WATER STABILISATION THROUGH A LIMESTONE MEDIATED SIDESTREAM PROCESS

BY

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A thesis submitted to the Department of Chemical Engineering of the Cape Technikon in fulfillment of the requirements for the Masters Degree in Chemical Engineering.

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Cape Technikon
December 2001

DECLARATION

I hereby certify that this thesis is my own original work, except where specifically acknowledged in the text. It is submitted for the Master's degree in Chemical Engineering to the Cape Technikon, Cape Town. The opinions and conclusions drawn are not necessarily those of the Cape Technikon.

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SYNOPSIS

Approximately 40% 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. 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 stabilization) 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 troublesome lime, high chemical operating costs, and the need for high quality white lime which is currently in short supply in South Africa. An alternative stabilization process is stabilisation via contact with limestone (solid calcium carbonate), which has been shown to have many advantages over lime-mediated stabilization. However, the use of limestone mediated stabilization has hitherto been limited to smaller water treatment works as a result of the large contact tanks required. Use of limestone for larger water treatment works was made viable by the development by CSIR of the limestone mediated Sidestream Stabilisation Process (SSP).

The SSP consists of taking a sidestream of approximately 2 – 5% of the unstabilised water, dosing high levels of 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. After CO_2 stripping, the sidestream is blended with the main stream in the correct proportions to allow for a fully stabilized 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 stabilization. SSP technology and its derivations are patented internationally.

The original aims of the project were to:

- Successfully operate the SSP pilot plant using the eductor as a mechanism for recovering CO_2 and thus saving significant operational costs of the project.
- 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 limits of SSP, and (ii), identify means to improve the performance and optimize the operation 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. These are mentioned below:

- Programming and software development. The original project objectives required the use of a commercially available process modelling package to model the SSP. At an advanced stage in the project it became apparent that the chosen package had fatal limitations regarding modeling of aqueous-gaseous phase interactions, and that for this reason further use of the package was pointless. Accordingly, originally unenvisaged programming and software development was carried out.

Of the many process modeling packages for modelling the SSP PRO/II was identified. 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 CO_2 addition and dissolution, and the condition of the sidestream after $CaCO_3$ dissolution.
- The model was, however, unable to accurately simulate CO_2 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 CO_2 stripping and recovery step is critical in the SSP process, the use of PRO/II was abandoned.

As a result of PRO/II not being suitable for modeling the SSP, the project team undertook previously unenvisaged 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%).

- Increasing the amount of "fresh" CO_2 added to the sidestream increases the CO_2 recovered, to a maximum of ~ 70%.

- An increase in vacuum pressure (i.e. closer to absolute zero pressure - - kPa) within the recovery vessels 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 that* addition of air would aid CO_2 recovery, the addition of 5 L atmospheric air/L sidestream decreased the final water 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.

In order to assess the accuracy of SSP-MOD developed in predicting the behavior of the SSP process, the model 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 optimize 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 CO_2 is essential in the SSP and that maximizing CO_2 recovery at economical "fresh" CO_2 doses was of primary importance in an attempt to optimize the process. Previous pilot plant work had shown that CO_2 recovery using vacuum pumps was potentially problematic, and therefore in this project the use of an eductor was chosen. Eductors have the potential advantages over vacuum pumps of low cost, simplicity and reliability, ease of installation, non-electrical unit, corrosion and erosion resistance.

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 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 or the USA manufacturers. This poor service puts the use of eductors in a negative light.

- Three "Long Run" pilot plant experiments were conducted. From these tests the following observations were made:
    - Data obtained from Long Run 1 (low vacuum – approximately 62 – 68 kPa (absolute), high "fresh" CO_2 dose – 788 mg/L) showed that even though pilot plant performance was not optimal (due to poor performance of the eductor) CO_2 recoveries of 30 – 40% were obtained.

  - Data obtained from Long Run 2 and 3 (high vacuum – approximately 40 – 45 kPa, low "fresh" CO_2 dose – 302 mg/L and 319 mg/L respectively) showed that CO_2 recoveries of 20 – 40% were obtained

Due to the non-performance of the eductor, a long run incorporating high vacuum and a high "fresh" CO_2 dose was not possible.

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

- The model accurately predicted the characteristics of the feed, CO_2 acidified sidestream and sidestream after $CaCO_3$ uptake.
- The model, however, predicted a significantly lower CO_2 recovery than what had been experienced during pilot plant operation (e.g. for Long Run 1 the model predicted a CO_2 recovery of ~ 8%, while a CO_2 recovery of 30 – 40% had been obtained from pilot plant operation).
- Subsequent extensive 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 the introduction of small amounts of air improved CO_2 recovery, further modeling with the addition of air to the recovery vessels was investigated. The SSP-MOD showed that the addition of small amounts of air (0.1 – 1 L air/L sidestream) could aid CO_2 recovery, and that, based on data from Long Run 1, CO_2 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 vessels. This result therefore confirms historical pilot plant observation
- 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 CO_2 recovery.

ACKNOWLEDGEMENTS

The work contained in this thesis was performed at the Centre for Science and Industrial Research (CSIR) between September 1999 and March 2001.

I wish to thank the following persons and/or institutions for their assistance and contributions in the completion of this thesis:

- The CSIR in Stellenbosch for the use of their research facilities and financial support.
- The National Research Foundation (NRF) for their financial contribution.
- My supervisors, Grant Mackintosh and Prof. FW Petersen for their guidance and encouragement throughout the course of my studies. Their advice and assistance is greatly appreciated.
- The CSIR water treatment project team and the Cape Water Programme staff in general, for all their support and assistance.
- My family and friends for their support and encouragement throughout my years of studying.

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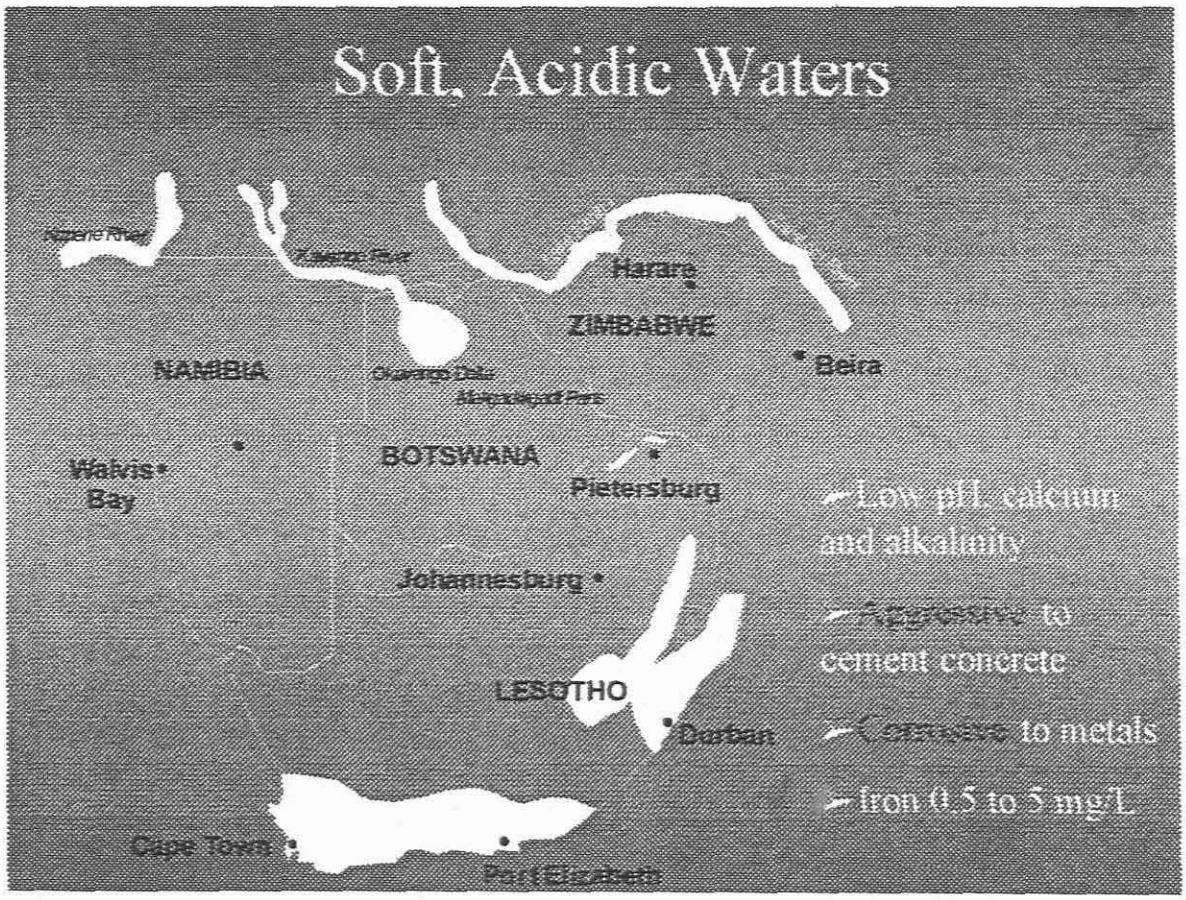
CHAPTER 1

INTRODUCTION

1.1 STABILISATION OF SOFT ACIDIC WATERS

Throughout the world, where snow melt and mountain catchment waters are found and where the underlying geology is lacking in calcitic deposits, calcium and carbonate-deficient waters with low pH occur. Typically these soft, acidic waters have low conductivity (5 – 50 mS/m), low total alkalinity (0 –20 mg/l as $CaCO_3$) and low pH (pH < 6). Examples of such waters are found in Sydney (Australia), Sierra Nevada (US), Vancouver (Canada), the Harz region (Germany) and the southern and eastern seaboard of Southern Africa. In addition, virtually all of the ground waters of the southern and eastern fringes of South Africa (approximately 200 km inland) have similar characteristics.



Soft, Acidic Waters

- Low pH, calcium and alkalinity
- Aggressive to cement concrete
- Corrosive to metals
- Iron 0.5 to 5 mg/L

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

Common problems developing from the transportation of waters with such qualities are those of aggressive attack of cement-lined pipes and corrosive attack of metal pipes. Most of the water distribution pipes (approximately 90 %) in municipal water distribution systems are either made of cement or composed of cement-based material. These cement-lined materials are attacked by aggressive waters by dissolving free lime and calcium carbonates, silicates and aluminates from the cement matrix. This results in two undesirable effects: Firstly, the reliability of both the cement type pressure channels and containing structures is lost, resulting in pipe bursts, leakage and structural failure. Secondly, for reinforced concrete structures, the concrete cover is removed, exposing the steel to a corrosive environment, resulting in rusting and eventual failure.(Mackintosh *et al* ,1999)

These attacks also impose considerable financial consequences in distribution networks and at consumer level. These include lost water from pipe bursts and leaks, costs incurred towards repairing the reservoirs and pipelines and a decrease in the quality of the water as a result of increased levels of dissolved metal corrosion by-products to the extent where it can be unsuitable for utilization thus resulting in niggling problems such as laundry and wall discolouration. Such problems thus necessitate that water treatment authorities stabilize the water prior to any distribution.

The predominant control measure used by water utilities to prevent such attack is pH adjustment for calcium carbonate saturation control, through the addition of lime or sodium alkalis, as well as carbon dioxide. These treatment technologies and the related know-how are readily available for larger systems as found in large towns and cities. The operation of such systems is however costly and often problematic, and not suitable for smaller water treatment works or small users in rural environments due to the lack of well trained staff and reliable equipment which are both seldom in the many small towns and communities receiving such waters.

Stabilization of calcium and carbonate species deficient waters requires increasing both Ca^{2+} and alkalinity concentrations to values satisfying the minimum criteria to control aggression and corrosion, i.e. increasing both to ≥ 50 mg/l as $CaCO_3$, and adjusting pH so that the final water has pH in the range $6.5 < pH < 9.5$ and is supersaturated by about 4 mg/l as $CaCO_3$. Chemical conditioning to achieve these criteria involves the addition of lime, $Ca(OH)_2$, for Ca^{2+} and alkalinity adjustment, and addition of CO_2 for pH adjustment. However, such full stabilization, although well understood is not ideal for small users and secondly, lime dosing is troublesome and problematic. Furthermore, the increasing limited availability of high quality (white) lime in some parts of South Africa will result in increased operating chemical costs at water treatment facilities, as lime will need to be sourced outside the country.

1.2 SIDESTREAM STABILISATION PROCESS (SSP)

An alternative means of stabilizing low pH, calcium and alkalinity-deficient water is by contact with naturally occurring solid calcium carbonate or limestone. In this process, the natural $CaCO_3$ demand is the 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. Such stabilization significantly reduces the aggressive and corrosive characteristics of water.

Field test work and municipal units have shown that limestone mediated stabilization is more effective and advantageous than the lime/CO_2 process taking into consideration the fact that the limestone mediated stabilization is more economically viable and efficient. However these municipal water purification works are only limited to about 30 Ml/day. The advantages of limestone-mediated stabilization include:

- The water treats itself, taking up calcium and alkalinity to satisfy equilibrium requirements.
- The 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 is impractical for use in small-scale water treatment plants.
- Limestone can be obtained at a relatively lower price than lime [SAR 160/t against SAR 900/t at 2000 prices].
- The chemical cost of stabilization is greatly reduced.
- Complicated dosing of expensive carbon dioxide is not required

This has led to the development of the Sidestream Stabilization Process (SSP) by the Centre for Science and Industrial Research (CSIR). This process is suitable for larger water purification installations and it is patented internationally. This process is also the subject of ongoing research and development. This particular study focused on the following aspects:

i) The operation of the SSP pilot plant, laboratory and further pilot plant investigations.
ii) The development and calibration of a process model describing the aqueous, gaseous and solid phase chemistry of the carbonate weak acid/base system.

1.3 DEVELOPMENT OF APPROPRIATE PROCESS SIMULATION MODELS TO MODEL THE SSP

PRO/II is a comprehensive computer simulation system used in a variety of process industries e.g. chemical, petroleum, natural gas and polymer industries. It combines the data resources of a large chemical component library and extensive thermodynamic property prediction methods with the most advanced and flexible unit operational techniques. It also provides users with computational facilities to perform all mass and energy balance calculations required to model steady-state processes (*PRO/II Version 5*).

The simulation packages will be used to perform rigorous mass and energy balances for a wide range of SSP scenarios such as evaluating the various plant configurations and optimising the developed process models. This investigation will also aim to use the PRO/II modelling package to accurately predict the behaviour of the SSP and describe the aqueous, gaseous and solid phase chemistry of the process. Once the model is developed and assessed, a sensitivity analysis will be performed to test whether the model works under a series of conditions. This would then further allow for the consideration and optimization of the process, and understanding of its limitations, prior to any commissioning for industrial construction.

The results obtained from PRO/II would be verified using an aquatic chemistry package, STASOFT version 4 (2001).

STASOFT, an interactive user-friendly computer program, is a program based on the chemical equilibrium model of the Ca-Mg-CO_3 system. It provides rapid numerical solutions to characterization of a water and the dosing requirements to obtain the desired chemical water quality for a prescribed input. Updated versions are extended to also incorporate ion pairing between principal cation species (Ca^{2+}, Mg^{2+} and Na^+) and anion species (SO_4^{2-}, CO_3^{2-} and HCO_3^-).

1.4 WORK APPROACH

The original aims of the project were to:

- Assess the suitability of the eductor as a tool for recovering CO_2 from the recovery vessels
- 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 the SSP, and (ii), identify means to improve the performance and optimise the operation 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 pilot plant operation. These are mentioned below:

- Programming and software development. At an advanced stage in the project it became apparent that the chosen modelling 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 unenvisaged programming and software development was carried out.
- Consideration of a simplified sidestream stabilisation process. This process is however not included in this thesis.

Chapter two describes the fundamental aqueous phase carbonate chemistry which forms the basis for this investigation.

Chapter three addresses the chemistry of calcium carbonate in aqueous, gaseous and solid phases, and the interdependence between the various phases. It also focuses on the dissolution kinetics models used to describe the process.

Chapter four describes the concept of a sidestream stabilization process.

Chapter five describes the development of the SSP-MOD program for predicting the behaviour of the SSP. However, only the equations, algorithms and sub-routines are included.

Chapter six is based on the pilot plant operation using an eductor for carbon dioxide recovery and the assessment of the SSP-MOD program.

Chapter seven addresses the use of PRO/II as a process-modelling package for predicting the behaviour of the SSP.

CHAPTER 2

THE CARBONATE CHEMISTRY SYSTEM IN AQUEOUS PHASE EQUILIBRIUM

2.1 INTRODUCTION

The carbonate system is a weak acid-base system which exists in aqueous solutions as dissolved carbon dioxide (CO_{2aq}), carbonic acid (H_2CO_3), bicarbonate (HCO^-_3) and carbonate ions (CO_3^{2-}) and the complexes of these ions. Interaction of these ions with water results in a displacement of equilibrium between H^+ and OH^- ions. Basically the system is derived from the dissolution of carbon dioxide gas and carbonate minerals into the water. Addition of an acid or a base to an aqueous solution of carbonate species gives rise to changes in pH and concomitant changes in the concentrations of all the species that constitute the system.

A distinguishing feature of the carbonate system is that the gas phase forms an integral part of it. For a system initially in equilibrium, any change in the partial pressure of CO_2 in the gas phase induces a state of non-equilibrium between gas and aqueous phases. This causes, with time, an exchange of CO_2 between the phases resulting in a shift in pH and the species concentrations until equilibrium between the phases is re-established. A further feature is the relative insolubility of many carbonate minerals; the precipitation and dissolution of these minerals have a significant effect on the system behaviour. As consequence of these two features it is often necessary to consider all three phases, aqueous, gas and solid, in order to describe the response of the systems to external influences.

This chapter covers the application of aqueous phase equilibrium chemistry to the carbonate system with two principal objectives. Firstly, characterization of the carbonate system in solution. This involves the measurement of the fundamentally important selected mass parameters, alkalinity and acidity, such that carbonate species concentrations can be determined. Secondly, prediction of change in state arising from some form of chemical dosing. This aspect may involve either specifying the type and amount of chemical dosage and determining the final state, or the initial and final states are specified and the chemical dosage must be determined. In both cases the approach will be to utilise equilibrium chemistry as the basis from which the development is affected.

2.2 CARBONATE SPECIES EQUILIBRIA

Carbonate species ($H_2CO_3^*$, HCO_3^-, and CO_3^{2-}) dissolved in water exist in equilibrium with each other and with the water molecules (H^+ and OH^-). The relationships between these species are governed by a set of thermodynamic equilibrium equations all of which must be satisfied simultaneously.

For the water species:

$$(H^+)(OH^-) = k_w / F_m = K_W' \tag{2.1}$$

For the carbonate species:

$$(H^+)(HCO_3^-) / (H_2CO_3^*) = k_1 / F_m = K_1' \tag{2.2}$$

$$(H^+)(CO_3^{2-}) / (HCO_3^-) = k_2 / F_d = K_2' \tag{2.3}$$

where ($H_2CO_3^*$) = the sum of molecularly dissolved carbon dioxide and carbonic acid, (H_2CO_3), mol/l

The equilibrium constants k_w, k_1 and k_2 in Equations **(2.1)**, **(2.2)** and **(2.3)** vary with temperature as follows:

(a) For pK_w

$$pK_w = 4787.3 / (T) + 7{,}1321 \log (T) + 0{,}01037 (T) - 22{,}801$$
$$= 14{,}165 \text{ at } 20°C$$

(b) For pK_1

$$pK_1 = 17052 / (T) + 215{,}21 \log (T) - 0{,}12675 (T) - 545{,}56$$
$$= 6{,}394 \text{ at } 20°C$$

(c) For pK_2

$$pK_2 = 2902{,}39 / (T) + 0{,}02379 (T) - 6{,}498$$
$$= 10{,}377 \text{ at } 20°C$$

where : $pK = -\log K$

In the dissociation Equations **(2.1)** to **(2.3)** above the hydrogen ion concentration is expressed in the active form, (H^+). This arises because this parameter is measured in this form via pH using potentiometric methods where

$$pH = -\log(H^+) \qquad \textbf{(2.4)}$$

and thus the numerical value of (H^+) is as follows:

$$(H^+) = 10^{-pH}$$

The three equilibrium equations above (i.e. Equations **2.1** to **2.3**) incorporate five unknowns, i.e. (H^+), $[H_2CO_3^*]$, $[CO_3^{2-}]$, $[HCO_3^-]$ and $[OH^-]$, therefore to determine values for all these parameters (i.e. to characterise the system) two independent parameters must be measured. From Equation **(2.4)** it can be seen that the measurement of pH satisfies one of these requirements; direct measurement of any one of the other parameters is not possible, However, there exists further parameters for the system which "are linked" to the individual species concentrations and which can be measured. These include various capacity parameters such as total carbonate species concentrations and various forms of alkalinity and acidity.

2.3 TOTAL CARBONATE SPECIES, ALKALINITY AND ACIDITY

2.3.1 Total carbonate species

The total carbonate species concentration, C_T, is the sum of the various dissolved carbonate species concentration, i.e.

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad \textbf{(2.5)}$$

Clearly, if C_T and pH are measured the system can be characterised. The distribution of carbonate and water species with pH for a fixed C_T is shown graphically in a log species-pH diagram in **Figure 2.1**. However, the measurement of C_T requires expensive laboratory equipment (i.e. an inorganic carbon analyser) so that this parameter is seldom used explicitly in characterisation.

Invariably as an alternative to C_T measurement, one (or more) of the various forms of alkalinity or acidity are measured and used in characterisation. Definitions and equations for the various forms of alkalinity and acidity are not as obvious as that for total carbonate species and are, therefore, introduced only after a conceptual explanation in the following section. (Suffice to note, however, that these parameters are relatively easily measured in practice and thus are commonly used with pH for characterisation purposes).

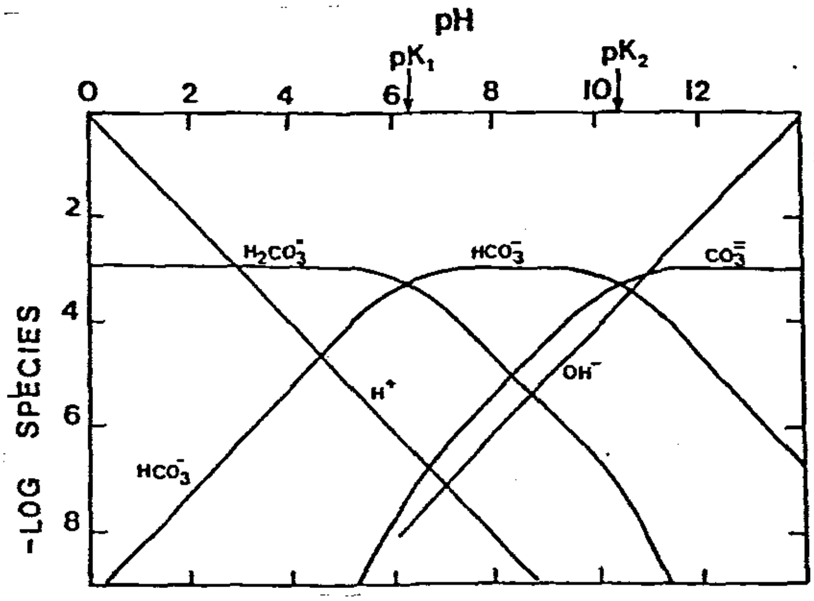


Figure 2.1: *log[species]* – pH diagram for the carbonate system in water with C_T = 0.0002 mole/l.

2.3.2 Alkalinity and acidity

Over the years the terms "alkalinity" and "acidity" have been applied to a variety of different capacity parameters, the following section is included to define meanings assigned to these terms in the work presented here.

If a carbonate species is added to pure water, either as a salt (e.g. HCO_3^-, CO_3^{2-}) or as a gas (CO_2), the solution formed is known as an equivalent solution, with the pH established at the equivalence point for the particular weak acid species added. The carbonate species added to the water is termed the reference species, and the solution itself is termed an equivalent solution. If a strong base (acid) is added to this equivalent solution the pH increase (decrease) above (below) the equivalence point of the solution. The mass concentration of the base (acid) added to the solution to effect this change is known as the alkalinity (acidity) of the solution with respect to the original equivalent solution established by addition of the reference species to pure water.

Using the Arrhenius definition of an acid (i.e. an acid when added to water releases protons (H^+), the above definition can be rephrased as; **alkalinity (acidity) is the proton accepting (donating) capacity of the solution relative to some reference state.**

It is possible to derive equations linking alkalinity (acidity) to each of the carbonate species ($H_2CO_3^*$, HCO_3^- and CO_3^{2-}) and the water species (H^+ and OH). These equations are given below; their derivations can be obtained from (**Loewenthal and Marais, 1976**).

$$\begin{aligned} H_2CO_3^* \text{ alkalinity} &= 2[CO_3^{2-}] + H[CO_3^-] + [OH^-] - [H^+] \\ &= -H_2CO_3^* \text{ acidity} \end{aligned} \qquad \textbf{(2.6)}$$

Similarly using HCO_3^- or CO_3^{2-} as reference species (addition of sodium carbonate or sodium bicarbonate) the following expressions can be obtained

$$\begin{aligned} HCO_3^- \text{ alkalinity} &= [CO_3^{2-}] + [OH^-] - [H_2CO_3^*] - [H^+] \\ &= -HCO_3^- \text{ acidity} \end{aligned} \qquad \textbf{(2.7)}$$

$$\begin{aligned} CO_3^{2-} \text{ alkalinity} &= -2[H_2CO_3^*] - [HCO_3^-] - [H^+] + [OH^-] \\ &= -CO_3^{2-} \text{ acidity} \end{aligned} \qquad \textbf{(2.8)}$$

Conventionally the $H_2CO_3^*$ alkalinity is written as **"Alkalinity"** and the CO_3^{2-} acidity as **"Acidity"**, and is the nomenclature used throughout this investigation.

It must be remembered that the above alkalinities (acidities) are a measure of the mass concentration of acid (base) required to bring the pH of a solution to a specified equivalence point. Thus a relationship between total carbonate species, alkalinity and acidity exists.

2.4 INTERDEPENDENCE BETWEEN MASS PARAMETERS, ALKALINITY AND ACIDITY, AND TOTAL SPECIES CONCENTRATION

The mass parameters, alkalinity and acidity, and total species concentration are parameters which can be used to determine (or characterise) the state of a water. Consequently, in terms of what was stated previously, one would expect that if values for any two of these parameters are known then the remaining parameters can be determined. That is, one expects some form of interdependency between these parameters. Two forms of interdependency exist:

(a) between alkalinities and acidities with the same reference equivalent solution, and

(b) between alkalinities and acidities relative to different equivalent solutions.

For the alkalinity and acidity associated with the same equivalence solution, the alkalinity value is simply the negative of the acidity value, e.g. from Equations **(2.6)** to **(2.8)**

$$H_2CO_3^* \text{ alkalinity} = -H_2CO_3^* \text{ acidity} \qquad \textbf{(2.9)}$$

The sum of alkalinity with respect to a selected equivalent solution and acidity with respect to the next lower protonated equivalent solution equals total carbonate species concentration, i.e.

$$H_2CO_3^* \text{ alkalinity} + HCO_3^- \text{ acidity} = C_T \tag{2.10}$$

$$HCO_3^- \text{ alkalinity} + CO_3^{2-} \text{ acidity} = C_T \tag{2.11}$$

More broadly, if the reference species for the equivalent solution relative to which alkalinity and acidity are defined are "n" protons apart the sum is 'n' times C_T, e.g.

$$H_2CO_3^* \text{ alkalinity} + HCO_3^- \text{ acidity} = C_T \quad (n = 1) \tag{2.12}$$

$$H_2CO_3^* \text{ alkalinity} + CO_3^{2-} \text{ acidity} = 2C_T \quad (n = 2) \tag{2.13}$$

These relationships can be represented graphically as shown in **Figure 2.2**. This plot shows that if values are known for two independent mass parameters then values for the remaining mass parameters can be determined directly.

