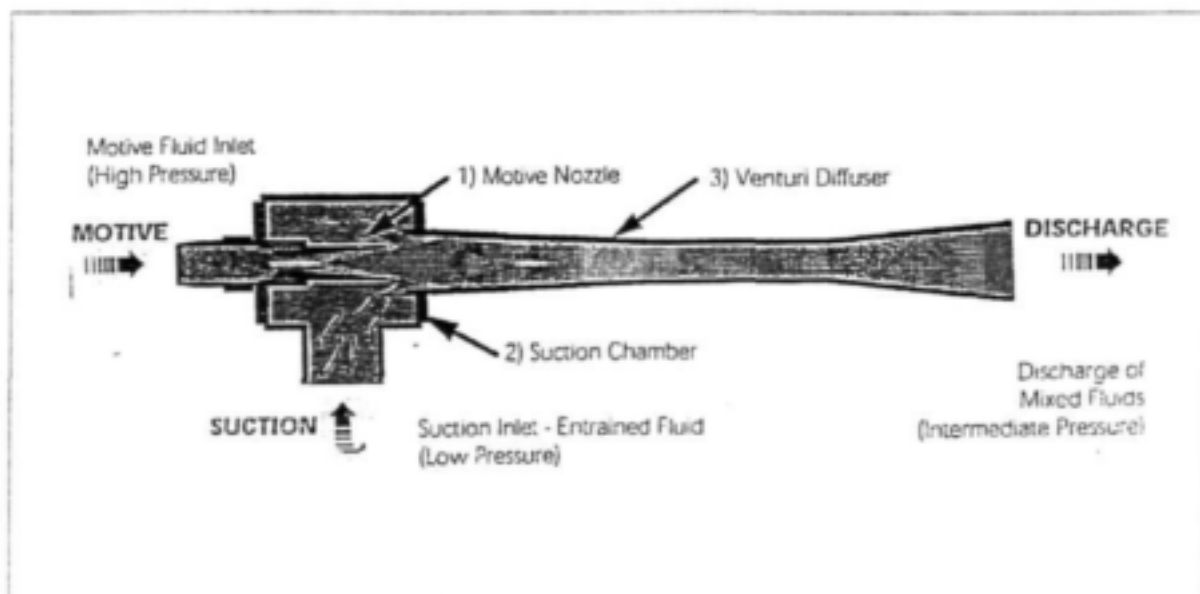


Figure 6.1: A basic outline of an venturi device (Source: www.chemguard.com)

6.4 EDUCTORS FOR EXHAUSTING GASEOUS STREAMS

Eductors are often used in industry to pump liquids and exhaust gases. Eductors are constant flow devices that produce accurate proportioning data, specified flow and pressure. It is therefore critical to match the eductor with downstream devices. This includes any friction loss associated with delivering the flow to the discharge device at its given operating pressure. An imbalance in this calculation will likely cause the eductor to malfunction. Eductors are typically portable devices although they can be used with great care in fixed system applications.

Eductors can be attributed with the following advantages:

- **Low cost**

Eductors are relatively inexpensive in relation to systems performing similar tasks.

- **Easy to install**
Either threaded or flanged connections are available. Units are compact, relatively light and can be adapted to a variety of piping configurations.
- **Non-electrical**
Eductors can be used in hazardous locations where electrically operated alternatives would require expensive explosion-proofing.
- **Corrosion and erosion resistant**
Eductors can be made resistant to the corrosive effects of the liquid handled and the environment because they can be made from most materials or coated with corrosion resistant materials.
- **Simple and reliable**
Since the basic eductor has no moving parts to wear or break, only periodic inspection is required. Eductors are also easy to operate and are relatively small. They thus take up less space and require less supplementary equipment than conventional vacuum pumps. They are suitable for wet or dry mixtures of gases containing sticky or solid matter.
- **Self priming**
Eductors require no priming and can be used in either continuous or intermittent operation.
- **Multi-functional**
Eductors can be used in various industrial applications for a variety of purposes e.g. mixing, pumping or moving many types of liquids and gases in the petrochemical, process and power industries. If adequate mixing of the gas and liquid phases occurs, then the use of an eductor may eradicate the need for large dissolution vessels in the SSP pilot plant.

The choice of the most suitable eductor for a given application depends on the following factors:

- Motive pressure and temperature
- Suction pressure and temperature
- Required capacity
- Discharge pressure

6.5 SIZING SPECIFICATION AND ACQUISITION OF EDUCTOR

For SSP pilot plant operation, the following eductor criteria were selected:

- Motive flow: 300 – 340 L/hr
- Discharge pressure: 300 kPa
- Suction pressure: 50 kPa to 20 kPa

Various manufacturers and suppliers of eductor equipment were contacted and from these investigations a Penberthy Model LM ½" B PVC eductor (manufactured in the United States of America) was purchased. The specifications for the eductor as supplied by the South African distributor were:

- Motive flow: 340 L/hr
- Motive pressure: 650 kPa
- Discharge pressure: 300 kPa
- Suction pressure: 50 kPa to 20 kPa

The following figure shows the relative size of the eductor device.

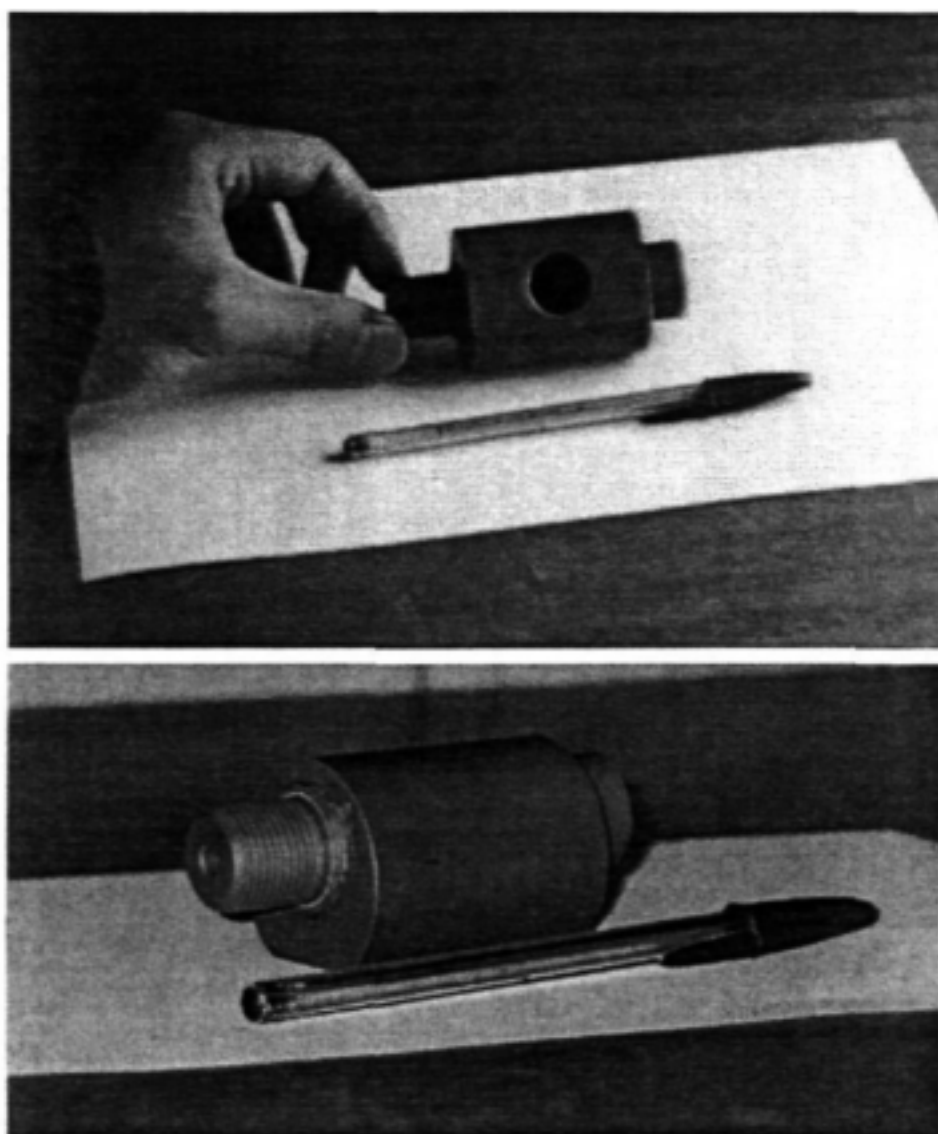


Figure 6.2: Penberthy Model LM 1/2" B PVC eductor

The sidestream of untreated feed is pumped to the inlet of the eductor (at the pressure required for its operation i.e. 650 kPa). After the water stream has passed through the CO₂ and limestone dissolution vessels, CO₂ is stripped by aeration as it enters the CO₂ recovery vessels (using spray nozzles). The eductor is designed to create a vacuum of between 50 and 20 kPa (depending on the specific requirements), drawing off the recovered CO₂ and allowing "CO₂-free" water to trickle to the bottom of the recovery vessel. One eductor is used to draw the recovered CO₂ from both recovery vessels (RV1 and RV2). The recovered CO₂ enters the eductor where it is mixed with the incoming untreated feed stream. The eductor then ejects a CO₂-water mixture as product at 300 kPa, the operating pressure of the dissolution vessel. In operation, raw water flows through the eductor, which causes the pressure to drop below atmospheric levels. CO₂ is then "sucked" up through the pick-up tube into the water stream. Piping limitations and other precautionary measures were investigated to ensure optimum eductor operability.

6.7 PRELIMINARY EXPERIMENTS USING THE MODEL LM ½ " B EDUCTOR

Preliminary experiments using the Model LM ½" B eductor were conducted by the project team in order to obtain a greater understanding of the functioning of eductor systems. It was expected that this information would be used to "fine tune" operational aspects of the SSP pilot plant. In these experiments problems were encountered with the operation of the eductor (loss of vacuum, discharge water splash-back, etc.) and the distributors/manufacturers of the eductor were contacted on several occasions in an attempt to solve these problems. This resulted in testing various eductor orientations (45° and 180°) and piping configurations (use of water traps, etc) on the SSP pilot plant. In addition, a test program was established which consisted of:

- Isolating the eductor from the SSP and conducting separate tests.
- Re-installing the eductor into the SSP and drawing a vacuum from the recovery columns without any water flowing into the columns (i.e. no aeration – water runs to waste).
- Drawing a vacuum from the recovery columns with water flowing through the spray nozzles into the columns (i.e. with aeration in RV1 and RV2).
- Normal SSP operation (i.e. dosing CO₂ into the plant and trying to recover it through the eductor from the recovery columns).

In the isolated eductor test it was proven that a vacuum could be obtained using the eductor. The eductor was then re-installed into the pilot plant. In this experiment, a by-pass line was created so that water would not flow into the recovery vessels (RV1 and RV2). The eductor would therefore attempt to create vacuum conditions within RV1 and RV2 without water being passed into either column. The conditions were set as follows:

- Flow: 340 L/hr
- Motive Pressure: 650 kPa
- Discharge Pressure: 300 kPa

In this configuration, pilot plant operation showed that no vacuum was generated. During this experiment continuous back-splashing was experienced (as encountered during the previous experiments). This back-splashing continued to decrease any vacuum generation that had been obtained. During subsequent further testing, the source of non-optimal operation was discovered.

During start-up, with the vacuum valve completely closed (i.e. the vacuum valve isolates the recovery vessels from the eductor), the vacuum gauge at the suction end of the eductor increased to ~20 kPa, with the motive pressure increasing to 650 kPa. The discharge pressure gradually ascended to its controlled value of 300 kPa. The discharge pressure was maintained at 300 kPa as this is the desired pressure for effective CO₂ dissolution (and the design discharge pressure of the eductor – the maximum allowable discharge pressure of the eductor is 305 kPa – above this pressure the eductor “chokes” and vacuum generation ceases).

However, by experiment it was found that when the discharge pressure increased beyond 260 kPa the vacuum generated dropped at a rapid rate. When the discharge pressure reached 300 kPa the pressure had already dropped to 100 kPa (i.e. atmospheric conditions – no vacuum generated).

The discharge pressure was therefore controlled at 260 kPa so that decreases in the vacuum generated could be avoided (but still maintaining plant operations close as possible to optimal conditions of 300 kPa). This resulted in vacuum generation that increased with time suggesting that running the pilot plant for longer periods would result in the generation of high vacuums. From the short tests conducted a vacuum as high as 37 kPa was generated.

At this stage the South African distributors of the eductor device were contacted and discussions relating to the unexpected poor performance of the eductor ensued. During these extensive discussions, which included both review of design specifications and performance data it became apparent that the South African distributors had supplied incorrect design specifications (with regards discharge pressure conditions) to the manufacturers of the eductor in the United States of America, which resulted in the acquisition of an incorrectly sized eductor. This error had resulted in a major set back in the project, as a lot of time had been wasted trying to optimise plant operation using the incorrectly sized eductor. Therefore, to prevent any further delays the project team felt that this eductor would be further tested in a set of preliminary pilot plant trials (maintaining the system at the required conditions) such that a broader understanding of operating eductor systems

could be achieved. These preliminary pilot plant trials would therefore be conducted during the lag period in which a new, correctly sized eductor would be acquired.

Following the above findings, it was decided that the plant could be tested with water being sprayed (aerated) into one of the recovery columns. Results obtained from this experiment showed that if the required motive flow, motive pressure and discharge pressure conditions were maintained, vacuums as high as 42 kPa could be maintained within the CO₂ recovery vessels.

Following the success of the previously described experiments it was decided that the plant be tested in normal operating mode.

However, prior to the discussion of the results obtained from this preliminary operation of the SSP pilot plant, it is necessary to describe the methodology used to calculate the amount of CO₂ recovered, as this aspect is discussed throughout this chapter.

6.8 METHODOLOGY FOR CALCULATING PERCENTAGE CO₂ RECOVERY

The percentage CO₂ recovered is calculated by division of the recovered CO₂ by the sum of the "fresh" CO₂ added and the recovered CO₂, which is then multiplied by 100.

$$\% \text{ CO}_2 \text{ Recovered} = [\text{Actual CO}_2 \text{ recovered} / (\text{"Fresh" CO}_2 \text{ added} + \text{Actual CO}_2 \text{ recovered})] \times 100$$

Therefore, by way of example, if the amount of "fresh" CO₂ added to the sidestream was 300 mg/L, and 200 mg/L of CO₂ was recovered, the percentage CO₂ recovered would be $200 / (300 + 200) \times 100 = 40\%$.

The amount of CO₂ recovered can be determined in two ways:

- STASOFT 4
- "Bones Curve"

STASOFT 4

Using the raw water characteristics and STASOFT 4, the amount of CO₂ required to obtain recorded pH levels (from the on-line pH probes) in the dissolution vessels (prior to addition of "fresh" CO₂) is calculated. The figure obtained is the amount of CO₂ that is recovered (mg/L). The following figure shows the methodology used in STASOFT 4 to calculate the amount of CO₂ recovered.

STASOFT 4				STASOFT 4			
NAME:				NAME:			
TREATMENT PROCESS:	Initial	CO2		TREATMENT PROCESS:	Initial	CO2	CO2
Unit:	Water	mg/l		Unit:	Water	mg/l	mg/l
Purity of Process Chemical:		100.0%		Purity of Process Chemical:		100.0%	100.0%
Amount:		100.0		Amount:	50.0		100.0
PARAMETERS (mostly mg/l)				PARAMETERS (mostly mg/l)			
Temperature	C	20	20	Temperature	C	20	20
Conductivity	mS/m	10	10	Conductivity	mS/m	10	10
Calcium, dissolved	Ca	2.0	2.0	Calcium, dissolved	Ca	2.0	2.0
pH		8.00	5.05	pH		8.00	5.33
Alkalinity	CaCO3	5.0	5.0	Alkalinity	CaCO3	5.0	5.0
Carbonic Species	CO2	4.4	104.4	Carbonic Species	CO2	4.4	54.4
CaCO3 PP	CaCO3	-8.7	-105.1	CaCO3 PP	CaCO3	-8.7	-105.6

Figure 6.4: Example of using STASOFT 4 to calculate CO₂ recovered

The above figure describes the following case study. The raw water has conditions as shown in the figure. After the addition of 100 mg/L CO₂ a water with a pH of 5.05 is expected. However, after the addition of 100 mg/L CO₂ on the pilot plant the pH of the stream is 4.89. This can only occur if an additional 50 mg/L of CO₂ is added to the sidestream and must be as a result of recovery of CO₂. Therefore the amount of CO₂ recovered is 50 mg/L and the percentage CO₂ recovery is $[50 / (100 + 50)] \times 100 = 33\%$.

The STASOFT 4 method for calculating the amount of CO₂ recovery is based on pH measurements and therefore a great deal of accuracy in pH determinations are required.

"Bones Curve"

The so-called "Bones Curve" is used to determine the amount of CO₂ recovered during long runs. During a long run, two "Bones Curves" are produced, one at the beginning of the run (the "A" curve) and another at the end of the run (the "B" curve). During such operation the pilot plant is run in a non-CO₂ recovery mode. Each of these curves is a plot of total alkalinity in the sidestream after contact with limestone vs. the amount of "fresh" CO₂ added to the sidestream. Each "Bones Curve" requires approximately 15 hours of pilot plant operation to produce. For ease of reference, operation of the pilot plant to determine the "Bones Curves" is hereinafter referred to operating the SSP plant in "Bones Mode".

A typical "Bones Curve" is shown in the following figure. **Note:** the y-axis can reflect either calcium or total alkalinity.

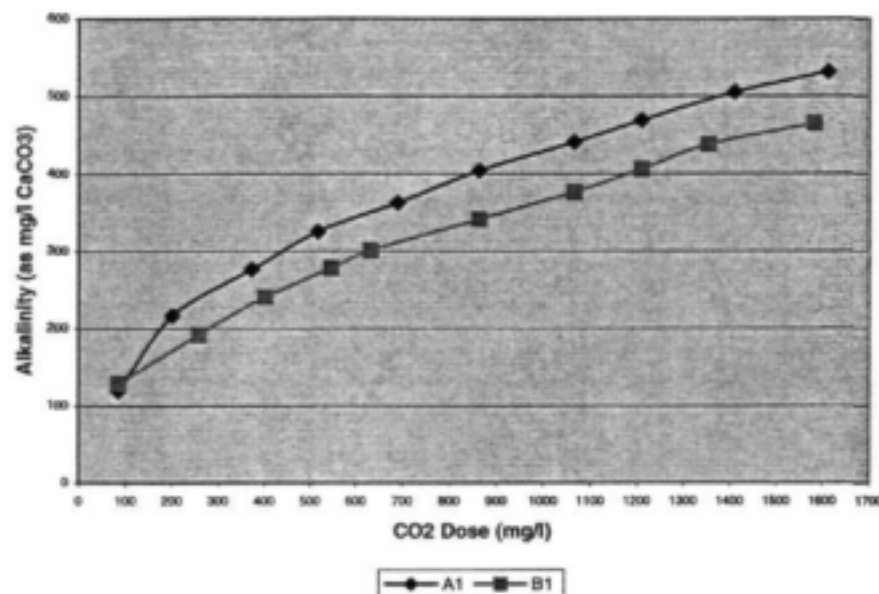


Figure 6.5: Typical "Bones Curve"

Therefore, as an example as to how the "Bones Curve" is used to measure the percentage CO₂ recovery let us assume that 350 mg/L of "fresh" CO₂ was dosed to the sidestream and a total alkalinity of ~ 300 mg/L was recorded in the final stream leaving the pilot plant. However, from the above "Bones Curve" it is clear that to obtain a final total alkalinity of 300 mg/L a CO₂ dose of ~ 430 mg/L (based on "A" curve) and ~ 620 mg/L (based on "B" curve) is necessary. The amount of CO₂ recovered is thus 430 - 350 = 80 mg/L (based on "A" curve) and 620 - 350 = 270 mg/L (based on "B" curve), and the percentage CO₂ recovery based on the calculation method as described above is ~ 19% (A) and ~ 43% (B). The actual CO₂ recovered will lie between the maximum and minimum percentage CO₂ recoveries calculated (previous pilot plant experience, however, has shown that the actual CO₂ recovered follows the "B" curve more closely).

6.9 PRELIMINARY "NORMAL" SSP OPERATION WITH INCORRECTLY SIZED EDUCTOR

6.9.1 Short Run

Up until this stage the experiments conducted did not incorporate injection of CO₂ into the system. Therefore it was necessary to operate the plant in its normal operating mode. This would both show the influence of CO₂ dosed on the vacuums

generated (i.e. does CO₂ dosing decrease the vacuums) and the ability of the eductor (via vacuum generation) to recover CO₂. In this preliminary experiment, CO₂ recovery was monitored through pH measurement which would serve as an indication of whether CO₂ was recovered using the eductor.

During the short run experiment the plant was operated for approximately 8 hours. CO₂ dosing was maintained at 0.57 g/L and the sidestream flow rate at 350 L/hr.

The results indicated that the vacuums generated within the recovery vessels increased progressively over the first two hours (as the air within the recovery vessels was displaced). After this period the vacuum generated stayed more or less constant (between 31 and 36 kPa) for the remaining duration of the experiment. The experiment showed that high vacuums could potentially be maintained for extended period of time using an eductor (this is in strong contrast to what had previously been achieved using vacuum pumps).

pH was monitored for the duration of the experiment. CO₂ was added after approximately two hours of plant operation (when the vacuums generated were more or less stable). Approximately an hour after CO₂ dosing commenced, the pH reading in DV1 started decreasing suggesting that CO₂ was being recovered from the recovery vessels (RV1 & RV2) and dissolving in the feed water. This is evident from the results which indicate a decrease in the pH of the feed from pH ~8.30 to about pH ~5.40 in DV1, the dissolution vessel into which the discharge of the eductor enters.

Preliminary calculations (to calculate the quantity of CO₂ recovered) were performed using the aquatic chemistry software package, *STASOFT 4*. The percentage CO₂ recovered was calculated by dividing the amount of CO₂ recovered (by calculation using *STASOFT 4*), by the sum of the quantity of "fresh" CO₂ dosed (0.57 g/L) and the CO₂ recovered. These preliminary results indicate that CO₂ recoveries of approximately 40% could be expected.

Detailed results for this experiment are shown in **APPENDIX 6A**.

6.9.2 Long Run

Following the short run, a long run was initiated with the objective of determining:

- If the eductor could maintain the vacuum pressure over an extended period of time, and
- If the amount of CO₂ recovered would vary with operational time.

The plant operated in the same configuration as used during the short run. The plant was initially operated to determine the so-called "Bones Curve" (i.e. a calibrated graph quantifying the influence of CO₂ dosing on the uptake of CaCO₃).

This graph is used as a means of determining the amount of CO₂ recovered during normal SSP operation.

After operation in "Bones Mode" (i.e. no CO₂ recovery), the plant was run in its normal mode (i.e. in CO₂ recovery mode) for 74 hours. Vacuum pressures and pH readings were recorded every half-hour while samples were collected on an hourly basis for laboratory determination of calcium and total alkalinity. After being run in normal mode, the plant was again operated without any CO₂ recovery (i.e. in "Bones Mode") to again determine the influence of CO₂ dosing on the uptake of calcium carbonate at the end of the run (at the end of the run less solid CaCO₃ is available in the limestone contactors).

Long run data showed that for the duration of the experiment, once normal operation in CO₂ recovery mode had commenced, the vacuum pressure within the recovery vessels were maintained at approximately 40 kPa. This result indicates that the use of an eductor as a vacuum generating device is advantageous, as it is able to sustain high vacuums for extended periods of time. This should therefore result in a continuously high CO₂ recovery, which would lower the requirements for fresh CO₂ usage.

pH was also monitored for the duration of the experiment. Approximately 0.57 g/L "fresh" CO₂ was dosed into DV3. A short time after dosing with CO₂ had commenced it was noted that the pH reading in DV1 started decreasing to similar levels as had been previously recorded during the short run, suggesting once again that the eductor was recovering CO₂ from the recovery vessels (RV1 & RV2). This is evident from the results which indicate a decrease in the pH of the feed from pH ~8.1 – 8.6 to about pH ~4.6 – 5.0 in DV1, the dissolution vessel into which the discharge of the eductor enters.

CO₂ gas had leaked (from the CO₂ regulator) during the time the plant operated in "Bones Mode". This resulted in inaccurate measures of the influence of CO₂ dosed on CaCO₃ uptake, and for this reason the "Bones Curve" was not used to determine CO₂ recovery. Preliminary calculations using STASOFT 4 showed that a CO₂ recovery of approximately 35 - 45% was obtained during the run.

Detailed results for this experiment are shown in **APPENDIX 6B**.

6.10 CORRECTIVE IMPROVEMENTS TO THE SSP PILOT PLANT

Following the preliminary experiments described in section 6.8, efforts were made to identify and overcome possible problematic areas on the pilot plant that may be decreasing the effectiveness of the CO₂ stripping and recovery process. This investigation included:

- Reconfiguration of pilot plant
- Use of a correctly sized eductor

- Replacement of spray nozzles used in recovery vessels
- Replacement of pH probes

6.10.1 Reconfiguration of Pilot Plant

Review of the pilot plant configuration, and information gathered during pilot plant operation, showed that potentially large amounts of CO₂ were lost at the first dissolution vessel (DV1) as a result of both insufficient contact time between water and recovered CO₂, and the possible purging of recovered CO₂ with excess air. In the original pilot plant configuration (prior to the use of an eductor), separate recovered gas and water streams were used (counter-current flow), but due to the operating principles of the eductor this was no longer possible (the eductor discharges a liquid-gas stream).

The pilot plant was therefore reconfigured such that water and recovered CO₂ would enter at the bottom of DV1, thereby allowing additional contact time between the water and recovered CO₂. The second dissolution vessel (DV2) was reconfigured such that excess air could be purged at this stage, thereby attempting to minimize the loss of recovered CO₂.

Physical inspection of the pilot plant found that no leaks within the eductor suction line and surrounding vessels were present.

6.10.2 Use of a Correctly Sized Eductor

Due to the fact that the previously purchased eductor had not met the required design specifications (due to the provision of incorrect information from the South African distributor to the American-based manufacturer) exceptional thoroughness and care was now taken by the project team to ensure that a correctly sized eductor was obtained. Both the South African distributor and manufacturer from the United States of America of the previously tested eductor (Penberthy Model LM ½" B) were contacted with regards obtaining a correctly sized eductor for use on the SSP pilot plant.

Following discussions, a written order was placed for an eductor with the following specifications:

- Motive pressure: 650 kPa
- Motive flow: 340 L/hr
- Suction flow (CO₂): 0.16 kg/hr
- Suction pressure: 20 kPa
- Discharge pressure: 300 kPa

Investigation revealed that Penberthy were able to supply a Model LM ½" A eductor with the following specifications:

- Motive pressure: 650 kPa
- Motive flow: 463 L/hr
- Suction flow (CO₂): 36.1 kg/hr (for • CO₂ = 1.9 kg/m³ at 20 °C)
- Suction pressure: 20 kPa
- Discharge pressure: 300 kPa

Review of the Penberthy proposed Model LM ½" A eductor specifications yielded two possible areas of concern; namely motive flow and suction flow, which were carefully considered.

- **Motive Flow**

The flowrate of the Penberthy proposed Model LM ½" A eductor was significantly higher than what the pilot plant had been originally designed for (463 L/hr vs. 300 L/hr). This could be problematic in terms of limestone contact only. However, review of the pilot plant showed that even at this flowrate sufficient limestone contact time would occur. However, the spray nozzles in the recovery vessels (which allow aeration and therefore stripping of CO₂) would need to be resized and replaced (this can be readily implemented).

- Hence, an oversized motive flow was deemed to be non-problematic.

- **Suction Flow**

The gas suction flow specification forwarded to the manufacturers was based on previous experimental data. The specification supplied by Penberthy for suction flow was approximately 200 times larger than that which was thought to be required. Whilst this was not thought to be problematic by the project team, clarification was sought from the manufacturers. The manufacturers confirmed that an oversized suction flow would not retard eductor performance if a lower gas suction flow existed.

- Hence, an oversized suction flow was deemed to be non-problematic.

Following these investigations the above mentioned eductor was purchased, installed and commissioned on the SSP pilot plant. (The eductor was the same size and looked similar to the previously purchased Model LM ½" B). Preliminary testing (without CO₂ dosing) showed that the eductor operated as expected from the specifications.

6.10.3 Replacement of Spray Nozzles used in Recovery Vessels

Due to the new eductor requiring a higher motive flowrate than what was previously required, the spray nozzles within the recovery vessels were resized. More suitably sized spray nozzles were obtained and subsequently installed on the pilot plant.

Preliminary testing showed that efficient atomisation of the water stream was once again occurring.

6.10.4 Replacement of pH Probes

During preliminary pilot trials it was noted that on a number of occasions, the in-line pH probes had malfunctioned. Although they were frequently calibrated, problems with respect to ease of calibration and accuracy during the test run persisted. The suppliers of the pH probes were therefore contacted. The suppliers agreed to test/check all the pH probes and controllers used on the SSP pilot plant. These investigations revealed that:

- Two of the pH controller units required immediate replacement.
- Four of the pH probes required immediate replacement. In addition, it was noted that the lifespan of the other four pH probes was limited and would require replacement within a year. As pilot plant testing was approaching its end it was decided that only four of the pH probes would be replaced.

This unexpected set back resulted in a further delay of pilot plant trials by approximately two months. Once the new units had been obtained, the suppliers re-calibrated all the pH probes and controllers to original factory standards. The probes and controllers were subsequently re-installed on the SSP pilot plant. At this stage the SSP pilot plant was ready for follow-up testing.

6.11 PILOT PLANT OPERATION USING THE MODEL LM ½" A EDUCTOR AND CONCURRENT ASSESSMENT OF SSP-MOD

Following implementation of upgrades as described in section 6.9 above, the pilot plant was ready for operation. SSP system optimisation by concurrent use with the SSP-MOD model could therefore commence. It was envisaged that during this process the following would occur:

- Firstly, using understanding gained in CHAPTER 5, the required system parameters would be set.
- Secondly, a series of short runs (8 hour duration) would be carried out to confirm the optimal settings obtained and undertake preliminary calibration of the model (i.e. pilot plant optimisation would be based on feedback from the model and model calibration would be based on feedback from the pilot plant).
- Finally, a series of three weeklong (Monday to Friday) trials, with the plant under 24 hour supervision over a period of 105 hours, would be conducted with the objectives of further refining the calibration of the model and optimisation of the pilot plant in an iterative manner.

6.11.1 Short Runs

Experimental Design and Objectives

The plant was operated for approximately 8 hours during the short run experiments. Each short run performed had a different "fresh" CO₂ dosing and the sidestream flowrate was maintained at 463 L/hr. In this way an understanding of the pilot plant performance at various doses of CO₂ could be obtained. The results obtained from these runs were then compared to what was predicted by the SSP-MOD model.

Experimental Results and Discussion

The following graphs (Figure 6.6) show the actual (from SSP pilot plant operation – shown first) and predicted (from SSP-MOD model- shown second) CaCO₃ uptake vs. the CO₂ dose. It must be noted that the graph obtained from the SSP-MOD model is for a particular vacuum generated (namely 30 kPa), whereas the pilot plant results were obtained at varying vacuum pressures. (This will be discussed in more detail shortly).

The graphs show that the SSP-MOD model predicts that a higher CaCO₃ uptake can be achieved for a particular CO₂ dose than what is predicted from pilot plant operation. This is due to the fact that the SSP-MOD model does not include limestone dissolution kinetics (but assumes CaCO₃ dissolved to equilibrium quantities). The SSP-MOD model output shows that for high CO₂ recoveries (in excess of 60%) very high CO₂ doses (> 1000 mg/L) are required. At lower doses of CO₂ (e.g. at 700 mg/L), relatively low CO₂ recoveries (~ 25%) can be expected. In addition, from the SSP-MOD model it appears as though at a dose of approximately 800 mg/L, no additional benefit is gained from the subsequent addition of CO₂ (as evidenced from the levelling off of the "CaCO₃ uptake/CO₂ dose" curve). Although, from the SSP pilot plant data, it generally appears as though the "CaCO₃ uptake/CO₂ dose" curve is also levelling off this cannot be stated with much certainty.

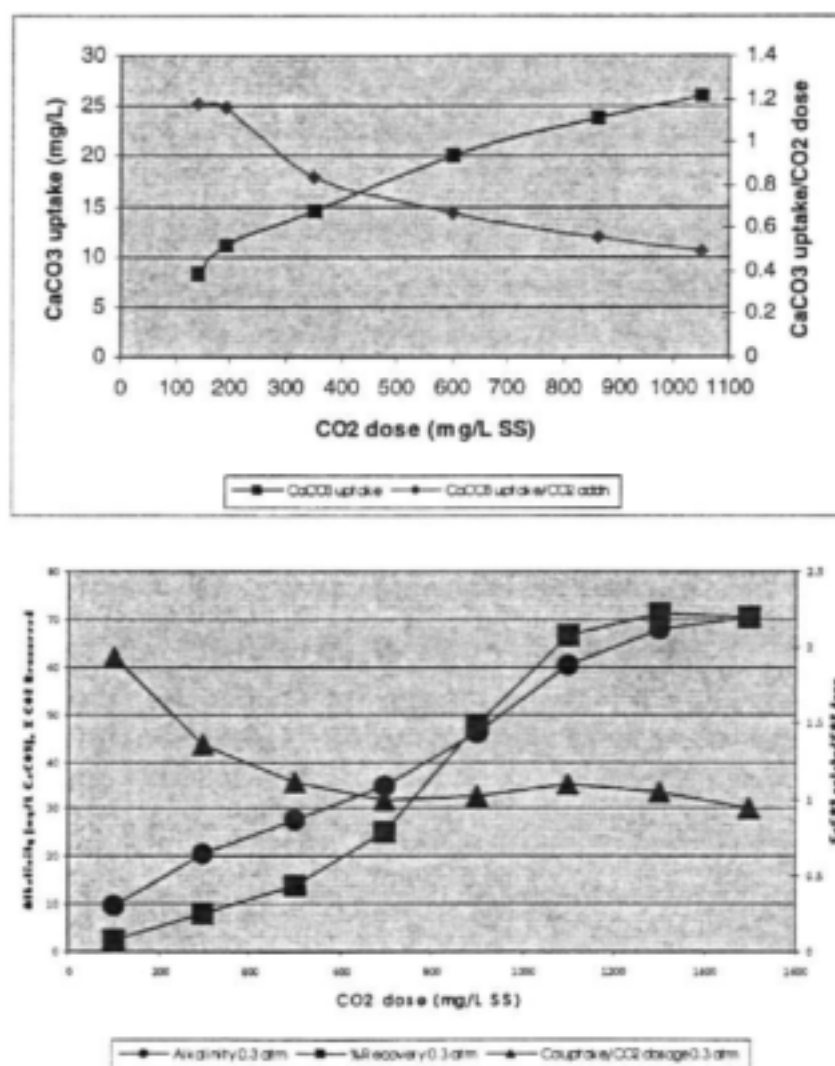


Figure 6.6: Short runs: actual and predicted CaCO₃ uptake vs. CO₂ dosage

Furthermore, the short runs revealed that with an increase in fresh CO₂ dose into the third dissolution vessel (DV3) (and therefore a increase in the amount of CO₂ the eductor must recover at the recovery vessels), the vacuum generated in the recovery vessels decreased. Results obtained are shown in the following table (vacuums recorded are maximum values obtained during the short run experiment).

Table 6.1: Maximum vacuums generated during short runs for a particular CO₂ dose

CO ₂ DOSE (MG/L)	CO ₂ DOSE (KG/HR)	VACUUM GENERATED IN RV1 (KPA)	VACUUM GENERATED IN RV2 (KPA)
140	0.065	34	30
190	0.088	39	35
350	0.16	45	40
600	0.28	58	54
860	0.40	70	66
1050	0.49	84	79

The above table clearly shows the decrease in vacuum with increasing "fresh" CO₂ dose. However, of critical importance is the fact that if we were able to recover all the CO₂ dosed (i.e. 100% CO₂ recovery) the resultant recovered gas stream would still be significantly smaller than the design suction flow in all cases (design criteria of the eductor is a suction capacity of ~36.1 kg/hr of CO₂ and a vacuum pressure of 20 kPa). Both leak checks and analysis of the pressure measuring equipment showed that no discrepancies/malfunctions had occurred. Although it is understandable that a vacuum of 20 kPa might not necessarily be obtained (due to piping configuration, friction losses, etc), the eductor should be able to maintain the desired vacuum conditions of ~ 30 kPa, for any of the above CO₂ doses. As the experiments were only conducted for a period of one day it was thought that by operating the pilot plant for longer periods of time, the vacuum generated might increase further. It was therefore decided to conduct a long run experiment using the knowledge gained from the short runs.

Another aspect that was tested during the short runs was the use of air to aid CO₂ stripping. In preliminary investigations using SSP-MOD it was found that the addition of approximately 5 L air/L sidestream decreased the amount of CO₂ that was recovered. The project team, however, felt that the use of air may be beneficial and assist CO₂ stripping, as this had been assessed and verified in previous pilot plant trials.

Studies were therefore conducted to assess the influence of air on the CO₂ stripping efficiency within the recovery columns on the pilot plant. These tests revealed that with the addition of air into the recovery columns, the vacuum steadily decreased and that atmospheric pressure (i.e. 100 kPa – i.e. no vacuum)

was obtained between 1 – 3 hours after the addition of air had started (depending on the amount of air that was added). This is a practical limitation brought about by the use of eductors on the existing pilot plant. Therefore if investigation using SSP-MOD revealed that air does aid CO₂ stripping, the use of eductors in full-scale industrial applications would be compromised.

Conclusions: Short Run Experiments

Short run experiments conducted showed that:

- Although the SSP-MOD model showed higher CaCO₃ uptakes (due to the fact that CaCO₃ dissolution kinetics are not used), the model showed similar trends to what was obtained from operation of the pilot plant.
- Analysis of short run data showed that an increasing “fresh” CO₂ dose resulted in a decrease in the vacuum generated. This was a cause for concern as the amount of CO₂ in the SSP pilot plant system was much lower than the oversized design specifications of the eductor. The project team, however, felt that decreased vacuum readings recorded at this stage could be temporary (and therefore exaggerated on short runs), and hence would not be evident in the longer operational time period of subsequent long runs.
- During experiments it became apparent that the eductor was sensitive to the addition of air to the recovery vessels. Experiments showed that the vacuum generated with the recovery vessels decreased to atmospheric pressure within a few hours of operation, once air had been added (regardless of the amount of air that was added). This is in contrast to prior plant observations (using vacuum pumps), which showed that the addition of air could aid CO₂ stripping, and recovery. If subsequent modelling found that air addition was beneficial, the use of eductors would be compromised.

Following the short runs, a series of long runs were conducted.

6.11.2 Long Run 1

Experimental Design and Objectives

From analysis of both the short run data and the output from the SSP-MOD model, it was decided to run the SSP pilot plant with a “fresh” CO₂ dose of approximately 800 mg/L. This run would therefore confirm the results obtained from the previous short run and provide further data for comparison with SSP-MOD. In addition, following the results obtained from the short run experiments, the behaviour of the SSP pilot plant with respect to vacuum generation would also be monitored.

During the first 15 hours of operation the pilot plant was operated to determine the “Bones Curve”. During this period the “fresh” CO₂ dose was varied between approximately 90 to 1600 mg/L. The resultant product water total alkalinity at these CO₂ doses would then be used to construct the so-called “Bones Curve A” of CaCO₃ uptake vs. CO₂ dose. At the end of this procedure, the plant was operated in CO₂ recovery mode for a further 72 hours. The average “fresh” CO₂ dosed

during this period was found to be 788 mg/L. Finally, at the end of pilot plant operation in CO₂ recovery mode, the pilot plant was operated to determine the "Bones Curve B".

Experimental Results and Discussion

After the run was completed, the following graph of CaCO₃ uptake vs. vacuum pressure in the recovery vessels was drawn.

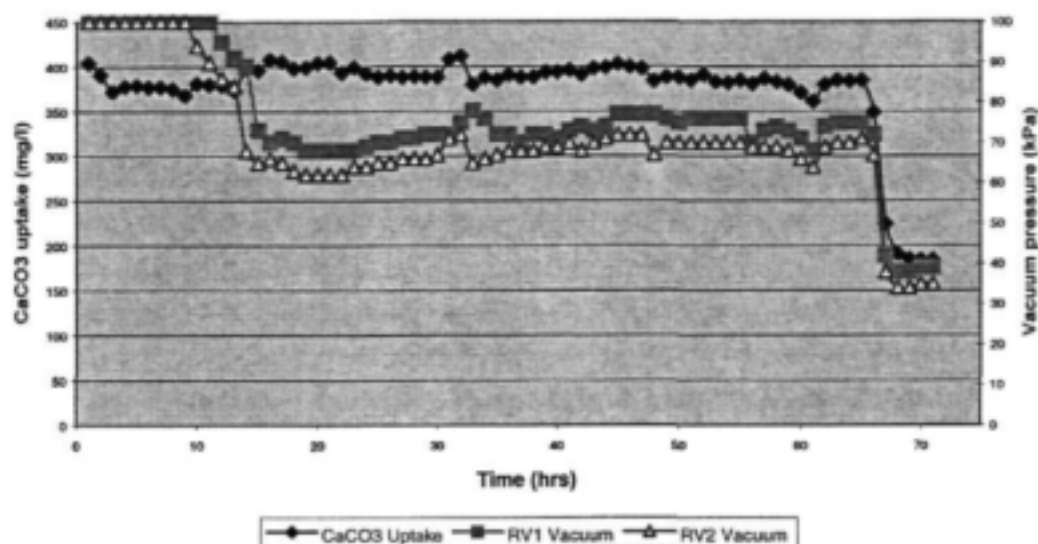


Figure 6.7: Long Run 1: Calcium carbonate uptake and vacuum pressure in recovery vessels

The graph indicates the calcium carbonate uptake of the sidestream. The average feed total alkalinity was 18.3 mg/L (as CaCO₃) and the total alkalinity in the final sidestream varied between 386 mg/L (as CaCO₃) (low) and 422 mg/L (as CaCO₃) (high), and was generally between 400 and 410 mg/L (as CaCO₃) for the duration of the experiment. In addition, the results indicate that the vacuums generated within the recovery vessels gradually increased and levelled off after approximately 18 hours of operation at 62 and 68 kPa. Vacuum pressures recorded for the remaining duration of the experiment were more or less constant after this. These low vacuum pressures were similar to what was experienced during the short run experiments (i.e. decreased vacuums at higher "fresh" CO₂ dose). Due to this inefficient operation of the eductor, the amount of "fresh" CO₂ dosed was lowered towards the end of the experiment to approximately a quarter of the original dose. This immediately resulted in a significant increase in the vacuum pressure generated and after approximately four hours of operation, the vacuum pressure was approximately 38 kPa in RV1 and 34 kPa in RV2. This confirmed that the eductor was not operating according to its design specifications, and that a decrease in vacuum was being experienced with an increase in "fresh" CO₂ dosed.

The Model LM ½" A eductor was oversized and should therefore be able to draw a high vacuum at much higher CO₂ doses than was dosed in the experiment. The eductor was therefore not operating according to its design specifications. This problem was raised with both the South African distributors and manufacturers from the United States of America. Neither party, however, could provide meaningful comment as to why the eductor failed or what solutions could be employed to rectify the situation. The project team expressed their concern and disappointment over this state of affairs, and appealed to both parties to set matters straight. At the end of the project, a meaningful response had not yet been received.

The "Bones Curves" were used to calculate the quantity of CO₂ recovered. The percentage CO₂ recovered was calculated by dividing the actual amount of CO₂ recovered (by calculation from the "Bones Curve"), by the sum of the quantity of CO₂ dosed during that time period (788 mg/L) and the CO₂ recovered. The following graph shows the CO₂ recovered during the experiment.

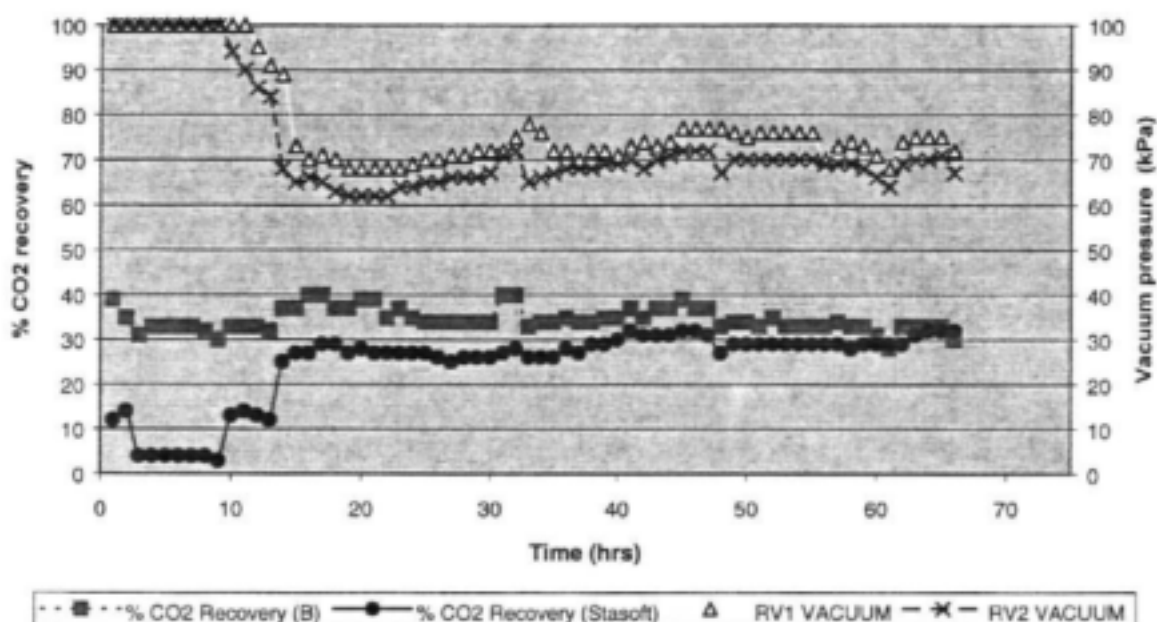


Figure 6.8: Long Run 1: CO₂ recovery

The results indicated that the CO₂ recovered varied between 30 – 40% (average of 35%) for the duration of the experiment. These results were confirmed using STASOFT 4.

Detailed results for this experiment are shown in **APPENDIX 6C**.

Conclusions: Long Run 1

The long run experiment showed that:

- The problem relating to the generation of low vacuums in the recovery vessels (first observed during the short run experiments) persisted in the long run experiment (increasing "fresh" CO₂ dose decreases the vacuum generated). The vacuum pressure within the recovery vessels during the long run experiment was approximately 62 – 68 kPa. When the "fresh" CO₂ dose was lowered at the end of the long run the vacuum increased to approximately 34 – 38 kPa. This problem was raised with both the South African distributors and manufacturers from the United States of America, but neither party could provide meaningful comment as to the reason why the eductor failed.

Therefore, although considerable efforts were made to ensure that a correctly sized eductor was obtained; the eductor could not meet the required design specifications. The project team expressed their concern and disappointment over this state of affairs, and appealed to both parties to respond meaningfully as a matter of urgency. (At the end of the project a meaningful response had not yet been received.)

- With the aforementioned sub-optimal performance of the eductor, a CO₂ recovery of approximately 30 – 40% (average of 35%) was measured.

In addition, due to the problems experienced with the eductor it was felt that it was premature to calibrate the SSP-MOD model at the end of Long Run 1, and that calibration would occur at the end of subsequent long runs, once a better understanding of the limitations of the pilot plant was obtained.

6.11.3 Long Run 2 and 3

Experimental Design and Objectives

Due to the problems experienced in Long Run 1 (low vacuums and lack of meaningful comment from the manufacturers) it was decided to operate the pilot plant at a "fresh" CO₂ dose of approximately 300 mg/L, the motivation being that although the SSP-MOD model had shown that at such a dose, a lower CO₂ recovery would be achieved, short run data showed that this CO₂ dose would allow one to obtain a relatively high vacuum of 40 kPa. The data gathered could then be used to further assess the effectiveness of the SSP-MOD model for predicting the behaviour of the SSP. The same procedure as in Long Run 1 was again followed.

Experimental Results and Discussion

After the run was completed, the following graphs of CaCO₃ uptake vs. vacuum pressure in the recovery vessels were drawn.