For example, if say, $H_2CO_3^*$ alkalinity = 2 mmol/l and HCO_3^- acidity = 1 mmol/l, then from the above section:

C_T = $H_2CO_3^*$ alkalinity + HCO_3^- acidity
= 3 mmol/l

HCO_3^- alkalinity = - HCO_3 acidity
= -1 mmol/l

CO_3^{2-} alkalinity = - CO_3^{2-} acidity
= -4 mmol/l

$H_2CO_3^*$ acidity = - H_2CO_3 alkalinity
= -2 mmol/l

CO_3^{2-} acidity = $C_T - HCO_3^-$ alkalinity
= 4 mmol/l

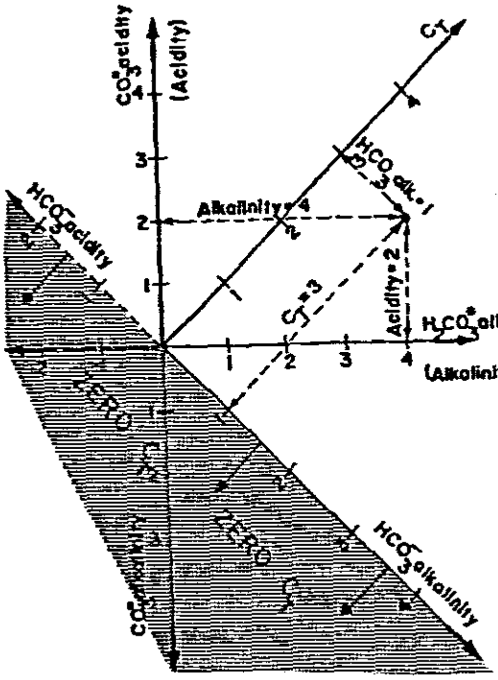


Figure 2.2: Interdependence between mass parameters for the carbonate system.

2.5 INTERDEPENDENCE BETWEEN pH AND MASS PARAMETERS

The interdependence between pH, alkalinity and acidity is established via the equilibrium equations (Equations **2.1 to 2.3**) and the equations for the capacity parameters alkalinity (Equation **2.7**) and acidity (Equation **2.8**), to give:

$$\text{Acidity} = \text{Alkalinity}\,[1 + 2.10^{(pH - pK_2')} \;/\; 1 + 2.10^{(pK_1' - pH)}]$$

$$- 10^{(pH - pK_w')} + 10^{(-pH)} \qquad \textbf{(2.14)}$$

Examination of Equation **(2.14)** shows that for a chosen pH value there exists a linear relationship between alkalinity and acidity. **Figure 2.3**, known as the Deffeyes type-conditioning diagram (**Loewenthal and Marais, 1976**), shows that the measurement of any two independent parameters completely defines the values for the remaining ones. For example, if pH and alkalinity are known then the value for acidity is simply read off the appropriate ordinate. The alkalinity-acidity-pH diagram can also be used to predict the change in state of a water due to chemical dosing and thus constituting a single phase conditioning diagram.

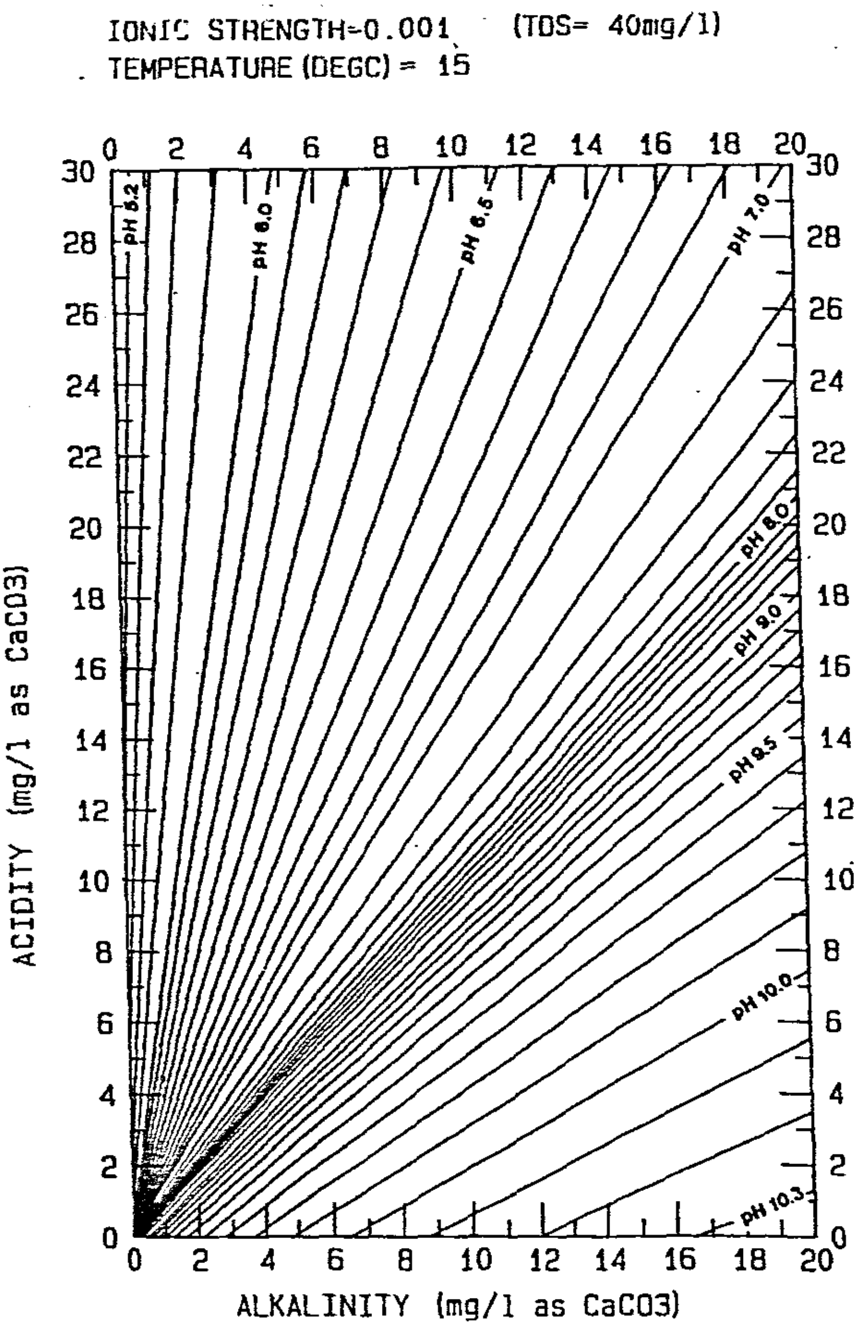


Figure 2.3: Plot of pH lines with Alkalinity and Acidity as axes parameters constitutes a Deffeyes type diagram

2.6 CHANGES IN MASS AND CAPACITY PARAMETERS WITH CHEMICAL DOSING

The various forms of alkalinity and acidity discussed above change in a simple stoichiometric manner with the mass concentration of a chemical dosage (or removal)(**Loewenthal et al, 1986**). The corresponding changes in pH are however more complex and need to be calculated using equilibrium considerations.

From the definitions of alkalinity and acidity, the changes in the parameters alkalinity and acidity with chemical dosage are as follows:

$$\Delta\ \text{Alkalinity} = \text{Alk}_{added}$$

$$= 2[CO_3^{2-}]_{added} + [HCO_3^-]_{added} + [OH^-]_{added} - [H^+]_{added} \qquad \textbf{(2.15)}$$

$$\Delta\ \text{Acidity} = \text{Acid}_{added}$$

$$= 2[H_2CO_3^*]_{added} + [HCO_3^-]_{added} - [OH^-]_{added} + [H^+]_{added} \qquad \textbf{(2.16)}$$

where Δ indicates a positive change

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

2.7 MEASUREMENT OF ALKALINITY

Ideally, to determine the alkalinity of a water with respect to a specific reference species, a titration should be carried out to the equivalence point of the selected reference species. The alkalinity being a measure of the strong acid added to the sample to reach that selected equivalence point. The problem often arising in this regard hinges around identifying the selected equivalence point.

The $H_2CO_3^*$ equivalence point varies with C_T which is initially unknown; consequently the end point to the titration is unknown. For waters with alkalinity ≥ 30 mg/l as $CaCO_3$, various procedures have been developed for the best estimate of the endpoint to the titration (and hence the alkalinity value); For waters with alkalinity ≤ 30 mg/l alkalinity measurement should be measured using Gran titration methods (**Loewenthal *et al*, 1986**).

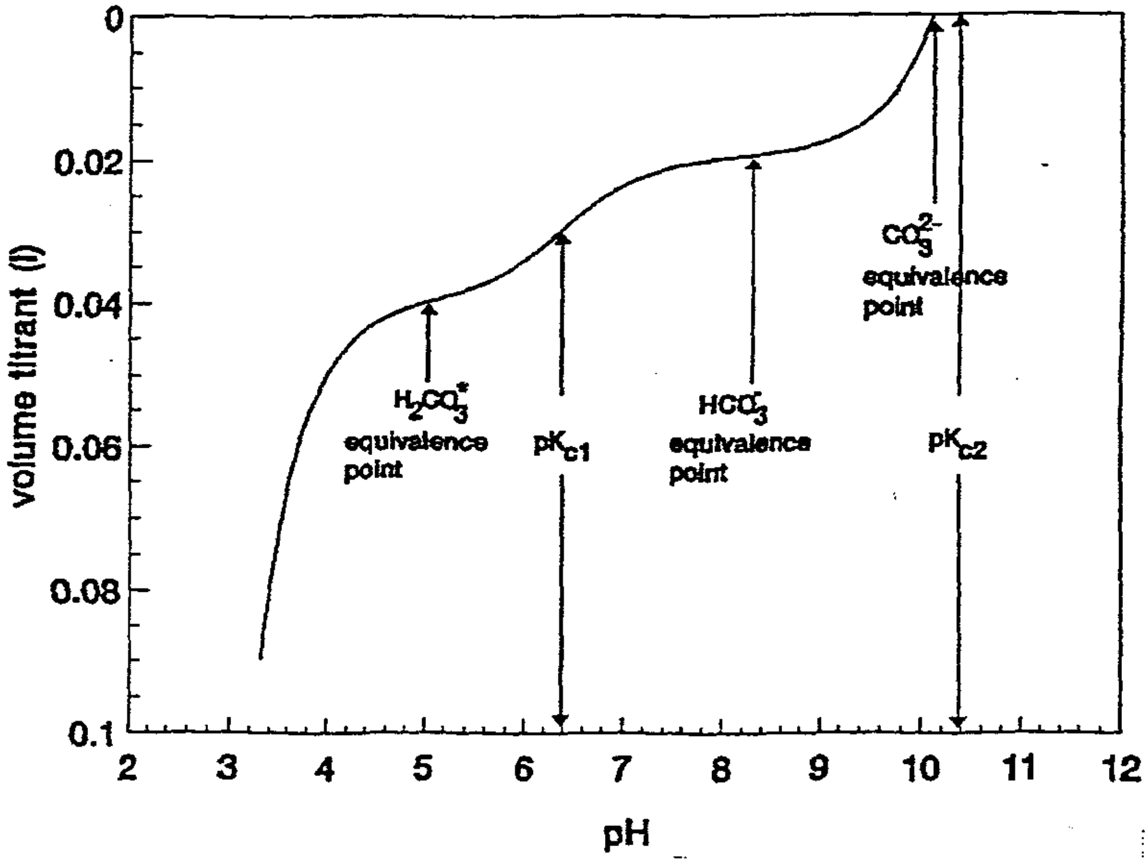


Figure 2.4: Volume of titrant versus pH curve for a 1l sample of 0.0002 mole/l $NaCO_3$ solution titrated with 0.001 mole/l HCl.

Where a potentiometric titration (i.e. pH measurement) is carried out, this data can be used to plot a *volume of titrant* versus *pH* curve. Certain inflection points are observed (see **Figure 2.4**). A maximum slope occurs at the pK values, and a minimum slope at the equivalence points. The slope of the *volume of titrant versus pH* curve thus gives an indication of the error in titrating to any particular pH value, a maximum slope indicating maximum possible error and vice versa. The slope of this curve introduces the concept of buffer capacity.

CHAPTER 3

CHEMISTRY OF THE CARBONATE SYSTEM IN THE AQUEOUS, GASEOUS AND SOLID PHASES AND ITS DISSOLUTION KINETICS

3.1 INTRODUCTION

In this chapter the aqueous phase is brought into contact with calcium and carbonate species. Changes in the aqueous phase chemical characteristics of a water *inter·alia* either exchanging carbon dioxide with the gaseous phase or dissolving/precipitating minerals, is assessed using single aqueous phase equilibrium considerations. However, no consideration was given to the "driving forces" with respect to interphase equilibrium, i.e. water brought into contact with gaseous phase (say carbon dioxide in the air) or a solid phase (say calcium carbonate).

For carbon dioxide exchange with the gas phase the driving force is induced by a state of disequilibria between molecular dissolved carbon dioxide in the aqueous phase and carbon dioxide in the gaseous phase. For calcium carbonate precipitation/dissolution, the driving force is induced by disequilibria between calcium and carbonate species in the aqueous phase and, say calcite ($CaCO_3$), in the solid phase. Compared with rates to equilibrium between species in the aqueous phase, rates for interphase equilibrium are inevitably very much slower and will depend on such factors as degree of disequilibria, mixing, etc.

In this investigation, equilibrium between species in the aqueous and solid phases is of primary interest. Various models describing the kinetics of attainment of interphase equilibrium for solutions with the solid phase are presented. However, before assessing quantitatively the changes which occur as interphase equilibrium is attained, it is necessary to discuss briefly the state of equilibrium occurring between both the aqueous and gaseous phases and/or the solid phase. With this background it is then possible to predict whether a water will be aggressive to cement type materials and to what extent.

3.2 AQUEOUS-GASEOUS PHASE EQUILIBRIUM

Carbon dioxide exchange between water and the atmosphere takes place until the carbon dioxide (CO_2) partial processes in the two phases are equal, i.e. at equilibrium between air and water the dissolved CO_2 concentration is fixed.

In the approach to aqueous-gaseous equilibrium the pH in the water changes and there is a redistribution of the dissolved carbonic concentrations, i.e. a change in the dissolved CO_2 concentration occurs and more CO_2 is exchanged with the air. The pH at which equilibrium is established depends on the alkalinity of the water. Exchange of CO_2 between air and water does not change the alkalinity, only the acidity and pH, provided no $CaCO_3$ precipitation occurs.

For equilibrium between dissolved and atmospheric CO_2 at a particular partial pressure of CO_2 (pCO_2) the concentration of dissolved CO_2 is defined by Henry's Law as:

$$[H_2CO_3^*] = K_{CO2} * pCO_2 \qquad \textbf{(3.1)}$$

$$pK_{CO2} = -1760.0/T + 9.619 - 0.00753T \qquad \textbf{(3.2)}$$

For CO_2 in equilibrium between a constant partial pressure of CO_2 in the atmosphere and water, alkalinity and pH are directly related as follows:

From Equation **(2.6)**

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

Solving for $[CO_3^{2-}]$ and $[HCO_3^-]$ from Equations (**2.2 and 2.3**) respectively, and substituting into the equation above for alkalinity,

$$\text{Alkalinity} = [H_2CO_3^*] * 10^{pH-pK_1'}(2.10^{pH-pK_2'} + 1) + 10^{pH-pK_w'} - 10^{-Ph} / F_m$$

And substituting for $[H_2CO_3^*]$ from Equation **(2.6)**

$$\text{Alkalinity} = P_{CO_2} * K_{CO2} * 10^{pH-Pk_1'}(2.10^{pH-Pk_2'} + 1) + 10^{pH-pK_w'} - 10^{-pH}/F_m \qquad \textbf{(3.3)}$$

Thus, from Equation **(3.3)** alkalinity is directly related to pH for a water at equilibrium with CO_2 in the air. Equilibrium between carbonate species in the aqueous phase and CO_2 in the gaseous phase (say air with $P_{CO_2} = 0.00032$ atmospheres) can be depicted in a Modified Caldwell-Lawrence diagram (see below in section 3.4) allowing for quick graphical assessment of whether aqueous-gaseous equilibrium exists in a water.

3.3 AQUEOUS-SOLID PHASE EQUILIBRIUM

When solid calcium carbonate dissolves in water, dissolution and precipitation reactions occur between species in the solid and aqueous phases. Precipitation and dissolution are the net results of precipitation and dissolution reactions occurring concurrently, when, with the former, precipitation rate exceeds the dissolution rate, and there is a decreasing difference between the two concurrent rates until the two are equal and no net precipitation or dissolution occurs. This limiting concentration is termed the solubility of the mineral (calcium carbonate) in the particular liquid. Assessment of the solubility status is achieved by considering the water saturation state.

Undersaturation, supersaturation and saturation are terms describing whether the chemical state of a water is respectively such that it causes dissolution of a solid (undersaturation), precipitation of a solid (supersaturation), or no precipitation or dissolution (saturation). Aggressive waters attack cement type pipes and structures by dissolving free lime and $CaCO_3$ from the solid into the aqueous phase giving rise to so called aggressive attack. Such waters are undersaturated with respect to both lime and $CaCO_3$. Chemically these waters are characterised as being "undersaturated" with respect to $CaCO_3$. For waters saturated or supersaturated with respect to $CaCO_3$, solid $CaCO_3$ will not dissolve and free lime in the cement in contact with the water will be transformed with time to solid $CaCO_3$ (see later). For this reason the solubility status of the water with respect to $CaCO_3$ is of critical importance whilst that of the considerably more soluble lime is not crucial.

Theoretically, the saturation state with respect to $CaCO_3$ is identified by comparing the activity product of calcium, Ca^{2+}, and carbonate, CO_3^{2-}, species with the solubility product constant, K_{sp}. The activity product is the product of the active molar concentration of calcium, Ca^{2+}, and carbonate, CO_3^{2-}, species, i.e.

$$\text{Activity Product} = [Ca^{2+}]\,[CO_3^{2-}] \qquad \textbf{(3.4)}$$

The activity product cannot increase *ad lib* but has a stable upper limit called the **solubility product**.

If the activity product is greater than the solubility product constant, K_{sp}, precipitation of solid $CaCO_3$ out of the water occurs; if less, dissolution of solid $CaCO_3$ into the water takes place; if equal, there will be no net dissolution or precipitation.

Hence, for dissolution of $CaCO_3$ (undersaturation),

$$[Ca^{2+}]\,[CO_3^{2-}] < K_{sp} \qquad \textbf{(3.5a)}$$

For precipitation of $CaCO_3$ (supersaturation),

$$[Ca^{2+}]\,[CO_3^{2-}] > K_{sp} \qquad \textbf{(3.5b)}$$

and, at saturation,

$$[Ca^{2+}]\,[CO_3^{2-}] = K_{sp} \qquad \textbf{(3.5c)}$$

The effects of ionic strength on equilibrium can be estimated by writing the solubility product equation in terms of concentration and activity coefficients i.e.

$$[Ca^{2+}]\,[CO_3^{2-}] = K_{sp} / f_d^2 = K_{sp}' \qquad \textbf{(3.6)}$$

In Equations **(3.5 a, b and c)**, K_{sp} is the solubility product for $CaCO_3$. The value of the thermodynamic solubility product depends on temperature, pressure and the type of $CaCO_3$ mineral precipitated (e.g. calcite, aragonite or vaterite). The type of mineral that will precipitate depends on the ionic constitution of the water (i.e. the concentration and types of salt present in solution), state of supersaturation, temperature and pressure. For low ionic strength waters in the temperature 0-60°C, at low degrees of supersaturation and atmospheric pressure, the usual $CaCO_3$ mineral that will precipitate, is calcite **(Loewenthal and Marais, 1976)**. The calcite solubility product is temperature dependent as follows (**Loewenthal and Marais, 1976**):

$$\begin{aligned} pK_{sp} &= 0.01183\,t + 8.03 \qquad \textbf{(3.7)} \\ &= 8.226 \text{ at } 20°C \end{aligned}$$

where $pK_{sp} = -\log_{10} K_{sp}$

The above solubility product value was determined without taking into account ion pairing effects between calcium and carbonate species in solution. Consequently, this effect is reflected in this solubility product value, i.e. species concentrations in Equation **(3.6)** reflect the sum of free and ion paired (total) species concentrations. However, this approximation is adequate for normal terrestrial waters where complexing of calcium and CO_3^{2-} by other ions in the solution is negligible.

If ion pairing is to be incorporated in computations then the solubility product function determined by **Plummer(1979)** should be used, i.e.

$$\text{Log } K_{sp} = -171.9065 - 0.077993\,T_K + (2839.319/T_K) + 71.595 \log T_K \qquad \textbf{(3.8)}$$

The investigations reported here were for very soft waters and consequently ion pairing has been neglected so that Equation **(3.7)** was used where necessary.

3.4 SATURATION STATE

The rate at which equilibrium is attained between the solid and aqueous phases is extremely slow as compared to the attainment of equilibrium between species in the aqueous phase only. Consequently, for water in contact with solid calcium carbonate ($CaCO_3$) the solution may either be under- or super- or just saturated with respect to $CaCO_3$. The states of under- or supersaturation may exist for protracted lengths of time. The calcium carbonate saturation state of water describes the condition of the water with respect to the above states.

In terms of the solubility product equation Equation **(3.6)**, the saturation state can be described by the relative saturation index, Ω, as follows.

$$\Omega = ([Ca^{2+}]\,[CO_3^{2-}]) \,/\, K'_{sp} \qquad \textbf{(3.9)}$$

If $\Omega = 1$ the water is just saturated

If $\Omega > 1$ the solution is supersaturated and precipitation will occur with time

If $\Omega < 1$ the solid $CaCO_3$ is present, dissolution will occur with time

From the treatment point of view it is important that the saturation state be known and if necessary adjusted prior to distribution (**Loewenthal *et al*, 1986**). In this context two problems arise, firstly a qualitative one, and secondly a quantitative one. As far as the qualitative description of saturation is concerned referring to Equation **(3.9)** values for K'_{sp}, Ca^{2+} and CO_3^{2-} need to be known. The first two can be obtained directly however, as shown in **Chapter Two**, the CO_3^{2-} concentration can be measured directly and needs to be determined from some other analytical measurement, in particular pH and alkalinity. In this regard the work of (**Langelier, 1936**) pioneered rapid means of assessing saturation state.

Langelier's saturation index, SI, is the difference between the actual pH of the water and the theoretical pH of the water at which it would be saturated for the measured alkalinity and calcium concentrations. Viz.

$$SI = pH_{actual} - pH_s$$

$$pH_s \approx pK_2 - pK_{sp} + p[\text{Alkalinity}] + p[Ca^{2+}] \qquad \textbf{(3.10)}$$

where pH_{actual} = measured pH of the water

pK'_2 = apparent equilibrium constant as defined in Equation **2.3**

pK'_{sp} = apparent solubility product for calcium carbonate

If $SI < 0$ the water is supersaturated

If $SI > 0$ indicates undersaturation

Langelier emphasized that the index must be considered only as a qualitative measure of super- or undersaturation. The numerical value determined for the SI has no bearing on the amount of $CaCO_3$ that can dissolve/precipitate from the solution (**Loewenthal *et al*, 1986**). Qualitative assessment of the saturation state is not sufficient quality criteria by which to effectively monitor the treatment of water prior to distribution. To this end a quantitative description of saturation state is required. The calcium carbonate precipitation/dissolution potential facilitates an accurate prediction of the amount of solid $CaCO_3$ that can precipitate from or dissolve into aqueous solution.

3.5 THE CALCIUM CARBONATE PRECIPITATION/ DISSOLUTION POTENTIAL

The calcium carbonate precipitation/dissolution potential is defined as the mass of $CaCO_3$ to be precipitated from, or dissolved into, a water to attain saturation with respect to $CaCO_3$, assuming that temperature and ionic strength effects have been considered and incorporated into the apparent equilibrium constant. It has been shown previously that the chemical state of water containing carbonate species can only be uniquely determined if any of the two parameters alkalinity, acidity or pH are known. By considering such an aqueous solution in contact with solid calcium carbonate the only species introduced/removed into/from the system are Ca^{2+} and CO_3^{2-}. By introducing the solubility product equation, expressed in concentration form Equation **(3.6)**, one more equation and one more unknown viz. $[Ca^{2+}]$, have been introduced to the characterization problem, thus the system of equations describing the chemical state of the water remains consistent.

There is a direct stoichiometric relationship between the amount of calcium carbonate dissolving/precipitating and the corresponding changes in both Ca^{2+} concentration and alkalinity in the solution. However, this does not hold for the individual weak acid species, CO_3^{2-}, involved in the dissolution/precipitation reaction, as this component of calcium carbonate speciates in solution and varies with pH according to the single phase equilibrium chemistry described previously (see **Chapter 2**). Because of this complex relationship between the solution species involved in the dissolution/precipitation reaction, it has not been possible to develop a single elegant equation that can be used to calculate the precipitation potential from the measured parameters alkalinity (or acidity), pH and calcium. To this end iterative procedures involving successive approximations have been developed, to determine the precipitation potential.

Theoretical determination of the saturated state and the CCPP/CCDP using equilibrium chemistry is carried out very easily either (i) graphically as proposed by **Loewenthal and Marais (1976)** using the **Modified Caldwell-Lawrence**

(MCL) diagram or, (ii) using user-friendly computer software such as *STASOFT* (**Loewenthal *et al*, 1989**).

The MCL diagram is probably the most frequently used as it is not only easy to use but imparts a good insight into the changes that the capacity parameters experience in attaining a metastable or equilibrium state. The MCL diagram is a three-phase (aqueous, solid and gaseous) equilibrium diagram for use for the carbonate system. Separate graphs are available for various ionic strengths (or Total Dissolved Solids i.e. TDS) and for the different temperature ranges. Its use can be extended to include *inter alias* determination of the precipitation/dissolution potential (i.e. aggressiveness).

The ordinate represents the solution acidity while the abscissa, the difference between the solution alkalinity and the calcium concentration (i.e. alkalinity minus Calcium or AMC). Sets of curves representing pH, alkalinity and calcium values are plotted on these axes. The calcium line that passes through the intersection point of given pH and alkalinity values is the calcium concentration that the water should have if it were saturated.

The theory involved in the construction of such diagrams is given by **Loewenthal and Marais (1976)** and examples of its use by **Loewenthal *et al* (1986)**. Unfortunately the parameters of alkalinity, acidity and the calcium concentration must be reported in units of mg/l as $CaCO_3$ which reduces the graphs usefulness in a fully metricated environment.