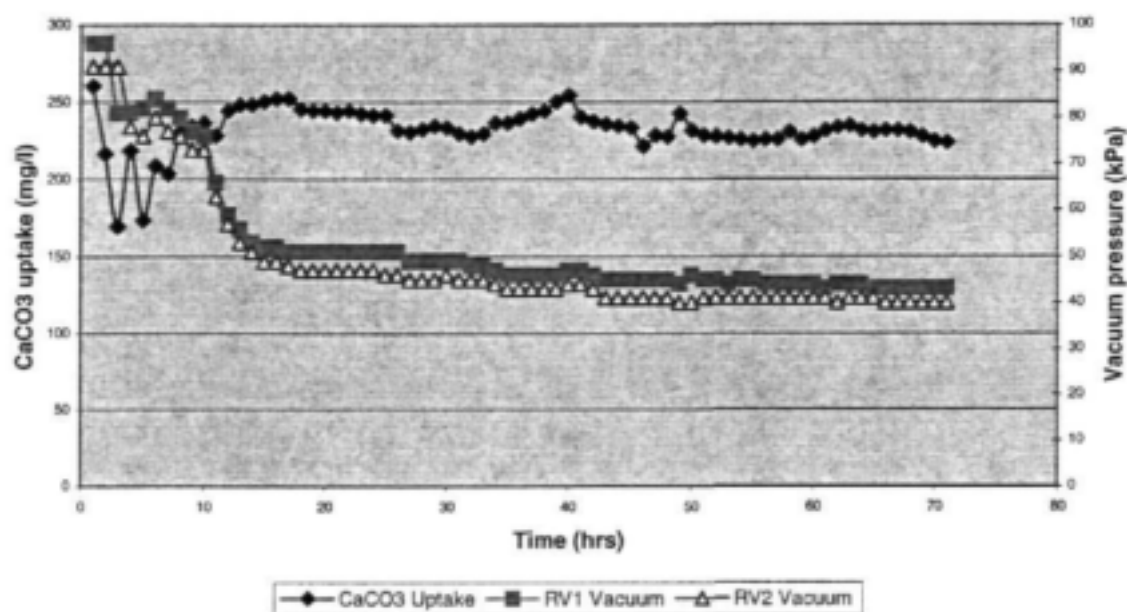


Figure 6.9: Long Run 2: Calcium carbonate uptake and vacuum pressure in recovery vessels

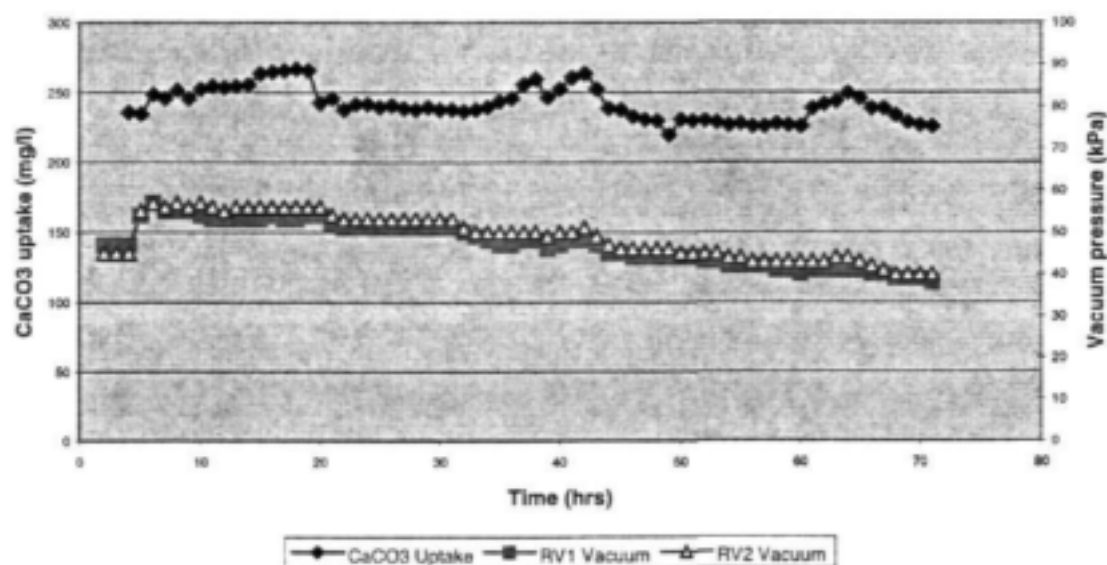


Figure 6.10: Long Run 3: Calcium carbonate uptake and vacuum pressure in recovery vessels

The graphs indicate the calcium carbonate uptake of the sidestream. In Long Run 2 (**Figure 6.9**) the average feed total alkalinity was 19.7 mg/L (as CaCO_3) and the total alkalinity in the final sidestream varied between 240 mg/L (as CaCO_3) (low) and 287 mg/L (as CaCO_3) (high), and was generally approximately 250 mg/L (as CaCO_3) for the duration of the experiment. In Long Run 3 (**Figure 6.10**) the average feed total alkalinity was 20.7 mg/L (as CaCO_3) and the total alkalinity in the final sidestream varied between 241 mg/L (as CaCO_3) (low) and 274 mg/L (as CaCO_3) (high), and was generally between 250 and 270 mg/L (as CaCO_3) for the duration of the experiment.

In Long Run 2, CO_2 dosing and vacuum generation occurred simultaneously. The results in **Figure 6.9** indicate that the vacuums generated within the recovery vessels gradually increased and levelled off at a vacuum of approximately 40 kPa. The graph further indicates that although the vacuum generally increased over time, no significant change in the calcium carbonate uptake occurred (indicating that no additional CO_2 was being recovered). This suggests that an increase in vacuum alone on the pilot plant may not be sufficient to achieve higher CO_2 recoveries (this will be further discussed once CO_2 recovery results are presented).

In Long Run 3 it was decided to first try and build a steady vacuum before dosing any CO_2 . This was to try and overcome any vacuum generation decrease (as a result of CO_2 dosing) and to see if first building a vacuum improved performance with respect to CO_2 recovery. **Figure 6.10** shows that after approximately 3 hours of operation the vacuum within the recovery vessels was approximately 45 kPa. At this stage CO_2 dosing commenced. At the start of CO_2 dosing the vacuum within the recovery vessels immediately decreased after which it again gradually increased over the course of the experiment. The vacuum generated within the recovery vessels levelled off at a vacuum of approximately 40 kPa. The graph again indicates that although the vacuum generally increased over time, no significant change in the calcium carbonate uptake occurred (indicating that no additional CO_2 was being recovered). This confirms results obtained in Long Run 2.

Again, the "Bones Curve" data was used to calculate the quantity of CO_2 recovered. The percentage CO_2 recovered was calculated by dividing the actual amount of CO_2 recovered (by calculation from the "Bones Curve"), by the sum of the quantity of "fresh" CO_2 dosed during that time period (302 mg/L Run 2 and 319 mg/L Run 3) and the CO_2 recovered. The following graphs show CO_2 recovery data for both Long Run 2 and Long Run 3.

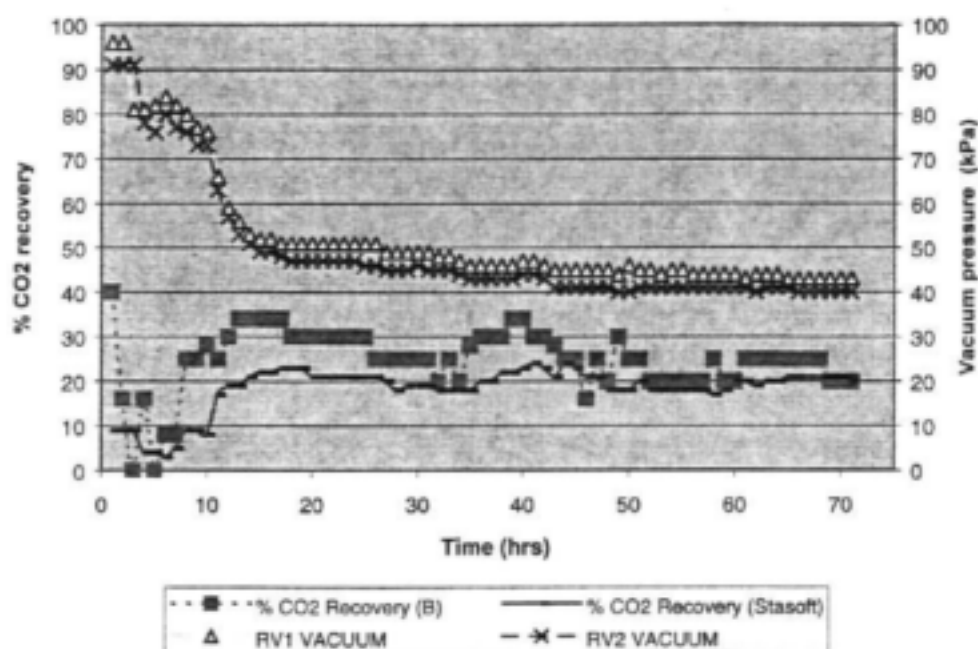


Figure 6.11: Long Run 2: CO₂ recovery

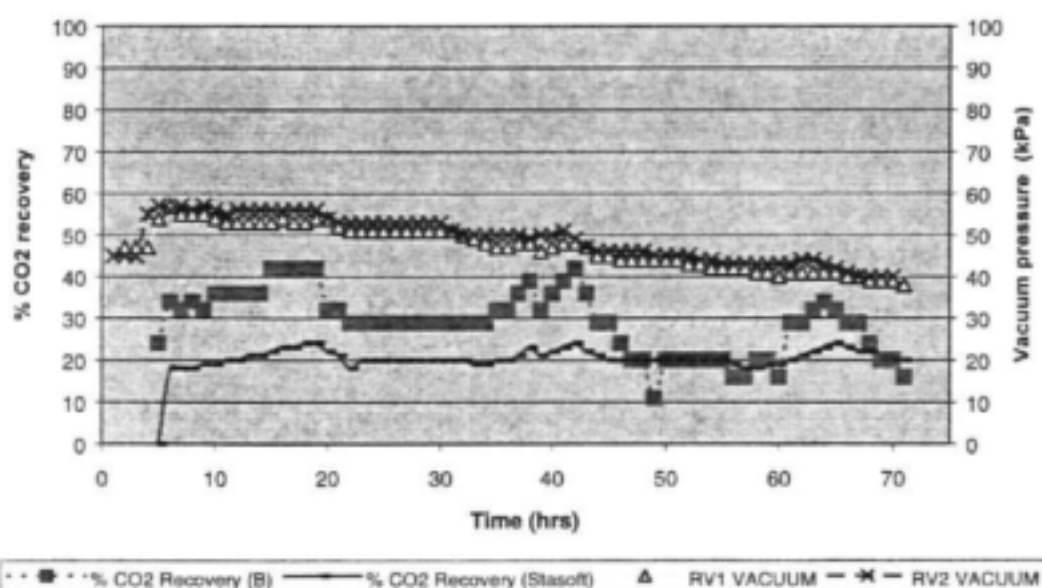


Figure 6.12: Long Run 3: CO₂ recovery

The results indicated that for Long Run 2, the CO₂ recovered generally varied between 20 – 30% (average of 25 %) and that CO₂ recovered in Long Run 3 generally varied between 20 – 40% (average of 29 %) for the duration of the experiment. From the graphs it also appears as though an increase in vacuum in the range of 15 kPa over the course of the experiment did not necessarily result in an increase in CO₂ recovery. This result correlates with model predictions at low “fresh” CO₂ doses (see CHAPTER 5 – section 5.7.2).

Detailed results for this experiment are shown in **APPENDIX 6D** and **6E**.

Conclusions: Long Run 2 and 3

The long run experiments showed that:

- Reasonable vacuums of approximately 40 kPa could be obtained in the recovery vessels if a lower CO₂ dose of approximately 300 mg/L was added to the sidestream.
- CO₂ recoveries of approximately 20 – 30% (average of 25%) were measured for a vacuum of 40 kPa in Long Run 2 and 20 – 40% (average of 29%) for a vacuum of 40 kPa in Long Run 3.
- An increase in vacuum from ~ 55 kPa to ~ 40 kPa over the course of the experiment did not appear to influence the amount of CO₂ recovered. This result correlates with model predictions at low “fresh” CO₂ doses (below ~ 500 mg/L “fresh” CO₂ – see CHAPTER 5, section 5.7.2).
- Comparison of Long Run 2 and Long Run 3 data showed that SSP pilot plant experiments were reproducible.

Data gathered from the long runs would subsequently be used to calibrate the model.

6.11.4 Analysis of Long Run Results using the SSP-MOD Model

Following the pilot plant trials, calibration of the *SSP-MOD* model could commence. The following data obtained from the long runs were used as input parameters for the model:

- Raw water characteristics (as from sample analysis)
- Average “fresh” CO₂ dosed to the sidestream (as measured from mass loss of a CO₂ cylinder)
- CaCO₃ uptake (from calcium and total alkalinity determinations)
- Vacuum pressure within the recovery vessels

Using these inputs model simulations were carried out. Analysis of the output results obtained showed that:

- The model accurately predicts conditions of the sidestream for the stages CO₂ addition/dissolution and CaCO₃ dissolution.
- Discrepancies exist between model predictions and the SSP pilot plant with regards to the amount of CO₂ stripped and recovered. For example, in Long Run 1 a CO₂ recovery of 30 – 40% was recorded, using the “Bones Curve” analysis method. This method of analysis was thought to be an accurate way of determining the amount of CO₂ recovered. *STASOFT 4* was used to correlate data obtained from Long Run 1, and showed that the method for calculating CO₂ recovery was appropriate, with results obtained from the “Bones Curve” method correlating *STASOFT 4* CO₂ recovery calculations. The *SSP-MOD* model,

however, predicted that when using the specified input parameters, a much lower CO₂ recovery of approximately 5% would be obtained.

This procedure was repeated for both Long Run 2 and 3. This showed that the model again predicted a very low CO₂ recovery of ~ 4.5%, compared to an observed recovery of ~ 20 – 40%.

Results obtained from pilot plant operation therefore showed that higher CO₂ recoveries were obtained than what was predicted from the SSP-MOD model.

Following this result the following actions were carried out:

- The validity of the assumptions used in model generation were reviewed and confirmed.
- The algorithms developed and used in the SSP-MOD model were reviewed, checked and verified.
- Manual materials mass-balances were conducted for the inert gases ("air") and carbonic species, and were found to be accurate.
- The Henry/Dalton equations used in the in the dissolution and recovery vessels were reviewed and verified.
- Carbonate chemistry calculations in the dissolution, recovery and limestone vessels were verified using STASOFT 4 determinations.

During this review and validation period a number of minor mistakes were found in the SSP-MOD model. However, after correction, the model still predicted much lower CO₂ recoveries than what had been obtained from pilot plant operation.

Additional Gas-Liquid Equilibrium Stages

The original SSP-MOD program utilised a single stage gas-liquid equilibrium stage tripper to model the CO₂ stripping and recovery step of the SSP. The project team therefore investigated the influence of additional gas-liquid phase equilibrium stages on model predictions of CO₂ recovery. The model was altered to allow the user to include a number of equilibrium stages (i.e. similar to simulating a distillation column), in an attempt to address the low recoveries obtained. Using a 3 stage gas-liquid equilibrium stripping model, the CO₂ recoveries obtained increased, but were still not similar to results obtained from pilot plant operation (e.g. for Long Run 1 the amount of CO₂ recovered was approximately 8% - vs. 5% for a single stage gas-liquid equilibrium stripping model and 30 – 40% obtained from pilot plant operation). In addition, analysis showed that the amount of CO₂ that could be recovered started to

taper off after 3 stages (and would therefore not reach a CO₂ recovery level of 30 – 40% with additional stages.

"B" Factor

The "B" factor used in the *SSP-MOD* model is related to the amount of undissolved gas that is purged from the dissolution vessels after the addition of the recovered CO₂ (and before the addition of "fresh" CO₂) (discussed in more detail in CHAPTER 5). By varying the "B" factor (between 0.1 and 1), different amounts of both CO₂ and air would be purged from the dissolution vessels. In previous model simulations a "B" factor input of 1 had been used (i.e. all the undissolved gas is purged). This was a reasonable assumption as undissolved gas is constantly purged from the dissolution vessels on the SSP pilot plant.

However, due to discrepancies experienced, the project team investigated the influence of varying the "B" factor. These investigations showed that CO₂ recoveries similar to what was obtained during pilot plant operation, could only be simulated at very low "B" factors between 0.2 and 0.1 (i.e. the majority of the undissolved gas is retained within the system). This was, however, not the case during pilot plant operation as this would have led to a visible accumulation of gas within the dissolution vessels, which did not occur.

At this stage it became clear that despite considerable efforts by the project team, deviations between model predictions and pilot plant operation occurred when no air was introduced into the CO₂ recovery vessels. At the close of the project a meaningful explanation as to why such discrepancies existed when no air was added into the recovery vessels had not been reached. Nevertheless, based on observations from historical pilot plant operation where it seemed that small amounts of air improved CO₂ recovery, further modelling with the addition of air to the recovery vessels would be investigated.

Influence of Air on CO₂ Stripping and Recovery

In pilot plant operation prior to this project, air had been used to aid CO₂ stripping and recovery, and the belief existed that nominal doses of air improved CO₂ recovery. However, in the preliminary investigation using the *SSP-MOD* model (see CHAPTER 5), the model predicted that with the addition of a significant amount of air (5 L air/L sidestream) the amount of CO₂ that was recovered decreased. In order to address this apparent contradiction, the project team therefore now used the model to simulate the addition of smaller amounts of air in an attempt to aid CO₂ stripping and recovery. (Unfortunately, this could not be assessed using the pilot plant as a result of the negative impact on performance of the eductor, in turn resulting in decrease in vacuum).

The SSP-MOD investigation revealed that if small amounts of air were added to the recovery vessels (between 0.1 – 1 L air/L sidestream) CO₂ stripping and recovery could theoretically improve, if high vacuums could be maintained. The results obtained are presented in Figure 6.12 below. The model simulation was based on results obtained from Long Run 1 and utilises a 3 stage gas-liquid equilibrium stripping vessel (as apposed to the use of a single stage gas-liquid equilibrium stripping vessel).

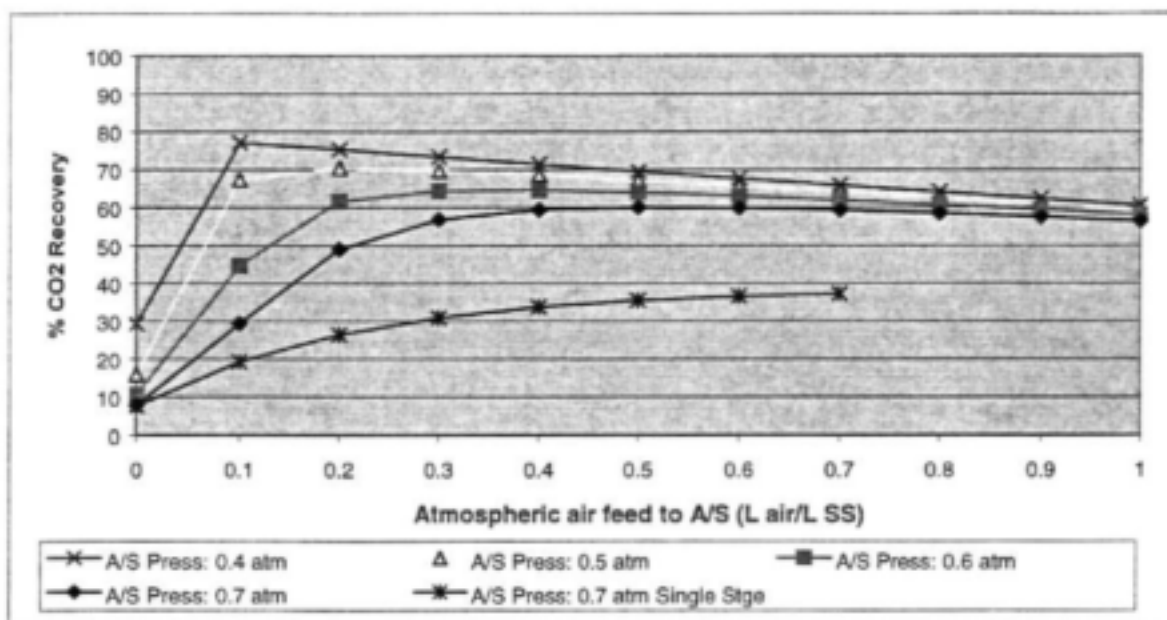


Figure 6.13: Three stage CO₂ stripping and recovery model based on a "fresh" CO₂ dose of 788 mg/L (i.e. Long Run 1)

The graph indicates that increased vacuum pressure results in increased CO₂ recoveries (e.g. if the vacuum pressure can be increased from 70 kPa to 40 kPa, an increase in CO₂ recovery from ~ 10% to ~ 30% could be expected). Furthermore, the graph indicates that the addition of very small quantities of air aids CO₂ stripping and recovery and that theoretical CO₂ recoveries of almost 80% could be expected if 0.1 L air/L sidestream was added, while maintaining a vacuum pressure of 40 kPa (for current pilot plant operation using the Model LM ½" A eductor this would translate into the addition of ~ 46 L/h of air).

These modelling based observations need to be seen in relation to historic pilot plant results. Historical pilot plant operation using vacuum pumps (vacuum pressure ~ 50 kPa) and a "fresh" CO₂ dose of ~ 333 mg/L, yielded a CO₂ recovery of ~ 62% (see CHAPTER 2, section 2.4). During this experiment a small amount of air was added, as it was believed to assist CO₂ recovery. Subsequent pilot plant tests using the eductor (vacuum pressure ~ 40 kPa) and a "fresh" CO₂ dose of ~ 302 mg/L (Long Run 2) and ~ 319 mg/L (Long Run 3), yielded a CO₂ recovery of ~ 25% (average) and 29% (average) respectively (see section 6.10.3). Bearing the relative poor performance

of the eductor in mind, the only other significant difference between the experiments was as a result of the introduction of air into the recovery vessels. This result therefore supports model findings of improved CO₂ recovery with the addition of low amounts of air.

Experiments were therefore conducted on the pilot plant to assess the performance of the SSP process with the introduction of air into the recovery vessels. Air was bled in using air rotameters (calibrated between 0 - 2500 L/hr of air) that had previously been employed in the SSP pilot plant trials using vacuum pumps. Using the eductor it was found that when air was added to the recovery vessels, the vacuum generated in the recovery vessels decreased with time, and that within 1 - 3 hours (depending on the amount of air added) the pressure within the recovery vessel was at atmospheric pressure (i.e. no vacuum). This is a serious limitation of the use of eductors as the SSP-MOD model has shown that the addition of small amounts of air into the recovery vessels will benefit CO₂ stripping and recovery. Previous experiments using vacuum pumps showed that air could be added into the recovery vessels without a decrease in vacuum in the recovery vessel being experienced. This result compromises the further use of eductors. Due to these significant developments further testing of the eductor was discontinued.

6.12 CONCLUSIONS: PILOT PLANT OPERATION AND ASSESSMENT OF SSP-MOD

Use of an eductor as opposed to vacuum pumps was chosen as eductors have the following potential advantages over vacuum pumps: low cost, simple and reliable, ease of installation, non-electrical unit, corrosion and erosion resistant.

During the testing and operation of the SSP pilot plant using an eductor, the following important observations were made:

- The use of an eductor ensures that a steady vacuum can be obtained. This is in contrast to what could previously be obtained on the pilot plant using vacuum pumps, where decreases in vacuum generation efficiency often occurred.
- For the successful operation of the SSP, the use of a correctly sized eductor is of critical importance. However, during this project both eductors tested did not operate at the required design specifications. This was despite considerable effort being made by the project team to ensure that correctly sized eductor's were obtained.
 - ♦ Investigation revealed that in the first instance the distributors provided incorrect specifications for the eductor. In the second instance, it again became apparent that the eductor was not operating as expected. This problem was raised with both the South

African distributors and manufacturers from the United States of America, but neither party could provide meaningful comment as to the reason why the eductor failed.

- ♦ Therefore, although considerable efforts were made to ensure that a correctly sized eductor was obtained, the eductor could not meet the required design specifications. The project team expressed their concern and disappointment over this state of affairs, and appealed to both parties to respond meaningfully as a matter of urgency. At the end of the project, a meaningful response had not yet been received. This poor service puts the use of eductors in a negative light.
- Three "Long Run" pilot plant experiments were conducted under the following conditions:
 - ♦ Low vacuum, high "fresh" CO₂ dose (Long Run 1)
 - ♦ High vacuum, low "fresh" CO₂ dose (Long Run 2 and 3)

From these tests the following observations were made:

- ♦ Data obtained from Long Run 1 (low vacuum – approximately 62 - 68 kPa, high "fresh" CO₂ dose – 788 mg/L) showed that even though pilot plant performance was not optimal (due to poor performance of the eductor) CO₂ recoveries of 30 – 40 % were obtained.
- ♦ In addition, data obtained from Long Run 2 and Long Run 3 (high vacuum – approximately 40 - 45 kPa, low "fresh" CO₂ dose – 302 mg/L and 319 mg/L respectively) showed that CO₂ recoveries of 20 – 40 % were obtained.

Due to the non-performance of the eductor, a long run incorporating high vacuum and a high "fresh" CO₂ dose could not be conducted.