STASOFT, an interactive user-friendly computer program, is a program based on the chemical equilibrium model of the Ca-Mg-CO_3 system. It provides rapid numerical solutions to characterization of a water and the dosing requirements to obtain the desired chemical water quality for a prescribed input. Updated versions are extended to also incorporate ion pairing between principal cation species (Ca^{2+}, Mg^{2+} and Na^{+}) and anion species (SO_4^{2-}, CO_3^{2-} and HCO_3^{-}).

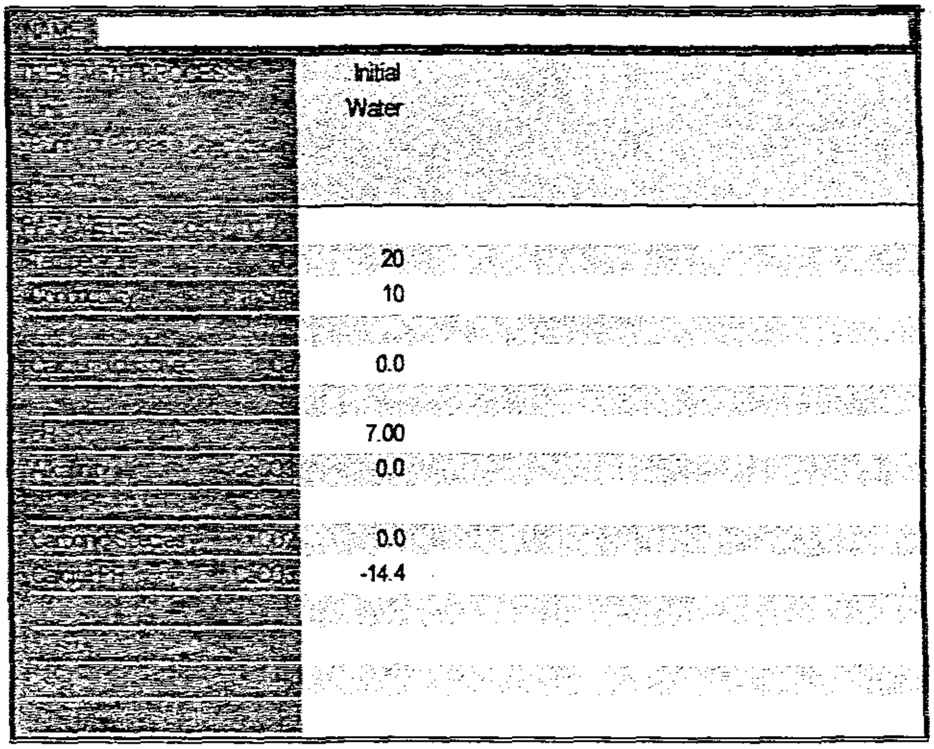
STASOFT is designed for application to both "terrestrial" waters (i.e. those where ion pairing effects are negligible and the Total Dissolved Solids (TDS) less than about 1000 mg/l and "higher" salinity waters (i.e. those where ion pairing effects are significant). For both waters this program is designed to provide solutions to a broad range of problems that are likely to be encountered by water treatment authorities. These include the following:

- Calcium and magnesium softening and stabilization
- Blending of two or more waters with different chemical characteristics
- pH adjustment of a water through chemical dosing
- Effects of temperature and concentration changes on a water's characterization
- Evaluation of underground or treated waters when achieving two-or-three-phase equilibrium
- Treatment of calcium and $H_2CO_3^*$ alkalinity deficient waters
- Stabilization of waters to a specified calcium carbonate precipitation potential

The latest STASOFT package, STASOFT 4, due to be released within 2001 consists of two programs, namely one user friendly Graphical User Interface (called here Standard STASOFT 4), and a DOS version which is used together with data and output files, (called here Watchem).

When STASOFT is started, an initial page appears, as in **Figure 3.1**. 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 then 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.

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.



Initial
Water

20
10
0.0
7.00
0.0
0.0
-14.4

Figure 3.1: A typical screen in standard STASOFT 4

3.6 CALCIUM CARBONATE (LIMESTONE) DISSOLUTION KINETICS

The rate at which a mineral dissolves in aqueous solution is influenced by a number of factors such as temperature, chemical composition, physical and chemical properties of the dissolving mineral and the manner in which the mineral is brought into contact with the solution.

Models to describe the kinetics of calcium carbonate precipitation/dissolution have been developed by numerous authors. However, most of the work was done from a geological standpoint with the view to describing limestone formations. Many of these models are totally empirical **Mills (1984)**, however in some cases mechanistic models have been postulated, for example **Plummer *et al* (1979)**.

Plummer (1979), investigated the dissolution of marble chips. Their observations indicated that the dissolution rate is linearly to the degree of mineral undersaturation, i.e.

$$d[Ca^{2+}]/dt = k_{(D+G)}S([Ca^{2+}]_{sat} - [Ca^{2+}]) \qquad \textbf{(3.11)}$$

where $d[Ca^{2+}]/dt$ = rate of dissolution reaction
$[Ca^{2+}]$ = concentration of Ca^{2+} in the bulk solution
$[Ca^{2+}]_{sat}$ = saturation equilibrium concentration of Ca^{2+} in the monolayer
$K_{(D+G)}$ = dissolution rate constant used in the Dorange and Guetchidjan equation (ms^{-1})

Subsequent investigations in this field by **Plummer *et al* (1979))**, have shown that such a first order reaction does not give a general description of dissolution kinetics of calcium carbonate.

It was further postulated that the rate of precipitation in any seeded solution is proportional to the surface area of seed and the degree of supersaturation viz. the concentration of the zero ion pair, $CaCO_3^0$, of the bulk solution. They presented order model (Equation **3.12** below) for the net precipitation rate.

$$-d[Ca^{2+}]/dt = k_{(R+N)}S\{[Ca^{2+}][CO_3^{2-}] - K_{sp}/f_d^2\} \qquad \textbf{(3.12)}$$

where $k_{(R+N)}$ = dissolution/precipitation rate constant used in the Reddy and Nancollas equation ($m^{-2}s^{-1}$)

This form of equation was utilized to describe precipitation kinetics in surface controlled processes, i.e. processes independent of mixing phenomena.

However, other authors noted an inconsistency in that the rate constant depended on the initial pH of the solution where $5 \leq pH_{initial} \leq 9$. Using the hypothesis, **Sturrock *et al (1976)*** formulated the following equation for calcium carbonate precipitation kinetics processes governed by surface controlled reactions and with bulk solution pH in the region $5 \leq pH \leq 9$ as,

$$- d[Ca^{2+}]/dt = k_{(D+J)} S f_d^2 \{[Ca^{2+}]^{½}[CO_3^{2-}]^{½} - (k_{sp}/f_d^2)^{½}\}^2 \qquad \textbf{(3.13)}$$

where $k_{(D+J)}$ = precipitation rate constant used in the Davies and Jones equation ($mole^{-1}m^4s^{-1}$)

Mills (1984) attempted to apply the **Davies and Jones (1955)** hypothesis to the dissolution of limestone chips in acidified terrestrial waters ($pH \leq 2.5$). He found no agreement for the initial dissolution rate up to pH of approximately 5. In order to model the process more closely he incorporated an additional term dependent on the proton activity in the bulk solution, i.e.

$$- d[Ca^{2+}]/dt = k_{(M1)} f_d^2 \{[Ca^{2+}]^{½}[CO_3^{2-}]^{½} - (k_{sp}/f_d^2)^{½} + k_{(M2)} (H^+)^{0.584} \qquad \textbf{(3.14)}$$

where $k_{(M1)}$, $k_{(M2)}$ = dissolution rate constants used by Mills, includes surface area effects for a pebble size

Mills (1984) showed that the second term above dominates calcium carbonate dissolution kinetics where $pH \leq 4.5$, at higher pH values the second term becomes negligible and kinetics is governed by the first term.

An important criticism that can be levelled at the work reported by **Mills (1984)** is that he did not investigate whether he was dealing with a surface controlled or a diffusion controlled process. That is, he did not investigate the effects of variable mixing energy on the dissolution kinetics. This omission has serious implications because the first term in his equation was formulated for surface controlled reactions (**Sturrock *et al*, 1976**), such surface controlled reactions should be independent of mixing energy.

Furthermore, virtually all his experiments were conducted in the low pH region, $2.5 \leq pH_{initial} \leq 5$, where proton activity terms totally dominated dissolution kinetics and very little correlation is reported for the higher pH region, $5 \leq pH$ where the first term dominates.

The first point above has been reassessed, **Kommüller et *al* (1995)**, using an upflow reactor system and limestone granules from Bredasdorp. Mineral dissolution phenomena are usually controlled by a diffusion mechanism **(Stumm &Morgan, 1981). Kommüller *et al* (1995)**, observed that the rates of dissolution varied according to flow characteristics in the pH region $5 \leq pH \leq 9$ followed a linear pattern and were equal to the rate constant $k_{(D+J)}$ in Equation **(3.13)** when plotted versus the **Sturrock *et al,1976*** function. This observation indicated that the dissolution rate is not controlled by surface phenomena (as required by the **Sturrock *et al,1976*** equation), but by transport/diffusion phenomena between the surface of the dissolving mineral and the bulk solution.

Stumm and Morgan (1981) and others proposed that for mineral dissolution processes the kinetics is best described by a first order type of equation, i.e.

$$d[Ca^{2+}]/dt = k_{(S+M)} S (c_{sat} - c) \tag{3.15}$$

where $k_{(S+M)}$ = dissolution rate constant used in the Stumm &Morgan equation

The rate constant $k_{(S+M)}$ in Equation **(3.15)** above depends on a number of factors including the physical characteristics of the dissolving mineral and the hydraulic flow characteristics, i.e. flow rate.

This form of equation seems to have been derived from Fick's Law which states: In a quiescent aqueous environment, the driving force of the molecular diffusion process is the concentration difference between two regions of solution at some distance, l, from each other.

According to this law, it is a first order equation of the following form:

$$\mathrm{Flux}_i = D_i/l\,(\Delta c_i) \qquad \textbf{(3.16)}$$

Where Flux_i = flux of ion species, i

Kommüller *et al* (1995), explains the derivation of Equation **(3.15)** in much detail and further describe the equations derived for calcium carbonate dissolution kinetics in the region $5 \leq pH \leq 9$. However, all these derivations, outside this pH range and under extraordinary environmental conditions (such as high partial pressure of carbon dioxide), needed further considerations to be addressed.

Plummer *et al* (1979) proposed that calcium carbonate dissolution kinetics may be dominated by either or both proton activity and carbonic acid species concentrations in the bulk solution. That is, when either H^+ activity and or $H_2CO_3^*$ concentration in the bulk solution are sufficiently high, these species accelerate reactions at the crystal surface thereby accelerating the overall dissolution reaction.

$$d[Ca^{2+}] / dt = k_{(P1)}\, S\, a_{H^+} + k_{(P2)}\, S\, a_{H_2CO_3^*} + k_{(P3)}\, S\, a_{H_2O} \qquad \textbf{(3.17)}$$

According to **Plummer *et al,(1979)*** the first term in Equation **(3.17)** is significant only for pH less than about 5, and the second term for greater than 0.1 atmospheres. Their third term, formulated as a function of the activity of water links to the dissolution rate in pure water. This term however does not appear to be linked to the typical diffusion controlled type of equation.

With respect to dissolution rate, they observed that the H^+ attack [i.e. the first term in Equation **(3.17)**] depended on stirring rate, reflecting a transport-controlled process. However, the CO_2 and the water dependence of the dissolution rate (i.e. the second and third term respectively) did not appear to be significantly affecting the stirring. This would indicate dissolution processes which are not diffusion controlled. By including terms describing the dissolution of calcium carbonate due to high concentration of H^+ and/or $H_2CO_3^*$, the dissolution model becomes:

$$d[Ca^{2+}]/dt = k_1S\{k'_{sp}{}^{1/2} - [Ca^{2+}]^{1/2}[CO_3^{2-}]^{1/2}\} + k_2S[H^+] + k_3S[H_2CO_3^*] \qquad \textbf{(3.18)}$$

Each of the three rate constants in the above equation depend on a number of factors including the physical characteristics of the dissolving mineral and the hydraulic flow characteristics, i.e. flow rate. As far as the physical characteristics are concerned calcium carbonate occurring in natural deposits may vary from a dense metamorphosed marble through a pure non-metamorphosed chalk to a friable impure permeable form. In general each calcium carbonate deposit will give rise to different rate constants. For natural terrestrial waters usually only the first term is of any significance and it is this term that is investigated in this work.

Kornmüller *et al* (1995) applied this model to the dissolution of limestone from the Bredasdorp deposit in the soft waters representative of those found in the Western Cape. The last two terms of the model above, do not play a significant role in the dissolution of limestone in the natural waters relevant to this study. For practical purposes **Kornmüller *et al*, (1995)** combined the surface area, S, and the rate constant, k_1, to form a compound rate constant, $k_{DC\ compound}$, which he found to vary with mixing energy (i.e. hydrological conditions) for a specific granule size – an observation consistent with the diffusion controlled model. Thus, the equation becomes:

$$d[Ca^{2+}]/dt = k_{DC\ compound}\, f_d\, \{k'_{sp}{}^{1/2} - [Ca^{2+}]^{1/2}[CO_3^{2-}]^{1/2}\} \qquad \textbf{(3.19)}$$

where $k_{DC\ compound}$ = compound rate constant for a diffusion controlled reaction, which varies with temperature, ionic strength, physico-chemico properties of the mineral and hydraulic characteristics.

In the following chapter the Sidestream Stabilization Process is described in the treatment of typical Cape waters. This process encompasses the investigations described in the previous chapters.

CHAPTER 4

BACKGROUND OF THE SIDESTREAM STABILIZATION PROCESS (SSP)

4.1 STABILISATION

4.1.1 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, 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 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 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 $CaCO_3$.

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. Chemical conditioning of potable water to ameliorate such attack is referred to as stabilisation.

4.1.2 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. (CCPP is a measure of the amount of solid $CaCO_3$ that will precipitate from a water to reach aqueous-solid phase equilibrium. For example, water with a CCPP of 30 mg/L as $CaCO_3$ will precipitate 30 mg/L $CaCO_3$, to reach chemical 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 the 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 highly supersaturated, with respect to $CaCO_3$, and that the calcium and alkalinity values should not be less than 50 mg/L (as $CaCO_3$). 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 minimizing 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.

Stabilisation is usually achieved via the addition of lime ($Ca(OH)_2$), to increase calcium (Ca^+) 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.

4.1.3 The Sidestream Stabilisation Process (SSP)

The sidestream stabilization process (SSP) is a limestone mediated stabilization process developed by the CSIR for larger water purification installations, illustrated conceptually in Figure 4.1. The process involves taking a sidestream of unstabilized water, dosing high levels of gaseous carbon dioxide (CO_2) and then contacting the CO_2 acidified stream with limestone. The acidified stream takes up considerable amounts of the solid $CaCO_3$/limestone, thereby increasing the 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 stabilized mainstream.

Carbon dioxide recovery and re-use can be sufficient that the use of 'fresh' carbon dioxide in the process is minimal. This type of stabilization also has significant advantages over the traditional use of powdered lime and carbon dioxide:

- The process uses inexpensive limestone as a calcium and alkalinity source
- Limestone can be obtained at relatively lower prices than lime (SAR 225/t against SAR 1200/t at 2001 prices)
- Capital costs are reduced as a result of treating only a portion of the feed water in a sidestream
- The SSP allows for full stabilization as required in large distribution networks

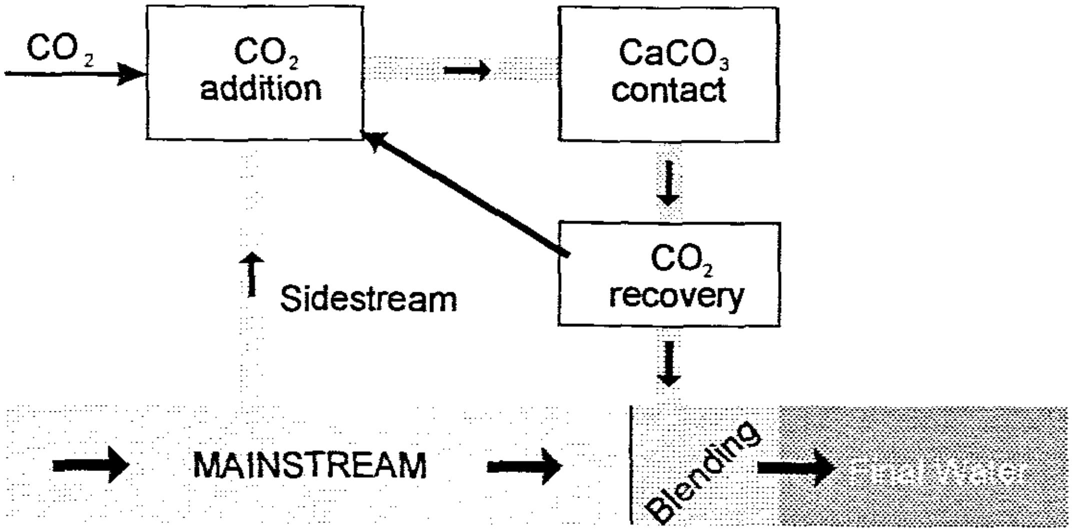


Figure 4.1: Conceptual representation of the Sidestream Stabilization Process

4.2 THEORETICAL CONSIDERATIONS

The principles governing the carbonate system in the aqueous, gaseous and solid phases (explained in detail in **Chapters 2 and 3**) play a significant role in the Sidestream Stabilization Process development. In particular, the dissolution of gaseous carbon dioxide (CO_2) into liquid phase, the dissolution of solid calcium carbonate into a liquid phase, and the recovery of excess dissolved carbon dioxide from the liquid phase to the gaseous phase are of tremendous interest and thus have to be considered. Considering the above, it is useful to note the following:

The kinetics of **carbon dioxide dissolution** into 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 carbonate species and the dosing chemical type (CO_2) lead to a water with exceptionally high total acidity and calcium carbonate dissolution potential (CCDP).

The **dissolution of calcium carbonate (limestone)**, $CaCO_3$, can only occur if the solution is undersaturated with regard to the solid carbonate. Temperature and pressure of the system, calcium and carbonate species distribution and partial pressure of carbon dioxide influence the solubility of $CaCO_3$. 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. However, suffice to note that waters with high total 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.

4.3 PROCESS DESCRIPTION (EXISTING CSIR PILOT PLANT)

The basic laboratory pilot plant and the conceptual configuration of the sidestream stabilization pilot plant is shown in **Figure 4.3**. The raw water feed is split, with a desired percentage sidestream being extracted from a constant mainstream into the pilot plant; for a 5% sidestream the flowrate is controlled at 300 L/hr using a rotameter, thereby treating a total stream of 6000 L/hr. The sidestream water is then pumped through the eductor as a high-pressure stream.

The water-CO_2 mixture then passes into 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 CO_2 dissolution vessels receive recovered CO_2. "Fresh" CO_2 from a commercial cylinder is pumped into the last dissolution vessel (DV3). The CO_2 is added into DV3 via a diffuser located near the base of the dissolution column, and is therefore added counter flow. Excess gas build-up in the water-CO_2 mixture from the eductor discharge port is vented to atmosphere in DV1 and DV2.

Having passed through the dissolution vessels, the acidified water enters the up-flow, flooded packed column calcium carbonate (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. 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 CO_2 recovery vessels, RV1 and RV2 (dimension: total height = 2050 mm, diameter = 200 mm), in series. Water is sprayed into the top of the recovery vessels via spray nozzles and percolates downwards over a packing of Pall rings, and collects at the bottom. The recovery vessels are operated at reasonably high vacuums; the required vacuum being created by the eductor. The sidestream is blended with the balance of the feed. The blended water then undergoes a final stripping of any excess carbon dioxide, by spraying the water through nozzles in 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 in the SSP is the commercially available limestone pebbles from Bredasdorp, Western Cape. 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 limestone used in the pilot plant trials has a grading of +12 mm –15 mm.

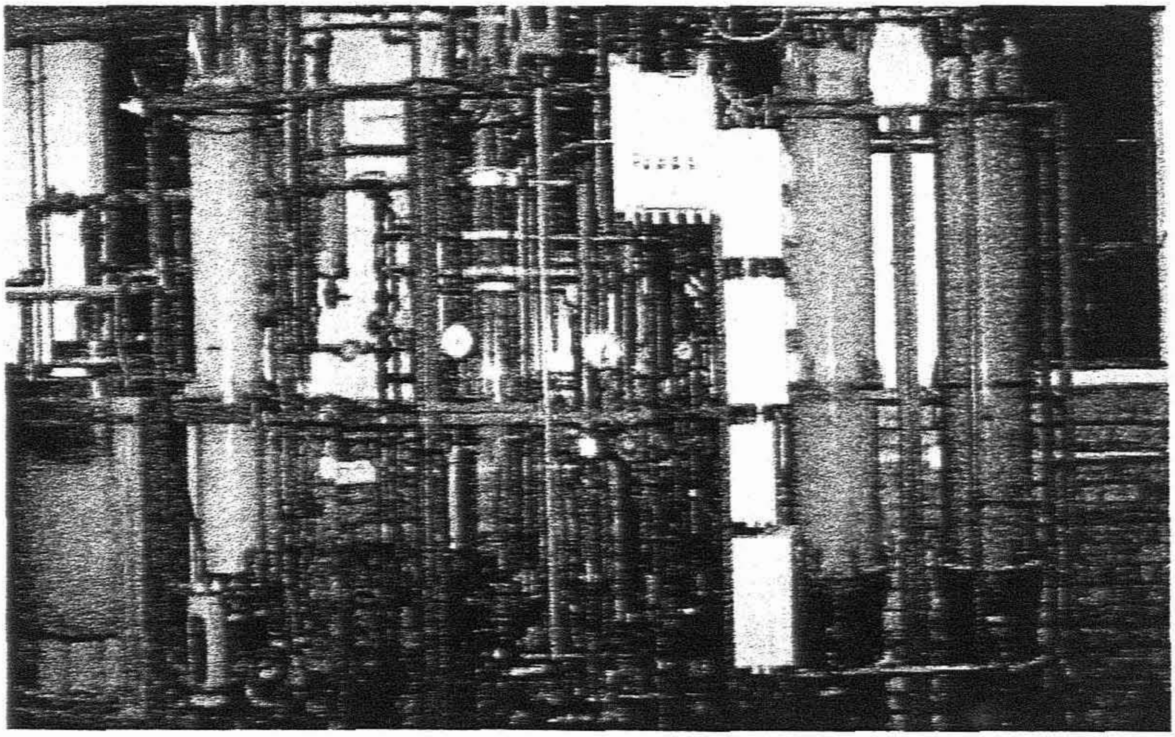


Figure 4.2: A photographic diagram of the Sidestream Stabilization Process

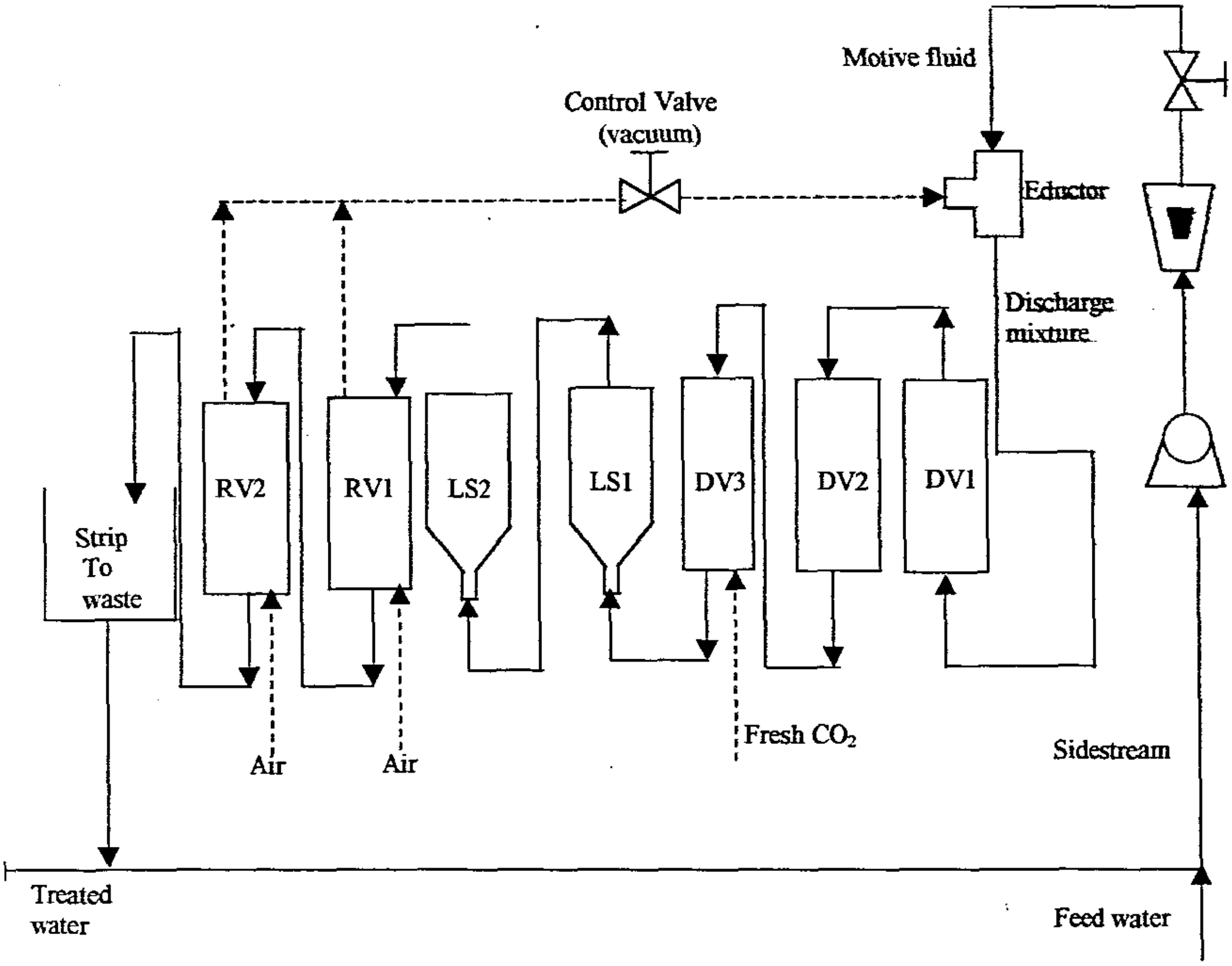


Figure 4.3: Process diagram for the Sidestream Stabilization Process

4.4 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:

4.4.1 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 stabilize the mainstream with a sidestream of about 5% of the total plant throughput, the required characteristics of the acidified water were: pH of about 3.5, Acidity of about 3000 mg/L (as $CaCO_3$) and 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 Acidity calculations (using STASOFT (5) based on in-line pH measurement), and/or 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.

4.4.2 Limestone Dissolution

This stage entails the dissolution of $CaCO_3$ from solid phase into the aqueous phase. Desktop calculations indicated that in order to introduce sufficient calcium and Alkalinity into the mainstream 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 rata of about 1.2 g/L with vessel pressure of 300 kPa. Alkalinity was measured via strong acid titration and calcium was measured by atomic absorption spectrophotometry.

4.4.3 Calcium and Alkalinity Dosing Prediction

A relationship between CO_2 dose and the mass of $CaCO_3$ 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 $CaCO_3$ dissolution at different CO_2 dosages. The empirically derived relationship was used for the prediction of calcium carbonate uptake, and for the interpretation of CO_2 recovery results.