- At the end of the pilot plant trials, outputs from the SSP-MOD model were compared with data obtained from pilot plant operation. These investigations revealed that:
 - ♦ The model accurately predicted the characteristics of the feed, CO₂ acidified sidestream and sidestream after CaCO₃ uptake.
 - ♦ The model, however, predicted a significantly lower CO₂ recovery than what had been experienced during pilot plant operation (e.g. for Long Run 1 the model predicted a CO₂ recovery of ~ 8 %, while a CO₂ recovery of 30 – 40 % had been obtained from pilot plant operation).
 - ♦ Subsequent review and analysis of the model yielded no significant errors in the model, and at the close of the project a meaningful explanation as to why such discrepancies had occurred had not been reached.
 - ♦ Based on observations from historical pilot plant operation where it seemed that small amounts of air improved CO₂ recovery, further modelling with the addition of air to the recovery vessels was

investigated. The SSP-MOD model showed that the addition of small amounts of air (0.1 – 1 L air/L sidestream) could aid CO₂ recovery, and that, based on data from Long Run 1, CO₂ recoveries as high as 70% could be achieved if a high vacuum pressure could be maintained within the recovery vessel. This result therefore confirms historical pilot plant observations.

- ♦ A significant limitation with regards to the use of eductors is the unit's non-capability of maintaining a vacuum with addition of even nominal levels of air to the recovery vessels. This result compromises the further use of eductors.

6.13 CHAPTER 6 - REFERENCES

- (1) Chemguard: Hand line nozzles and Eductors (1999) www.chemguard.com
- (2) Penberthy: Installation, operation, maintenance for models LL, LH, ELL, GL, GH jet pumps –CGM MATERIALS manufacturers.

APPENDIX 6A

SHORT RUN

Table 6A-1: Pressure measurements

TIME	P ₁ kPaG	P ₂ kPaG	P ₃ kPaG	P ₄ kPaG	V ₁ kPaG	V ₂ kPaG	RV2 kPaG	M ₁ mmHg	M ₂ mmHg	M ₁ kPaG	M ₂ kPaG
9:25	550	555	170	160	-38	-40	-42	300	297	-40.00	-39.59
9:35	550	550	170	155	-46	-48	-48	356	354	-47.46	-47.19
9:45	540	550	170	155	-46	-47	-50	336	335	-44.79	-44.66
9:55	540	550	170	160	-48	-56	-56	387	387	-51.59	-51.59
10:05	540	550	169	160	-48	-53	-54	383	417	-51.06	-55.59
10:15	540	550	170	160	-48	-53	-54	381	376	-50.79	-50.12
10:25	540	550	170	160	-46	-52	-54	376	370	-50.12	-49.32
10:35	540	550	170	160	-50	-44	-54	350	366	-46.66	-48.79
10:45	540	550	170	160	-52	-44	-52	340	344	-45.32	-45.86
10:55	540	550	170	160	-44	-46	-50	332	335	-44.22	-44.66
11:05	550	560	170	160	-50	-53	-56	385	384	-51.32	-51.19
11:15	550	560	160	150	-56	-58	-60	422	430	-56.22	-57.32
11:25	550	560	160	150	-60	-64	-66	471	469	-62.79	-62.52
11:35	550	560	160	150	-62	-64	-66	472	471	-62.92	-62.79
11:45	550	560	160	150	-61	-64	-66	470	470	-62.66	-62.66
11:55	550	560	160	150	-61	-66	-66	465	463	-61.99	-61.72
12:05	550	560	160	150	-62	-65	-66	475	470	-63.32	-62.66
12:15	560	565	160	150	-64	-65	-66	481	480	-64.12	-63.99
12:25	560	560	160	150	-64	-65	-66	491	485	-65.46	-64.66
12:35	560	560	160	150	-65	-66	-68	487	486	-64.92	-64.79
12:45	560	560	160	150	-65	-67	-68	482	480	-64.26	-63.99
12:55	560	560	160	150	-64	-65	-68	474	470	-63.19	-62.66
13:05	560	560	160	150	-63	-65	-68	468	468	-62.39	-62.39
13:15	560	560	160	150	-63	-65	-66	470	465	-62.66	-61.99
13:25	560	565	160	150	-64	-65	-68	477	475	-63.59	-63.32
13:35	560	560	160	150	-64	-65	-68	483	478	-64.39	-63.72
13:45	550	560	160	150	-64	-65	-68	482	476	-64.26	-63.46
13:55	550	560	160	150	-64	-65	-70	483	477	-64.39	-63.59
14:05	550	560	160	150	-64	-66	-68	484	480	-64.52	-63.99
14:15	550	560	160	150	-65	-67	-70	494	487	-65.86	-64.92
14:25	550	560	160	150	-66	-67	-70	495	490	-65.99	-65.32
14:35	550	560	160	150	-66	-67	-70	496	495	-66.12	-65.99
14:45	550	565	160	150	-66	-68	-70	505	495	-67.32	-65.99
14:55	560	565	160	150	-67	-68	-70	503	498	-67.06	-66.39
15:05	560	565	160	150	-67	-68	-70	510	503	-67.99	-67.06
15:15	560	565	160	150	-67	-64	-70	513	507	-68.39	-67.59
15:25	560	565	160	150	-67	-64	-70	516	510	-68.79	-67.99
15:35	560	570	160	150	-67	-70	-70	520	513	-69.32	-68.39
15:45	560	570	160	150	-67	-72	-70	522	520	-69.59	-69.32
15:55	560	570	160	150	-67	-71	-72	526	525	-70.12	-69.99

RV2 - Vacuum gauge on RV2

M₂ - RV2's manometer

Table 6A-2: pH and CO₂ dosing using both RV1 and RV2

Time	Feed pH	Dischge pH	DV1 pH	DV2 pH	DV3 pH	L/stone pH	RV1 pH	RV2 pH	CO ₂ dose (g/L)	STASOFT CO ₂ (g/L)	% CO ₂ Recovery
9:25	8.3	8.68	8.40	8.37	8.05	8.67	8.17	8.48			
9:35	8.42	8.64	8.67	8.11	8.11	8.75	8.15	8.49			
9:45	8.48	8.78	8.75	8.31	8.20	8.78	8.09	8.53			
9:55	8.53	8.82	8.81	8.36	8.33	8.80	8.02	8.54			
10:05	8.53	8.79	8.83	8.42	8.39	8.86	8.27	8.56			
10:15	8.53	8.78	8.82	8.43	8.41	8.87	8.30	8.56			
10:25	8.53	8.80	8.78	8.43	8.41	8.89	8.32	8.54			
10:35	8.53	8.64	8.80	8.38	8.39	8.92	8.34	8.58			
10:45	8.51	8.73	8.76	8.38	8.39	8.94	8.37	8.58			
10:55	8.51	8.80	8.75	8.37	8.36	8.94	8.38	8.58			
11:05	8.51	8.64	8.72	8.35	8.33	8.98	8.41	8.60			
11:15	8.48	8.77	8.72	8.33	8.31	8.98	8.43	8.62			
11:25	8.48	8.63	8.69	8.30	8.28	8.98	8.43	8.60			
11:35	8.48	8.62	8.66	8.26	8.28	8.98	8.43	8.62			
11:45	8.43	8.61	8.64	8.26	8.26	9.00	8.44	8.62			
11:55	8.42	8.60	8.64	8.25	8.25	9.00	8.44	8.60	0.57	1.5E-4	0
12:05	8.41	8.57	8.63	8.23	4.25	9.01	8.44	8.60	0.57	1.5E-4	0
12:15	8.40	8.56	8.61	8.20	4.26	8.99	8.44	8.60	0.57	1.7E-4	0
12:25	8.38	8.57	8.59	8.20	4.22	7.32	7.68	8.09	0.57	1.7E-4	0
12:35	8.37	7.06	8.34	8.17	4.25	6.67	6.92	7.56	0.57	1.7E-4	0
12:45	8.37	6.3	6.51	7.39	4.24	6.47	6.37	6.82	0.57	1.4E-3	0
12:55	8.35	5.94	6.16	6.09	4.26	6.40	6.21	6.50	0.57	0.027	5
13:05	8.35	5.73	5.89	5.68	4.30	6.36	6.10	6.26	0.57	0.07	11
13:15	8.35	5.55	5.73	5.42	4.25	6.36	6.05	6.13	0.57	0.13	19
13:25	8.36	5.55	5.63	5.23	4.21	6.36	6.04	6.11	0.57	0.20	26
13:35	8.37	5.56	5.6	5.18	4.25	6.36	6.02	6.06	0.57	0.22	28
13:45	8.35	5.55	5.63	5.12	4.21	6.34	6.00	6.02	0.57	0.26	31
13:55	8.35	5.55	5.66	5.18	4.17	6.34	6.00	6.02	0.57	0.22	28
14:05	8.33	5.47	5.56	5.21	4.21	6.33	6.00	6.01	0.57	0.21	27
14:15	8.33	5.39	5.47	5.02	4.24	6.31	6.00	6.02	0.57	0.33	37
14:25	8.34	5.42	5.49	4.98	4.26	6.31	6.00	6.00	0.57	0.36	39
14:35	8.34	5.4	5.47	5.03	4.20	6.31	6.00	6.00	0.57	0.32	36
14:45	8.33	5.38	5.47	5.00	4.20	6.31	6.00	5.99	0.57	0.35	38
14:55	8.32	5.34	5.43	4.96	4.20	6.31	6.00	5.99	0.57	0.38	40
15:05	8.34	5.37	5.4	4.92	4.19	6.31	6.00	5.99	0.57	0.42	42
15:15	8.34	5.33	5.4	4.92	4.20	6.31	5.99	5.99	0.57	0.42	42
15:25	8.33	5.34	5.4	4.9	4.38	6.32	6.00	5.97	0.57	0.44	44
15:35	8.33	5.29	5.37	4.9	4.37	6.32	5.99	5.97	0.57	0.44	44
15:45	8.33	5.34	5.38	4.9	4.38	6.34	5.99	5.97	0.57	0.44	44
15:55	8.33	5.34	5.4	4.91	4.38	6.38	5.97	5.97	0.57	0.43	43

APPENDIX 6B

LONG RUN

Table 6B-1: Pressure and vacuum recorded during extended operation of the SSP

TIME	Sample no.	P ₁ kPaG	V ₁ kPaG	V ₂ kPaG	RV2 kPaG	M ₁ kPaG	M ₂ kPaG
23:00	M1	550	-34	-36	-23	-37	-38
00:00	M2	550	-48	-51	-38	-51	-51
01:00	M3	550	-56	-58	-42	-57	-56
02:00	M4	550	-60	-63	-46	-59	-59
03:00	M5	550	-60	-64	-46	-59	-60
04:00	M6	550	-60	-64	-46	-61	-60
05:00	M7	550	-60	-64	-46	-63	-62
06:00	M8	550	-60	-64	-50	-61	-59
07:00	M9	550	-59	-63	-49	-61	-60
08:00	M10	550	-57	-61	-47	-59	-57
09:00	M11	550	-60	-63	-50	-61	-60
10:00	M12	550	-59	-63	-48	-61	-61
11:00	M13	550	-57	-60	-46	-58	-57
12:00	M14	550	-60	-64	-48	-61	-60
13:00	M15	550	-60	-62	-48	-62	-60
14:00	M16	550	-30	-32	-22	-34	-32
15:00	M17	550	-50	-53	-40	-52	-51
16:00							
17:00	M18	550	-60	-62	-48	-61	-60
18:00	M19	550	-60	-63	-48	-61	-60
19:00	M20	550	-60	-59	-48	-63	-62
20:00	M21	550	-59	-59	-48	-61	-61
21:00	M22	550	-59	-58	-48	-62	-61
22:00	M23	550	-59	-63	-48	-63	-59
23:00	M24	550	-59	-63	-48	-60	-59
00:00	M25	550	-58	-62	-48	-58	-58
01:00	M26	550	-57	-62	-46	-58	-58
02:00	M27	550	-57	-62	-46	-58	-58
03:00	M28	550	-60	-63	-50	-62	-62
04:00	M29	550	-57	-63	-46	-58	-58
05:00	M30	550	-57	-62	-46	-57	-60
06:00	M31	550	-57	-62	-46	-61	-60
07:00	M32	550	-59	-62	-48	-62	-61
08:00	M33	550	-60	-64	-49	-62	-61
09:00	M34	550	-60	-64	-50	-62	-61
10:00	M35	550	-61	-64	-50	-62	-62
11:00	M36	550	-62	-68	-50	-61	-61
12:00	M37	550	-61	-66	-50	-63	-63
13:00	M39	550	-62	-68	-50	-62	-61
14:00	M40	550	-61	-65	-50	-62	-61
15:00	M41	550	-61	-65	-50	-62	-61
16:00	M42	550	-60	-64	-48	-60	-59
17:00	M43	550	-60	-64	-50	-61	-59
18:00	M44	550	-61	-58	-50	-63	-62
19:00	M45	550	-60	-58	-48	-62	-62
20:00	M46	550	-60	-59	-48	-61	-61
21:00	M47	550	-60	-59	-50	-64	-64
22:00	M48	550	-61	-64	-50	-62	-61
23:00	M49	550	-60	-64	-50	-62	-61
00:00	M50	550	-61	-65	-50	-63	-62
01:00	M51	550	-61	-65	-50	-63	-62
02:00	M52	550	-60	-64	-50	-62	-61
03:00	M53	550	-61	-64	-50	-62	-61
04:00	M54	550	-61	-65	-50	-63	-62
05:00	M55	550	-61	-65	-50	-63	-63
06:00	M56	550	-61	-64	-50	-63	-62
07:00	M57	550	-61	-65	-50	-63	-62
08:00	M58	550	-62	-65	-50	-64	-62

09:00	M59	550	-60	-65	-50	-63	-61
TIME	Sample no.	P ₁ KPaG	V ₁ kPaG	V ₂ KpaG	RV2 kPaG	M ₁ kPaG	M ₂ kPaG
10:00	M60	550	-60	-64	-50	-61	-60
11:00	M61	550	-62	-65	-50	-61	-60
12:00	M62	550	-61	-65	-50	-62	-61
13:00	M63	550	-61	-64	-50	-62	-61
14:00	M64	550	-60	-64	-50	-61	-60
15:00	M65	550	-63	-66	-52	-64	-62
16:00	M66	550	-59	-63	-48	-59	-58
17:00	M67	550	-61	-65	-50	-61	-61
18:00	M68	550	-62	-60	-50	-61	-59
19:00	M69	550	-60	-59	-48	-61	-61
20:00	M70	550	-62	-61	-51	-65	-64
21:00	M71	550	-61	-60	-50	-63	-62
22:00	M72	550	-63	-66	-52	-65	-64
23:00	M73	550	-62	-65	-50	-63	-62
00:00	M74	550	-62	-65	-50	-63	-62

Table 6B - 2: pH readings recorded at various stages within the SSP

TIME	Sample No.	FEED pH	ONLINE pH	DV1 pH	DV2 pH	DV3 pH	L/STONE PH	RV1 pH	RV2 pH
23:00	M1	8.57	6.39	4.36	4.49	3.99	5.81	5.59	5.97
00:00	M2	8.56	5.93	4.48	4.67	4.06	5.79	5.59	6.07
01:00	M3	8.54	6.06	4.57	4.76	4.09	5.83	5.77	6.12
02:00	M4	8.53	5.98	4.63	4.84	4.11	5.84	5.80	6.18
03:00	M5	8.51	6.01	4.65	4.80	4.12	5.84	5.00	6.17
04:00	M6	8.49	6.19	4.66	4.86	4.14	5.84	5.83	6.19
05:00	M7	8.49	6.20	4.71	4.89	4.31	5.95	5.80	6.13
06:00	M8	8.47	5.40	5.01	5.35	4.25	5.80	5.85	6.28
07:00	M9	8.46	6.71	4.92	5.08	4.21	5.84	5.83	6.18
08:00	M10	8.46	5.17	4.86	5.05	4.21	5.84	5.82	6.16
09:00	M11	8.44	5.33	4.75	4.92	4.16	5.86	5.83	6.18
10:00	M12	8.39	5.20	4.75	4.95	4.20	5.84	5.80	6.14
11:00	M13	8.34	2.37	4.73	4.89	4.21	5.83	5.78	6.14
12:00	M14	8.31	5.22	4.73	4.87	4.19	5.81	5.78	6.16
13:00	M15	8.23	5.21	4.80	4.89	4.20		6.05	6.18
14:00	M16	8.21	5.31	4.71	4.84	4.20	5.83	5.73	6.22
15:00	M17	8.21	5.15	4.68	4.84	4.18	5.81	5.77	6.18
16:00		8.21	5.26	4.75	4.89	4.20	5.81	5.77	6.14
17:00	M18	8.23	5.28	4.74	4.90	4.18	5.83	5.80	6.14
18:00	M19	8.21	5.37	4.78	4.92	4.19	5.84	5.80	6.13
19:00	M20	8.23	5.27	4.75	4.92	4.14	5.84	5.80	6.13
20:00	M21	8.23	5.25	4.71	4.92	4.14	5.84	5.78	6.10
21:00	M22	8.23	5.27	4.71	4.92	4.17	5.83	5.77	6.10
22:00	M23	8.25	5.21	4.78	4.95	4.19	5.84	5.77	6.10
23:00	M24	8.25	5.35	4.81	4.98	4.16	5.84	5.77	6.10
00:00	M25	8.26	5.42	4.81	5.01	4.16	5.84	5.76	6.10
01:00	M26	8.28	5.40	4.83	5.01	4.14	5.84	5.76	6.10
02:00	M27	8.28	5.40	4.83	5.01	4.16	5.84	5.76	6.10
03:00	M28	8.31	5.40	4.86	4.98	4.19	5.57	5.80	6.10
04:00	M29	8.31	5.49	4.86	5.03	4.21	5.85	5.77	6.10
05:00	M30	8.31	5.40	4.83	5.03	4.16		5.80	6.13
06:00	M31	8.31	5.38	4.81	5.01	4.19	5.16	5.77	6.10
07:00	M32	8.34	5.37	4.76	4.96	4.21	5.84	5.78	6.12
08:00	M33	8.34	5.29	4.74	4.95	4.21	5.83	5.80	6.13
09:00	M34	8.34	5.28	4.76	4.96	4.18	5.83	5.78	6.10
10:00	M35	8.31	5.27	4.77	4.98	4.19	5.81	5.78	6.12
11:00	M36	8.26	5.27	4.83	5.03	4.21	5.81	5.78	6.14
12:00	M37	8.21	5.30	4.83	5.02	4.29	5.81	5.79	6.16
13:00	M39	8.16	5.22	4.78	5.13	4.24		5.82	6.22
14:00	M40	8.13	5.21	4.80	5.00	4.23	5.82	5.80	6.17

TIME	Sample no.	FEED	ONLINE	DV1	DV2	DV3	L/STONE	RV1	RV2
		pH	pH	pH	pH	pH	pH	pH	pH
15:00	M41	8.13	5.16	4.78	4.95	4.23	5.81	5.81	6.19
16:00	M42	8.14	5.18	4.77	4.95	4.19	5.83	5.79	6.19
17:00	M43	8.16	5.09		4.95	4.28	5.81	5.79	6.19
18:00	M44	8.16	5.24	4.78	4.95	4.17	5.82	5.79	6.17
19:00	M45	8.16	5.25	4.75	4.91	4.16	5.81	5.80	6.19
20:00	M46	8.19	5.30	4.77	4.92	4.13	5.81	5.80	6.18
21:00	M47	8.21	5.23	4.75	4.95	4.23	5.83	5.79	6.16
22:00	M48	8.23	5.40	4.77	4.95	4.20	5.84	5.79	6.16
23:00	M49	8.23	5.32	4.80	4.98	4.18	5.83	5.79	6.14
00:00	M50	8.24	5.28	4.73	4.89	4.23	5.81	5.80	6.18
01:00	M51	8.26	5.26	4.71	4.89	4.16	5.81	5.79	6.16
02:00	M52	8.28	5.24	4.75	4.90	4.18	5.81	5.77	6.14
03:00	M53	8.31	5.22	4.75	4.92	4.18	5.81	5.79	6.14
04:00	M54	8.31	5.25	4.73	4.89	4.16	5.81	5.78	6.16
05:00	M55	8.32	5.24	4.73	4.89	4.19	5.81	5.78	6.16
06:00	M56	8.34	5.25	4.75	4.88	4.21	5.83	5.80	6.14
07:00	M57	8.32	5.25	4.81	4.98	4.16	5.83	5.78	6.12
08:00	M58	8.31	5.60	4.76	4.92	4.18	5.83	5.80	6.12
09:00	M59	8.32	5.44	4.77	4.92	4.23	5.80	5.77	6.14
10:00	M60	8.26	5.12	4.77	4.91	4.20	5.78	5.77	6.12
11:00	M61	8.18	5.16	4.73	4.91	4.15	5.78	5.77	6.14
12:00	M62	8.09	5.17	4.82	5.00	4.23	5.83	5.79	6.17
13:00	M63	8.06	5.35	4.82	4.99	4.20		5.80	6.17
14:00	M64	8.11	5.14	4.79	4.99	4.20		5.81	6.14
15:00	M65	8.13	5.12	4.70	4.99	4.17	5.82	5.84	6.20
16:00	M66	8.14	5.10	4.75	4.91	4.14	5.80	5.79	6.17
17:00	M67	8.12	5.14	4.75	4.91	4.17	5.80	5.81	6.17
18:00	M68	8.14	5.25	4.72	4.90	4.17		5.81	6.19
19:00	M69	8.16	5.26	4.72	4.90	4.10		5.82	6.19
20:00	M70	8.19	5.27	4.79	4.90	4.09		5.86	6.22
21:00	M71	8.22	5.22	4.72	4.90	4.75		5.82	6.19
22:00	M72	8.24	5.45	5.33	4.25	4.25		5.94	6.28
23:00	M73	8.26	5.39	4.90	5.05	4.18		5.80	6.18
00:00	M74	8.28	5.30	4.78	4.95	4.17	5.85	5.80	6.20

Table 6B - 3: Calculated CO₂ Recovery from SSP operation

TIME	Sample No.	CO ₂ DOSAGE g/l	CO ₂ Recovery (stasoft) g/l	% Recovery (Stasoft)
23:00	M1	0.57	1.20	>100
00:00	M2	0.57	0.77	>100
01:00	M3	0.57	0.60	>100
02:00	M4	0.57	0.51	89
03:00	M5	0.57	0.57	100
04:00	M6	0.57	0.49	86
05:00	M7	0.57	0.45	79
06:00	M8	0.57	0.15	26
07:00	M9	0.57	0.29	51
08:00	M10	0.57	0.31	54
09:00	M11	0.57	0.42	74
10:00	M12	0.57	0.39	68
11:00	M13	0.57	0.45	79
12:00	M14	0.57	0.47	82
13:00	M15	0.57	0.45	79
14:00	M16	0.57	0.51	89
15:00	M17	0.57	0.51	89
16:00		0.57		
17:00	M18	0.57	0.45	79
18:00	M19	0.57	0.44	77
19:00	M20	0.57	0.42	74
20:00	M21	0.57	0.42	74
21:00	M22	0.57	0.42	74
22:00	M23	0.57	0.42	74
23:00	M24	0.57	0.39	68
00:00	M25	0.57	0.36	63
01:00	M26	0.57	0.34	60
02:00	M27	0.57	0.34	60
03:00	M28	0.57	0.34	60
04:00	M29	0.57	0.36	63
05:00	M30	0.57	0.32	56
06:00	M31	0.57	0.32	56
07:00	M32	0.57	0.34	60
08:00	M33	0.57	0.38	67
09:00	M34	0.57	0.38	67
10:00	M35	0.57	0.38	67
11:00	M36	0.57	0.36	63
12:00	M37	0.57	0.32	56
13:00	M39	0.57	0.33	58
14:00	M40	0.57	0.25	44

TIME	Sample no.	CO ₂ DOSAGE g/l	CO ₂ Recovery (stasoft) g/l	% Recovery (stasoft)
15:00	M41	0.57	0.35	61
16:00	M42	0.57	0.39	68
17:00	M43	0.57	0.39	68
18:00	M44	0.57	0.39	68
19:00	M45	0.57	0.39	68
20:00	M46	0.57	0.43	75
21:00	M47	0.57	0.42	74
22:00	M48	0.57	0.39	68
23:00	M49	0.57	0.39	68
00:00	M50	0.57	0.36	63
01:00	M51	0.57	0.45	79
02:00	M52	0.57	0.45	79
03:00	M53	0.57	0.44	77
04:00	M54	0.57	0.42	74
05:00	M55	0.57	0.45	79
06:00	M56	0.57	0.45	79
07:00	M57	0.57	0.46	81
08:00	M58	0.57	0.36	63
09:00	M59	0.57	0.42	74
10:00	M60	0.57	0.42	74
11:00	M61	0.57	0.43	75
12:00	M62	0.57	0.43	75
13:00	M63	0.57	0.34	60
14:00	M64	0.57	0.35	61
15:00	M65	0.57	0.35	61
16:00	M66	0.57	0.35	61
17:00	M67	0.57	0.43	75
18:00	M68	0.57	0.43	75
19:00	M69	0.57	0.43	75
20:00	M70	0.57	0.44	77
21:00	M71	0.57	0.44	77
22:00	M72	0.57	0.44	77
23:00	M73	0.57	0.44	77
00:00	M74	0.57	0.30	53

APPENDIX 6C

LONG RUN 1

"Bones Curve A"

Sample ID	Time	CO ₂ setting	Weight kg	Dose kg/hr	Dose g/l	Calcium mg/l	Alkalinity mg/l
BA1	08:00	1	22.04			47	119
	08:30	1	22.02	0.04	0.0864		
	09:00	1	22	0.04	0.0864		
	09:30	1	21.98	0.04	0.0864		
		AVG	22.01	0.04	0.0864		
BA2	10:00	2	21.94	0.08	0.1728	86	216
	10:30	2	21.9	0.08	0.1728		
	11:00	2	21.84	0.12	0.2592		
		AVG	21.89	0.0933	0.2016		
BA3	11:30	3	21.76	0.16	0.3456	109	276
	12:00	3	21.68	0.16	0.3456		
	12:30	3	21.58	0.2	0.432		
		AVG	21.67	0.1733	0.3744		
BA4	13:00	4	21.46	0.24	0.5184	128	325
	13:30	4	21.34	0.24	0.5184		
	14:00	4	21.22	0.24	0.5184		
		AVG	21.34	0.24	0.5184		
BA5	14:30	5	21.06	0.32	0.6911	147	362
	15:00	5	20.9	0.32	0.6911		
	15:30	5	20.74	0.32	0.6911		
		AVG	20.9	0.32	0.6911		
BA6	16:00	6	20.54	0.4	0.8639	163	404
	16:30	6	20.34	0.4	0.8639		
	17:00	6	20.14	0.4	0.8639		
		AVG	20.34	0.4	0.8639		
BA7	17:30	7	19.88	0.52	1.1231	179	441
	18:00	7	19.64	0.48	1.0367		
	18:30	7	19.4	0.48	1.0367		
		AVG	19.64	0.4933	1.0655		
BA8	19:00	8	19.12	0.56	1.2095	189	469
	19:30	8	18.84	0.56	1.2095		
	20:00	8	18.56	0.56	1.2095		
		AVG	18.84	0.56	1.2095		
BA9	20:30	9	18.22	0.68	1.4687	201	505
	21:00	9	17.9	0.64	1.3823		
	21:30	9	17.58	0.64	1.3823		
		AVG	17.9	0.6533	1.4111		
BA10	22:00	10	17.22	0.72	1.5551	218	531
	22:30	10	16.84	0.76	1.6415		
	23:00	10	16.46	0.76	1.6415		
		AVG	16.84	0.7467	1.6127		

"Bones Curve B"

Sample ID	Time	CO ₂ setting	Weight kg	Dose kg/hr	Dose g/l	Calcium mg/l	Alkalinity mg/l
BB1	23:00	1	13.3			53	129
	23:30	1	13.3	0	0		
	00:00	1	13.26	0.08	0.1728		
	00:30	1	13.24	0.04	0.0864		
		AVG	13.26	0.04	0.0864		
BB2	01:00	2	13.18	0.12	0.2592	80	192
	01:30	2	13.12	0.12	0.2592		
	02:00	2	13.06	0.12	0.2592		
		AVG	13.12	0.12	0.2592		
BB3	02:30	3	12.98	0.16	0.3456	102	241
	03:00	3	12.88	0.2	0.432		
	03:30	3	12.78	0.2	0.432		
		AVG	12.88	0.1867	0.4032		
BB4	04:00	4	12.66	0.24	0.5184	112	278
	04:30	4	12.54	0.24	0.5184		
	05:00	4	12.4	0.28	0.6048		
		AVG	12.53	0.2533	0.5472		
BB5	05:30	5	12.26	0.28	0.6048	121	301
	06:00	5	26.22	0.28	0.6048		
	06:30	5	26.06	0.32	0.6911		
		AVG	21.51	0.2933	0.6335		
BB6	07:00	6	25.88	0.36	0.7775	137	341
	07:30	6	25.66	0.44	0.9503		
	08:00	6	25.46	0.4	0.8639		
		AVG	25.66	0.4	0.8639		
BB7	08:30	7	25.22	0.48	1.0367	153	376
	09:00	7	24.96	0.52	1.1231		
	09:30	7	24.72	0.48	1.0367		
		AVG	24.96	0.4933	1.0655		
BB8	10:00	8	24.46	0.52	1.1231	163	406
	10:30	8	24.18	0.56	1.2095		
	11:00	8	23.88	0.6	1.2959		
		AVG	24.17	0.56	1.2095		
BB9	11:30	9	23.58	0.6	1.2959	177	438
	12:00	9	23.26	0.64	1.3823		
	12:30	9	22.94	0.64	1.3823		
		AVG	23.26	0.6267	1.3535		
BB10	13:00	10	22.58	0.72	1.5551	190	465
	13:30	10	22.2	0.76	1.6415		
	14:00	10	21.84	0.72	1.5551		
		AVG	22.20	0.7333	1.5839		

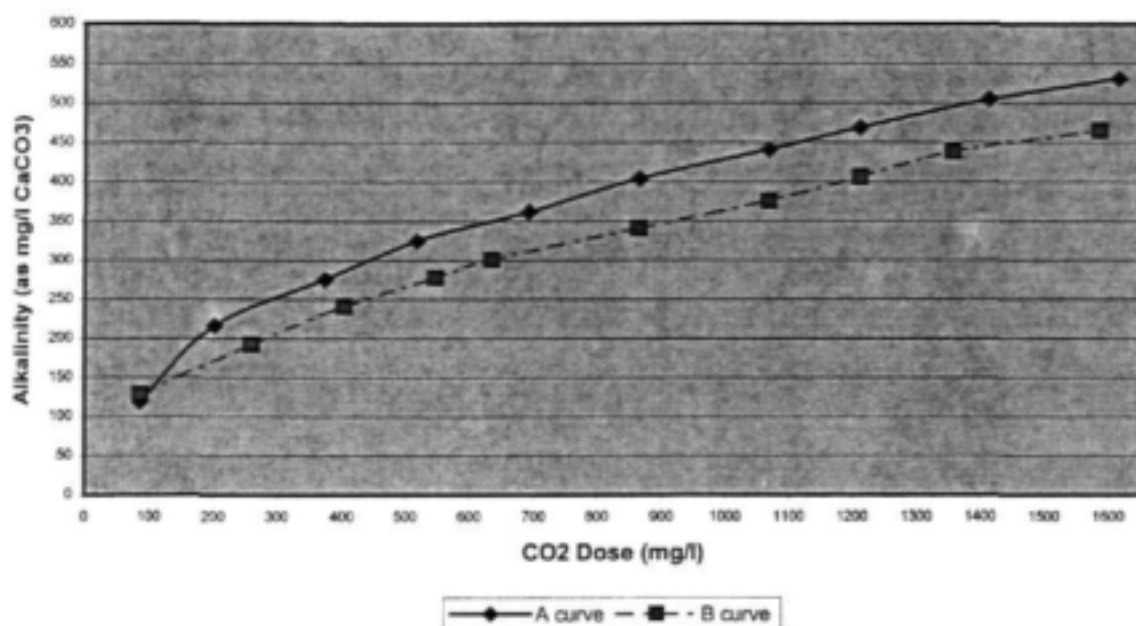


Figure 6C-1: Bones Curves

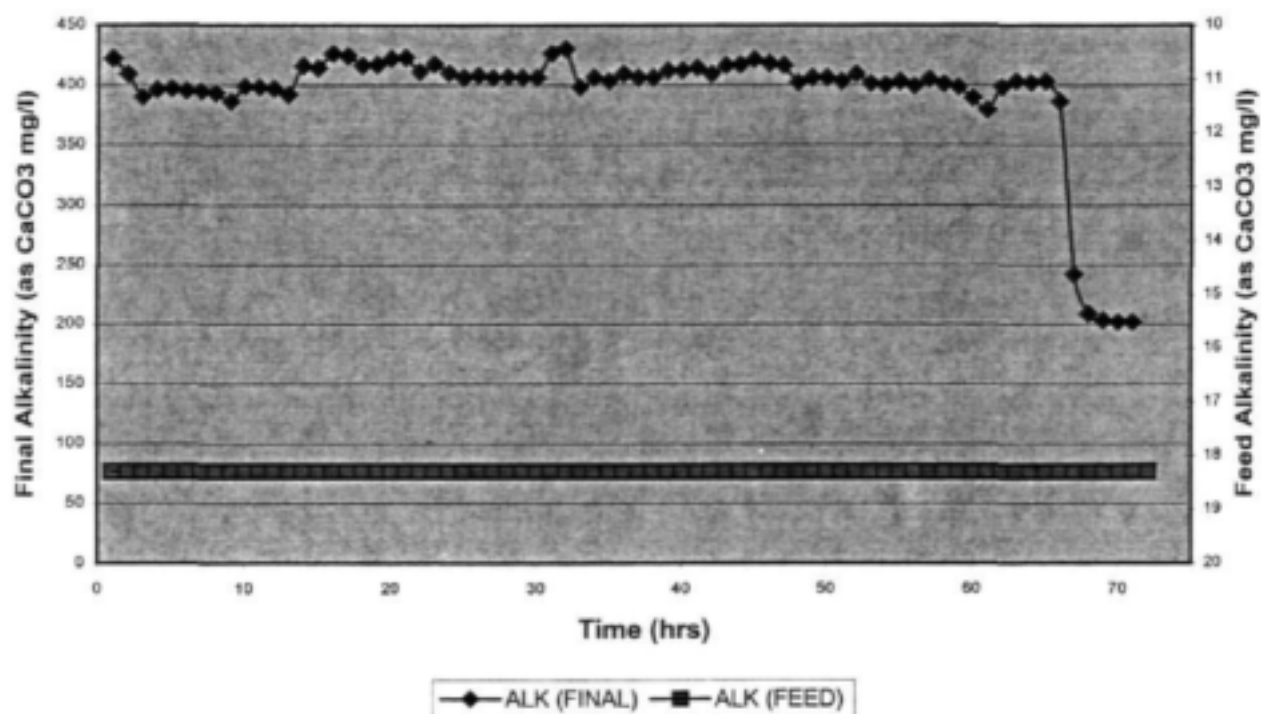


Figure 6C-2: Feed and final Alkalinities

Long Run 1 Data

Time	Sample ID	Calcium Ca mg/l	Calcium CaCO ₃ mg/l	Alkalinity CaCO ₃ mg/l	RV1 kPa	RV2 kPa	Dose mg/l	% CO ₂ Recovery	
								A	B
0:00	M1	171	427.5	422	100	100	788	14	39
1:00	M2	168	420	409	100	100	788	10	35
2:00	M3	152	380	390	100	100	788	4	31
3:00	M4	159	397.5	396	100	100	788	6	33
4:00	M5	158	395	397	100	100	788	6	33
5:00	M6	162	405	395	100	100	788	6	33
6:00	M7	161	402.5	395	100	100	788	6	33
7:00	M8	158	395	393	100	100	788	5	32
8:00	M9	157	392.5	386	100	100	788	2	30
9:00	M10	159	397.5	399	100	94	788	8	33
10:00	M11	157	392.5	398	100	90	788	8	33
11:00	M12	155	387.5	397	95	86	788	6	33
12:00	M13	154	385	392	91	84	788	5	32
13:00	M14	166	415	416	89	68	788	13	37
14:00	M15	164	410	414	73	65	788	13	37
15:00	M16	169	422.5	426	70	66	788	17	40
16:00	M17	164	410	424	71	65	788	17	40
17:00	M18	160	400	416	70	63	788	13	37
18:00	M19	161	402.5	417	68	62	788	13	37
19:00	M20	161	402.5	422	68	62	788	14	39
20:00	M21	160	400	423	68	62	788	14	39
21:00	M22	163	407.5	411	68	62	788	10	35
22:00	M23	164	410	417	68	64	788	13	37
23:00	M24	164	410	410	69	64	788	10	35
0:00	M25	164	410	406	70	65	788	8	34
1:00	M26	163	407.5	408	70	65	788	8	34
2:00	M27	164	410	406	71	66	788	8	34
3:00	M28	163	407.5	407	71	66	788	8	34
4:00	M29	163	407.5	406	72	66	788	8	34
5:00	M30	164	410	406	72	67	788	8	34
6:00	M31	168	420	426	72	71	788	17	40
7:00	M32	171	427.5	430	75	72	788	17	40
8:00	M33	161	402.5	398	78	65	788	8	33
9:00	M34	158	395	406	76	66	788	8	34
10:00	M35	160	400	403	72	67	788	8	34
11:00	M36	165	412.5	409	72	68	788	10	35
12:00	M37	162	405	406	70	68	788	8	34
13:00	M38	164	410	406	72	68	788	8	34
14:00	M39	166	415	412	72	69	788	10	35
15:00	M40	166	415	412	71	69	788	10	35
16:00	M41	166	415	414	73	70	788	13	37
17:00	M42	164	410	409	74	68	788	10	35
18:00	M43	167	417.5	416	73	70	788	13	37
19:00	M44	167	417.5	417	74	71	788	13	37
20:00	M45	167	417.5	421	77	72	788	14	39
21:00	M46	167	417.5	418	77	72	788	13	37
22:00	M47	164	410	416	77	72	788	13	37

Time	Sample ID	Calcium Ca mg/l	Calcium CaCO ₃ mg/l	Alkalinity CaCO ₃ mg/l	RV1 kPa	RV2 kPa	Dose mg/l	% CO ₂ Recovery	
								A	B
23:00	M48	162	405	402	77	67	788	8	33
0:00	M49	164	410	406	76	70	788	8	34
1:00	M50	163	407.5	406	75	70	788	8	34
2:00	M51	164	410	403	76	70	788	8	33
3:00	M52	162	405	409	76	70	788	10	35
4:00	M53	164	410	401	76	70	788	8	33
5:00	M55	162	405	400	76	70	788	8	33
6:00	M56	160	400	403	76	70	788	8	33
7:00	M57	159	397.5	399	70	69	788	8	33
8:00	M58	164	410	405	73	69	788	8	34
9:00	M59	162	405	401	74	69	788	8	33
10:00	M60	164	410	398	73	68	788	8	33
11:00	M61	160	400	389	71	66	788	4	31
12:00	M62	153	382.5	379	68	64	788	0	28
13:00	M63	158	395	398	74	69	788	8	33
14:00	M64	159	397.5	403	75	70	788	8	33
15:00	M65	164	410	402	75	70	788	8	33
16:00	M66	167	417.5	403	75	71	788	8	33
17:00	M67	149	372.5	386	72	67	788	2	30
18:00	M68	99	247.5	242	42	38	788	17	43
19:00	M69	87	217.5	209	38	34	788	0	11
20:00	M70	83	207.5	203	38	34	788	0	23
21:00	M71	83	207.5	202	39	35	788	0	8
22:00	M72	84	210	202	39	35	788	0	8

APPENDIX 6D

LONG RUN 2

"Bones Curve A"

Sample ID	Time	CO ₂ setting	Weight kg	Dose kg/hr	Dose g/l	Calcium mg/l	Alkalinity mg/l
BA1	08:00	1	21.78			47	120
	08:30	1	21.76	0.04	0.0864		
	09:00	1	21.74	0.04	0.0864		
	09:30	1	21.72	0.04	0.0864		
		AVG	21.75	0.04	0.0864		
BA2	10:00	2	21.68	0.08	0.1728	89	229
	10:30	2	21.62	0.12	0.2592		
	11:00	2	21.56	0.12	0.2592		
		AVG	21.62	0.1067	0.2304		
BA3	11:30	3	21.48	0.16	0.3456	113	288
	12:00	3	21.38	0.2	0.432		
	12:30	3	21.3	0.16	0.3456		
		AVG	21.38	0.1733	0.3744		
BA4	13:00	4	21.18	0.24	0.5184	133	335
	13:30	4	21.06	0.24	0.5184		
	14:00	4	20.94	0.24	0.5184		
		AVG	21.06	0.24	0.5184		
BA5	14:30	5	20.8	0.28	0.6048	146	369
	15:00	5	17.78	0.28	0.6048		
	15:30	5	17.64	0.28	0.6048		
		AVG	18.74	0.28	0.6048		
BA6	16:00	6	17.44	0.4	0.8639	164	417
	16:30	6	17.24	0.4	0.8639		
	17:00	6	17.02	0.44	0.9503		
		AVG	17.23	0.4133	0.8927		
BA7	17:30	7	16.78	0.48	1.0367	175	450
	18:00	7	16.54	0.48	1.0367		
	18:30	7	16.3	0.48	1.0367		
		AVG	16.54	0.48	1.0367		
BA8	19:00	8	16	0.6	1.2959	186	479
	19:30	8	15.7	0.6	1.2959		
	20:00	8	15.44	0.52	1.1231		
		AVG	15.71	0.5733	1.2383		
BA9	20:30	9	15.12	0.64	1.3823	199	516
	21:00	9	14.8	0.64	1.3823		
	21:30	9	14.46	0.68	1.4687		
		AVG	14.79	0.6533	1.4111		
BA10	22:00	10	14.08	0.76	1.6415	214	546
	22:30	10	13.72	0.72	1.5551		
	23:00	10	13.36	0.72	1.5551		
		AVG	13.72	0.7333	1.5839		

"Bones Curve B"

Sample ID	Time	CO ₂ setting	Weight kg	Dose kg/hr	Dose mg/l	Calcium mg/l	Alkalinity mg/l
BB1	23:00	1	14.44			43	110
	23:30	1	14.44	0	0		
	00:00	1	14.44	0	0		
	00:30	1	14.4	0.08	0.1728		
		AVG	14.43	0.04	0.0864		
BB2	01:00	2	14.34	0.12	0.2592	74	189
	01:30	2	14.28	0.12	0.2592		
	02:00	2	14.22	0.12	0.2592		
		AVG	14.28	0.12	0.2592		
BB3	02:30	3	14.14	0.16	0.3456	94	242
	03:00	3	14.06	0.16	0.3456		
	03:30	3	13.96	0.2	0.432		
		AVG	14.05	0.1733	0.3744		
BB4	04:00	4	13.84	0.24	0.5184	112	286
	04:30	4	13.72	0.24	0.5184		
	05:00	4	13.6	0.24	0.5184		
		AVG	13.72	0.24	0.5184		
BB5	05:30	5	13.44	0.32	0.6911	126	323
	06:00	5	13.28	0.32	0.6911		
	06:30	5	13.12	0.32	0.6911		
		AVG	13.28	0.32	0.6911		
BB6	07:00	6	12.92	0.4	0.8639	142	362
	07:30	6	12.74	0.36	0.7775		
	08:00	6	12.54	0.4	0.8639		
		AVG	12.73	0.3867	0.8351		
BB7	08:30	7	12.32	0.44	0.9503	158	401
	09:00	7	17.92	0.4	0.8639		
	09:30	7	17.6	0.64	1.3823		
		AVG	15.94	0.4933	1.0655		
BB8	10:00	8	17.4	0.4	0.8639	170	426
	10:30	8	17.12	0.56	1.2095		
	11:00	8	16.84	0.56	1.2095		
		AVG	17.12	0.5067	1.0943		
BB9	11:30	9	16.54	0.6	1.2959	182	460
	12:00	9	16.2	0.68	1.4687		
	12:30	9	15.9	0.6	1.2959		
		AVG	16.21	0.6267	1.3535		
BB10	13:00	10	15.52	0.76	1.6415	200	495
	13:30	10	15.14	0.76	1.6415		
	14:00	10	14.8	0.68	1.4687		
		AVG	15.15	0.7333	1.5839		

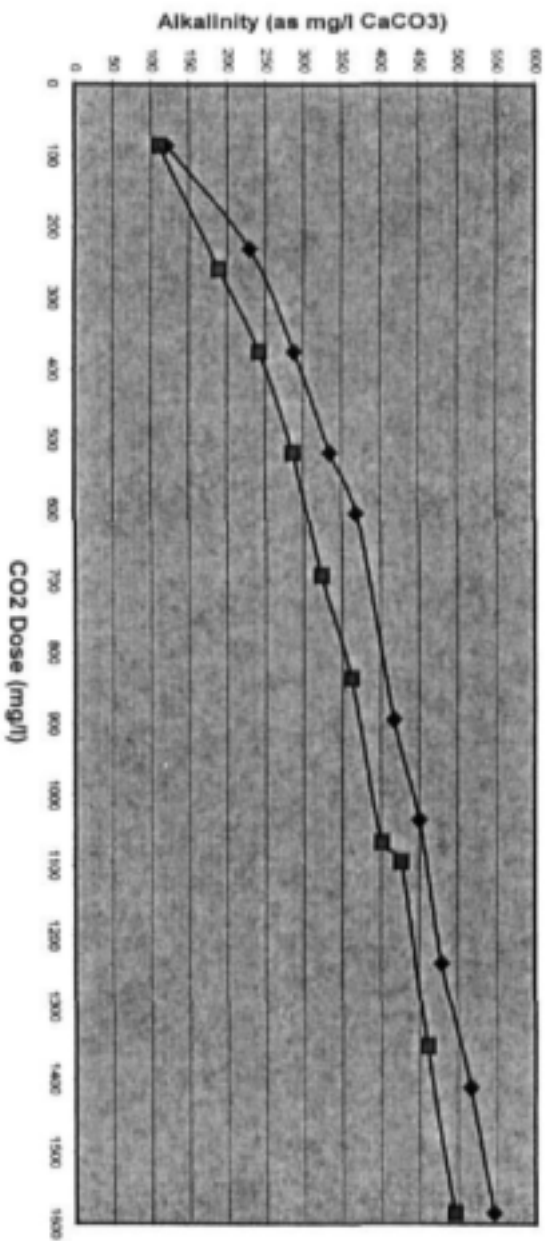


Figure 6D-1: Bories curve

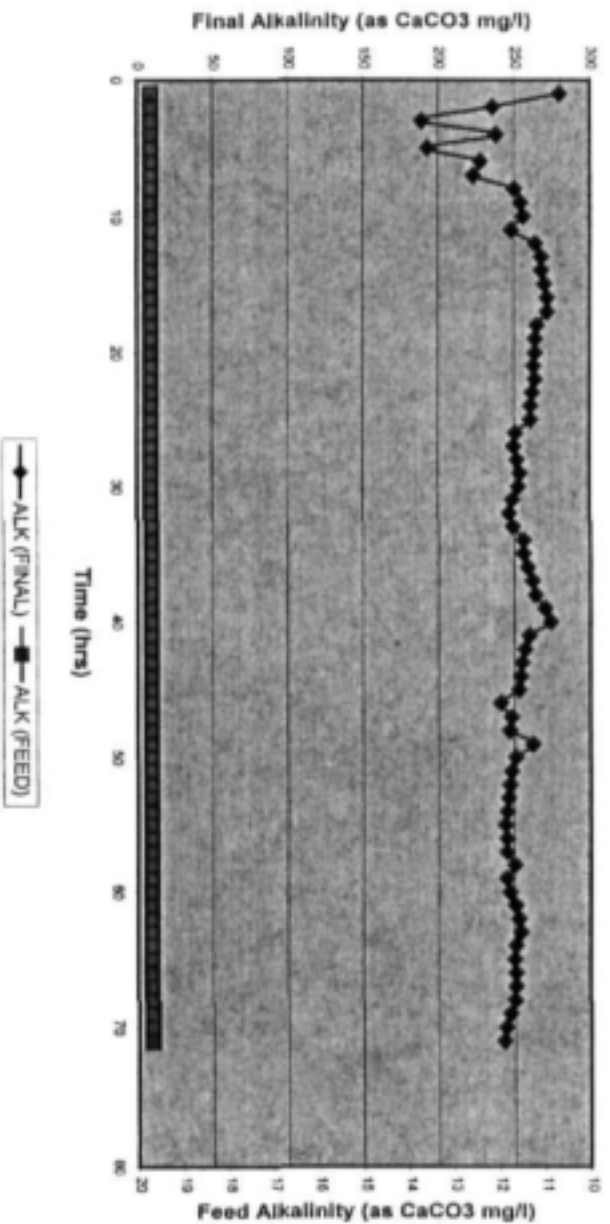


Figure 6D-2: Feed and final Alkalinities

Long Run 2 Data

Time	Sample ID	Calcium Ca mg/l	Calcium CaCO ₃ mg/l	Alkalinity CaCO ₃ mg/l	RV1 kPa	RV2 kPa	Dose mg/l	% CO ₂ Recovery	
								A	B
0:00	M1	109	272.5	280	96	91	302	11	40
1:00	M2	92	230	236	96	91	302	0	16
2:00	M3	74	185	189	81	91	302	0	0
3:00	M4	93	232.5	238	81	78	302	0	16
4:00	M5	74	185	193	82	76	302	0	0
5:00	M6	88	220	228	84	80	302	0	8
6:00	M7	86	215	223	82	77	302	0	8
7:00	M8	97	242.5	250	80	76	302	0	25
8:00	M9	99	247.5	254	77	73	302	0	25
9:00	M10	100	250	256	76	73	302	0	28
10:00	M11	99	247.5	248	66	63	302	0	25
11:00	M12	105	262.5	264	59	57	302	0	30
12:00	M13	108	270	268	56	53	302	6	34
13:00	M14	107	267.5	268	53	51	302	6	34
14:00	M15	106	265	270	52	49	302	6	34
15:00	M16	109	272.5	272	52	49	302	6	34
16:00	M17	109	272.5	272	51	48	302	6	34
17:00	M18	108	270	265	51	47	302	0	30
18:00	M19	107	267.5	264	51	47	302	0	30
19:00	M20	105	262.5	264	51	47	302	0	30
20:00	M21	105	262.5	263	51	47	302	0	30
21:00	M22	106	265	264	51	47	302	0	30
22:00	M23	106	265	262	51	47	302	0	30
23:00	M24	105	262.5	261	51	47	302	0	30
0:00	M25	103	257.5	261	51	46	302	0	30
1:00	M26	105	262.5	251	51	46	302	0	25
2:00	M27	99	247.5	250	49	45	302	0	25
3:00	M28	100	250	252	49	45	302	0	25
4:00	M29	102	255	254	49	45	302	0	25
5:00	M30	102	255	253	49	46	302	0	25
6:00	M31	102	255	249	49	45	302	0	25
7:00	M32	100	250	247	48	45	302	0	20
8:00	M33	99	247.5	249	48	45	302	0	25
9:00	M34	99	247.5	256	47	44	302	0	20
10:00	M35	102	255	256	46	43	302	0	28
11:00	M36	102	255	259	46	43	302	0	30
12:00	M37	104	260	262	46	43	302	0	30
13:00	M38	104	260	264	46	43	302	0	30
14:00	M39	105	262.5	270	46	43	302	6	34
15:00	M40	107	267.5	274	47	44	302	6	34
16:00	M41	107	267.5	260	47	44	302	0	30
17:00	M42	102	255	257	46	43	302	0	30
18:00	M43	104	260	255	45	41	302	0	28
19:00	M44	105	262.5	254	45	41	302	0	25
20:00	M45	101	252.5	253	45	41	302	0	25
21:00	M46	100	250	241	45	41	302	0	16
22:00	M47	99	247.5	248	45	41	302	0	25