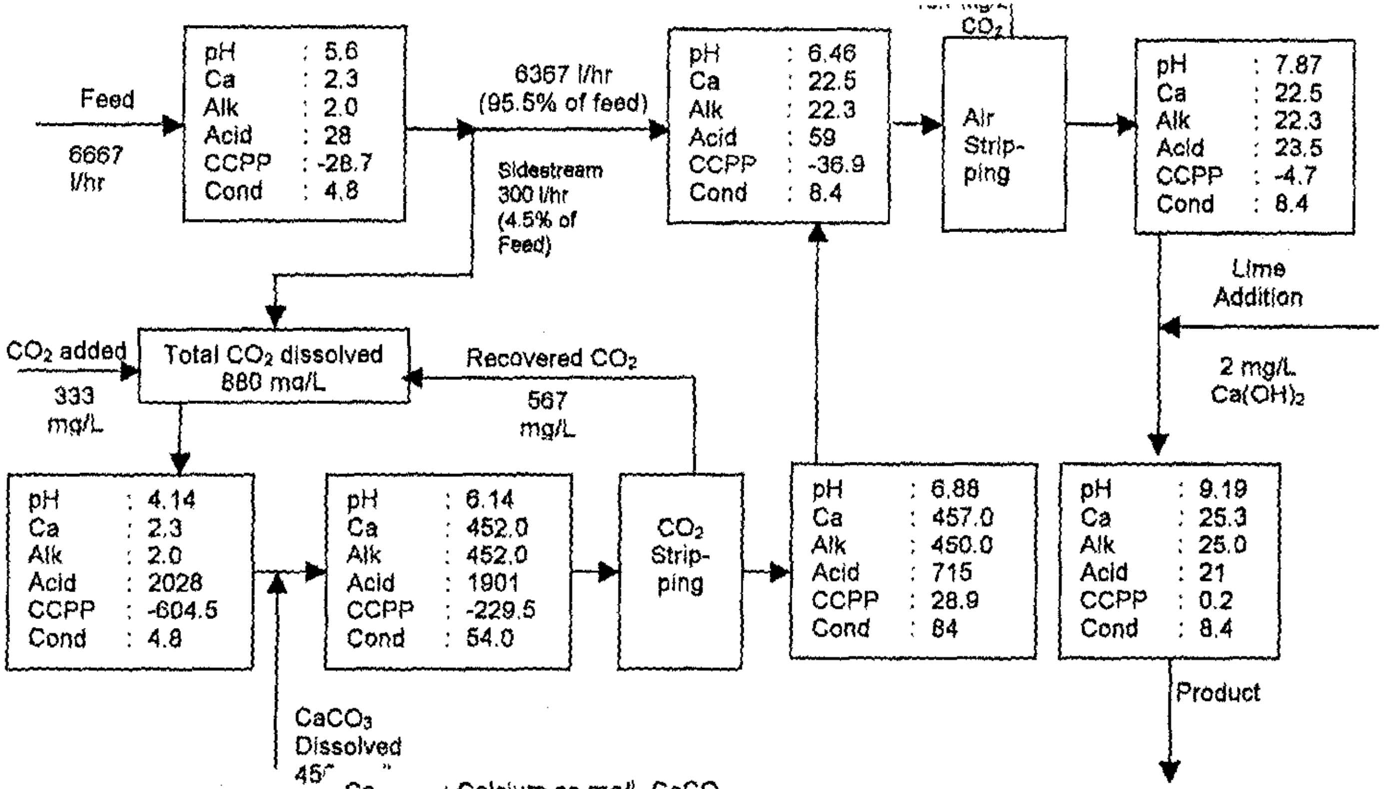
4.4.4 Determination of Percentage CO_2 Recovery

Probably the most critical stages in the process are the recovery of CO_2 after limestone contact, and reintroduction of the recovered CO_2 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 CO_2 dosage requirement. Initial investigations utilized a single stage CO_2 recovery and re-use system, i.e. referring to **Figure 4.3**. The following historical results presented pertain only to single stage recovery. The empirically derived relationship described in Section 4.4.3 was used to determine the total CO_2 dissolved in the water entering the limestone contact columns.

4.4.5 Single Stage Plant Results

Results of pilot plant trials using single stage CO_2 recovery are shown in **Figure 4.4** 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 CO_2 dissolved (880 mg/L) was determined by measuring the amount of $CaCO_3$ dissolved in the water leaving the limestone contactors and by using the empirically determined relationship described in Section 4.4.3. The amount of CO_2 (547 mg/L) was then calculated by subtracting the amount of CO_2 added (333 mg/L) from the total amount of CO_2 dissolved (880 mg/L). This amounted to a CO_2 recovery of 62%.

After CO_2 stripping and re-blending of the sidestream with the balance of the feed, a considerable amount of CO_2 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 $CaCO_3$. Using theoretical calculations, air stripping to atmosphere was employed to remove the excess CO_2, which raised the pH to 7.87, and reduce the negative precipitation potential to –4.7 mg/L as $CaCO_3$. Thereafter, nominal lime dosage was required to obtain a product with a slightly positive precipitation potential.



Ca : Calcium as mg/L $CaCO_3$
Alk : Total alkalinity as mg/L $CaCO_3$
Acid : Total acidity as mg/L $CaCO_3$
CCPP : Calcium carbonate precipitation potential as mg/L $CaCO_3$
Cond : Electrical conductivity as mS/m

Figure 4.4: Single stage pilot plant results

CHAPTER 5

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

5.1 INTRODUCTION

In trying to address the problems with *PRO/II,* modelling routines were developed for crosscheck purposes. As a result of difficulties of addressing the *PRO/II* limitations, these routines became progressively more complex. Eventually, as a response to growing concern that *PRO/II* would prove to be fatally flawed for use in modeling the SSP, and despite considerable effort and time having being invested into *PRO/II*, it was necessary to develop a JAVA program that models the SSP process. However, this chapter is based primarily on the mathematical development of the program. The model was termed "SSP-MOD".

5.2 HISTORY OF DEVELOPMENT OF SSP-MOD MODEL

A spreadsheet was developed to model the dissolution of calcium carbonate in a limestone column. This required the following routines:

- Calculation of acidity from pH, calcium, alkalinity and electrical conductivity
- Calculation $[CO_3^{2-}]$
- Calculation of pH after calcium and 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
- Determine 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* 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 modeling packages, such as *PRO/II*, or through programming. It will be shown in

CHAPTER 7 that *PRO/II* does not contain adequate routines to model the CO_2 stripping step. Since this step is crucial in the modeling 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

The model was further developed to allow calculation of the composition of both the product gas and water streams flowing from a theoretical equilibrium flash vessel, given the composition of both the input water and gas streams.

In addition, a steady state mass balance was calculated over the whole SSP. This was built into the model, to allow determination of the conditions at which the process will reach a steady state, given all the input parameters. This involved several iterative calculation loops, which made the program rather slow. The program was further adapted to allow runs at multiple input ranges, to produce multiple outputs, which can be exported to *MSExcel* for graphical representation.

The program developed therefore models the various unit processes of the SSP (assuming liquid and gas phase steady-state equilibrium conditions in the gas and water streams that leave each unit). The following diagram shows the system structure on which the model is based.

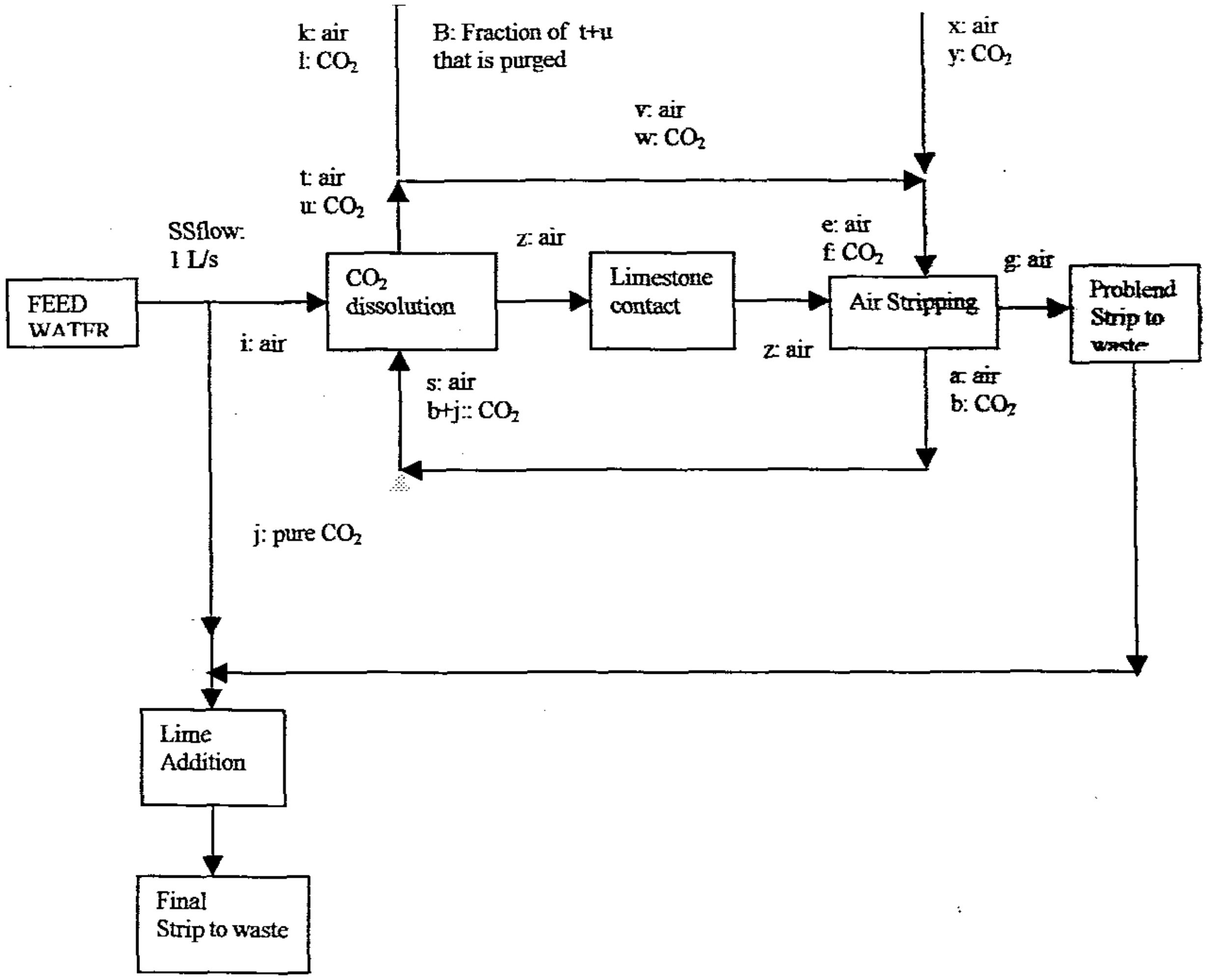


Figure 5.1: Process diagram for SSP-MOD model

5.3 SSP-MOD MODEL DEVELOPMENT

The SSP-MOD model developed is based on the following principles:

- Materials mass balances for carbonic species and inert gases (N_2/O_2) over each unit and the whole sidestream section.
- Dalton's Law (partial pressure of a component gas = molar fraction of that gas in gas phase * total pressure) for CO_2 and for the inert gases.
- Henry's Law (partial pressure of a component gas = liquid molar fraction of that gas * Henry's constant).
- 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

Sub routines were developed to simulate the aquatic chemistry processes.

5.4.1 Aquatic Chemistry Sub-routines

- CO_2 dosage to a water:
  The pH, 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

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 input 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 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 mole per litre sidestream water) are named by alphabetic letters in the figure.

Basis for mass balance:

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

$1\,l\ of\ water = 1000\ g$

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

$W = {1000}/{18} = 55.556\ moles$

$$Air\ in \quad = \quad Air\ out \tag{5.1}$$

$$z + e \quad = \quad a + g$$

$$CO_2\ \text{exp}elled\ by\ water\ stream \ = \ b - f \tag{5.2}$$

Dalton's Law for air:

$$y\Pi \ = \ p_{air} \tag{5.3}$$

Henry's Law for dissolution of air in water:

$$p_{air} \ = \ X_{air}\, H_{air} \tag{5.4}$$

H_{air} : Henry's Law Constant for air, taken as 7.2×10^4 atm/mole fraction @ 25°C. The constant given by Perry was calculated from the absorption coefficients of O_2 and N_2, 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 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 = 6.64×10^4 atm/mole fraction).

The molar amount of air dissolved in the water stream is very small compared to the molar amount of water (1.4×10^{-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}:

$$X_{air} = \frac{g}{W} \tag{5.5}$$

Substituting Equation **5.5** into **5.4**, and equalizing Equation **5.3** and **5.4**

$$\frac{a}{a+b}\Pi = \frac{g}{W}H_{air} \tag{5.6}$$

From Equation **5.1**:

$$g = z+e-a$$

Substituting Equation **5.1** into **5.6**:

$$\frac{a}{a+b}\Pi = \frac{z+e-a}{W}H_{air} \tag{5.7}$$

Equation **5.7** 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 onwards:

$$0 = -a^2 + \left(z+e-\frac{\Pi}{H_{air}}W-b\right)a + (z+e)b \tag{5.8}$$

'**a**' may be determined using:

$$\mathbf{a} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{5.9}$$

where:

$$a = -1$$

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

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

Since **a** in Equation **5.9** is negative, the denominator of Equation. **5.9** 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 conditions have to be met:

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

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:

$$\mathbf{a} = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \tag{5.10}$$

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 of air in the gas stream entering the flash vessel.

f: The molar amount CO_2 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, 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 CO_2 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 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 CO_2 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_b, the partial pressure of CO_2 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 opposed to being expelled.

(iii) **b** (the molar amount CO_2 in the gas stream leaving the flash vessel) is calculated from equation **5.2**

(iv) **a** (the molar amount air in the gas stream leaving the flash vessel) is calculated using equation **5.9** (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 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 **5.6**.

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 flow rate 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":

$$i + x = k + g \tag{5.11}$$

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

$$e = v + x \tag{5.12}$$

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 utilisation 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:

$$v = (1-B)t \qquad \textbf{(5.13)}$$

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

$$t = k + v \qquad \textbf{(5.14)}$$

Substituting t in Equation **5.13** with the above gives:

$$v = (1-B)(k+v) \qquad \textbf{(5.15)}$$

Solving the above for v:

$$v = \frac{k(1-)B}{B} \qquad \textbf{(5.16)}$$

Substituting v above in Equation **5.12:**

$$e = \frac{k(1-B)}{B} + x \tag{5.17}$$

From Equation **5.1**:

$$a = e - g + z$$

All the air in the product gas stream from the stripper (a) is reintroduced to the CO_2 dissolution stage, therefore the air in the dissolution feed gas stream (s) equals a:

$$s = a \tag{5.18}$$

Substituiting e above with Equation **5.17** gives:

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

Substituting k above, using Equation **5.11**:

$$s = \frac{(1+x-g)(1-B)}{B} + x + z - g \tag{5.19}$$

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 CO_2 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 **5.6**:

$$\frac{a}{a+b}\Pi_{AS} = \frac{g}{W}H_{air}$$

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:

$$g_{\max} = \frac{\Pi_{AS}W}{H_{air}} \qquad \textbf{(5.20)}$$

Similarly, the upper limit for z can be established:

$$z_{\max} = \frac{\Pi_{DV}W}{H_{air}} \qquad \textbf{(5.21)}$$

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

$$g_{\min} = 0$$

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 substituted in Equation **5.19**. The upper limit for $z-g$ can be calculated as follows:

$$(z-g)_{\max} = z_{\max} - g_{\min}$$

$$= z_{\max}$$

Substituting g with $g_{\min}$ and $(z-g)_{\max}$ in Equation **5.19**, to obtain $s_{\max}$:

$$s_{\max} = \frac{(1+x)(1-B)}{B} + x + z_{\max} \tag{5.22}$$

Substituting g with $g_{\max}$ and $(z-g)_{\min}$ in Equation **5.19**, to obtain $s_{\min}$:

$$s_{\min} = \frac{(1+x-g_{\max})(1-B)}{B} + x - g_{\max} \tag{5.23}$$

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 Equation **5.23** to be less than 0, it should be changed to 0.

The algorithm formulated to solve the CO_2-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 CO_2 entering the CO_2 dissolution vessel. The latter amount also depends on the output from the 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 CO_2 fed into the dissolution vessel. In the outer loop, the value of R is "guessed" and adjusted iteratively, and in the inner loop, the value of R is "guessed" and adjusted. R is the fraction of the CO_2 in the feed gas to the dissolution vessel that originates from the air stripper product gas:

$$R = \frac{b}{b+j} \tag{5.24}$$

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

$$b = \frac{jR}{1-R} \tag{5.25}$$

$$s_{\max} = \frac{(1+x)(1-B)}{B} + x + z_{\max} \tag{5.22}$$

Substituting g with $g_{\max}$ and $(z-g)_{\min}$ in Equation **5.19**, to obtain $s_{\min}$:

$$s_{\min} = \frac{(1+x-g_{\max})(1-B)}{B} + x - g_{\max} \tag{5.23}$$

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 Equation **5.23** to be less than 0, it should be changed to 0.

The algorithm formulated to solve the CO_2-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 CO_2 entering the CO_2 dissolution vessel. The latter amount also depends on the output from the 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 CO_2 fed into the dissolution vessel. In the outer loop, the value of R is "guessed" and adjusted iteratively, and in the inner loop, the value of R is "guessed" and adjusted. R is the fraction of the CO_2 in the feed gas to the dissolution vessel that originates from the air stripper product gas:

$$R = \frac{b}{b+j} \tag{5.24}$$

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

$$b = \frac{jR}{1-R} \tag{5.25}$$

5.4.5 Algorithm for CO_2 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 CO_2 dosed to the sidestream.
- π_{DV}, the total pressure in the CO_2 dissolution vessel.
- π_{RV}, the total pressure in the air stripping vessel.
- The flow and composition (in terms of percentage air and CO_2) 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:

$$s_{guess} = \frac{s_{upper\,\mathrm{lim}\,it} - s_{lower\,\mathrm{lim}\,it}}{2}$$

The initial upper and lower limits for s are given in Equations **5.22** and **5.23**, respectively.

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

$$R_{guess} = \frac{R_{upper\,\mathrm{lim}\,it} - R_{lower\,\mathrm{lim}\,it}}{2}$$

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 **5.25**.

(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:

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

(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:

(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 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 **5.18** and **5.24**.

(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 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 of 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 the SSP process, 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**:

- Calcium, alkalinity (both as mg/L $CaCO_3$), pH, electrical conductivity (mS/m) and temperature (°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 8.297×10^{-4} mole/L.
- A flow for the feed water need not be specified – the models is based on a timescale of 1second 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 L air/L "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 $CaCO_3$)
- Alkalinity (mg/L as $CaCO_3$)
- pH
- Electrical conductivity (mS/m)
- Temperature (°C)
- Total inorganic carbon content (as mg/L CO_2) – calculated from the acidity and 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 $CaCO_3$ 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 L gas/L "sidestream" water)
- Molar fraction air (assuming air is mainly nitrogen and oxygen)
- Molar fraction CO_2
- Temperature (°C)
- Total pressure (atmospheres absolute pressure)
- Total molar flow (moles/ L "sidestream" water)
- Molar flow air (moles/L "sidestream" water)
- Molar flow CO_2 (moles/L "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, eqbrm 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 STREAMS? 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 STREAMS?  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:
```

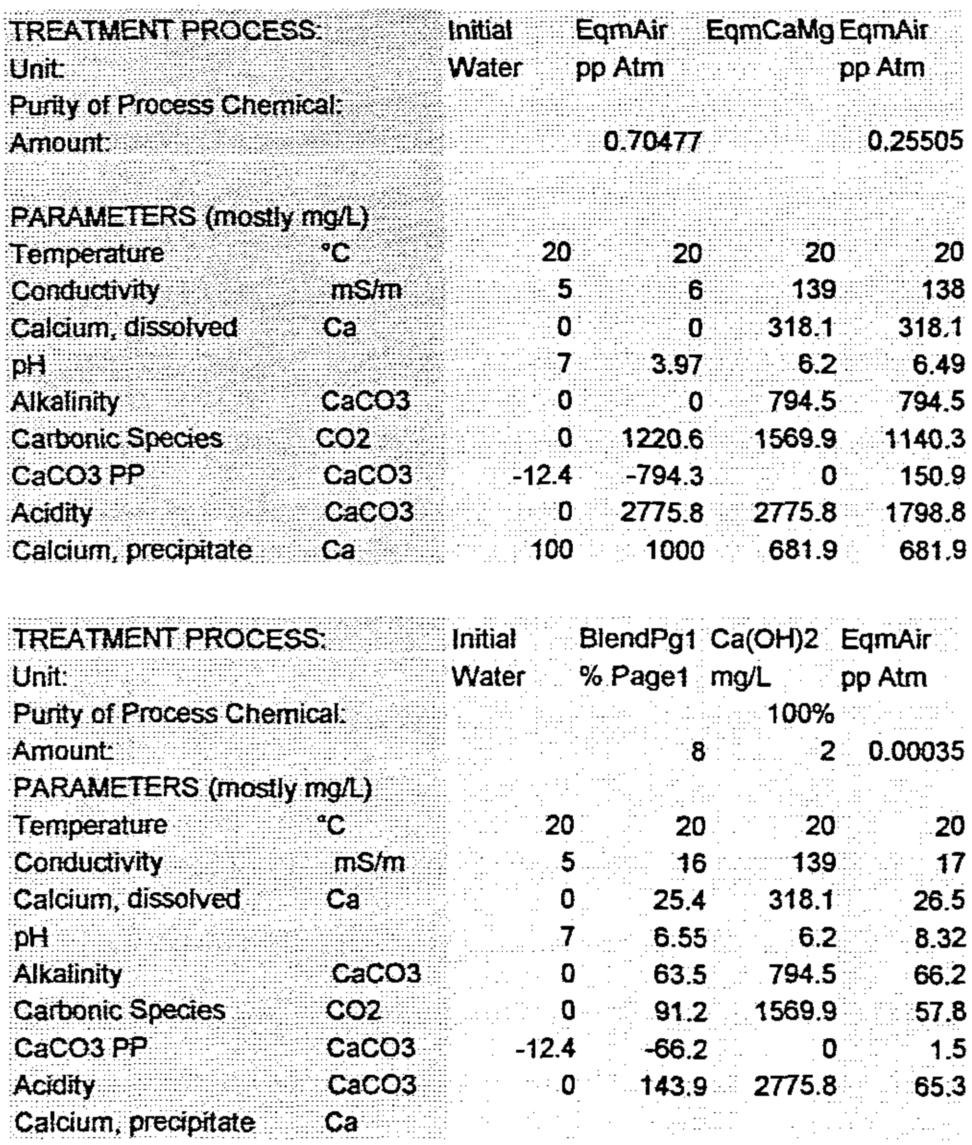
PROC	Dosage	Ca	Alk	EC	T	Ct	Ac	CCPP	PH	Air
FEED		0.0	0.0	5.0	20	-0.0	-0.0	-14.2	7.0	8.297E-4
CO2	1222.8	0.0	0.0	5.0	20	1222.8	2279	-669.2	3.97	0.001771
EQCA	792.4	792.4	792.4	95.0	20	1571.4	2779	-0.0	6.23	0.001771
CO2	-433.21	792.4	792.4	95.0	20	1137.9	1793	134.6	6.53	3.47E-5
% STRM	8.0	63.4	63.4	12.0	20	91.0	143.5	-66.8	6.56	3.47E-5
LIME	2.0	66.1	66.1	12.0	20	91.0	140.8	-62.1	6.61	3.47E-5
EQAIR	3.5E-4	66.1	66.1	12.0	20	58.1	65.9	0.7	8.34	3.47E-5
			MfAir	MfCO2	T	Vol	Press	nMole	moleAir	MoleCO2
DV Feed-gas			0.76508	0.9417	20	0.24	3.0	0.02977	0.001736	0.028034
DV Prod-gas			0.76508	0.2349	20	0.01	3.0	0.00104	7.9501E-4	2.441E-4
Gas off-bleed			0.76508	0.2349	20	0.01	3.0	0.00104	7.9501E-4	2.441E-4
Air feed			0.99965	3.5E-4	20	0.0	1.0	0.0	0.0	0.0
AS Feed-gas			0.0	0.0	20	0.0	3.0	0.0	0.0	0.0
AS Prod-gas			0.14983	0.8502	20	0.93	0.3	0.01159	0.001736	0.009853