23:00	M48	97	242.5	247	45	41	302	0	20
Time	Sample ID	Calcium Ca mg/l	Calcium CaCO ₃ mg/l	Alkalinity CaCO ₃ mg/l	RV1 kPa	RV2 kPa	Dose mg/l	% CO ₂ Recovery	
								A	B
0:00	M49	98	245	262	44	40	302	0	30
1:00	M50	105	262.5	251	46	40	302	0	25
2:00	M51	99	247.5	248	45	41	302	0	25
3:00	M52	99	247.5	247	45	41	302	0	20
4:00	M53	97	242.5	246	44	41	302	0	20
5:00	M55	97	242.5	245	45	41	302	0	20
6:00	M56	97	242.5	244	45	41	302	0	20
7:00	M57	97	242.5	245	44	41	302	0	20
8:00	M58	97	242.5	245	44	41	302	0	20
9:00	M59	100	250	250	44	41	302	0	25
10:00	M60	97	242.5	245	44	41	302	0	20
11:00	M61	97	242.5	247	44	41	302	0	20
12:00	M62	100	250	251	43	41	302	0	25
13:00	M63	100	250	253	44	40	302	0	25
14:00	M64	100	250	254	44	41	302	0	25
15:00	M65	99	247.5	251	44	41	302	0	25
16:00	M66	99	247.5	250	43	41	302	0	25
17:00	M67	97	242.5	251	43	40	302	0	25
18:00	M68	97	242.5	251	43	40	302	0	25
19:00	M69	97	242.5	250	43	40	302	0	25
20:00	M70	96	240	247	43	40	302	0	20
21:00	M71	96	240	244	43	40	302	0	20
22:00	M72	96	240	243	43	40	302	0	20

APPENDIX 6E

LONG RUN 3

"Bones Curve A"

Sample ID	Time	CO ₂ setting	Weight kg	Dose kg/hr	Dose g/l	Calcium mg/l	Alkalinity mg/l
BA1	08:00	1	14.76			46	117
	08:30	1	14.76	0	0		
	09:00	1	14.74	0.04	0.0864		
	09:30	1	14.72	0.04	0.0864		
		AVG	14.74	0.0267	0.0864		
BA2	10:00	2	14.68	0.08	0.1728	91	224
	10:30	2	14.62	0.12	0.2592		
	11:00	2	14.56	0.12	0.2592		
		AVG	14.62	0.1067	0.2304		
BA3	11:30	3	14.48	0.16	0.3456	115	285
	12:00	3	14.4	0.16	0.3456		
	12:30	3	14.32	0.16	0.3456		
		AVG	14.45	0.16	0.3456		
BA4	13:00	4	14.2	0.24	0.5184	134	331
	13:30	4	14.08	0.24	0.5184		
	14:00	4	13.96	0.24	0.5184		
		AVG	14.17	0.24	0.5184		
BA5	14:30	5	13.8	0.32	0.6911	150	375
	15:00	5	13.62	0.36	0.7775		
	15:30	5	13.48	0.28	0.6048		
		AVG	13.76	0.32	0.6911		
BA6	16:00	6	13.28	0.4	0.8639	167	408
	16:30	6	13.08	0.4	0.8639		
	17:00	6	12.88	0.4	0.8639		
		AVG	13.25	0.4	0.8639		
BA7	17:30	7	12.64	0.48	1.0367	172	440
	18:00	7	12.4	0.48	1.0367		
	18:30	7	18.36	0.48	1.0367		
		AVG	14.16	0.48	1.0367		
BA8	19:00	8	18.08	0.56	1.2095	181	468
	19:30	8	17.82	0.52	1.1231		
	20:00	8	17.54	0.56	1.2095		
		AVG	16.90	0.5467	1.1807		
BA9	20:30	9	17.22	0.64	1.3823	200	496
	21:00	9	16.88	0.68	1.4687		
	21:30	9	16.56	0.64	1.3823		
		AVG	16.89	0.6533	1.4111		
BA10	22:00	10	16.18	0.76	1.6415	208	517
	22:30	10	15.8	0.76	1.6415		
	23:00	10	15.42	0.76	1.6415		
		AVG	16.07	0.76	1.6415		

"Bones Curve B"

Sample ID	Time	CO ₂ setting	Weight kg	Dose kg/hr	Dose mg/l	Calcium mg/l	Alkalinity mg/l
BB1	23:00	1	13.66			42	109
	23:30	1	13.64	0.04	0.0864		
	00:00	1	13.62	0.04	0.0864		
	00:30	1	13.6	0.04	0.0864		
		AVG	13.63	0.04	0.0864		
BB2	01:00	2	13.54	0.12	0.2592	76	190
	01:30	2	13.48	0.12	0.2592		
	02:00	2	13.44	0.08	0.1728		
		AVG	13.48	0.1067	0.2304		
BB3	02:30	3	13.4	0.08	0.1728	100	250
	03:00	3	13.26	0.28	0.6048		
	03:30	3	13.16	0.2	0.432		
		AVG	13.27	0.1867	0.4032		
BB4	04:00	4	13.1	0.12	0.2592	110	289
	04:30	4	13.04	0.12	0.2592		
	05:00	4	12.78	0.52	1.1231		
		AVG	12.97	0.2533	0.5472		
BB5	05:30	5	12.62	0.32	0.6911	133	339
	06:00	5	12.44	0.36	0.7775		
	06:30	5	12.36	0.16	0.3456		
		AVG	12.47	0.28	0.6048		
BB6	07:00	6	26.18	0.48	1.0367	141	356
	07:30	6	26	0.36	0.7775		
	08:00	6	25.8	0.4	0.8639		
		AVG	25.99	0.4133	0.8927		
BB7	08:30	7	25.54	0.52	1.1231	152	389
	09:00	7	25.32	0.44	0.9503		
	09:30	7	25.08	0.48	1.0367		
		AVG	25.31	0.48	1.0367		
BB8	10:00	8	24.78	0.6	1.2959	163	418
	10:30	8	24.54	0.48	1.0367		
	11:00	8	24.28	0.52	1.1231		
		AVG	24.53	0.5333	1.1519		
BB9	11:30	9	23.96	0.64	1.3823	175	452
	12:00	9	23.66	0.6	1.2959		
	12:30	9	23.32	0.68	1.4687		
		AVG	23.64	0.64	1.3823		
BB10	13:00	10	23	0.64	1.3823	175	484
	13:30	10	22.62	0.76	1.6415		
	14:00	10	22.24	0.76	1.6415		
		AVG	22.62	0.72	1.5551		

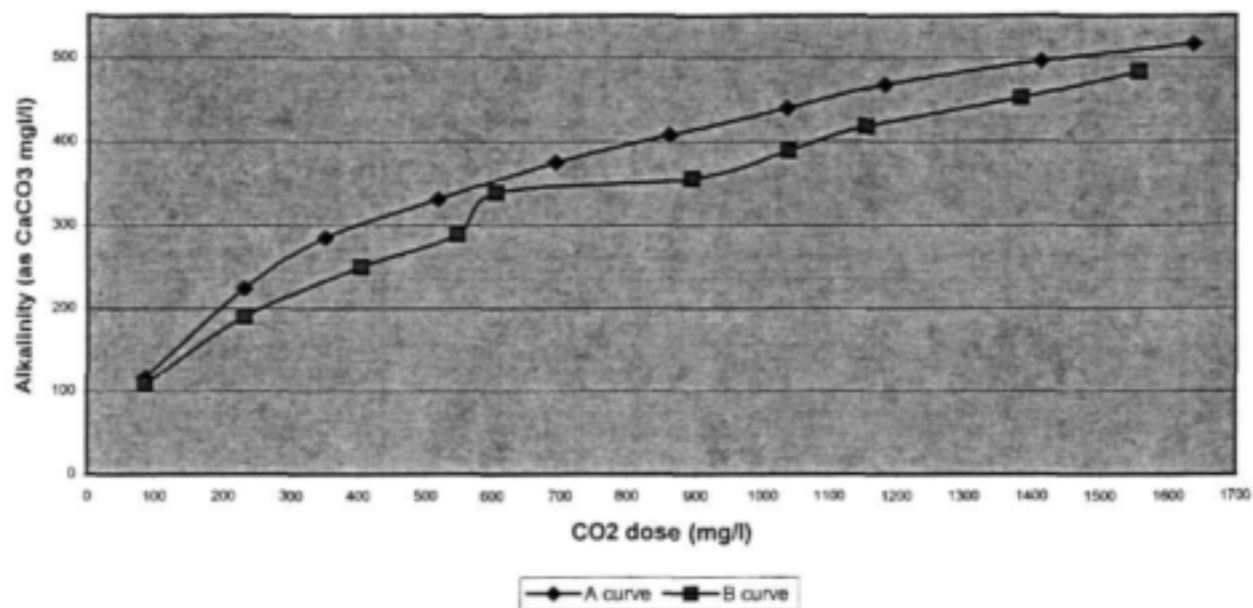


Figure 6E-1: *Bones curve*

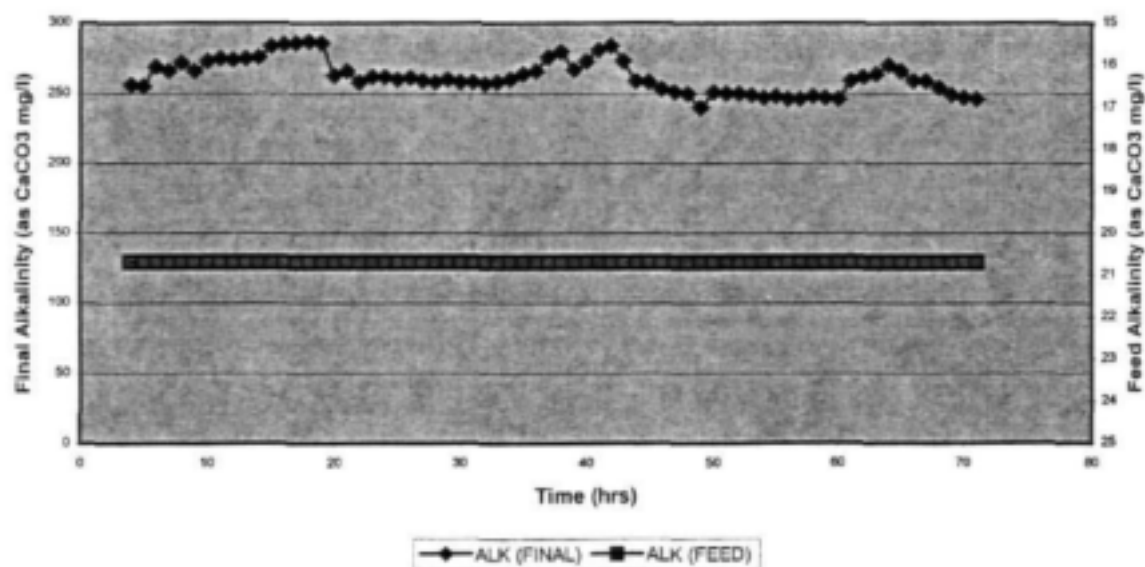


Figure 6E-2: *Feed and final Alkalinities*

Long Run 3 Data

Time	Sample ID	Calcium Ca mg/l	Calcium CaCO ₃ mg/l	Alkalinity CaCO ₃ mg/l	RV1 kPa	RV2 kPa	Dose mg/l	% CO ₂ Recovery	
								A	B
0:00	M1								
1:00	M2				47	45			
2:00	M3				47	45			
3:00	M4	105	210	256	47	45			
4:00	M5	104	208	255	54	55	319	0	24
5:00	M6	111	222	269	57	57	319	0	34
6:00	M7	105	210	266	55	56	319	0	32
7:00	M8	106	212	272	55	57	319	0	34
8:00	M9	107	214	266	55	56	319	0	32
9:00	M10	110	220	273	54	57	319	3	36
10:00	M11	108	216	275	53	56	319	3	36
11:00	M12	107	214	274	53	55	319	3	36
12:00	M13	108	216	275	53	56	319	3	36
13:00	M14	108	216	276	53	56	319	3	36
14:00	M15	117	234	284	53	56	319	11	42
15:00	M16	117	234	285	54	56	319	11	42
16:00	M17	117	234	286	53	56	319	11	42
17:00	M18	116	232	287	53	56	319	11	42
18:00	M19	114	228	286	54	56	319	11	42
19:00	M20	105	210	263	54	56	319	0	32
20:00	M21	107	214	266	52	54	319	0	32
21:00	M22	102	204	258	51	53	319	0	29
22:00	M23	104	208	262	51	53	319	0	29
23:00	M24	104	208	262	51	53	319	0	29
0:00	M25	104	208	260	51	53	319	0	29
1:00	M26	104	208	261	51	53	319	0	29
2:00	M27	103	206	259	51	53	319	0	29
3:00	M28	103	206	258	51	53	319	0	29
4:00	M29	105	210	260	51	53	319	0	29
5:00	M30	104	208	258	51	53	319	0	29
6:00	M31	100	200	258	51	53	319	0	29
7:00	M32	101	202	257	50	51	319	0	29
8:00	M33	104	208	258	49	50	319	0	29
9:00	M34	102	204	260	48	50	319	0	29
10:00	M35	105	210	264	47	50	319	0	32
11:00	M36	105	210	266	47	50	319	0	32
12:00	M37	111	222	276	48	50	319	3	36
13:00	M38	112	224	280	48	50	319	6	39
14:00	M39	108	216	267	46	49	319	0	32
15:00	M40	110	220	273	47	50	319	3	36
16:00	M41	112	224	281	48	50	319	6	39
17:00	M42	114	228	284	48	51	319	11	42
18:00	M43	109	218	273	47	49	319	3	36
19:00	M44	104	208	259	45	47	319	0	29
20:00	M45	104	208	258	45	46	319	0	29
21:00	M46	99	198	253	44	46	319	0	24

Time	Sample ID	Calcium Ca mg/l	Calcium CaCO ₃ mg/l	Alkalinity CaCO ₃ mg/l	RV1 kPa	RV2 kPa	Dose mg/l	% CO ₂ Recovery	
								A	B
22:00	M47	100	200	251	44	46	319	0	20
23:00	M48	100	200	250	44	46	319	0	20
0:00	M49	100	200	240	44	46	319	0	11
1:00	M50	101	202	251	44	45	319	0	20
2:00	M51	101	202	250	44	45	319	4	20
3:00	M52	101	202	250	43	45	319	0	20
4:00	M53	101	202	249	43	45	319	0	20
5:00	M55	97	194	247	42	44	319	0	20
6:00	M56	97	194	248	42	44	319	0	20
7:00	M57	96	192	246	42	43	319	0	16
8:00	M58	98	196	246	42	43	319	0	16
9:00	M59	98	196	248	41	43	319	0	20
10:00	M60	99	198	247	41	43	319	0	20
11:00	M61	103	206	246	40	43	319	0	16
12:00	M62	105	210	259	41	43	319	0	29
13:00	M63	105	210	262	41	43	319	0	29
14:00	M64	108	216	264	41	44	319	0	32
15:00	M65	108	216	270	41	44	319	0	34
16:00	M66	104	208	266	41	43	319	0	32
17:00	M67	102	204	259	40	42	319	0	29
18:00	M68	103	206	259	40	41	319	0	29
19:00	M69	100	200	254	39	40	319	0	24
20:00	M70	98	196	249	39	40	319	0	20
21:00	M71	99	198	247	39	40	319	0	20
22:00	M72	98	196	246	38	40	319	0	16

CHAPTER 7

**PRELIMINARY ASSESSMENT OF
THE SSP FOR THE LESOTHO
HIGHLANDS SCHEME, INCLUDING
FINANCIAL EVALUATION**

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7.1 INTRODUCTION

A primary motivator for this project was Rand Water's considerations with regards water transport and treatment requirements for the Lesotho Highlands scheme. Historically, Rand Water has abstracted some 95% of its raw water from the Vaal Dam. At the time of submitting the project proposal it was envisaged that by 1999 some 25% of raw water would originate from Lesotho Highlands, and that by 2008 this would increase to about 50% of Rand Water raw water (i.e. some 70 cubic metres/second). Studies are under way by Rand Water to assess whether the large flows should be via natural watercourse or via gravity pipeline. Piping of water has advantages in that both environmental degradation and water loss are significantly less than if natural watercourses transport the water. The pipeline would carry the water from the Katze Dam tunnel outlet near Clarens to a termination point south of Johannesburg. As the envisaged pipe is likely to cost around 3 billion Rand, protection thereof from aggressive and corrosive attack is of high priority.

Lesotho Highlands water is chemically very different to Vaal Dam water, and in particular is relatively soft and acidic, requiring conditioning to prevent attack of cement concrete and metal structures and conduits. Rand Water identified the Sidestream Stabilisation Process (SSP) as a potentially attractive alternative to conventional lime and carbon dioxide mediated stabilisation.

It is important to note that during the course of this project, Rand Water has considerably revised annual growth in water demand. Initially an assumption of 4,5% annual growth was used, however this growth has slowed down for a number of reasons and it is now regarded that growth may well be less than 2,5% per annum. On the foregoing assumption augmentation is not required before 2016 i.e. 2 years of detailed design should commence in 2009 allowing five years for construction from 2011 and commissioning by 2016. Accordingly, Rand Water has not finalised water treatment requirements for the Lesotho Highlands Scheme.

This WRC project was required to determine *inter alia* the desirability and suitability of an optimised SSP for the Lesotho Highlands scheme, and assess the motivation for potential industrialisation and full-scale implementation of the process. Considering the inability of both:

- (i) The CSIR project team to optimise operation of the SSP pilot plant at high percentage carbon dioxide recovery levels (i.e. carbon dioxide recovery greater than 50%), and
- (ii) The inability of the Rand Water project team to finalise water treatment and stabilisation requirements.

It was agreed that the objectives would be sufficiently met if the desirability and suitability of the SSP process was considered as follows:

- Assume that As River outfall water is representative of raw water quality.
- Assume that water treatment will be via use of either micro-filtration, or filtration using ferric chloride as a flocculation agent with the latter process being the more likely.
- Assume that stabilised water quality should closely represent existing Rand Water stabilisation requirements.
- Basic financial attractiveness should be assessed for via simple chemical running cost comparisons for a range of SSP performances.
- More detailed financial attractiveness should be considered for ferric chloride based treatment.
- For the more detailed financial assessment, the assessment should take place within the CO₂ stripping and recovery limitations achieved using the pilot plant (see Chapter 6).

7.2 WATER QUALITY AND TREATMENT CONSIDERATIONS

7.2.1 Raw Water Quality

Rand Water monitored raw water quality via on-site sample collection. Samples were collected in and around the Katse Dam as shown in **Figure 7.1**.



Figure 7.1: Katse Dam Sampling Points

Table 7.1 gives a summary of various sampling points in and around the Katse dam. Inspection of the Rand Water sampling results reveals that:

- Raw water quality is not that of typical soft, acidic water as first expected. In particular, calcium and total alkalinity levels are noticeably higher than expected at the outset of the project.
- Raw water quality may not have stabilised as changes in certain parameters (especially total alkalinity) have been observed over the past two years. The data from the various inflows to the dam seems to indicate that the calcium and total alkalinity levels could be contributed from the geological formations in the catchment area of the Katse Dam.

For the purposes of this project, it is suffice to note that, at present, Rand Water Process Engineers regard the shaded column in **Table 7.1** as a reasonably accurate representation of the As River water, which will require treatment.

Table 7.1: Water quality data in and around the Katse Dam.

	AS RIVER OUTFALLS	AS RIVER OUTFALLS	KATSE DAM TOWER	AS RIVER OUTFALLS	INLET TOWER (SURFACE)	INLET TOWER (BOTTOM)	MALIBAMATSO RIVER	PELALENG RIVER	LIPHOFUNG RIVER	MOKHOUTANE RIVER	BOKONG RIVER
Time period	Typical	Nov 00	Nov 00	Jun/ Jul 00	May 96/Sept 99						
pH	7.27	6.7	8.5	6.8	7.9	7.3	7.6	7.4	7.7	7.9	7.6
Conductivity (mS/m)	8.1	5.9	6.6	8.3	8.2	7.8	7.4	5.7	9.4	11.4	5.0
Hardness (as mg/l CaCO ₃)	41.75	36.5	38.5	35.5	37.0	37.0	48.0	26.0	42.0	52.0	22.0
Total alkalinity (as mg/l CaCO ₃)	35.55	29.4	28.9	37.3	36.0	35.0	33.0	26.0	39.0	48.0	23.0
Ca (as mg/l Ca)	9.25	10.0	8.6	8.5	9.1	9.1	9.0	6.7	10.9	13.1	5.8
Mg (as mg/l Mg)	4.13	2.8	4.2	3.4	3.4	3.3	3.0	2.1	3.6	4.9	1.9
Na (as mg/l Na)	3.3			2.2	2.5	2.0	2.1	1.7	2.8	2.9	1.9
Dissolved oxygen (mg/l)					8.2	6.0	9.0	8.8	9.3	9.3	8.6

7.2.2 Treatment Options

Rand Water has carried out various laboratory scale experiments assessing water treatment options. In particular, tests have been carried out assessing both direct and indirect filtration in which ferric chloride is used as the coagulant. Direct filtration using membranes for micro filtration is also being considered; however, preliminary costings indicate that this approach will be 50% more expensive.

Rand water carried out tests using a mini plant (2 L/min) on stabilised Katse water, the results of which are shown in **Table 7.2**. 21.5 mg/l $\text{Ca}(\text{OH})_2$ and 20.7 mg/l CO_2 were dosed to water collected from the As-river outfalls. 3.3 mg/l FeCl_3 as Fe was dosed in the trial. The pH of the final water (direct and in-line filtration) does not comply to the stabilisation requirements in the next paragraph. The emphasis in these tests was on the removal of suspended matter. Considerable further work still needs to be done to find the best treatment method for the water.

Table 7.2: Results from the direct and in-line filtration tests.