```
CO2 dosage to SS:  800.0
Partial CO2 pressures (atm) DV:  0.704766  AS:  0.255051
Percentage recycled CO2 in DV  feed  35.144
(Dissolved CO2 – fresh CO2)/ (Dissolved CO2)  0.346
Number of iterations to calculate mole air into diss vessel:  15
CO2 recovery calculation converged
```

Figure 5.2: Example of a SSP-MOD run with distilled water, dosing 800 mg/L pure CO_2, without pre-blended strip-to-waste step

In the fifth line from the bottom, the CO_2 partial 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 CO_2 pressures were used as input in *STASOFT 4* for this comparison. The *STASOFT 4* output is shown in the following figure.



TREATMENT PROCESS:		Initial	EqmAir	EqmCaMg	EqmAir
Unit:		Water	pp Atm		pp Atm
Purity of Process Chemical:					
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	318.1	318.1
pH		7	3.97	6.2	6.49
Alkalinity	CaCO3	0	0	794.5	794.5
Carbonic Species	CO2	0	1220.6	1569.9	1140.3
CaCO3 PP	CaCO3	-12.4	-794.3	0	150.9
Acidity	CaCO3	0	2775.8	2775.8	1798.8
Calcium, precipitate	Ca	100	1000	681.9	681.9

TREATMENT PROCESS:		Initial	BlendPg1	Ca(OH)2	EqmAir
Unit:		Water	% Page1	mg/L	pp Atm
Purity of Process Chemical:				100%	
Amount:			8	2	0.00035
PARAMETERS (mostly mg/L)					
Temperature	°C	20	20	20	20
Conductivity	mS/m	5	16	139	17
Calcium, dissolved	Ca	0	25.4	318.1	26.5
pH		7	6.55	6.2	8.32
Alkalinity	CaCO3	0	63.5	794.5	66.2
Carbonic Species	CO2	0	91.2	1569.9	57.8
CaCO3 PP	CaCO3	-12.4	-66.2	0	1.5
Acidity	CaCO3	0	143.9	2775.8	65.3
Calcium, precipitate	Ca				

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)

DETER-MINANT	**FEED**		**POST– CO_2 DISSOLN (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% SS)**		**POST LIME DOSAGE (2 mg/L LIME)**		**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	6.61	6.55	6.61	6.60	8.34	8.32
Ca	0	0	0	0	317	318	317	318	25.4	25.4	26.4	26.5	26.4	26.5
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
Acidity	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 SSS 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 "CO_2 dissolution" vessels connected in series. In the first dissolution vessel, DV1, recovered CO_2 is contacted with the feed water. The water then only passes through DV2, and in DV3, pure ("fresh") CO_2 is added from a gas cylinder. From there, the water passes through two limestone columns, and then through two CO_2 stripping/recovery vessels, RV1 and RV2. The two recovery vessels are connected in parallel to the suction side of an eductor (an vacuum generating venturi device – see CHAPTER 6 for further details). Gas containing CO_2 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/STONE	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)
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 (absolute) throughout the run and a vacuum of approximately 35 kPa (abs) was maintained within the recovery vessels. Pure CO_2 was fed into DV3 at a measured rate of 570 mg/L (the amount of CO_2 added was measured based on mass loss from a CO_2 cylinder). No air was fed to the recovery vessels.

A SSP-MOD run was carried out using the above input values. The SSP-MOD program has the option of allowing water to reach $CaCO_3$ saturation in the limestone contact vessel, or to specify a $CaCO_3$ dosage. In this case, the $CaCO_3$ dosage was specified to reflect the actual amount of CO_2 taken up by the water.

The SSP-MOD output is summarized in **Table 5.3**.

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
Alkalinity (as mg/L $CaCO_3$)	15	15	387.0	387.8
ElectricalConductivity (mS/m)	8	8	58	58
CCPP (as mg/L $CaCO_3$)	-5.5	-506.2	-190.7	-143.5
Carbonic species (as mg/L CO_2)	13.3	652.9	816.6	707.2

The SSP-MOD simulation predicts that 70 mg/L of recovered CO_2 can be re-dissolved in the dissolution vessels, which results in a total CO_2 dosage of 570 + 70 = 640 mg/L. However, correlation between the post-CO_2 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 CO_2 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 CO_2 recovered), the pure CO_2 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 CO_2 dosage is specified as 820 mg/L, the pH values after limestone contact and CO_2 stripping were similar. This result indicates that more CO_2 was dissolved (and therefore more CO_2 was recovered) than what was predicted using the SSP-MOD model. (The amount of "fresh" CO_2 dosed was measured via mass loss and therefore decreases in pH measured in the dissolution vessels were as a result of recovered CO_2.) 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 if 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 optimize 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 CO_2 dosage
- Effect of pressure in the stripping/recovery vessel
- Effect of atmospheric air flow into the air stripper/recovery vessel

5.7.1 Effect of CO_2 Dosage

A SSP-MOD model run was carried out whereby the "fresh" CO_2 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 alkalinity of the blended stream, and the percentage CO_2 recovery (percentage recovered CO_2 divided by the total CO_2 dosage, i.e. the pure plus the recovered CO_2). It can be seen that for this set of dissolution/stripping pressures the percentage CO_2 recovery increases to a maximum of ~ 70% (at a CO_2 dose of 1300 mg/L), after which it starts to decrease.

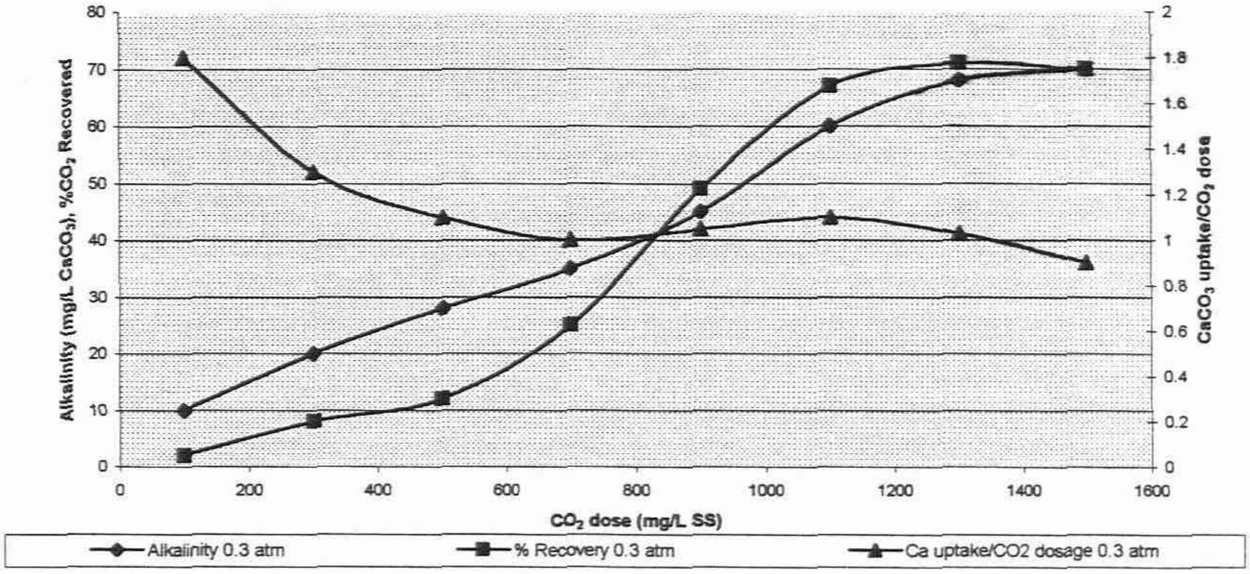


Figure 5.4: Output from a multiple SSP-MOD run, varying pure CO_2 dose between 100 and 1500 mg/L, i.e. showing alkalinity after blending

5.7.2 Effect of Pressure in Recovery Vessel

It was believed that the vacuum pressure in the recovery vessel influences the amount of CO_2 that is recovered which would therefore influence the total amount of $CaCO_3$ taken up (if more CO_2 is available, more $CaCO_3$ will dissolve). This concept was verified by the SSP-MOD model, which showed that an increase in vacuum pressure resulted in a greater $CaCO_3$ uptake, indicating that more CO_2 is being recovered. Furthermore, it was found that CO_2 recoveries only increased with increased vacuum at higher "fresh" CO_2 doses. These results are shown in **Figure 5.5**.

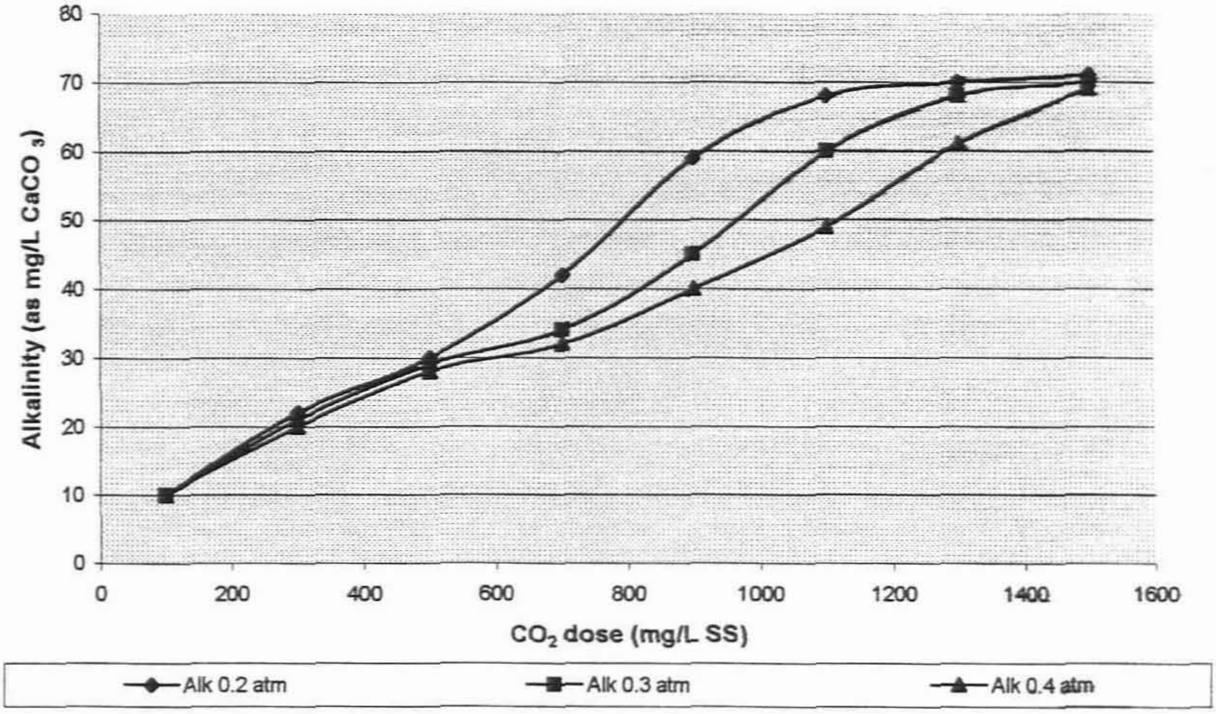


Figure 5.5: Alkalinity in the sidestream (after limestone contact at different recovery rates CO_2 doses, and for different pressures in the air stripping/recovery vessel)

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

It was believed that the addition of atmospheric air into the recovery vessel would improve CO_2 recovery, as the addition of air into the recovery vessel reduces the partial CO_2 pressure in the recovery vessel, thus allowing more CO_2 to be stripped from the water. This had been verified during previous pilot plant tests, which showed that the addition of air aided CO_2 stripping and recovery. **Figure 5.6** shows the alkalinities and percentage CO_2 recoveries at different CO_2 dosages, if no air flows into the recovery vessel (the alkalinities shown are after blending a 5% sidestream with the mainstream).

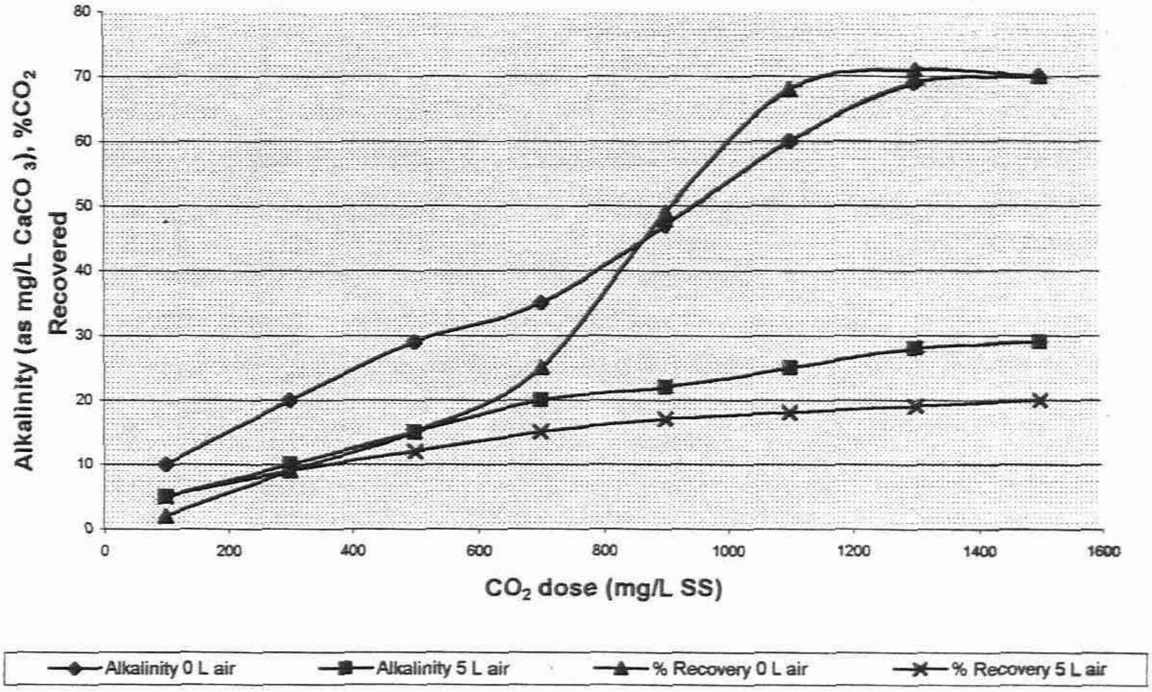


Figure 5.6: Alkalinity and percentage CO_2 recovery in a 5% sidestream in the blended stream, at different CO_2 doses, with and without air flow into the stripper

The above graph indicates that the addition of 5 L air/L sidestream reduces the final alkalinity and therefore the amount of CO_2 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 modeling packages and the recognised *STASOFT 4* aquatic chemistry software package, the project team undertook previously unenvisaged programming to create a model to describe the SSP process.

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

- Calcium, alkalinity, pH, electrical conductivity and temperature of the feed water.
- The "fresh" CO_2 dosage.
- The total pressure in the CO_2 dissolution vessel.
- The amount of $CaCO_3$ taken up in the limestone contactor (or if this is unknown the water is equilibrated with $CaCO_3$).
- The total pressure in the recovery vessel.
- Flow of an air stream 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.
- 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. Subsequently, this 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 CO_2 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 *STASOFT4* 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" CO_2 added to the sidestream increases the CO_2 recovered to a maximum of ~ 70% (at a "fresh" CO_2 dose of 1300 mg/L). At this stage an increase in fresh CO_2 dosed does not improve CO_2 recovery.

An increase in vacuum pressure (i.e. closer to absolute zero pressure – kPa) within the recovery vessel increases the amount of CO_2 recovered. This relationship was seen to only hold at higher CO_2 doses.

Previous pilot plant trials had showed that the addition of air aided CO_2 stripping and recovery. The SSP-MOD model, however showed that the addition of 5 L atmospheric air/L sidestream decreased the final water alkalinity and therefore decreased the amount of CO_2 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 CO_2 RECOVERY AND ASSESSMENT OF THE “SSP-MOD” PROGRAM

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 optimize 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 optimize 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 describes work undertaken to improve both the operation of the SSP pilot plant to achieve improved/optimized 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 columns (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 eductor devices may be suitable on the SSP pilot plant as their use provides a means of overcoming moisture related problems, without compromising vacuum generation efficiency.

6.3 EDUCTOR THEORY

An eductor is a device that uses the basic Bernoulli principle to relate fluid velocity to pressure. In this regard, an eductor 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.

Eductors (also known as jet pumps, ejectors, venturis, siphons) convert energy between two flows. These are highly efficient, differential pressure systems. In general, a pressure difference between the inlet and the outlet ports of the eductor creates a vacuum inside the eductor body, which then initiates suction through the suction port. When a pressurized motive (operating) fluid enters the eductor inlet, it is constricted towards the converging nozzle and changes into a high velocity jet stream. The increase in velocity through the nozzle results in a decrease in pressure, thereby enabling an additive material to be drawn through the suction port and entrained into the motive stream. As the jet stream is diffused toward the eductor outlet its velocity is reduced and it is re-converted into pressure energy (but at a pressure lower than the eductor inlet pressure)

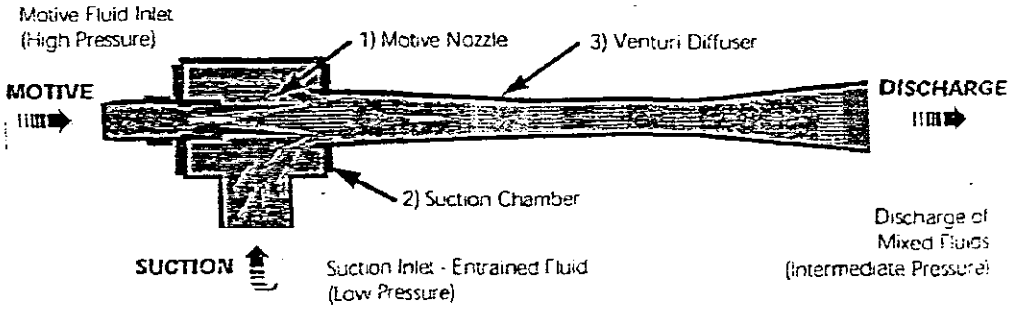


Figure 6.1: A basic outline of an eductor device (Source: www.chemguard.com)

6.4 EDUCTORS FOR EXHAUSTING GASEOUS STREAMS

Eductors are designed to be 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.
- **Non-electrical**
  Eductors can be used in hazardous locations where electrically operated alternatives would require expensive explosion proofing.
- **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.
- **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 and 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 or gases in the petrochemical, process and power industries.

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 (operating) Flow: 300 – 340 L/hr
- Discharge Pressure: 300 kPa
- Suction Pressure variations: 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.

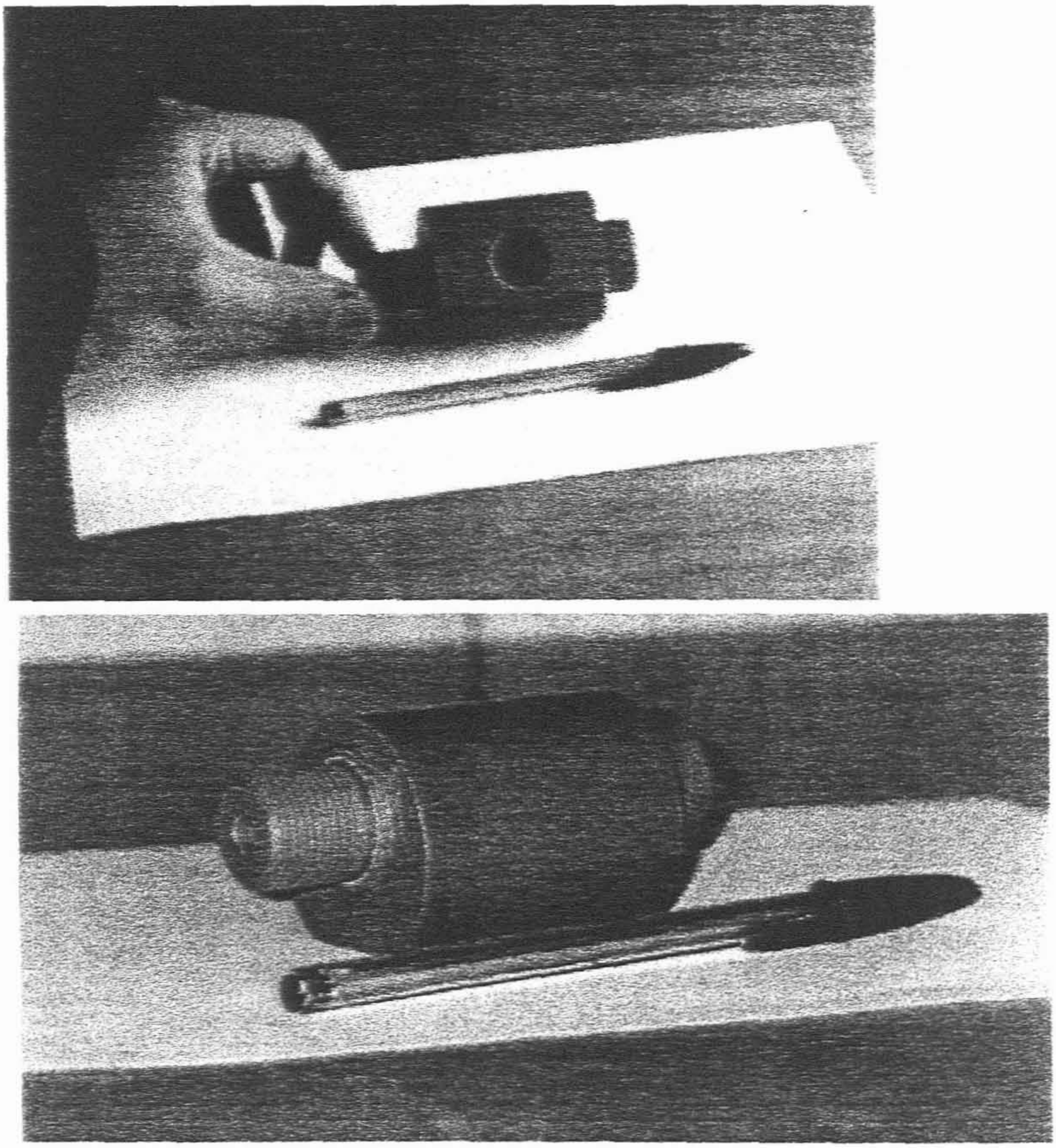


Figure 6.2: Penberthy Model LM½ "B PVC Eductor

6.6 EDUCTOR SYSTEM CONFIGURATION

The eductor was installed according to instructions supplied by the manufacturers. The basic configuration of the pilot plant showing the location of the eductor follows:

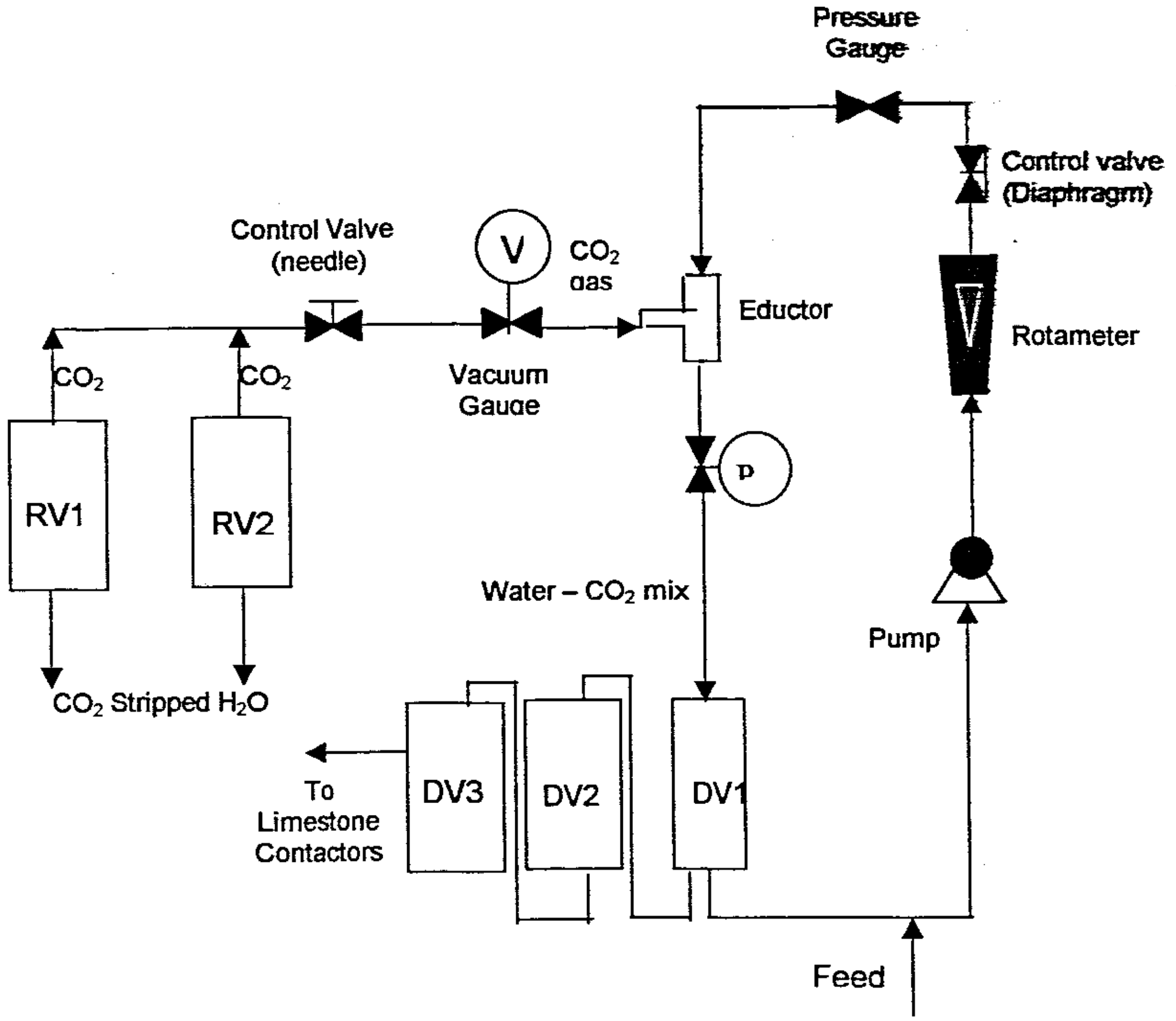


Figure 6.3: Process diagram for the recovery and dissolution of CO_2 using and eductor device

The water is pumped through a 50 mm pipe reduced to a 25 mm pipe into the SSP using a peripheral turbine pump which can effectively operate at a maximum head of 75 m and can also produce a maximum flowrate of 600 l/hr at 680 kPa. Its Net Positive Suction Head (NPSH) is less than 0.8 m. After the water stream has passed through the CO_2 and limestone dissolution columns, CO_2 is stripped by aeration as it enters the CO_2 recovery columns (using spray nozzles).

The eductor is designed to create a vacuum of between 50 to 20 kPa (depending on the specific requirements), drawing off the recovered CO_2 and allowing "CO_2-free" water to trickle to the bottom of the recovery column. One eductor is used to draw the recovered CO_2 from both recovery vessels (RV1 and RV2). The recovered CO_2 enters the eductor where it is mixed with the incoming untreated feed stream. The eductor then ejects a CO_2-water mixture as a product at 300 kPa, the operating pressure of the dissolution vessel. CO_2 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 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 theses 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 (with aeration in RV1 and RV2).
- Normal SSP operation (i.e. dosing CO_2 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. A simple configuration illustrating the eductor experiment isolated from the SSP pilot plant is shown in **Figure 6.4** below.

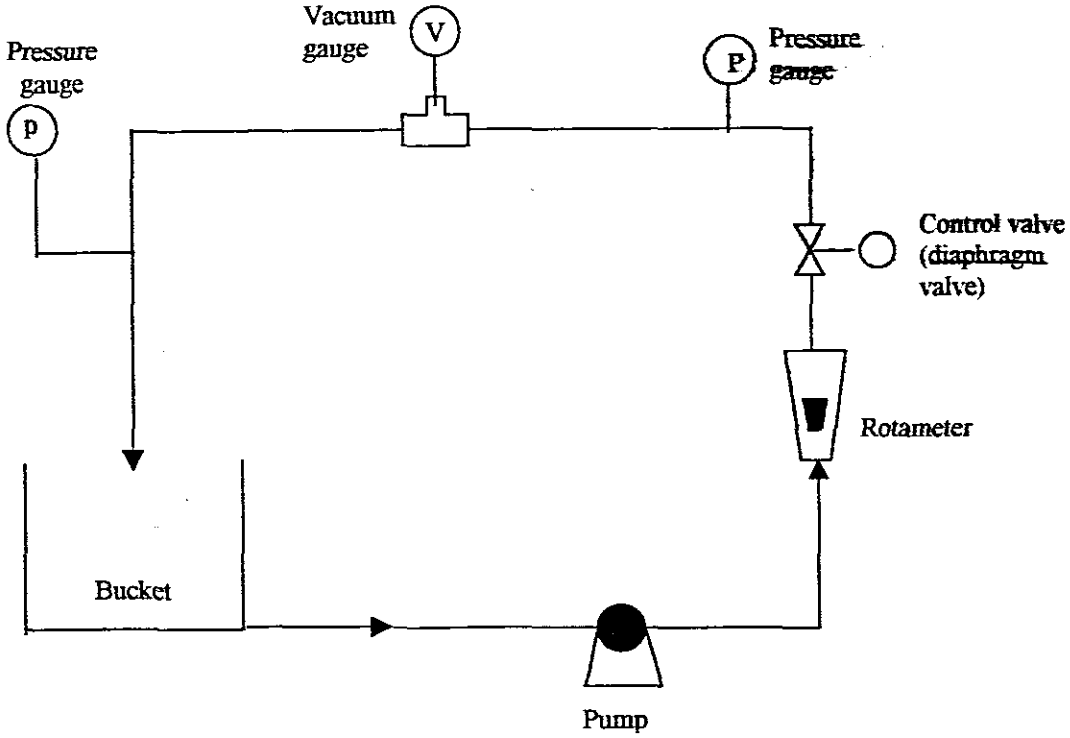


Figure 6.4: Schematic representation of the eductor experimental set-up

The eductor was then re-installed into the pilot plant. In this experiment, a by-pass line was created so that water could 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 CO_2 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 was therefore controlled at 260 kPa so that decreases in vacuum generated could be avoided (but still maintaining plant operations as 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 were contacted and discussions relating to the unexpected poor performance of the eductor ensued. During the extensive discussions, which included both the review of design specifications and performance data it became apparent that the South African distributors had supplied incorrect design specifications (with regards to discharge pressure conditions) to the manufacturers in the USA, which resulted in the acquisition of an incorrectly sized eductor. Therefore, to prevent any further delays 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 vessels. 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 CO_2 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 CO_2 recovered as well as the retention times in the various columns of the SSP, as this aspect is discussed throughout this chapter.

6.8 RETENTION TIMES OF THE SSP COLUMNS

The retention time of each column was calculated based on the actual volume, void ratio included, using the equation:

$$Column\ volume = \left(\frac{\Pi * (d)^2}{4}\right)h \qquad \textbf{(6.1)}$$

Once the volume is obtained the void ratio of a column, depending on whether it is a packed column, is taken into consideration. Thereafter, the retention time of a column is calculated based on the following equation:

$$Column\ \mathrm{Re}tention\ time = \frac{V}{Q} \qquad \textbf{(6.2)}$$

Table 6.1: Retention times of the SSP columns

Column	Flowrate L/hr	Flowrate m^3/hr	Diameter m	Height m	Volume m^3	Voidage fraction	Actual volume	Retention time	
								hrs	mins
DV 1	340	0.34	0.2	1.81	0.0569			0.167	10.02
DV 2	340	0.34	0.2	1.81	0.0569			0.167	10.02
DV3	340	0.34	0.15	2.05	0.0362			0.106	6.36
LS1	340	0.34	0.3	2.41	0.1704	0.4	0.068	0.200	12
LS2	340	0.34	0.3	2.41	0.1704	0.4	0.068	0.200	12
RV1	340	0.34	0.2	2.05	0.0644	0.8	0.052	0.153	9.18
RV2	340	0.34	0.2	2.05	0.0644	0.8	0.052	0.153	9.18

Using a flowrate of 300l/hr the retention times for the various columns were calculated in **Table 6.1** with voidage fractions taken into consideration for the limestone and carbon dioxide recovery columns. Since these columns are limestone columns packed with limestone pebbles and recovery columns packed with pall rings, the voidage fraction is considered to be the total space occupied by the packings which thus slows the rate at which the water passes through that particular column. Thus to calculate the retention time for the limestone and recovery columns the actual volume with voidage included is taken into consideration. The total time for a complete cycle is taken to be the sum of the time recorded for each column.

$$\textit{Total time per cycle} = \sum \text{Retention time} \qquad (6.3)$$

6.9 METHODOLOGY FOR CALCULATING PERCENTAGE CO$_2$ RECOVERY

The percentage CO$_2$ recovered is calculated by division of the recovered CO$_2$ by the sum of the "fresh" CO$_2$ added and the recovered CO$_2$, which is then multiplied by 100.

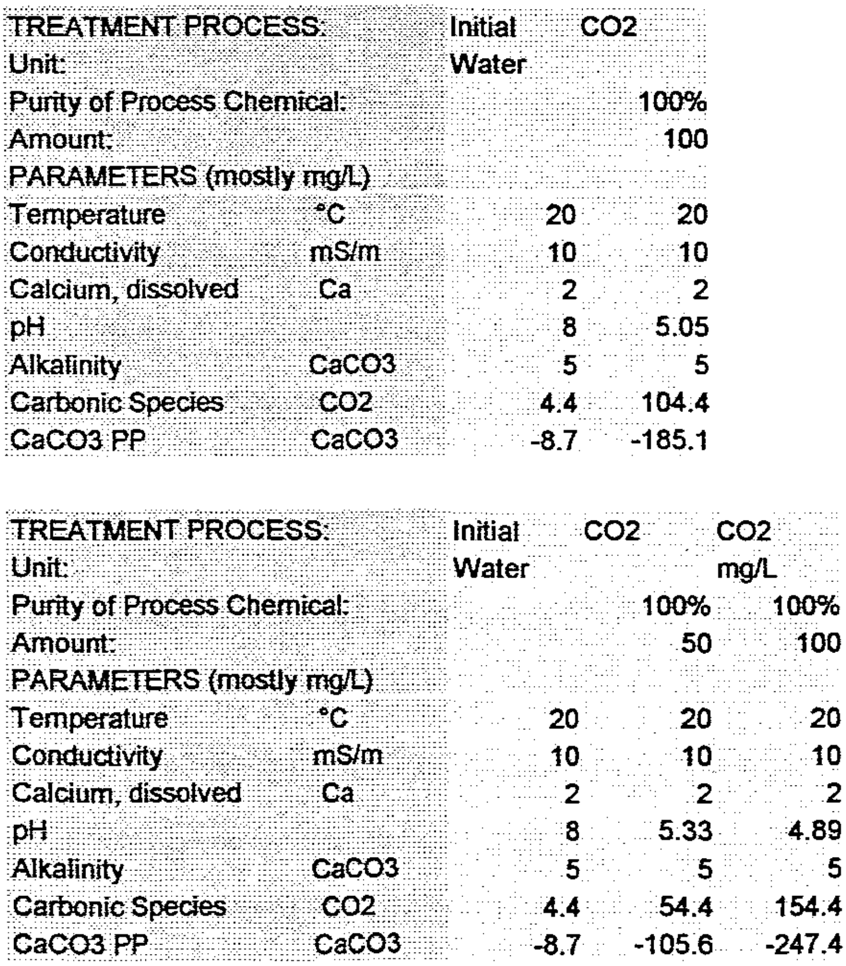
$$\%CO_2\ \text{Recovered} = \frac{Actual\ CO_2\ recovered}{\text{"}Fresh\text{"}\ CO_2\ added + Actual\ CO_2\ recovered} \times 100 \qquad (6.4)$$

Therefore, by way of example, if the amount of "fresh" CO_2 added to the sidestream was 300 mg/L, and 200 mg/L was recovered, the percentage CO_2 recovered would be 200 / (300 + 200) * 100 = 40%

The amount of CO_2 recovered can be determined in two ways:
STASOFT 4 and the "Bones Curve"

STASOFT 4

Using the raw water characteristics and *STASOFT 4*, the amount of CO_2 required to obtain recorded pH levels (from the on-line pH probes) in the dissolution vessels (prior to addition of "fresh" CO_2) is calculated. The figure obtained is the amount of CO_2 recovered (mg/L). The following figure shows the methodology used in *STASOFT 4* to calculate the amount of CO_2 recovered.



TREATMENT PROCESS:		Initial	CO2
Unit:		Water	
Purity of Process Chemical:			100%
Amount:			100
PARAMETERS (mostly mg/L)			
Temperature	°C	20	20
Conductivity	mS/m	10	10
Calcium, dissolved	Ca	2	2
pH		8	5.05
Alkalinity	CaCO3	5	5
Carbonic Species	CO2	4.4	104.4
CaCO3 PP	CaCO3	-8.7	-185.1

TREATMENT PROCESS:		Initial	CO2	CO2
Unit:		Water		mg/L
Purity of Process Chemical:			100%	100%
Amount:			50	100
PARAMETERS (mostly mg/L)				
Temperature	°C	20	20	20
Conductivity	mS/m	10	10	10
Calcium, dissolved	Ca	2	2	2
pH		8	5.33	4.89
Alkalinity	CaCO3	5	5	5
Carbonic Species	CO2	4.4	54.4	154.4
CaCO3 PP	CaCO3	-8.7	-105.6	-247.4

Figure 6.5: Example of using *STASOFT 4* to calculate CO_2 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 CO_2 a water with a pH of 5.05 is expected. However, after the addition of 100 mg/L CO_2 on the pilot plant the pH of the stream is 4.89. This can only occur if an additional 50 mg/L of CO_2 is added to the sidestream and must be as a result of recovery of CO_2. Therefore the amount of CO_2 recovered is 50 mg/L and the percentage CO_2 recovery is [50 / (100 + 50)] * 100 = 33%.

The *STASOFT 4* method for calculating the amount of CO_2 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" (developed by a former CSIR engineer) is used to determine the amount of CO_2 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-CO_2 recovery mode. Each of these curves is a plot of alkalinity in the sidestream after contact with limestone vs the amount of "fresh" CO_2 added to the sidestream. Each "Bones Curve" requires approximately 15 hours of the pilot plant to produce. For ease of reference, operation of the pilot plant to determine the "Bones Curve" 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 alkalinity.

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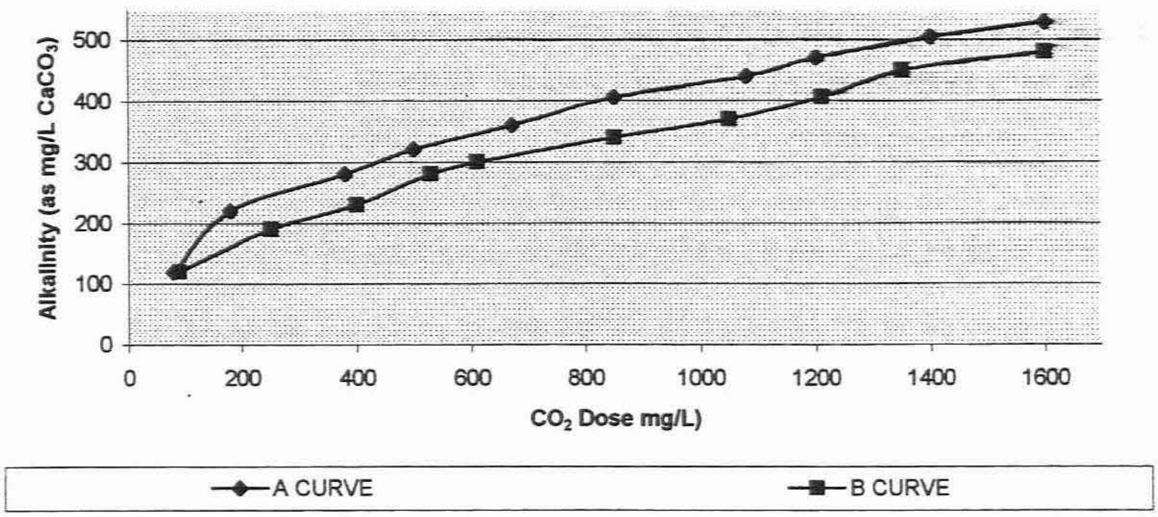


Figure 6.6: Typical "Bones Curve"

Therefore, as an example as to how the "Bone Curve" is used to measure the percentage CO_2 recovery let us assume that 350 mg/L of "fresh" CO_2 was dosed to the sidestream and an Alkalinity of ~300 mg/L (based on the laboratory analysis of the water) was recorded in the final stream leaving the pilot plant. However, from the above "Bones Curve" it is clear that to obtain a final Alkalinity of 300 mg/L a CO_2 dose of ~430 mg/L (based on "A" curve) and ~620 mg/L (based on "B" curve) is necessary. The amount of CO_2 recovered is thus;

430 – 350 = 80 mg/L (based on "A" curve)
620 – 350 = 270 mg/L (based on "B" curve)

The percentage CO_2 recovery based on the calculation method (eq. 6.1) as described above is ~19% (A) and ~43% (B). The actual CO_2 recovered will lie between the maximum and minimum percentage CO_2 recoveries calculated (previous pilot plant experience, however, has shown that the actual CO_2 recovered follows the "B" curve more closely.

6.10 PRELIMINARY "NORMAL" SSP OPERATION WITH INCORRECTLY SIZED EDUCTOR

6.10.1 Short Run

Up until this stage the experiments conducted did not incorporate injection of CO_2 into the system. Therefore it was necessary to operate the plant in its normal operating mode. This would both show the influence of CO_2 dosed on the vacuums generated (i.e. does CO_2 dosing decrease the vacuums) and the ability of the eductor (via vacuum generation) to recover CO_2. In this preliminary experiment, CO_2 recovery was monitored through pH measurement which would serve as an indication of whether CO_2 was recovered using the eductor.

During the short run experiment the plant was operated for approximately 8 hours. CO_2 dosing was maintained at ~0.6 g/L (a rotameter setting of 3.5 units) and the sidestream flow rate at 350 L/hr at a CO_2 pressure of 290 kPa.

The results indicated that the vacuums generated within the recovery columns increased progressively over the first two hours (as the air within the recovery columns 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 periods 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. CO_2 was added after approximately two hours of plant operation (when the vacuums generated were more or less stable). Approximately an hour after CO_2 dosing commenced, the pH reading in DV1 started decreasing suggesting that CO_2 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 CO_2 recovered) were performed using the aquatic chemistry software package, *STASOFT 4*. These preliminary results indicate that CO_2 recoveries of approximately 40% could be expected

Detailed results for this experiment are shown in **APPENDIX A**.

6.10.2 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 CO_2 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 "Bones Curve" (i.e. a calibrated graph quantifying the influence of CO_2 dosing on the uptake of $CaCO_3$).

After operation in "Bones Mode" (i.e. no CO_2 recovery), the plant was run in its normal mode (i.e. in CO_2 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 alkalinity. After being run in normal mode, the plant was again operated without any CO_2 recovery (i.e. in "Bones Mode") to again determine the influence of CO_2 dosing on the uptake of calcium carbonate at the end of the run (at the end of the run less solid $CaCO_3$ is available in the limestone contactors).

Long run data showed that for the duration of the experiment, once normal operation in CO_2 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 CO_2 recovery, which would lower the requirements for fresh CO_2 usage.

pH was also monitored for the duration of the experiment. Approximately 0.57 g/L "fresh" CO_2 was dosed into DV3. A short time after dosing with CO_2 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 CO_2 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.

CO_2 gas had leaked (from the CO_2 regulator) during the time the plant operated in "Bones Mode". This resulted in inaccurate measures of the influences of CO_2 dosed on $CaCO_3$ uptake, and for this reason the "Bones Curve" was not used to determine CO_2 recovery. Preliminary calculations using *STASOFT 4* showed that a CO_2 recovery of approximately 35 – 45% was obtained during the run.

Detailed results for this experiment are shown in **APPENDIX B**

6.11 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 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
- Replacement of pH probes

6.11.1 Reconfiguration of Pilot Plant

Review of the pilot plant configuration, and information gathered during pilot plant operation, showed that potentially large amounts of CO_2 were lost at the first dissolution vessel (DV1) as a result of both insufficient contact time between water and recovered CO_2, and the possible purging of recovered CO_2 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 CO_2 would enter at the bottom of DV1, thereby allowing additional contact time between the water and recovered CO_2. The second dissolution vessel (DV2) was reconfigured such that excess air could be purged at this stage, thereby attempting to minimise the loss of recovered CO_2.

Physical inspection of the pilot plant showed that no leaks within the eductor suction line and surrounding vessels were present.

6.11.2 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 to ensure that a correctly sized eductor was obtained. Both the South African distributor and the manufacturer from the United States of America of the previously tested eductor (Penberthy Model LM ½" B) were contacted with regards to 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 (CO_2):	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 (CO_2):	36.1 kg/hr (for $P_{CO_2} = 1.9$ kg/m^3 @ 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 flow rate of the proposed 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 flow rate sufficient limestone contact time would occur. However, the spray nozzles in the recovery vessels (which allow aeration and therefore stripping of CO_2) 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 acquired, installed and commissioned on the SSP pilot plant. (The eductor was the same size and resembled the previously acquired model). Preliminary testing (without

CO_2 dosing) showed that the eductor operated as expected from the specifications.

6.11.3 Replacement of Spray Nozzles used in Recovery vessels

Due to the new eductor requiring a higher motive flow rate than what was previously required, the spray nozzles within the recovery vessels were resized. More suitably sized nozzles were obtained and subsequently installed on the pilot plant. Preliminary testing showed that efficient atomisation of the water stream was once again occurring.

6.11.4 Replacement of pH probes

During preliminary pilot trial it was noticed that on a number of occasions, the in-line pH electrodes had malfunctioned. Although they were frequently calibrated, problems with respect to ease of calibration and accuracy during test runs persisted. The suppliers of these probes were thus contacted. The probes and controllers were then tested/checked by the suppliers. These investigations revealed that:

- Two of the pH controller units required immediate replacement
- Four pH probes also required immediate replacement. In addition, it was noted that the life span of the remaining four was limited and therefore would require replacing within a year. As pilot plant testing was approaching its end it was decided that only four of the probes would be replaced.

6.12 PILOT PLANT OPERATION USING THE MODEL LM ½" A EDUCTOR AND CONCURRENT ASSESSMENT OF SSP-MOD

Following implementation of upgrades as described in section 6.11 above, the pilot plant was ready for operation. SSP system optimization by concurrent use with the SSP-MOD model could therefore commence. It was envisaged that during this process the following would occur.

- Firstly, using the 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 optimization 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 optimization of the pilot plant in an iterative manner.

6.12.1 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" CO_2 dosing and the sidestream flow rate was maintained at 463 L/hr. In this way an understanding of the pilot plant performance at various doses of CO_2 could be obtained. The results obtained from these runs were then compared to what was predicted by the SSP-MOD.

Experimental Results and Discussion

The following graphs (Figure 6.7) show the actual (from SSP pilot plant operation – shown first) and predicted (from SSP-MOD model – shown second) $CaCO_3$ uptake vs. the CO_2 dose. It must be noted that the graph obtained from the SSP-MOD model is for a particular vacuum generation (namely 30 kPa), whereas the pilot plant results were obtained at varying vacuum pressures.

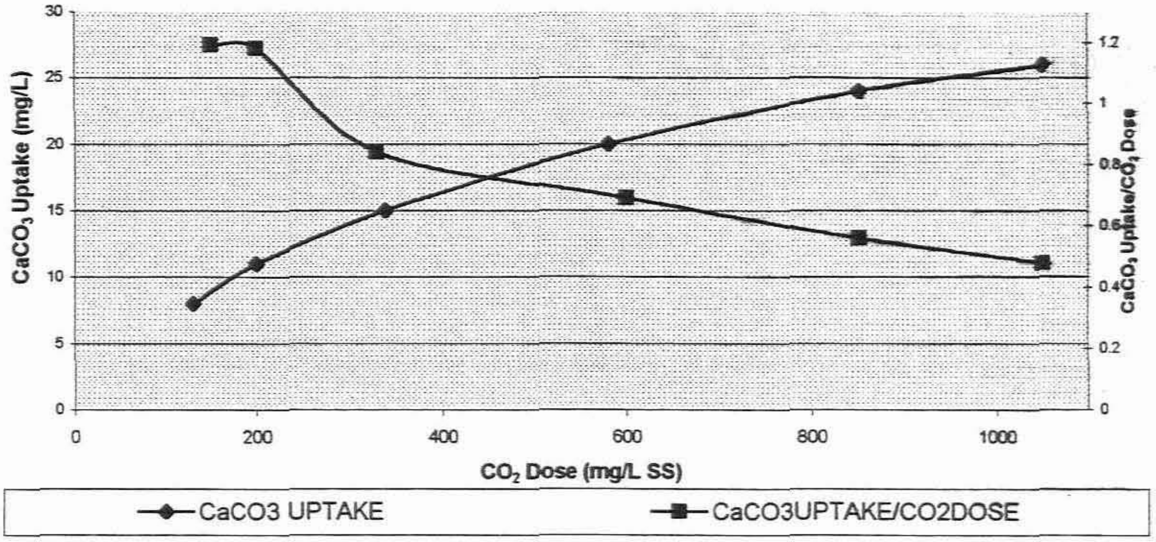


Figure 6.7: Short Run 1: actual and predicted $CaCO_3$ uptake vs. CO_2 dosage

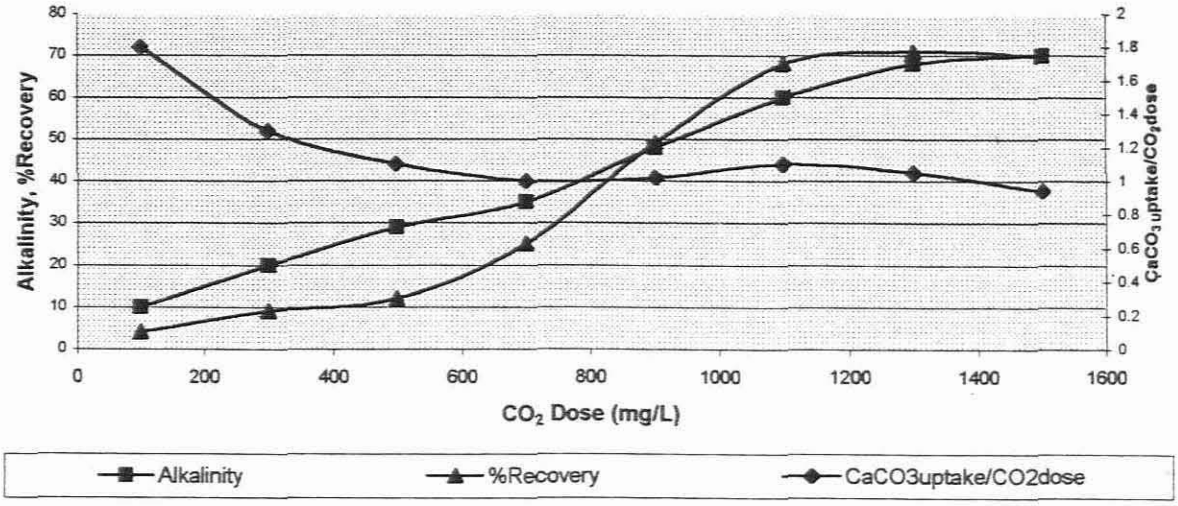


Figure 6.8: Short run 2: actual and predicted $CaCO_3$ uptake vs. CO_2 dosage

The graphs show that the SSP-MOD model predicts that a higher $CaCO_3$ uptake can be achieved for a particular CO_2 dose that 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 $CaCO_3$ dissolved to equilibrium quantities). The SSP-MOD model shows that for high CO_2 recoveries (in excess of 60%) very high CO_2 doses (> 1000 mg/L) are required. At lower doses of CO_2 (e.g. 700 mg/L), relatively low CO_2 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 CO_2 (as evidenced from the leveling off of the "$CaCO_3$ uptake/CO_2 dose" curve). Although, from the SSP pilot plant data, it generally appears as though the "$CaCO_3$ uptake/CO_2 dose" curve is also leveling but this cannot be stated with much certainty.

Furthermore, the short runs revealed that with an increase in fresh CO_2 dose into *the third dissolution vessel (DV3) (and therefore an increase in the amount of* CO_2 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 6.2: Maximum vacuums generated during short runs for a particular CO_2 dose

CO_2 DOSE (mg/L)	CO_2 DOSE (kg/hr)	VACUUM IN RV1 (kPa)	VACUUM IN RV2 (kPa)
140	0.065	34	30
190	0.088	39	35
350	0.16	49	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" CO_2 dose. However, of critical importance is the fact that if we were able to recover all the CO_2 dosed (i.e. 100% CO_2 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 CO_2 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 CO_2 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 CO_2 *stripping. In preliminary investigations using SSP-MOD it was found that the* addition of approximately 5 L air/L sidestream decreased the amount of CO_2 that was recovered. However, it was felt that the use of air may be beneficial and assist CO_2 stripping, as this had been assessed and verified in previous pilot plant trials.

Studies were therefore conducted to the influence of air on the CO_2 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 within 1 – 3 hours after the addition of air was 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 CO_2 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 $CaCO_3$ uptakes (due to the fact *that* $CaCO_3$ *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" CO_2 dose resulted in a decrease in the vacuum generated. This was cause for concern as the amount of CO_2 in the SSP pilot plant system was much lower than the oversized design specifications of the eductor. However, it was 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 CO_2 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.

6.12.2 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 "fresh" CO_2 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 SSP was operated to determine the "Bones Curve". During this period the "fresh" CO_2 dose was varied between approximately 90 to 1600 mg/L. The resultant product water Alkalinity at these CO_2 doses would then be used to construct the so-called "Bones Curve A" of $CaCO_3$ uptake vs. CO_2 dose. At the end of this procedure, the plant was operated in CO_2 recovery mode for a further 72 hours. The average "fresh" CO_2 dosed during this period was found to be 788 mg/L. Finally, at the end of the pilot plant operation in CO_2 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 $CaCO_3$ uptake vs. vacuum *pressure in the recovery vessel was constructed.*

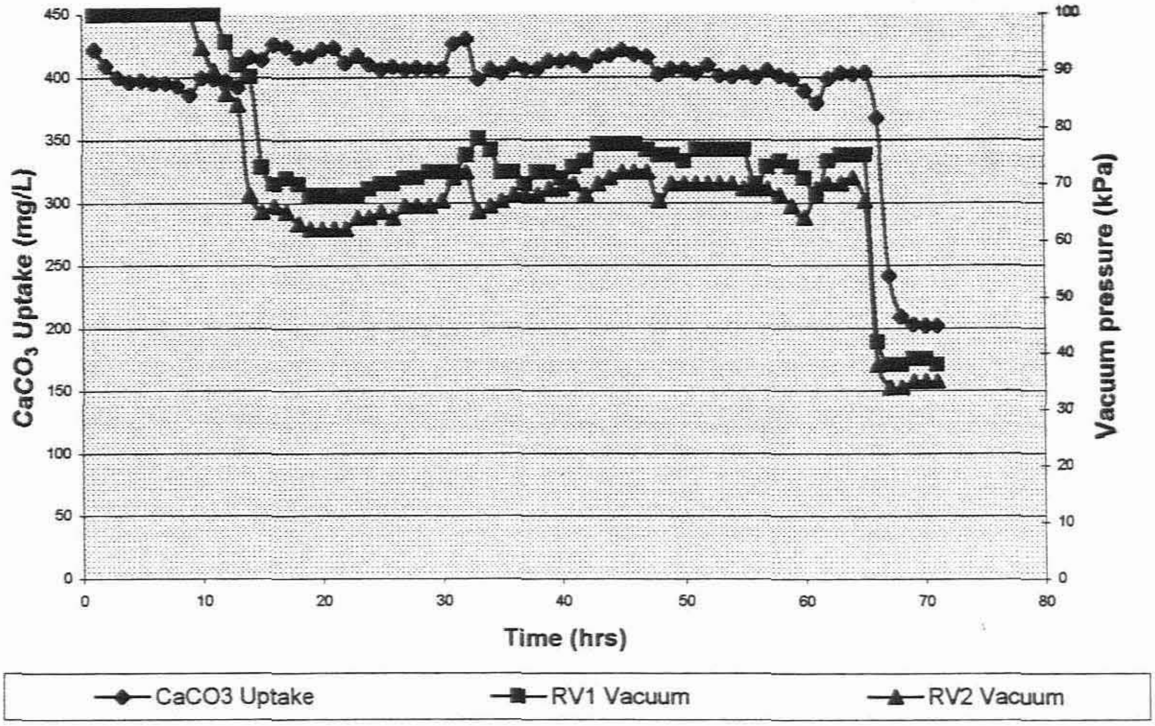


Figure 6.9: Long Run1: Calcium carbonate uptake and vacuum pressure in recovery vessels

The graph indicates the calcium carbonate uptake of the sidestream. The average feed alkalinity was 18.3 mg/L (as $CaCO_3$) and the alkalinity in the final sidestream varied between 386 mg/L (as $CaCO_3$) (low) and 422 mg/L (as $CaCO_3$) (high), and was generally between 400 and 410 mg/L (as $CaCO_3$) for the duration of the experiment. In addition, the results indicate that the vacuums generated within the recovery vessels gradually increased and leveled 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 (decreased vacuums at higher "fresh"* CO_2 dose). Due to this inefficient operation of the eductor, the amount of "fresh" CO_2 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 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" CO_2 dosed.

The Model LM ½" A eductor was oversized and should therefore be able to draw a high vacuum at much higher CO_2 doses than what was dosed in the experiment. The eductor was therefore not operating according to its design specifications. This problem was 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 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 CO_2 dosed during that time period (788 mg/L) and the CO_2 recovered. **Figure 6.10** shows the CO_2 recovered during the experiment.

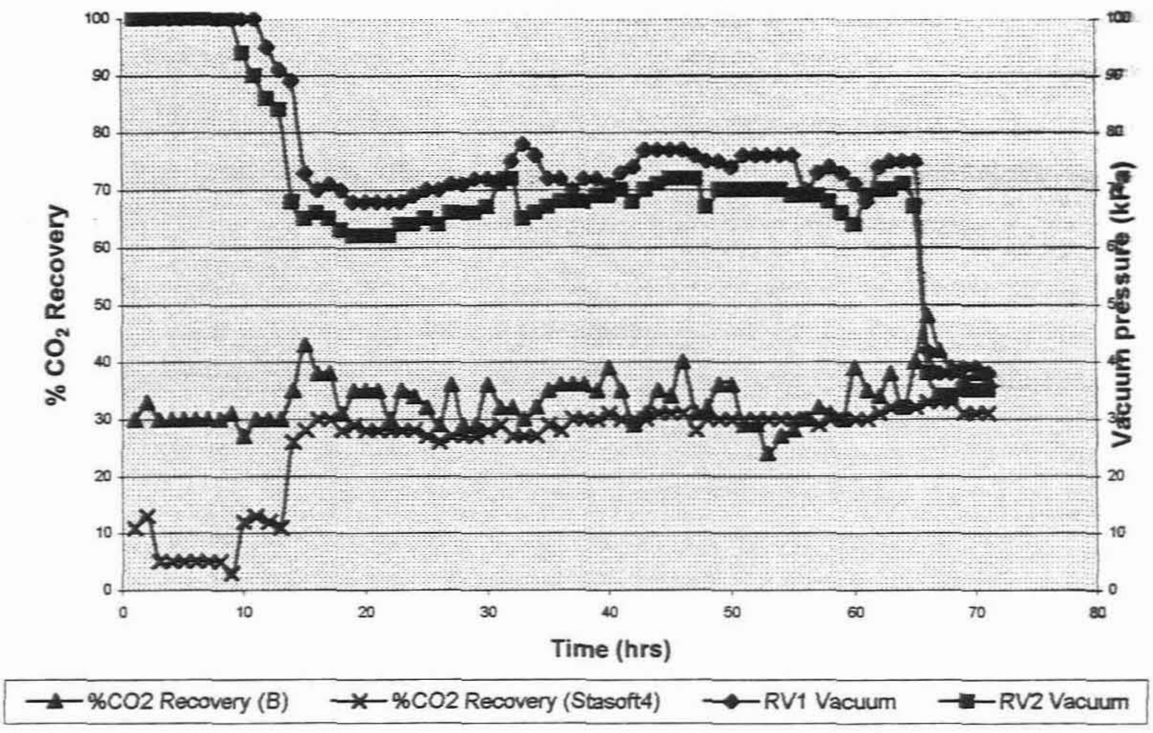


Figure 6.10: Long Run 1: CO$_2$ recovery

The results indicated that the CO$_2$ recovered varied between 30 – 40% (average 35%) for the duration of the experiment. These results were confirmed using *STASOFT 4*.

Detailed results for this experiment are shown in **APPENDIX C**.

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" CO$_2$ dose decreases the vacuum generated). The vacuum pressure within the recovery vessels during the long run experiment was approximately 34 –38 kPa. This problem was raised with both the local and abroad manufacturers, but neither party could provide meaningful comment as to 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.

- With the aforementioned sub-optimal performance of the eductor, a CO_2 recovery of approximately 30 – 40% (average 35%) was recovered.

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.

6.12.3 Long Run 2 and 3

Experimental Design and Objectives

Due to the problems encountered 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" CO_2 dose of approximately 300 mg/L, the motivation being that although the SSP-MOD model had shown that at such a dose, a lower CO_2 recovery would be achieved, short run data showed that this CO_2 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 $CaCO_3$ uptake vs. vacuum pressure in the recovery vessels were drawn.

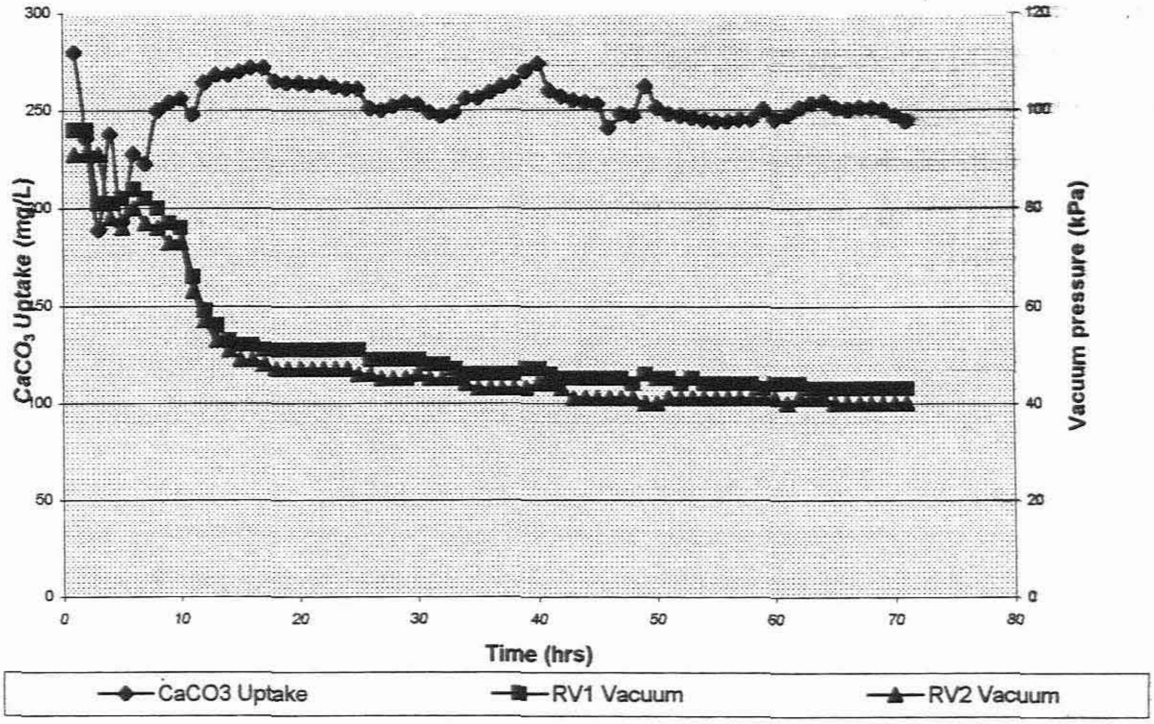


Figure 6.11: LongRun2:Calcium carbonate uptake and vacuum pressure in recovery vessels

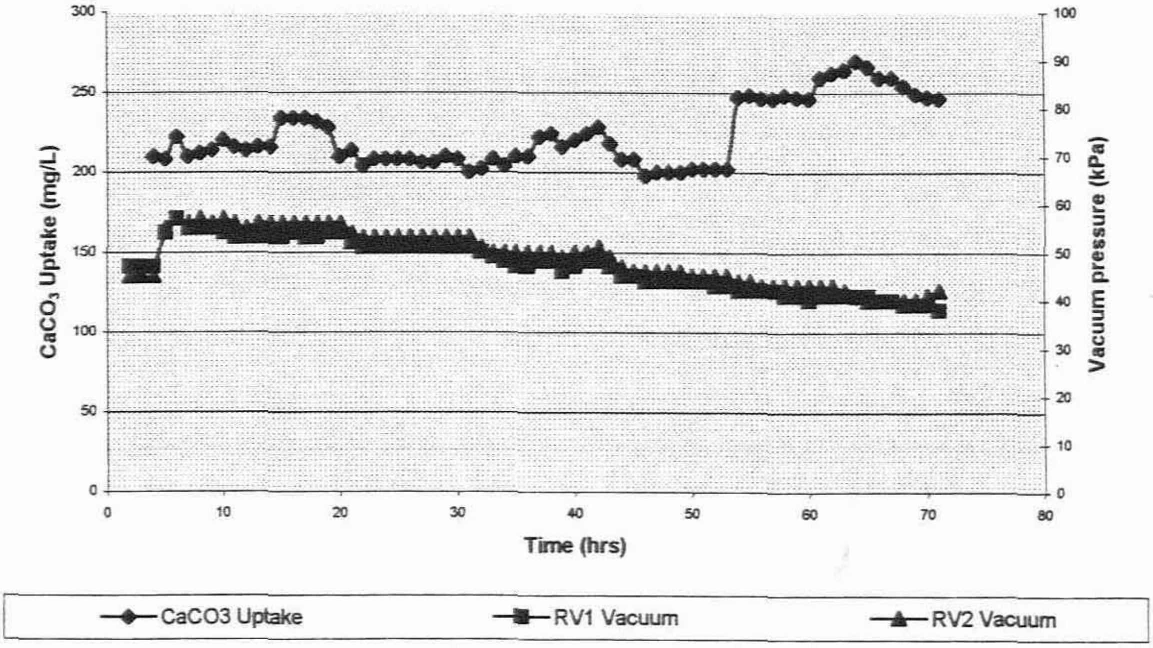


Figure 6.12: Long Run 3: Calcium carbonate uptake and vacuum pressure in recovery vessels

The graphs indicate the calcium carbonate uptake of the sidestream. In Long Run 2 (**Figure 6.11**) the average feed alkalinity was 19.7 mg/L (as $CaCO_3$) and the 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 6.12**) the average feed alkalinity was 20.7 mg/L (as $CaCO_3$) and the 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 6.11** 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 done in an attempt to 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 6.12** 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. **Figures 6.13 and 6.14** show CO_2 recovery data for both Long Run 2 and Long Run 3.

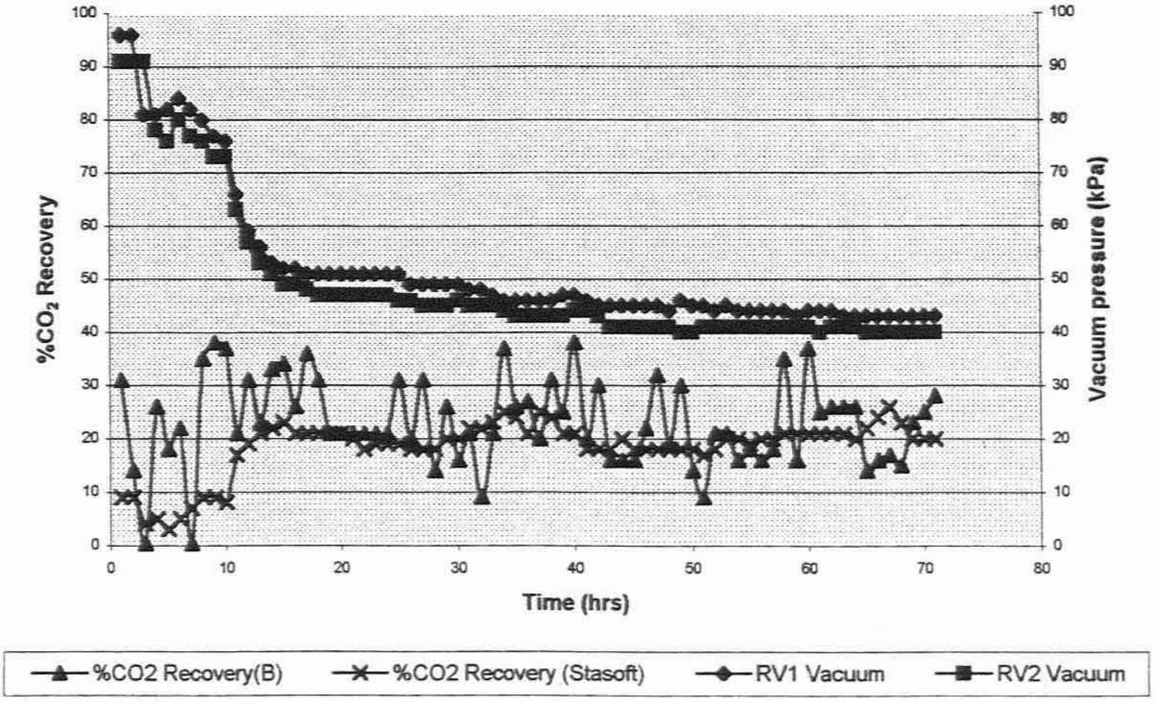


Figure 6.13:Long Run 2: CO_2 recovery

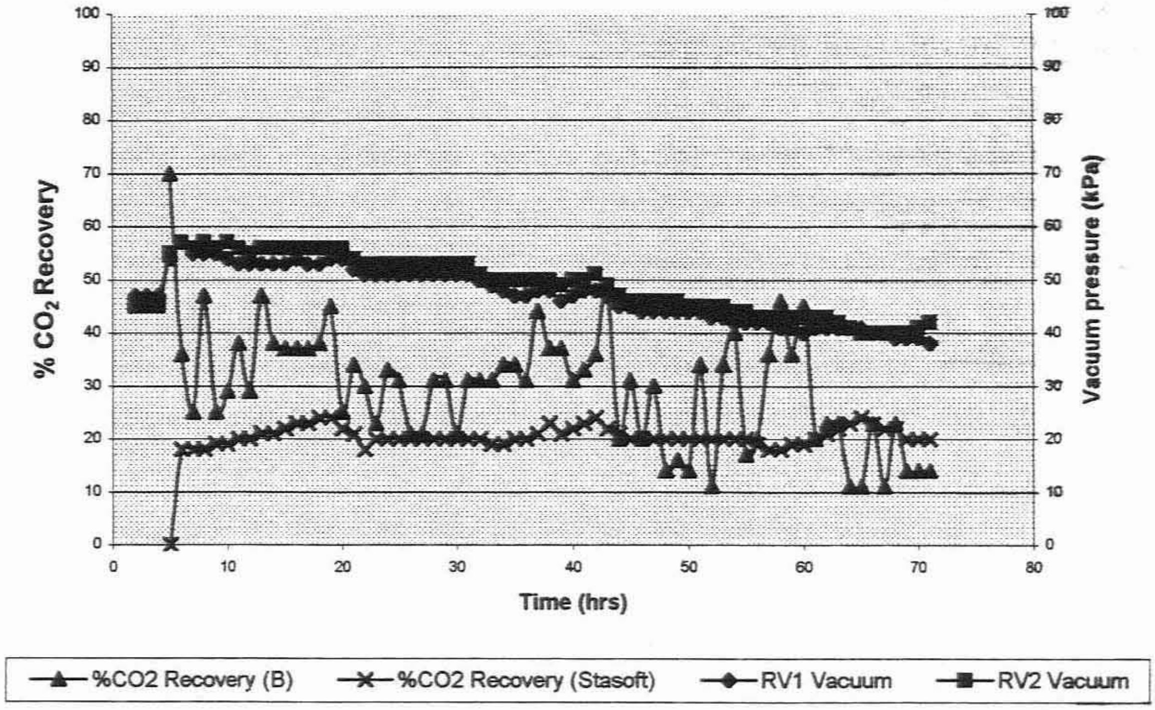


Figure 6.14: Long Run 3: CO_2 recovery

The results indicated that for Long Run 2, the CO_2 recovered generally varied between 20 – 30% (average 25%) and that CO_2 recovered in Long Run 3 generally varied between 20 – 40% (average 29%) for the duration of the experiments. 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 appear to result in an increase in CO_2 recovery. This result correlates with model predictions at low "fresh" CO_2 doses (see **CHAPTER 5** – section 5.7.2).

Detailed results for this experiment are shown in **APPENDIX D and E**.

Conclusions: Long Run 2 and 3

The long run experiments showed that:

- Reasonable vacuums of approximately 40 kPa could be achieved in the recovery vessels if a lower CO_2 dose of approximately 300 mg/L was added to the sidestream.

- CO_2 recoveries of approximately 20 – 30% (average 25%) were measured for a vacuum of 40 kPa in Long Run 2 and 20 – 40% (average 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 appear to influence the amount of CO_2 recovered. This result correlates with model predictions at low "fresh" CO_2 doses (below ~500 mg/L "fresh" CO_2 – 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.

6.12.4 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" CO_2 dosed to the sidestream (as measured from mass loss of a CO_2 cylinder)
- $CaCO_3$ uptake (from calcium and 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 CO_2 addition/dissolution and $CaCO_3$ dissolution.
- Discrepancies exist between model predictions and the SSP pilot plant with regards to the amount of CO_2 stripped and recovered. For example, in Long Run 1 a CO_2 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 CO_2 recovered. *STASOFT 4* was used to

correlate data obtained from Long Run 1, and showed that the method for calculating CO_2 recovery was appropriate, with results obtained from the "Bones Curve" method correlating *STASOFT 4* CO_2 recovery calculations. The SSP-MOD model, however, predicted that when using the specified input parameters, a much lower CO_2 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 CO_2 recovery of ~4.5%, compared to an observed recovery of ~20 – 40%.

Results obtained from pilot plant operation therefore showed that higher CO_2 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 algorithm 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 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 CO_2 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 stripper to model the CO_2 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 CO_2 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 CO_2 recoveries obtained increased, but were still not similar to results obtained from pilot plant operation (e.g. for Long Run 1 the amount of CO_2 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 CO_2 that could be recovered started to taper off after 3 stages (and would therefore not reach a CO_2 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 CO_2 (and before the addition of "fresh" CO_2) (discussed in more detail in **CHAPTER 5**). By varying the "B" factor (between 0.1 and 1), different amounts of CO_2 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, it was decided to investigate the influence of varying the "B" factor. These investigations showed that CO_2 recoveries similar to what was obtained during pilot plant operation, could only be simulated at very low "B" factor between 0.2 and 0.1 (i.e. the majority of 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, deviations between model predictions and pilot plant operation occurred when no air was introduced into the recovery vessels. At the close of the project a meaningful explanation as to why such discrepancies occurred when no air was added into the recovery vessels had not been reached. Nevertheless, based on observations from historical pilot plant operation when it seemed that small amounts of air improved CO_2 recovery, further modelling with the addition of air to the recovery vessels would be investigated.

Influence of Air on CO_2 Stripping and Recovery