	AS-RIVER WATER	AS-RIVER + LIME	AS-RIVER, LIME + CO_2	DIRECT FILTRATION	IN-LINE FILTRATION
pH	7.2	9.8	8.2	7.3	7.3
Conductivity (mS/m)	8.6	12	16	16	16
Hardness (as mg/l CaCO_3)	34	56	130	72	73
Total alkalinity (as mg/l CaCO_3)	39	60	78	70	70
Ca (as mg/l Ca)	8.3	17	43	24	24
Mg (as mg/l Mg)	3.3	3.3	5.2	3.0	3.2
Na (as mg/l Na)	1.4	1.4	1.5	1.4	1.4

7.2.3 Rand Water Stabilisation Requirements

Rand Water has determined their own stabilisation requirements to ensure that a water is non-corrosive. Details thereof are captured in the study "The effect of water quality and chemical composition on the corrosion of mild steel pipelines", performed by Scientific Services, Rand Water. A summary of these requirements is shown in **Table 7.3**.

Table 7.3: Chemical analysis for stable water according to Brits *et. al.*, March 1998
(WRC Report No 259/1/98)

ANALYSES	RANGE
Conductivity (mS/m)	14.5 - 17.0
pH	8.3 - 8.6
TDS (mg/l)	97.4 - 116.0
Total alkalinity (mg/l as CaCO ₃)	71 - 89
Hardness (mg/l as CaCO ₃)	69 - 73
Calcium (mg/l as Ca)	19 - 25
Magnesium (mg/l as Mg)	2.6 - 3.4
Sodium (mg/l as Na)	3.9 - 10.0
Ammonia (mg/l as NH ₃)	< 0.05
Sulphate (mg/l as SO ₄ ²⁻)	< 5
Chloride (mg/l as Cl ⁻)	< 5

In addition, Rand Water include consideration of the guidelines given by Loewenthal *et. al* (1986):

- A CCPP value of 1-2 mg/l.
- A total alkalinity of greater than 50 mg/l as CaCO₃.
- pH value of approximately 8.2.

7.3 BASIC FINANCIAL ASSESSMENT OF THE USE OF SSP FOR LESOTHO HIGHLANDS

7.3.1 Introduction

Using the water quality data from the untreated As River outfall of the Katse Dam, various treatment options were considered. Furthermore, stabilisation costs were compared using conventional lime and CO₂ versus the SSP process. Financial assessment includes:

- Basic financial assessment – in which the annual chemical operating costs of stabilisation using conventional lime and CO₂ are compared with those using SSP.
- Detailed financial assessment – in which a more comprehensive analysis considering *inter alia* capital costs, running costs and risk.

In all cases these financial assessments, and the associated water treatment requirements, should be regarded as no more than a preliminary basis for comparison of the relative stabilisation costs using conventional lime and CO₂ versus the SSP process.

In all financial assessments costs for the chemicals used were obtained from chemical suppliers (using year 2000 delivered prices):

- | | |
|------------------------|--------------------|
| • Bredasdorp Limestone | R370/ton |
| • Lime | R1400/ton |
| • CO ₂ | R700/ton + rental. |

NOTE: The prices for limestone and white lime vary considerably with both the quality of the product and the region to which the product must be transported. The cost of white lime has also been seen to fluctuate considerably in the past two years. The costs presented are typical costs for delivery of CO₂ and suitable quality limestone/white lime to the Lesotho Highlands Scheme, year 2000 prices. As the viability of the SSP is largely based on chemical cost savings, the cost of these chemicals for a particular application must be carefully considered.

7.3.2 CASE ONE: Micro-filtration- Small % sidestream combined with high percentage CO₂ recovery and re-use

When considering use of micro-filtration and where SSP is used with a small % sidestream combined with high percentage CO₂ recovery and re-use, an envisaged scenario is shown in **Table 7.4**. **SSP-MOD** was used to consider a SSP system where the sidestream had excess carbon dioxide stripped to waste and no nominal addition of lime. **SSP-MOD** showed that in this configuration SSP can be used to obtain a fully stabilised stream with a pH of 8.34, total alkalinity of 66.9 mg/L (as CaCO₃) and CCPP of 2 mg/L (as CaCO₃). This process requires a 2% sidestream (small) and CO₂ recovery of 69.6% (high). Conventional lime and CO₂ stabilisation would provide stabilised water with a pH of 9.02, total alkalinity of 72 mg/L (as CaCO₃) and CCPP of 10 mg/L (as CaCO₃). Chemical costs for a 2000 ML/day conventional lime and CO₂ stabilisation system would be about R33.5 million/annum, whilst chemical costs for SSP would be about R21.7 million/annum. This translates to **an annual chemical cost saving of about R11.8 million/annum.**

Table 7.4: Chemical cost comparison for the stabilisation of Lesotho Highlands water that has been treated via Microfiltration

SSP OP. CHARAC.	SSP FINAL WATER	CONV. FINAL WATER	CHEMICAL COST COMPARISON (2000 ML/DAY)	
% SS = 2	pH = 8.6	pH = 9.02	Lime/CO ₂	SSP
Recov = 70%	Alk = 72, Ca = 23	Alk = 72 Ca = 24	~ R33.5 M/year	~ R21.7 M/year
CO ₂ dose = 36.5 mg/L	CaCO ₃ dose = 36.5 mg/L	Lime dose = 27 mg/L CO ₂ dose = 24 mg/L	SAVINGS = ~R11.8 M/YEAR	
	CCPP = 2	CCPP = 10		

7.3.3 CASE TWO: Filtration assisted by ferric chloride dosing - High % sidestream combined with Low percentage CO₂ recovery and re-use

When considering filtration assisted by ferric chloride dosing, and where SSP is used with a high % sidestream and low percentage CO₂ recovery and re-use, the envisaged scenario's are shown in **Table 7.5**. SSP-MOD was used to consider a SSP system where the main stream had excess carbon dioxide stripped to waste and no nominal addition of lime. For both SSP and conventional stabilisation, two scenario's were considered. Namely, Scenario One where the treated but unstabilised water was equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation (i.e. a long retention time prior to stabilisation); and Scenario Two where the treated but unstabilised water was not equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation (i.e. a short retention time prior to stabilisation).

- SSP-MOD showed that in **Scenario One** SSP can be used to obtain a fully stabilised stream with a pH of 8.35, total alkalinity of 69 mg/L (as CaCO₃) and CCPP of 1 mg/L (as CaCO₃). This process requires a 10% sidestream (large) and CO₂ recovery of 10% (very low). Conventional lime and CO₂ stabilisation would provide stabilised water with a pH of 8.47, total alkalinity of 70.5 mg/L (as CaCO₃) and CCP of 3.3 mg/L (as CaCO₃). Chemical costs for a 2000 ML/day conventional lime and CO₂ stabilisation system would be about R56.2 million/annum, whilst chemical costs for SSP would be about R31.8 million/annum. This translates to an **annual chemical cost saving of about R24.4 million/annum**.

- SSP-MOD showed that in **Scenario Two** SSP can be used to obtain a fully stabilised stream with a pH of 8.35, total alkalinity of 69 mg/L (as CaCO₃) and CCPP of 1 mg/L (as CaCO₃). This process requires a 10% sidestream (large) and CO₂ recovery of 10% (very low). Conventional lime and CO₂ stabilisation would provide stabilised water with a pH of 8.47, total alkalinity of 70.5 mg/L (as CaCO₃) and CCP of 3.2 mg/L (as CaCO₃). Chemical costs for a 2000 ML/day conventional lime and CO₂ stabilisation system would be about R49 million/annum, whilst chemical costs for SSP would be about R31.9 million/annum. This translates to **an annual chemical cost saving of about R17.1 million/annum.**

Table 7.5: Chemical cost comparison for the stabilisation of Lesotho Highlands water that has been treated via filtration assisted by ferric chloride dosing: High % sidestream combined with Low percentage CO₂ recovery and re-use

SSP Op. CHARAC.	SSP FINAL WATER - EQBM WITH AIR	SSP FINAL WATER - NO EQBM WITH AIR	CONV. FINAL WATER	CONV. FINAL WATER	CHEMICAL COST COMPARISON (2000 ML/DAY)	
% SS = 10	pH = 8.35	pH = 8.35	pH = 8.47		Lime/CO ₂	SSP
Recov. = 10%	Alk = 69, Ca = 27.6	Alk = 69.3, Ca = 27.7	Alk = 70.5, Ca = 28.2	Alk = 70.5, Ca = 28.2	-R 56.2 M/year -R 49.0 M/year	-R 31.8 M/year -R 31.9 M/year
CO ₂ dose = 38 mg/L	CaCO ₃ dose = 45.8 mg/L	CaCO ₃ dose = 46.1 mg/L	Lime dose = 35 mg/L CO ₂ dose = 40 mg/L	Lime dose = 35 mg/L CO ₂ dose = 26 mg/L	SSP Savings = -R 24.4 M/year SSP Savings = -R 17.1 M/year	
	CCPP = 1	CCPP = 1	CCPP = 3.3	CCPP = 3.2		

7.3.4 CASE THREE: Filtration assisted by ferric chloride dosing - medium % sidestream combined with medium percentage CO₂ recovery and re-use

When considering filtration assisted by ferric chloride dosing, and where SSP is used with a medium % sidestream and a medium percentage CO₂ recovery and re-use, the envisaged scenario's are shown in **Table 7.6**. *SSP-MOD* was used to consider a SSP system where the main stream had excess carbon dioxide stripped to waste and no nominal addition of lime. For both SSP and conventional stabilisation, two scenario's were considered. Namely, Scenario One where the treated but unstabilised water was equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation (i.e. a long retention time prior to stabilisation); and Scenario Two where the treated but unstabilised water was not equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation (i.e. a short retention time prior to stabilisation).

Table 7.6: Chemical cost comparison for the stabilisation of Lesotho Highlands water that has been treated via filtration assisted by ferric chloride dosing: medium % sidestream combined with medium percentage CO₂ recovery and re-use

SSP Op. CHARAC.	SSP FINAL WATER - EQBM WITH AIR	SSP FINAL WATER - NO EQBM WITH AIR	CONV. FINAL WATER	CONV. FINAL WATER	CHEMICAL COST COMPARISON (2000 ML/DAY)	
% SS = 5	pH = 8.36	pH = 8.36	pH = 8.47	pH = 8.47	Lime/CO ₂	SSP
Recov. = 50%	Alk = 70.2, Ca = 28.1	Alk = 69.8, Ca = 27.9	Alk = 70.5, Ca = 28.2	Alk = 70.5, Ca = 28.2	-R 56.2 M/year -R 49.1 M/year	-R 36.2 M/year -R 35.7 M/year
CO ₂ dose = 46 mg/L CO ₂ dose = 45 mg/L	CaCO ₃ dose = 47 mg/L	CaCO ₃ dose = 47 mg/L	Lime dose = 35 mg/L CO ₂ dose = 40 mg/L	Lime dose = 35 mg/L CO ₂ dose = 26 mg/L	SSP Savings = -R 20.0 M/year SSP Savings = -R 13.4 M/year	
	CCPP = 1.1	CCPP = 1.1	CCPP = 3.3	CCPP = 3.2		

7.3.5 Discussion and Conclusions

In light of the possible practical full-scale limitations of the SSP process with regards to CO₂ stripping and recovery, the project team undertook a desktop analysis of a simplified SSP process. This entailed an investigation of the influence of:

- The presence and placement of stripping and alkali addition steps
- The CO₂ dosage to the sidestream
- The percentage sidestream.

The viability of the so-called "simplified SSP" was considered by the development by the project team of a model. The model included *JAVA* programming and the use of *STASOFT 4* and *Watchem*. (At the time, *STASOFT 4* development was in its final stages, and a preliminary test-version of the software was kindly made available by Mr Ian Morrison for the purpose of modelling the simplified SSP. The *Watchem* program is a command line and input file driven program supplied together with *STASOFT 4*). Since there is no gas recycling stream in the simplified SSP, *STASOFT 4* can model the whole process.

- *SSP-MOD* showed that in **Scenario One** SSP can be used to obtain a fully stabilised stream with a pH of 8.36, total alkalinity of 70.2 mg/L (as CaCO₃) and CCP of 1.1 mg/L (as CaCO₃). This process requires a 5% sidestream (medium) and CO₂ recovery of 50% (medium). Conventional lime and CO₂ stabilisation would provide stabilised water with a pH of 8.47, total alkalinity of 70.5 mg/L (as CaCO₃) and CCP of 3.3 mg/L (as CaCO₃). Chemical costs for a 2000 ML/day conventional lime and CO₂ stabilisation system would be about R56.2 million/annum, whilst chemical costs for SSP would be about R36.2 million/annum. This translates to **an annual chemical cost saving of about R20.0 million/annum.**
- *SSP-MOD* showed that in **Scenario Two** SSP can be used to obtain a fully stabilised stream with a pH of 8.36, total alkalinity of 69.8 mg/L (as CaCO₃) and CCP of 1.1 mg/L (as CaCO₃). This process requires a 5% sidestream (medium) and CO₂ recovery of 10% (medium). Conventional lime and CO₂ stabilisation would provide stabilised water with a pH of 8.47, total alkalinity of 70.5 mg/L (as CaCO₃) and CCP of 3.2 mg/L (as CaCO₃). Chemical costs for a 2000 ML/day conventional lime and CO₂ stabilisation system would be about R49.1 million/annum, whilst chemical costs for SSP would be about R35.7 million/annum. This translates to **an annual chemical cost saving of about R13.4 million/annum.**

7.4 DETAILED FINANCIAL ASSESSMENT

7.4.1 Introduction

Project Financial Evaluation methodology determines the financial viability of any new venture/project through a financial modelling exercise involving the quantification of various assumptions and a reasonable estimation of the project risk. It therefore provides a holistic financial view of the project as well as other benefits: focus on key factors, identification and prioritisation of tasks/issues, effective communication of results ideas.

In this instance the Financial Evaluation software was used to assess the financial viability of the SSP process. The detailed costing undertaken was based on a particular SSP scenario where the preliminary chemical running costs comparison of SSP and conventional lime/ CO_2 stabilisation shown above indicated that significant potential savings were potentially possible. I.e. **CASE TWO** (Filtration assisted by ferric chloride dosing - High % sidestream combined with Low percentage CO_2 recovery and re-use), **Scenario Two** (where the treated but unstable water was not equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation).

In this aforementioned scenario a SSP plant with a 10% sidestream and low CO_2 recovery of 10% was shown to be financially attractive. Both Rand Water process engineers and the CSIR project team considered this scenario appropriate in that it can be regarded as operationally and financially conservative with a relatively large percentage sidestream (increased capital cost) and low CO_2 recovery (lower than that achieved in pilot plant operation and with associated high chemical cost).

The financial model created took into account chemical costs, labour costs, maintenance shutdowns, capital cost recovery, inflation, required return on investment and risk. The detailed financial model considers the higher capital cost of SSP and the ongoing chemical savings of SSP and uses, and those other factors mentioned above, to essentially assess the ability of the SSP process to pay for itself. **At all stages estimates were skewed towards being conservative to the detriment of SSP.**

Model Description and Set-up

In setting up the model it was decided that the assessment should take place within the CO_2 stripping and recovery limitations achieved using the pilot plant. Accordingly, the following inputs and related assumptions were entered into the model:

- The lifespan of the project is 10 years. Note: this is conservative, as Rand Water usually looks at a 30-year project life.
- Inflation rate is 7% per annum.
- The minimum required return on investment is 10% per annum. Note: this is conservative, as Rand Water has generally used 6% per annum for Lesotho Highlands projects.
- The capacity of the proposed stabilisation plant is 2000 ML/day. This capacity is assumed from the first year of operation with no foreseen increase in capacity.
- The stabilisation plant operates for 350 days per year.
- In the financial model the SSP process with a 10% sidestream, a CO₂ recovery of 10%, and air stripping of the main stream was compared to the conventional lime/CO₂ stabilisation process that yielded the same final water quality. Note: this is conservative, as the pilot plant has consistently achieved a higher percentage CO₂ recovery than this (see Chapter 6).
- The following required chemical dosages (shown as required dosage to entire stream) were ascertained using *SSP-MOD* and *STASOFT 4*:
 - SSP (10% sidestream, 10% CO₂ recovery, air strip main)
 - CO₂ 38 mg/L
 - CaCO₃ 46.1 mg/L
 - Conventional lime/CO₂ stabilisation
 - CO₂ 26 mg/L
 - Ca(OH)₂ 35 mg/L
- The following chemical costs were used in the model:
 - CO₂ R700/ton
 - CaCO₃ R370/ton
 - Ca(OH)₂ R1400/ton

NOTE: The prices for limestone and white lime vary considerably with both the quality of the product and the region to which the product must be transported. The cost of white lime has also been seen to fluctuate considerably in the past two years. The costs presented are typical costs for delivery of CO₂ and suitable quality limestone/white lime to the Lesotho Highlands Scheme, year 2000 prices. As the viability of the SSP is influenced by the chemical cost savings, the cost of these chemicals for a particular application must be carefully reviewed.

- Wastage of 5% on all chemicals used was included.
- Required labour for both stabilisation plants was assumed equal, and therefore labour costs are cancelled in the model.
- Electricity costs for the SSP process were assumed to be R0.01/m³ higher than that for the conventional lime/CO₂ stabilisation process. Note: This additional electricity cost is included despite the fact that in the SSP process only 10% of the main stream undergoes treatment (therefore requiring less electricity).
- The following capital cost estimates were obtained from a real life costing of a 100 ML/day water stabilisation plant (year 2000 estimates) employing the following technology:
 - Conventional stabilisation (Lime/CO₂) R7 million
 - Limestone contactors (CaCO₃) R7 million

From these estimates the cost of a 100 ML/day SSP plant (utilising a 10% sidestream and 10% CO₂ recovery) was assumed to be:

- SSP (10% sidestream, 10% CO₂ recovery) R9 million

The following formula (often used for preliminary cost estimating) was utilised to determine the cost of a 2000 ML/day stabilisation plant:

$$C_2 = C_1 \times (Q_2 / Q_1)^x$$

Where C_2 is the estimated cost of the new project
 C_1 is the known cost of the existing comparable facility
 Q_1 and Q_2 are the respective capacities
 X is the cost capacity factor that usually varies between 0.6 and 0.8

Using the above formula and a cost capacity factor of 0.8, the following cost estimates were obtained:

- Conventional stabilisation (Lime/CO₂) R77 million
- SSP (10% sidestream, 10% CO₂ recovery) R99 million

As this is a green field project (an existing stabilisation plant does not exist), the additional capital cost of R22 million for the SSP plant was included in the financial model. In addition, a depreciation rate of 10% on cost was assumed.

- Maintenance costs of 5% per annum on the additional capital cost of the SSP plant were assumed.
- Tax of 35% was assumed to apply.

- The risk associated with this venture is not well defined. The risk discount factor was therefore set at 30% (high risk). In total, the discount factor amounts to 47%: 7% (inflation) + 30% (risk involved) + 10% (minimum required return on investment). Note: Rand Water felt that the associated risk of the 10% sidestream and 10% CO₂ recovery SSP plant would be lower than 30%.

7.4.2 Discussion of Financial Assessment Model Outputs

Once the financial model has been constructed using certain assumptions entered into the *MSExcel* spreadsheet (as listed above), various parameters are calculated and displayed in the form of graphs attached to an *MSExcel* spreadsheet. These parameters/graphs are:

- Cumulative Cash Flow
- Discounted Cash Flow
- Break-Even Capacity
- Cost Structure
- Net Present Value, Internal Rate of Return and Sensitivity Analysis

Cumulative Cash Flow

The total cumulative cash flow for the project (from initial investment to the end of the expected lifespan) includes the cash outflows that occur during the initial investment phase (e.g. total capital expenditure). Plotting this parameter against time provides a first estimate of the viability of the project. The cumulative cash flow for the SSP plant (10% sidestream, 10% CO₂ recovery) is shown in **Figure 7.2** below. The "nominal" curve, (dotted line), is the cumulative cash flow uncorrected for inflation, whereas the shaded curve represents the inflation corrected cash flow (more correct for assessing viability).

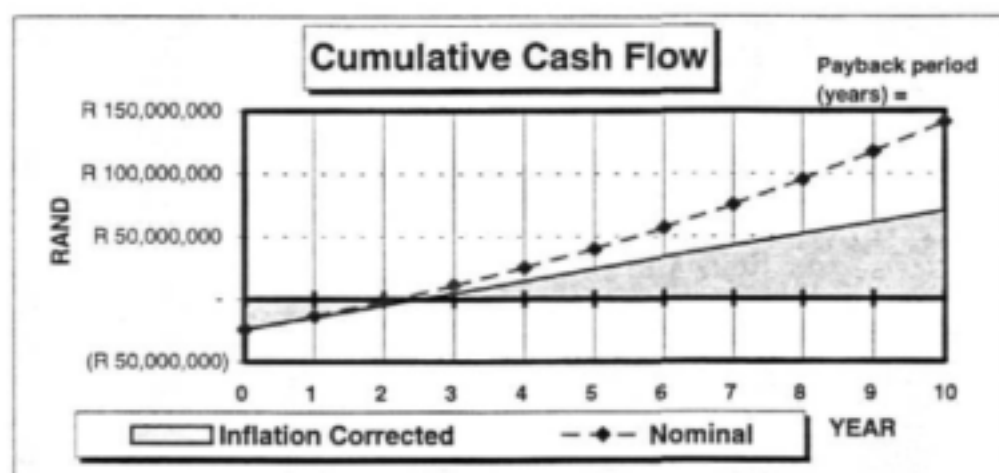


Figure 7.2: Cumulative Cash Flow

The point where the inflation corrected curve intersects the x-axis represents the payback period (i.e. the time taken for the money invested to be recovered). For the SSP plant under consideration, the payback period is 2.5 years (provided the assumptions made are correct). This parameter should be approximately a third of the project lifespan, and not more than half. The payback period shown here amounts to a quarter of the project lifespan, which gives a first indication of a healthy venture.

Discounted Cash Flow

The cumulative cash flow graph does not reflect the aspect of risk associated with a venture or project (i.e. the probability that the assumptions made in the model will turn out to be correct). In the same manner that the cash flow was "discounted" by a certain factor to account for inflation, it is possible to apply another "discount" factor to reflect the risk. The resulting cash flow obtained, the Discounted Cash Flow shown in **Figure 7.3**, now shows the effect of discounting for inflation (7%) and risk (30%). The resulting payback period has now shifted to 4.3 years, which is still financially viable.

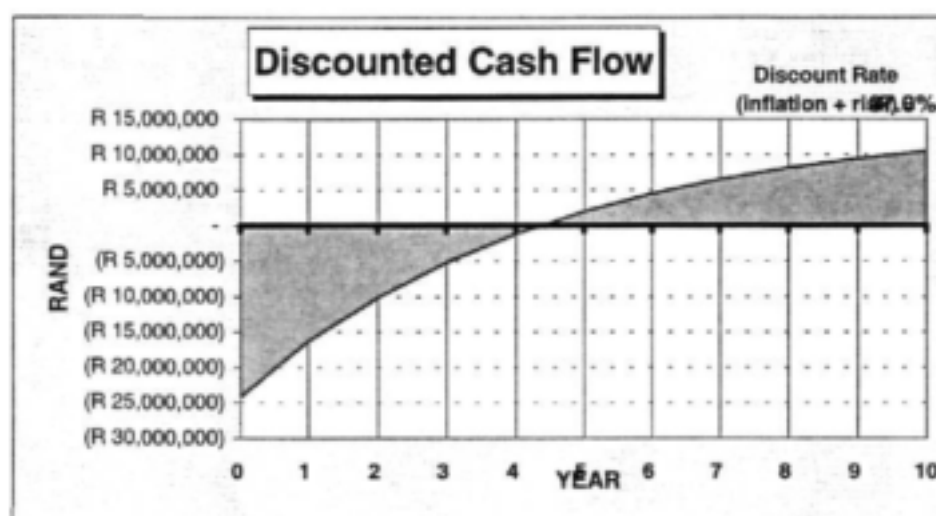


Figure 7.3: Discounted Cash Flow

Cost Structure

The cost structure of the project provides another cost-related view of the operating risk. The risk could be expected to increase if one of the slices of the pie chart was fairly large in comparison with the others. This would indicate that a small change in that cost could significantly affect the profit. **Figure 7.4** shows the cost structure graph associated with the SSP plant. The graph clearly indicates the importance of chemical and operating costs on the financial viability of the SSP plant.