In pilot plant operation prior to this project, air had been used to aid CO_2 stripping and recovery, and the belief that nominal doses of air improved CO_2 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 CO_2 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 CO_2 stripping and recovery. (Unfortunately, this could not be assessed using the pilot plant as a result of negative impact on performance of the eductor, in turn resulting in the 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) CO_2 stripping and recovery could theoretically improve, if high vacuums could be maintained. The results obtained are presented in **Figure 6.15** below. The model simulation was based on results obtained from Long Run 1 and utilises a stage 3 gas-liquid equilibrium stripping vessel (as opposed to the use of a single stage gas-liquid equilibrium stripping vessel).

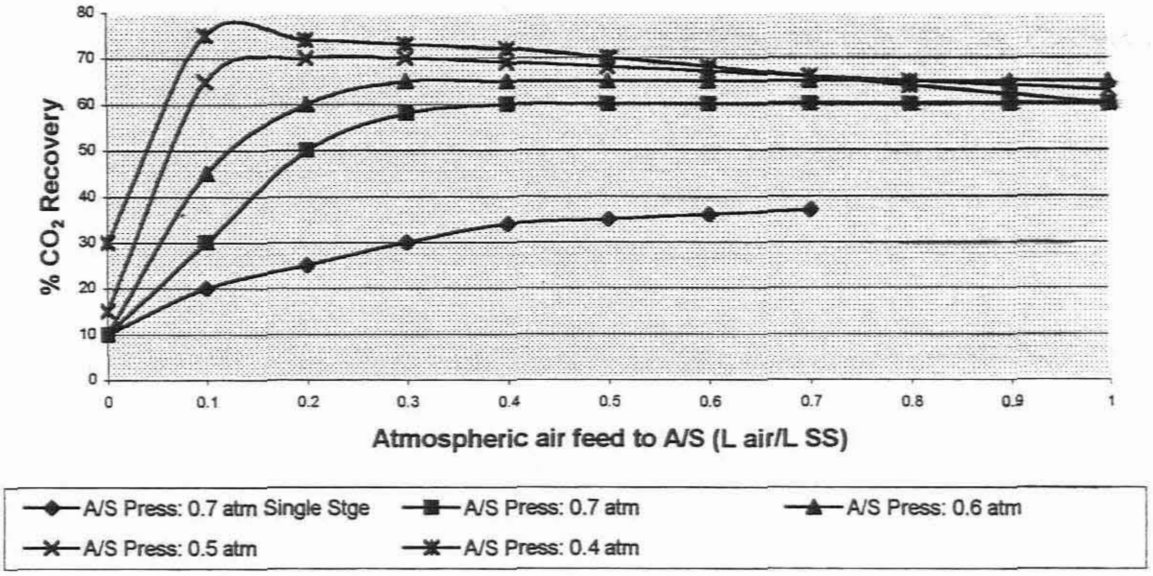


Figure 6.15: Three-stage CO_2 stripping and recovery model based on a "fresh" CO_2 dose of 788 mg/L (i.e. Long Run 1)

The graph indicates that increased vacuum pressure results in increased CO_2 recoveries (e.g. if the vacuum pressure can be increased from 70 kPa to 40 kPa, an increase in CO_2 recovery from ~ 10% to ~ 30% could be expected). Furthermore, the graph indicates that the addition of very small quantities of air aids CO_2 stripping and recovery and that theoretical CO_2 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/hr 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" CO_2 dose of ~ 333 mg/L, yielded a CO_2 recovery of ~ 62% (see **CHAPTER 4**, section 4.4). During this experiment a small amount of air (0.1 – 1 L air/L sidestream) was added, as it was believed to assist CO_2 recovery. Subsequent pilot plant tests using the eductor (vacuum pressure ~ 40 kPa) and a "fresh" CO_2 dose of 302 mg/L (Long Run 2) and ~ 319 mg/L (Long Run 3), yielded a CO_2 recovery of ~ 25% (average) and ~ 29% (average) respectively (see section 6.11.3).

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 vessels was at atmospheric pressure (i.e. no vacuum). This is a serious limitation of the use of eductors as the SSP-MOD model had shown that the addition of small amount of air into the recovery vessels would aid CO_2 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 vessels being experienced. This result compromises the further use of eductors. Due to these significant developments further testing of the eductor was discontinued.

6.13 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 units, 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 desired design specifications. This was despite

considerable effort being made by the project team to ensure that correctly sized eductor's were obtained.

  - Investigations 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 distributors and manufacturers, but neither party could provide meaningful comment as to the reasons 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" CO_2 dose (Long Run 1)
  - High vacuum, low "fresh" CO_2 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" CO_2 dose – 788 mg/L) showed that even though pilot plant performance was not optimal (due to poor performance of the eductor) CO_2 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" CO_2 dose – 302 mg/L and 319 mg/L respectively) showed that CO_2 recoveries of 20 – 40% were obtained.

Due to the non-performance of the eductor, a long run incorporating high vacuum and a high "fresh" CO_2 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, CO_2 acidified sidestream and sidestream after $CaCO_3$ uptake.
    - The model, however, predicted a significantly lower CO_2 recovery than what had been experienced during pilot plant operation (e.g. for Long Run 1 the model predicted a CO_2 recovery of ~ 8%, while a CO_2 recovery of 30 – 40% had been obtained from the 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 amount of air improved CO_2 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 CO_2 recovery, and that, based on data from Long Run 1, CO_2 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.

CHAPTER 7

THE USE OF *PRO/II* PROCESS MODELLING PACKAGE FOR PREDICTING THE BEHAVIOUR OF THE SIDESTREAM STABILISATION PROCESS

7.1 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 *PRO/II* as the commercially available process-modelling package. 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 model developed using the *PRO/II* simulation package would be largely based on the configuration of the pilot plant. The ability of this 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.

7.2 PRELIMINARY ASSESSMENT OF *PRO/II* AS A PROCESS SIMULATION PACKAGE

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:

- Drawing a flowsheet. Selection of the appropriate unit operations from the PROVISION suite of process icons and defining the streams (feed and product).
- *Defining the components selected from the PRO/II database.*
- Selecting thermodynamic calculation methods. Choosing from the list of commonly used methods, generalised correlations, equations-of-state methods, liquid-activity methods, and special data packages.

- Defining feed streams. Entering in required information such as flowrates, compositions, temperature and pressure.
- Provision of process conditions.
- Running the 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 minimisation, CSTR, PFR batch and in-line *FORTRAN* reaction kinetics reactors, pumps, compressors and expanders, pipes and valves, etc.

PRO/II also contains various functions that employ control (feedback, feedforward, etc.) and optimisation techniques. *PRO/II* also 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, splitter, mixer, 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 reason for this is 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

The 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". From reactions in aqueous solution that involve a "rearrangement" of icons, the reactor model is not necessary.

- *Gibbs Reactor*

  This reactor 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 a 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 system 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 the 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:
    - CO_2 addition
    - $CaCO_3$ dissolution
    - CO_2 stripping
    - CO_2 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 (see **Figure 7.1**).

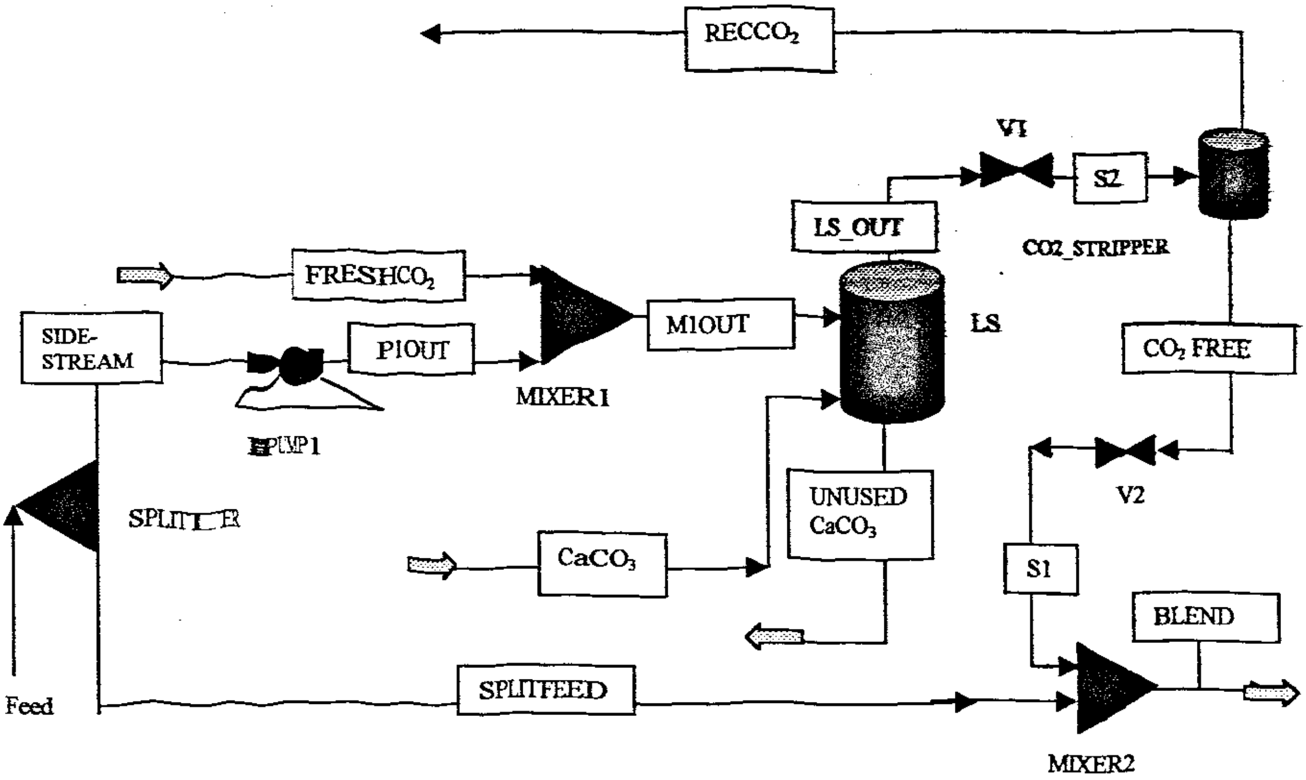


Figure 7.1: Process Flowsheet for the SSP as modelled in *PRO/II*

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

- Addition of CO_2 gas to the sidestream.
- Addition of limestone to the acidified stream.
- Stripping of CO_2 from the stabilised stream.
- Recovery and recycle of CO_2 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 the 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 Electrolyte module.

The sidestream then enters three CO_2 dissolution vessels in series (DV1, DV2 and DV3), which were modelled as a single mixer. The mixer 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 feed conditions. Fresh CO_2, at 300 kPa, is added, together with the sidestream, to the mixer and the blended CO_2-water stream then enters the limestone 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 CO_2-acidified stream. Any unused $CaCO_3$ will report to the stream provided. The stabilised water then enters the CO_2 recovery vessels (RV1, RV2), which strips and recovers CO_2 for further use. The recovery of CO_2 was modelled as follows. The stabilised stream passes through a valve, which generates the required vacuum conditions for CO_2 recovery, and then enters a flash drum which recovers CO_2 in the overhead product. The recovered CO_2 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 CO_2 dissolution columns (i.e. 300 kPa).

The CO_2-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 CO_2 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 modelled, 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 CO_2 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, the following results were generated.

Table 7.1: 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
Alkalinity as $CaCO_3$ (mg/L)	2.0	2.1
Acidity as $CaCO_3$ (mg/L)	28	24
CCPP 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.

CO_2 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 7.2: 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
Alkalinity as $CaCO_3$ (mg/L)	2.0	2.1
Acidity as $CaCO_3$ (mg/L)	2028	1998
CCPP 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 sidestreams after CO_2 *addition* closely resembles that found when operating the pilot plant.

$CaCO_3$ Dissolution

After the addition of CO_2, 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 at 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 solids 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 cannot be entered as final products). The following inputs are also required for the reaction 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.

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; stirred tank dissolver, but this operation does not occur in the SSP (i.e. limestone columns of the SSP act on plug flow basis). When using the dissolver unit operation, both the overhead and 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 using the dissolver function. The two limestone columns were modelled as a single dissolver (with volume equal to the sum of the two 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 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 7.3: Comparison between pilot plant and *PRO/II* model results for the stabilised sidestream

LIMESTONE ADDITION	**SIDESTREAM PILOT PLANT**	***PRO/II* MODEL**
pH	6.14	6.08
Calcium as $CaCO_3$ (mg/L)	452.0	452.7
Alkalinity as $CaCO_3$ (mg/L)	452.0	433.5
Acidity as $CaCO_3$ (mg/L)	1901	1983
CCPP 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.

CO_2 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) The required vacuum generated by the valve was 50 kPa.

On the SSP pilot plant, CO_2 recovery is affected via two vessels in series. Initially, these recovery columns were modelled as a single flash unit, with CO_2 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 CO_2 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 CO_2 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 CO_2 recovered in the overhead product). The unit operation was able to recover the desired quantity of CO_2, 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 CO_2 stream contained 70% of the total CO_2 (example) 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 CO_2 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 CO_2 recovered also increased. The following table briefly indicates the relationship between the vacuum pressure and the amount of CO_2 recovered.

Table 7.4: Amount of CO_2 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 CO_2 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 CO_2 from the mixed solution at a vacuum pressure of 14.14 kPa.

Table 7.5: Comparison between pilot plant and *PRO/II* model results for the Stabilised sidestream after CO_2 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
Alkalinity as $CaCO_3$ (mg/L)	450.0	327.0
Acidity as $CaCO_3$ (mg/L)	715	767
CCPP as $CaCO_3$ (mg/L)	28.9	-35.8
Electrical conductivity (mS/m)	84	61

From the above 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 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 $CaCO_3$ precipitate is formed (37% of the total $CaCO_3$ available in the stream). This was not taken into account when calculating the 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 $CaCO_3$ available in the stream) of solid $CaCO_3$ is present. This vacuum pressure, however, could not be used in the simulation, as no CO_2 could be recovered in *PRO/II* at this pressure (see above).

CO_2 Recycle

In the pilot plant operation, CO_2 is stripped, recovered and then re-used in the process. This minimises the required input of fresh CO_2 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 CO_2 and 547 mg/L of recovered CO_2 are added to the incoming sidestream. Initially, when constructing the process model, the total quantity of CO_2 added to the sidestream (880 mg/L), was added as fresh CO_2 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 pilot plant operation. Once this had been achieved, CO_2 could be recycled, and the quantity of fresh CO_2 lowered to the amount added on the pilot plant.

However, due to the problems experienced with CO_2 stripping and recovery in this preliminary investigation, CO_2 recycle was not thoroughly investigated. The recovered CO_2, at a pressure of 14.14 kPa was allowed to pass through a valve, thereby increasing the pressure of the recovered CO_2 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, CO_2 entering the dissolution columns from the recovery vessels does not undergo an increase in temperature.

Blend

After the CO_2 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 7.6: Comparison between pilot plant and *PRO/II* model 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
Alkalinity as $CaCO_3$ (mg/L)	22.3	22.3
Acidity as $CaCO_3$ (mg/L)	59	58
CCPP 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 CO_2 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 CO_2 from the blend stream
- Lime addition to yield a fully stabilised stream

When air stripping of excess CO_2 from the blended stream was modelled, similar problems as experienced when modelling CO_2 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.

Concluding remarks: Preliminary Assessment of *PRO/II*

The assessment showed that it was possible to readily model most of the critical steps of SSP in *PRO/II*. Difficulties were encountered when CO_2 was to be stripped and recovered from a mixed liquid stream. Nevertheless, interactions with *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.

7.3 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 CO_2 and $CaCO_3$ 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.

7.3.1 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 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 CO_2 gas to the sidestream**

  Unit operation: Mixer

  The three CO_2 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 while a solids product stream is present. Solid limestone is added to the flash unit together with the CO_2-acidified stream. If reaction kinetics are to be included the calculator unit operation should be employed.
- **Stripping, recovery and recycle of CO_2 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 stabilised 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.

7.3.2 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.

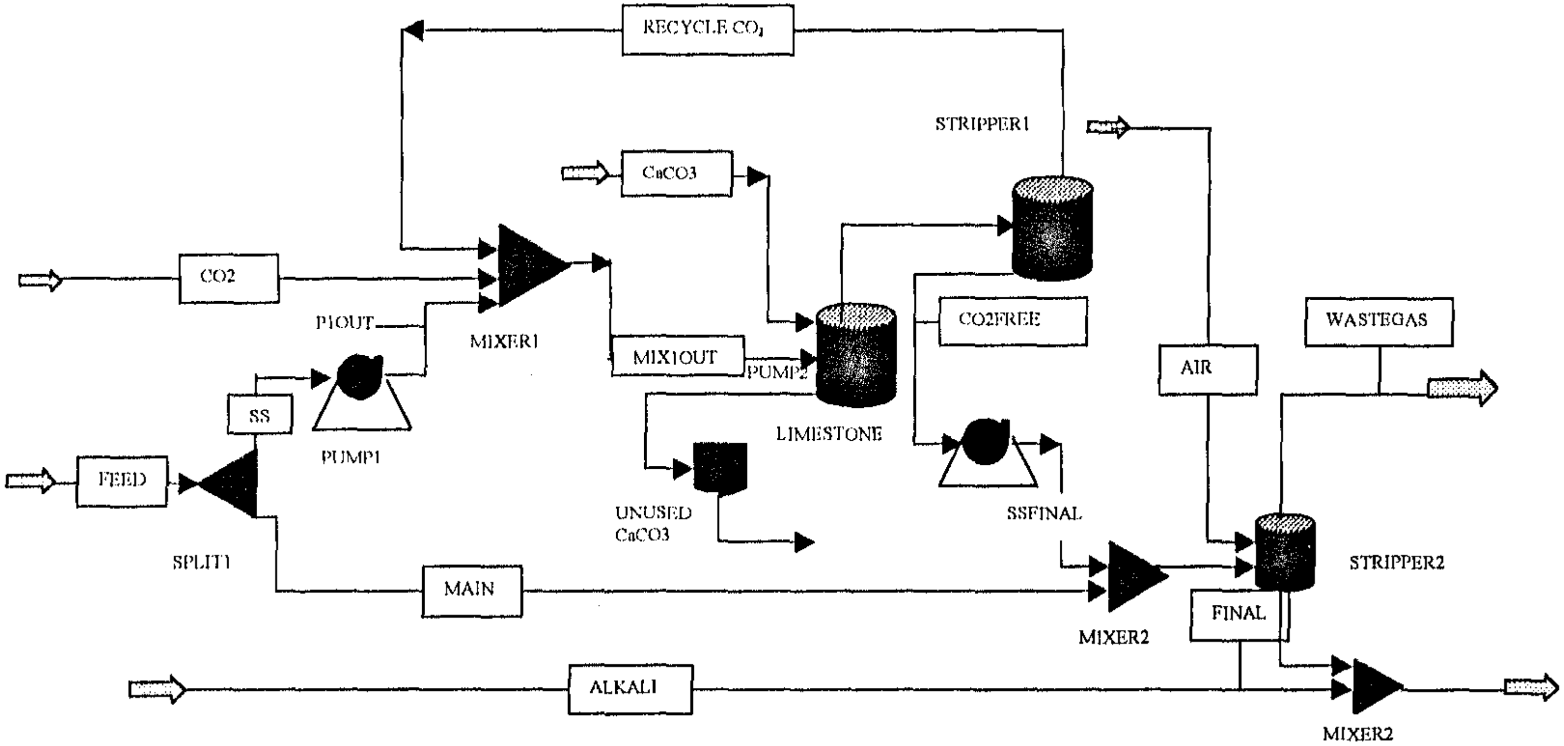


Figure 7.2: A complete Process Flowsheet of the SSP as modelled in *PRO/II*

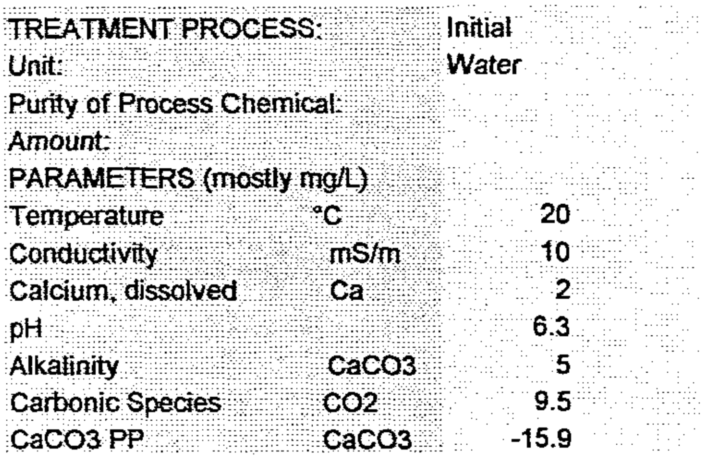
Raw water is fed into a splitter, with a decided percentage sidestream being abstracted and fed into the SSP pilot plant. A pump was then employed to raise the pressure of the sidestream to those conditions experienced on the pilot plant (300 kPa). The sidestream then enters three dissolution vessels in series (DV1, DV2 and DV3), which were modelled as a mixer. Fresh CO_2 is added together with the sidestream, to the mixer and the blended CO_2-water stream then enters the limestone 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 CO_2-acidified stream. Any unused $CaCO_3$ will report to the stream provided. The stabilised water then enters the CO_2 recovery columns (RV1, RV2), which strips and recovers CO_2 for further use.

Various unit operations were assessed to test the suitability of these units for modelling the CO_2 stripping step. The above figure shows the use of the flash drum unit operation (gas-liquid equilibrium vessel). The CO_2-free water is then mixed with the balance of the feed water to form a blended stabilised 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 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.



TREATMENT PROCESS:		Initial
Unit:		Water
Purity of Process Chemical:		
Amount:		
PARAMETERS (mostly mg/L)		
Temperature	°C	20
Conductivity	mS/m	10
Calcium, dissolved	Ca	2
pH		6.3
Alkalinity	CaCO3	5
Carbonic Species	CO2	9.5
CaCO3 PP	CaCO3	-15.9

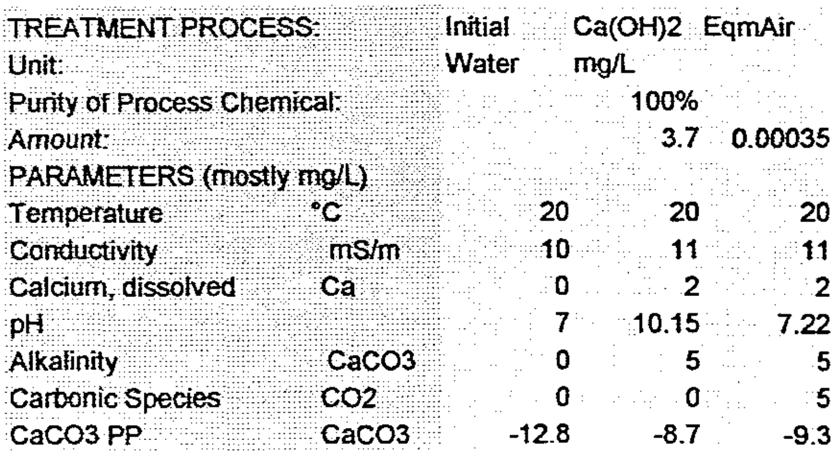
Figure 7.3: Manipulation of distilled water in *STASOFT 4* to form a specific feed water

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 result obtained in the output file then need to be analysed, and manual calculations are performed for calcium, 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 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 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 Alkalinity and pH are the result of the presence of a particular combination of hydroxide ions and carbon dioxide.)

Lime ($Ca(OH)_2$) 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 CO_2 partial pressure is 0.00035 atm). The feed water generated is illustrated below:



TREATMENT PROCESS:		Initial	Ca(OH)2	EqmAir
Unit:		Water	mg/L	
Purity of Process Chemical:			100%	
Amount:			3.7	0.00035
PARAMETERS (mostly mg/L)				
Temperature	°C	20	20	20
Conductivity	mS/m	10	11	11
Calcium, dissolved	Ca	0	2	2
pH		7	10.15	7.22
Alkalinity	CaCO3	0	5	5
Carbonic Species	CO2	0	0	5
CaCO3 PP	CaCO3	-12.8	-8.7	-9.3

Figure 7.4: 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 $Ca(OH)_2$ 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 $Ca(OH)_2$ stream is added to the distilled water and then together with a "large" air stream, is fed into a equilibrium flash vessel. The feed simulation follows:

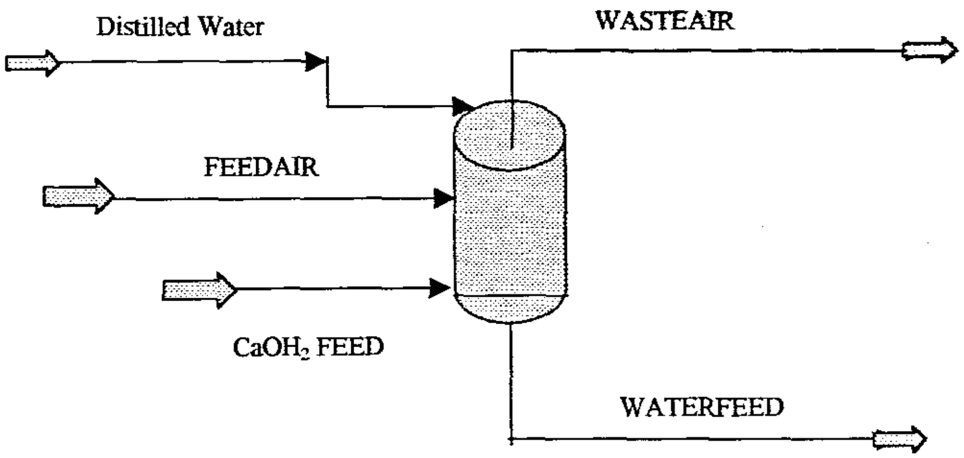


Figure 7.5: Flow diagram of model generated for feed in *PRO/II*

The result 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/II VERSION 5.1 ELEC V5.4386/EM
PROBLEM                                          OUTPUT
                            STREAM WEIGHT COMPONENT RATES  10/05/00
--------------------------------------------------------------------------
STREAM ID             UNUSEDCACO3 VENT          WASTEAIR     WATERFEED
NAME
PHASE                        SOLID        VAPOR        VAPOR        LIQUID
FLUID RATES, KG/HR
       1     CO2             0.0000       0.5395       8.7799       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       0.00000      0.00000
       6     HCN             0.0000       0.0000       0.00000      0.00000
       7     HCOOH           0.0000       0.0000       0.00000      0.00000
       8     SO2             0.0000       0.0000       0.00000      0.00000
       9     NAOH            0.0000       0.0000       0.00000      0.00000
      10     CACO3           0.0000       0.0000       0.00000      0.0332
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       0.00000
       2     N2              0.0000       0.0000       13272.8012   0.00000
       3     O2              0.0000       0.0000       4066.9209    0.00000
       4     H2O             0.0000       0.0000       259.2236     0.00000
       5     HCL             0.0000       0.0000       0.00000      0.00000
       6     HCN             0.0000       0.0000       0.00000      0.00000
       7     HCOOH           0.0000       0.0000       0.00000      0.00000
       8     SO2             0.0000       0.0000       0.00000      0.00000
       9     NAOH            0.0000       0.0000       0.00000      0.00000
      10     CACO3           0.1325       0.0000       0.00000      0.00000
TOTAL MW SOLID, KG/HR        0.1325       871.7923     17607.7255   6391.0250
TOTAL RATE, KG/HR            0.1325       871.7923     17607.7255   6391.0250
--------------------------------------------------------------------------
TEMPERATURE, C               20.0000      20.0000      20.0000      20.0000
PRESSURE, BAR                3.00000      3.00000      1.00000      1.00000
ENTHALPY, M*KW-HR/HR         -4.4459E-07  -1.8633E-05  -1.0148E-03  -0.0282
MOLECULAR WEIGHT             100.0872     28.7779      28.6079      18.0155
WEIGHT FRACTION VAPOR        0.00000      1.00000      1.00000      0.00000
WEIGHT FRACTION LIQUID       0.00000      0.00000      0.00000      0.00000
WEIGHT FRAC MW SOLID         1.00000      0.00000      0.00000      0.00000
pH                           N/A          N/A          N/A          7.31035
IONIC STRENGTH               N/A          N/A          N/A          1.55874E-04
MOLECULAR WEIGHT (AQ)        N/A          N/A          N/A          18.0157
```