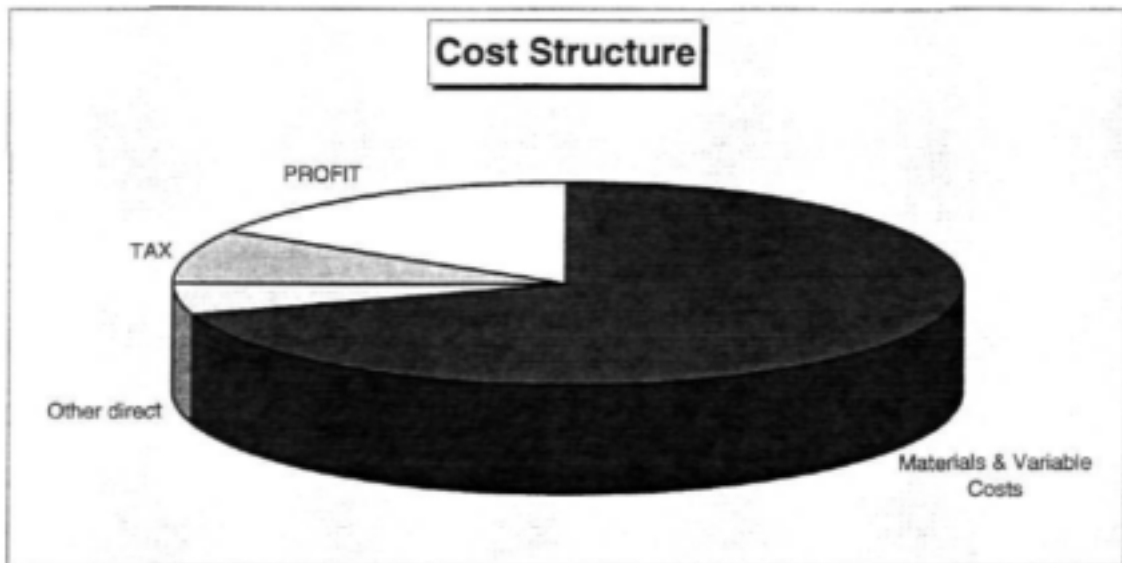


Figure 7.4: Cost Structure

Net Present Value, Internal Rate of Return and Sensitivity Analysis

The model finally calculates a Net Present Value (NPV) and an Internal Rate of Return (IRR) for the project lifespan. These two parameters represent an absolute measure of viability associated with any given project. To infer financial feasibility, the NPV needs only to be greater than zero. The IRR represents the total discount factor that gives a critical NPV of zero, therefore indicating whether this discount factor is large enough to account for inflation, the required return and the risk associated with the project.

Using the model inputs described in above, the NPV was calculated to be R2,7 million for the SSP process (with a 10% sidestream and a CO₂ recovery of 10%) and associated IRR of 52%. These two figures indicate that the project, with the assumptions made, is financially viable and that a risk factor of up to 35% (52% - 7% (inflation) - 10% (required return)), could still be applied and give an NPV of zero.

The most powerful way of evaluating the risk of the project is to do a sensitivity analysis. The sensitivity analysis tests the effect of each assumption on the NPV, by varying parameters (variables) by a specific amount (percentage). The resulting change in the NPV per variable indicates the degree of sensitivity of the project to that variable. However, the degree of impact alone does not determine the risk. The level of uncertainty associated to the impact gives an indication of the risk of the project. Using this approach the following key parameters were varied by 20% (i.e. a

20% increase in each of the following parameters in the SSP process – the conventional process is left unchanged):

- Capital cost
- Chemical operating cost
- Electricity cost

The following table shows the resultant effect of varying these parameters on the NPV and IRR (a bracketed NPV indicates a negative NPV).

Table 7.7: Effect of sensitivity analysis on NPV and IRR of the SSP plant

	NPV	IRR
Original	R2.7 million	52%
Capital cost +20%	(R2.2 million)	44%
Chemical operating cost +20%	(R7.3 million)	33%
Electricity cost +20%	R0.2 million	47%

The above table shows the significant variability of the financial viability of the specific SSP plant with regards to both capital cost and chemical operating cost.

Analysis of the NPV and IRR following variance in the **capital cost** shows that although the NPV is negative, an IRR of 44% is still obtained which indicates that the project can support an associated risk of 27% (7% inflation and 10% return on investment). In light of information supplied by Rand Water the project would still appear to be viable at this stage (no requirement for return on investment and projected lower risk than what predicted).

With a 20% increase in the **chemical operating costs** of the SSP plant, the NPV is significantly negative and the associated IRR is reduced to 33% (project can support a risk of 16%). However, in light of information supplied by Rand Water the project would still appear to be viable at this stage.

As only preliminary estimations for **electricity costs** were employed in the model created, it was felt necessary to determine the impact of varying this cost on the financial viability of the project. The table indicates that electricity has a significant effect on the project viability, and that more accurate electricity costs for the two alternative stabilisation options should be obtained and compared prior to project commencement.

7.4.3 Conclusions

The Financial Evaluation software is an effective tool for determining the viability of a new venture/business as well as providing a reasonable estimate of the risk associated to that venture/business. In this particular example a 2000 ML/day stabilisation plant incorporating the SSP process (with a 10% sidestream and 10% CO₂ recovery) was compared to a conventional stabilisation plant using lime and CO₂. The financial model generated showed that the SSP process is financially attractive with a positive NPV of R2.7 million and IRR of 52%. This positive result was based on the development of a financial model that described a "worst case" scenario with a relatively large percentage sidestream (increased capital cost) and low CO₂ recovery (high chemical cost).

Sensitivity analysis revealed that the financial viability of the SSP process is highly dependant on the capital cost and operating costs (chemical costs and electricity costs) of the SSP plant. In particular, it should be noted that the viability of the SSP process is strongly influenced by the cost of white lime/CO₂ and limestone. These factors will need to be thoroughly investigated prior to project commencement.

7.5 DISCUSSIONS AND CONCLUSIONS

This chapter addresses the desirability and suitability of an optimised SSP for the Lesotho Highlands scheme, and assess the motivation for potential industrialisation and full-scale implementation of the process.

Considering the inability of the CSIR project team to optimise operation of the SSP pilot plant at high percentage carbon dioxide recovery levels (i.e. carbon dioxide recovery greater than 50%), and the inability of Rand Water project team to finalise water treatment and stabilisation requirements, the approach was adopted that a number of conservative assumptions could be made. These included:

- Assume that As River outfall water is representative of raw water quality.
- Assume that water treatment will be via use of either micro-filtration, or filtration using ferric chloride as a flocculant with the latter process being the more likely.
- Assume that stabilised water quality should closely represent existing Rand Water stabilisation requirements.
- Basic financial attractiveness should be assessed for via simple chemical running cost comparisons for a range of SSP performances
- More detailed financial attractiveness should be considered for ferric chloride treatment
- For the more complex financial assessment, the assessment should take place within the CO₂ stripping and recovery limitations achieved using the pilot plant.

Accordingly, both basic financial assessment and more complex financial assessment were carried out. The basic financial assessment identified that where treatment is via filtration assisted by ferric chloride dosing, an appropriate stabilisation scenario is "high % sidestream (10%) combined with low percentage CO₂ recovery and re-use (10%) where the assumption is that the treated but unstable water was not equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation. In addition an airstrip of the blended stream is required. The basic financial assessment showed a potential chemical cost saving of approximately R17.1 million/annum.

Both Rand Water process engineers and the CSIR project team considered this scenario appropriate in that it can be regarded as operationally and financially conservative with a relatively large percentage sidestream (increased capital cost) and low percentage CO₂ recovery (lower than that achieved in pilot plant operation and with associated high chemical cost).

The detailed financial model considers the higher capital cost of SSP and the ongoing chemical savings of SSP and using these, and other running costs, to essentially assess the ability of the SSP process to pay for itself. The financial assessment showed that payback period corrected for inflation (7%) is 2.5 years, and payback period corrected for inflation and risk (37%) is 4.3 years. Both of these are very attractive.

Furthermore, the model calculates a Net Present Value (NPV) and an Internal Rate of Return (IRR) for the project lifespan. To infer financial feasibility, the NPV needs only to be greater than zero. The IRR represents the total discount factor that gives a critical NPV of zero. The NPV was calculated to be R2,7 million with an associated IRR of 52%. These two figures indicate that the project, with the assumptions made, is financially viable and that a risk factor of up to 35% (52% - 7% (inflation) - 10% (required return)), could still be applied and give an NPV of zero.

In summary, the detailed financial assessment showed that even with a number of conservative assumptions to the detriment of SSP (lifespan of 10 years, raised electricity costs for SSP, risk discount factor of 30% per annum, minimum required return of investment of 10% per annum, low percentage CO₂ recovery) the process potentially provides significant financial advantage over conventional lime/CO₂ stabilisation. The project team and Rand Water believes that SSP may present an opportunity for significant cost savings and the process should be subjected to further detailed evaluation in the future.

CHAPTER 8

FINAL CONCLUSIONS

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A significant proportion of the waters of South Africa and all of the waters of Lesotho, are soft and acidic with characteristically low calcium, total alkalinity and carbonate species concentration. Distribution of such waters results in aggressive attack of cement concrete pipes and linings, and corrosive attack of metal pipes and valves within the distribution network. The impact of such attack is significant, and results in the loss of water, the need for expensive repairs and a loss of water potability.

Water conditioning to prevent aggression and/or corrosion (termed stabilisation) is conventionally achieved by the addition of lime (Ca(OH)_2) and carbon dioxide (CO_2). Although this process is well documented and understood, it has a number of drawbacks which include the use of notoriously troublesome lime dosing equipment and the need for high quality white lime which is currently in short supply in South Africa. An alternative process is stabilisation via contact with limestone (solid calcium carbonate), which has been shown to have many advantages over lime-mediated stabilisation. The use of limestone mediated stabilisation has, however, hitherto been limited to smaller water treatment works as a result of the large contact tanks required. Use of limestone for large water treatment works was made viable by the development of the limestone mediated Sidestream Stabilisation Process (SSP). Indications from preliminary pilot plant trials and theoretical assessments have shown that the SSP process potentially provides significant cost savings and other advantages over conventional stabilisation.

As Rand Water is in the process of considering water transport and treatment requirements for the Lesotho Highlands Scheme Water (which are relatively soft and acidic therefore requiring stabilisation), the SSP was identified as a potentially attractive alternative to conventional stabilisation using lime and carbon dioxide.

8.1 THE USE OF PROCESS MODELLING PACKAGES FOR PREDICTING THE BEHAVIOUR OF THE SSP

One of the major aims of the project was to use a commercially available process modelling package to develop and calibrate a process model describing the SSP. The model developed would be used to both identify the operational limitations of SSP, and identify means to optimise the operation of the process.

Assessment of the *PRO/II* process modelling package showed that:

- The model developed was able to accurately simulate:
 - ♦ The incoming feed stream conditions (if correct inputs were added),
 - ♦ The condition of the sidestream after CO_2 addition and dissolution, and
 - ♦ The condition of the sidestream after CaCO_3 addition and dissolution (if the appropriate amount of CaCO_3 is added).
- Problems were, however, encountered when CO_2 stripping and recovery was modelled. The model was unable to accurately simulate what was occurring in practice from operation of the SSP pilot plant. The developers of the software were unable to positively identify the source of the problem and revealed that the package may have previously unidentified carbonate chemistry limitations. The developers stated that further review and analysis of the possible

limitations of the modelling package would only be investigated on a commercial basis. Due to this significant development, and the fact that CO₂ stripping and recovery step is a critical step in the SSP process, the use of *PRO/II* was abandoned.

- In light of the failure of the commercially available process modelling package, CSIR initiated development of its own model. Due to concerns of the practical limitations of CO₂ recovery and recycling, the project team first considered a "simplified SSP" process. This simplified SSP process does not include CO₂ recovery and subsequent recycling (but does incorporate CO₂ stripping to waste). It was envisaged that by using *STASOFT 4* and *Watchem* to model this simplified SSP.

8.2 CONSIDERATION OF THE VIABILITY OF A SIMPLIFIED SSP

Due to the aforementioned reasons a simplified SSP was considered in which no carbon dioxide recovery occurs. The theoretical viability of the simplified SSP was considered by the development by the project team of a model that included the use of *JAVA* programming, *STASOFT 4* and *Watchem*. If model development was successful it would be used as the basis for the further development of a model describing SSP (regardless of the viability of the simplified SSP).

Findings included *inter alia*:

- Stripping CO₂ to the atmosphere before blending the sidestream and mainstream was not financially attractive.
- Stripping CO₂ to the atmosphere after blending the sidestream and mainstream, was financially attractive. The financial attractiveness varied with the both the CO₂ stripping efficiency and the alkali's used for final pH adjustment. Use of sodium alkali's was found to provide little or no saving relative to the use of lime, as a result of the high cost of these chemicals.
- Where partial stripping of the mainstream was accompanied by lime dosing, an attractive chemical cost saving incurred.
- Importantly, where no stripping of CO₂ was practised and nominal lime dosing was employed, significant chemical savings relative to conventional lime and CO₂ mediated stabilisation were observed. For example,
 - ♦ Where a final total alkalinity of 50 mg/L and a CCPP of zero was required, use of a 20% sidestream would lead to a chemical cost saving of 2.63 c/kL. On a 100 ML/day treatment plant this would translate to a saving of R78 900 / month, and R959 950 / year.
 - ♦ Where a final total alkalinity of 30 mg/L and a CCPP of zero was required, a potential chemical cost saving of 1.25 c/kL is available at a 10% sidestream. On a 100 ML/day treatment plant this translates to a saving of R37 500 / month, and R456 250 / year.
- Considering the practical implications of CO₂ stripping from a main stream in a large water treatment works, it is of particular interest that the study showed that significant savings are potentially possible where no CO₂ stripping is required. It should, however, also be noted that the viability of the process is highly dependant on the costs of the

required chemicals (CO_2 /white lime vs. limestone). These costs need to be carefully considered at each particular application.

From this desktop investigation the project team gained a better understanding of the SSP process.

8.3 DEVELOPMENT OF "SSP-MOD" PROGRAM FOR PREDICTING THE BEHAVIOUR OF THE SSP

The steady state *SSP-MOD* model developed describes the various unit processes of the SSP process including CO_2 stripping, recovery and subsequent recycling.

- The model was compared with *STASOFT 4* and found to be accurate.

Subsequent to this the model was compared with actual data obtained from preliminary operation of the SSP pilot plant. This preliminary investigation had the following findings:

- The model predicted a significantly lower CO_2 recovery than what had been calculated (using pH measurements and *STASOFT 4*) from pilot plant operation.
- The model predicted that increasing the "fresh" CO_2 added to the sidestream increases the CO_2 recovered to a maximum of ~ 70 %.
- The model predicted that an increase in vacuum pressure (i.e. closer to absolute zero pressure – 0 kPa) within the recovery vessel increases the amount of CO_2 recovered (this relationship only holds at higher CO_2 doses).
- The model predicted that the addition of 5 L atmospheric air/L sidestream decreased the final water total alkalinity and the amount of CO_2 recovered. This result indicated that the addition of air may not always be beneficial and would have to be further investigated during pilot plant trials.

Following these findings efforts were made to identify and overcome possible problematic areas on the pilot plant that may be decreasing the effectiveness of the CO_2 stripping and recovery process. This investigation included: re-configuration of pilot plant, use of a correctly sized eductor, replacement of spray nozzles used in recovery vessels and replacement of faulty pH probes.

8.4 PILOT PLANT OPERATION USING AN EDUCTOR FOR CO_2 RECOVERY

In order to assess the accuracy of the *SSP-MOD* model developed, it needed to be verified and calibrated on data obtained from operation of the SSP pilot plant. In parallel with verification and calibration of the model, was the need to optimise SSP pilot plant operation. Assessment of the SSP process has shown that the stripping and recovery of CO_2 is an essential step in the SSP and maximizing CO_2 recovery is therefore of primary importance. Previous pilot plant studies had shown that CO_2 recovery using vacuum pumps is effective, yet potentially problematic in full-scale applications. Considering the potential benefits of eductors in full-scale applications, the use of an

eductor was selected for this project. Eductors have the following potential advantages over vacuum pumps: low cost, simple and reliable, ease of installation, non-electrical unit, corrosion and erosion resistant.

During the testing and operation of the SSP pilot plant using an eductor, the following important observations were made:

- The use of an eductor ensures that a steady vacuum can be obtained. This is in contrast to what could previously be obtained on the pilot plant using vacuum pumps, where decreases in vacuum generation efficiency often occurred.
- For the successful operation of the SSP, the use of a correctly sized eductor is of critical importance. However, during this project both eductors tested did not operate at the required design specifications. This was despite considerable effort being made by the project team to ensure that correctly sized eductor's were obtained.
 - Investigation revealed that in the first instance the distributors provided incorrect specifications for the eductor. In the second instance, it again became apparent that the eductor was not operating as expected. This problem was raised with both the South African distributors and manufacturers from the United States of America, but neither party could provide meaningful comment as to the reason why the eductor failed.
 - Therefore, although considerable efforts were made to ensure that a correctly sized eductor was obtained, the eductor could not meet the required design specifications. The project team expressed their concern and disappointment over this state of affairs, and appealed to both parties to respond meaningfully as a matter of urgency. At the end of the project, a meaningful response had not yet been received. This poor service puts the use of eductors in a negative light.
- Three "Long Run" pilot plant experiments were conducted under the following conditions:
 - Low vacuum, high "fresh" CO₂ dose (Long Run 1)
 - High vacuum, low "fresh" CO₂ dose (Long Run 2 and 3)

From these tests the following observations were made:

- Data obtained from Long Run 1 (low vacuum – approximately 62 - 68 kPa, high "fresh" CO₂ dose – 788 mg/L) showed that even though pilot plant performance was not optimal (due to poor performance of the eductor) CO₂ recoveries of 30 - 40 % were obtained.
- In addition, data obtained from Long Run 2 and Long Run 3 (high vacuum – approximately 40 - 45 kPa, low "fresh" CO₂ dose – 302 mg/L and 319 mg/L respectively) showed that CO₂ recoveries of 20 - 40 % were obtained.

Due to the non-performance of the eductor, a long run incorporating high vacuum and a high "fresh" CO₂ dose could not be conducted.

8.5 ASSESSMENT OF THE SSP-MOD MODEL BY COMPARISON WITH PILOT PLANT RESULTS

At the end of the pilot plant trials, outputs from the SSP-MOD model were compared with data obtained from pilot plant operation. These investigations revealed that:

- The model accurately predicted the characteristics of the feed, CO₂ acidified sidestream and sidestream after CaCO₃ uptake.
- The model, however, predicted a significantly lower CO₂ recovery than what had been experienced during pilot plant operation (e.g. for Long Run 1 the model predicted a CO₂ recovery of ~ 8 %, while a CO₂ recovery of 30 – 40 % had been obtained from pilot plant operation).
- Subsequent extensive review and analysis of the model by the project team and specialist third parties yielded no significant errors in the model, and at the close of the project a meaningful explanation as to why such discrepancies had occurred had not been reached.
- Based on observations from historical pilot plant operation where it seemed that small amounts of air improved CO₂ recovery, further modelling with the addition of air to the recovery vessels was investigated. The SSP-MOD model showed that the addition of small amounts of air (0.1 – 1 L air/L sidestream) could aid CO₂ recovery, and that, based on data from Long Run 1, CO₂ recoveries as high as 70% could be achieved if a high vacuum pressure could be maintained within the recovery vessel. This result therefore confirms historical pilot plant observations.
- A significant limitation with regards to the use of eductors is the unit's non-capability of maintaining a vacuum with addition of even nominal levels of air to the recovery vessels. This result compromises the further use of eductors.

8.6 ASSESSMENT OF THE SUITABILITY OF THE SSP FOR THE LESOTHO HIGHLANDS SCHEME

The second major aim of the project was to determine the desirability and suitability of the SSP process for the Lesotho Highlands scheme, and assess the motivation for industrialisation and full-scale implementation of the process.

Considering the inability of the CSIR project team to optimise operation of the SSP pilot plant at high percentage carbon dioxide recovery levels (i.e. carbon dioxide recovery greater than 50%), and the inability of Rand Water project team to finalise water treatment and stabilisation requirements, a number of conservative assumptions were made.

Both basic and more complex financial assessments were carried out. The basic financial assessment (encompassing chemical running costs only) identified that where treatment is via filtration assisted by ferric chloride dosing, an appropriate stabilisation scenario is "high %

sidestream (10%) combined with low percentage CO₂ recovery and re-use (10%) where the assumption is that the treated but unstable water was not equilibrated wrt aqueous-gaseous carbon dioxide prior to stabilisation. In addition an airstrip of the blended stream is required. The basic financial assessment showed a potential chemical cost saving of approximately R17.1 million/annum or 2.3 c/kL.

Both Rand Water process engineers and the CSIR project team considered this scenario appropriate in that it can be regarded as operationally and financially conservative with a relatively large percentage sidestream (increased capital cost) and low percentage CO₂ recovery (lower than that achieved in pilot plant operation and with associated high chemical cost).

The detailed financial model considers the higher capital cost of SSP and the ongoing chemical savings of SSP and using these, and other running costs, to essentially assess the ability of the SSP process to pay for itself. The financial assessment showed that payback period corrected for inflation (7%) is 2.5 years, and payback period corrected for inflation and risk (37%) is 4.3 years. Both of these are very attractive.

Furthermore, the model calculates a Net Present Value (NPV) and an Internal Rate of Return (IRR) for the project lifespan. To infer financial feasibility, the NPV needs only to be greater than zero. The NPV was calculated to be R2,7 million with an associated IRR of 52%. These two figures indicate that the project, with the assumptions made, is financially viable and that a risk factor of up to 35% [52% - 7% (inflation) - 10% (required return)], could still be applied and give an NPV of zero.

The detailed financial assessment therefore showed that even with a number of conservative assumptions to the detriment of SSP (lifespan of 10 years, raised electricity costs for SSP, risk discount factor of 30% per annum, minimum required return of investment of 10% per annum, low percentage CO₂ recovery) the process potentially provides significant financial advantage over conventional lime/CO₂ stabilisation.

8.7 FINAL THOUGHTS

Of obvious consideration for the financial assessments conducted (both simplified SSP vs. conventional lime-CO₂ stabilisation and SSP vs. conventional lime-CO₂ stabilisation) are the costs of the required chemicals (CO₂/white lime vs. limestone). The prices for both limestone and white lime vary geographically with transport costs. In recent years the price of high quality white lime has risen dramatically (depending on quality, the Rand exchange rate, and the region to which the product must be transported). Individual assessment of the relevant process therefore needs to be considered on a case-by-case basis. Due to these variations a direct comparison between the simplified SSP and the SSP cannot be made from the information presented in this report. The trend of chemical costs is that raw, graded limestone will always be significantly less expensive than use of beneficiated lime and CO₂ (with the latter two requiring considerable energy inputs). This cost difference is exaggerated by the

present South African need to import high quality white lime. Hence, whilst use of the simplified SSP and SSP needs to be considered on a case-by-case basis, these processes should always offer significant chemical cost savings over the use of lime and CO₂ based stabilisation.

A number of important conclusions can be made and these are summarised below.

In conclusion,

- The low risk simplified SSP was shown via desktop based equilibrium chemistry modelling to be a viable alternative for the full stabilisation of soft, acidic waters.
- The simplified SSP provides significant financial savings over conventional lime and carbon dioxide stabilisation. For example, on a 100 ML/day treatment plant treating a typical Stellenbosch raw water, and requiring a final Alkalinity of 50 mg/L and a CCPP of zero, the use of a 20% sidestream would result in a saving of R78 900 / month, and R959 950 / year.
- Although optimisation of SSP pilot plant operation could not be achieved, results from operation with sub-standard eductors revealed that CO₂ recoveries of 20 – 40% were obtained. It can therefore be assumed that higher CO₂ recoveries could be obtained if pilot plant operation was optimal.
- Conservative financial assessment of SSP for use at Clarens (Lesotho Highlands Scheme), in which CO₂ recovery and re-use assumptions were well within pilot plant performance, indicates that SSP provides significant financial savings over conventional lime and CO₂ stabilisation with a project payback period of 4.3 years, NPV of R2,7 million and IRR of 52%.

The above results serve as strong motivation for further investigation and industrialisation of both the simplified SSP and SSP.

Other related WRC reports available:

Additional treatment requirements of water abstracted from the Vaal River system following the importation of Lesotho Highland Water

Geldenhuys JC, Jones M and Joubert JHB

The latest of the interbasin transfer schemes designed and implemented to augment the Vaal River system is the Lesotho Highlands Water Project. The 22nd of January 1998 marked the official inauguration of the project, with the first releases of water to South Africa occurring in October 1997. At present the water released through the Ash River outfall follows the course of the Ash - Liebenbergsvlei - Wilge River system to the Vaal Dam, from where it is abstracted for treatment at Rand Water's treatment works or released for downstream users. With this in mind, this project was initiated to:

- Establish the possible changes that could take place in the chemical composition of water from the Vaal Dam catchment area due to the increasing effect of water imported from Lesotho; and
- Determine how different quality variables are likely to change the minimum water treatment required to produce chemically stable water of potable quality.

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