Figure 7.6: *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, Alkalinity, carbonic species, etc. These need to be calculated from the given fluid, solid and aqueous (ionic) species outputs. An *MSExcel* spreadsheet was employed in this regard.

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

Table 7.7: Comparison between *STASOFT 4* and *PRO/II* model results for the feed stream

FEED	***STASOFT 4***	***PRO/II* MODEL**
pH	7.22	7.31
Calcium as $CaCO_3$ (mg/L)	2.0	2.0
Alkalinity as $CaCO_3$(mg/L)	5.0	5.0
CCPP 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 with Electrical Conductivities are as a result of the shortcomings of the PRO/II Model with aqueous/carbonate chemistry calculations.

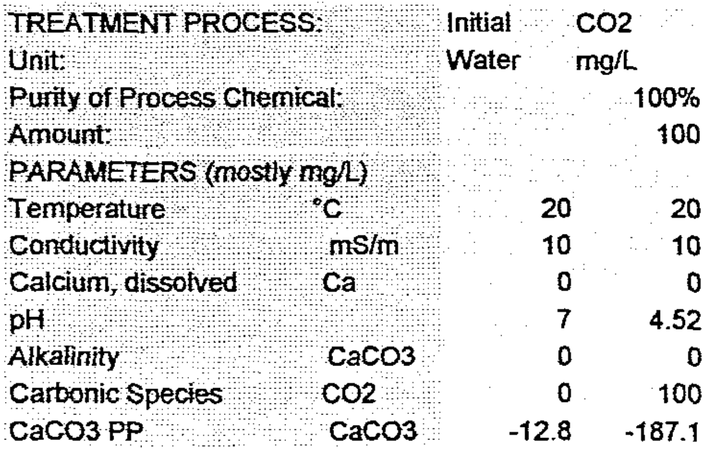
Concluding Remarks: Feed

- 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, alkalinity, etc.). Therefore, in order to simulate a specific feed water numerous iterative steps are required to obtain the desired results.

- In order to quickly simulate a specific feed water, inputs from *STASOFT 4* are required. Thus the interdependence of *PRO/II* with *STASOFT 4* to effectively model the required feed water is highlighted.

CO_2 Addition/Dissolution *STASOFT 4*

In *STASOFT 4*, when a certain dose of CO_2 is added to a particular water, the results are displayed immediately. This allows for easy process optimisation. The following example shows how CO_2 can be added to distilled water to obtain a *desired acidified water.*



TREATMENT PROCESS:		Initial	CO2
Unit:		Water	mg/L
Purity of Process Chemical:			100%
Amount:			100
PARAMETERS *(mostly mg/L)*			
Temperature	°C	20	20
Conductivity	mS/m	10	10
Calcium, dissolved	Ca	0	0
pH		7	4.52
Alkalinity	CaCO3	0	0
Carbonic Species	CO2	0	100
CaCO3 PP	CaCO3	-12.8	-187.1

Figure 7.7: *STASOFT 4* simulation for CO_2 addition to a distilled water stream

CO_2 Addition/Dissolution: *PRO/II*

The addition/dissolution of CO_2 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 CO_2 follows:

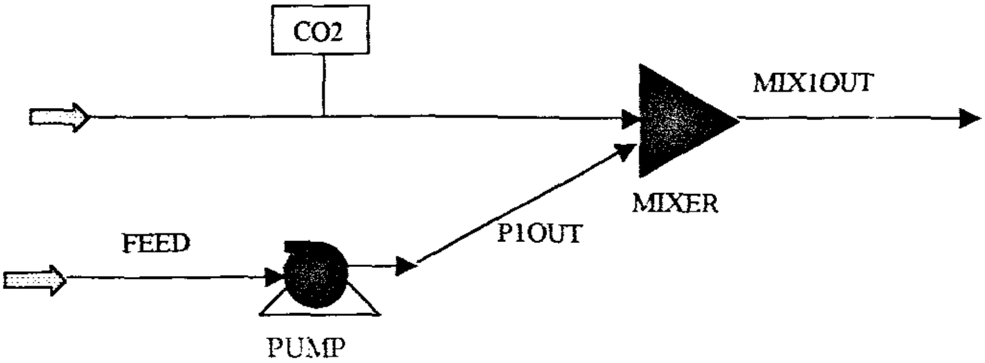


Figure 7.8: Flow diagram of model generated for CO_2 addition in *PRO/II*

However, as previously mentioned the generation of a specified final water quality after the addition of CO_2 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 CO_2 to distilled water, the following results were generated.

Table 7.8: 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
Alkalinity as $CaCO_3$(mg/L)	0.0	0.0
Total carbonic species as CO_2 (mg/L)	100.0	100.0
CCPP 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 CO_2 addition closely resembles that found when modelling the process in *STASOFT 4*.

Concluding Remarks: CO_2 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 CO_2) 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 CO_2 dosing) difficult for ever changing raw water quality, if only *PRO/II* is employed.

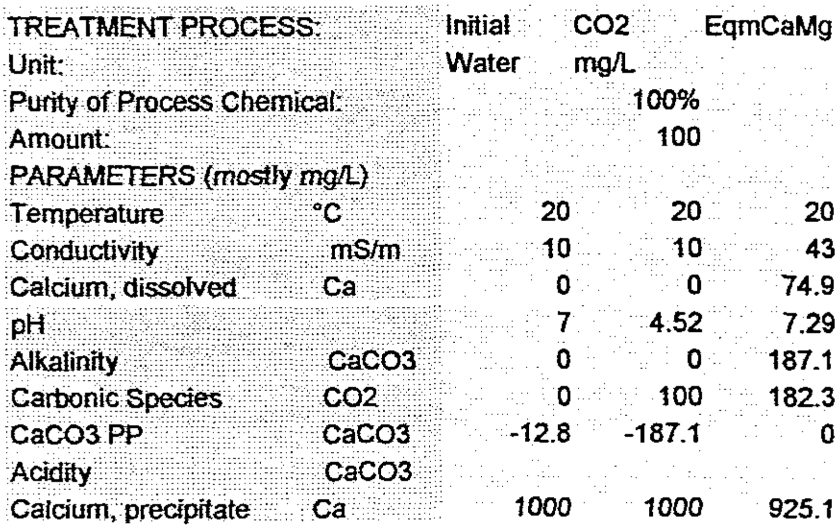
$CaCO_3$ Addition/Dissolution: *STASOFT 4*

The addition of $CaCO_3$ to the acidified stream in *STASOFT 4* can take either of the following two forms:

- ☐ A certain dose of $CaCO_3$ is added to a particular water, or

- $CaCO_3$ is added to reach equilibrium

The results obtained are displayed immediately which allows for easy process optimisation. The following example shows how $CaCO_3$ can be added to an acidified water. In this example $CaCO_3$ is added to equilibrium.



TREATMENT PROCESS:		Initial	CO2	EqmCaMg
Unit:		Water	mg/L	
Purity of Process Chemical:			100%	
Amount:			100	
PARAMETERS *(mostly mg/L)*				
Temperature	°C	20	20	20
Conductivity	mS/m	10	10	43
Calcium, dissolved	Ca	0	0	74.9
pH		7	4.52	7.29
Alkalinity	CaCO3	0	0	187.1
Carbonic Species	CO2	0	100	182.3
CaCO3 PP	CaCO3	-12.8	-187.1	0
Acidity	CaCO3			
Calcium, precipitate	Ca	*1000*	*1000*	925.1

Figure 7.9: *STASOFT 4* simulation for the addition of CO_2 to a distilled water stream

$CaCO_3$ 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 Electrolyte 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.

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 will 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 solid 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.

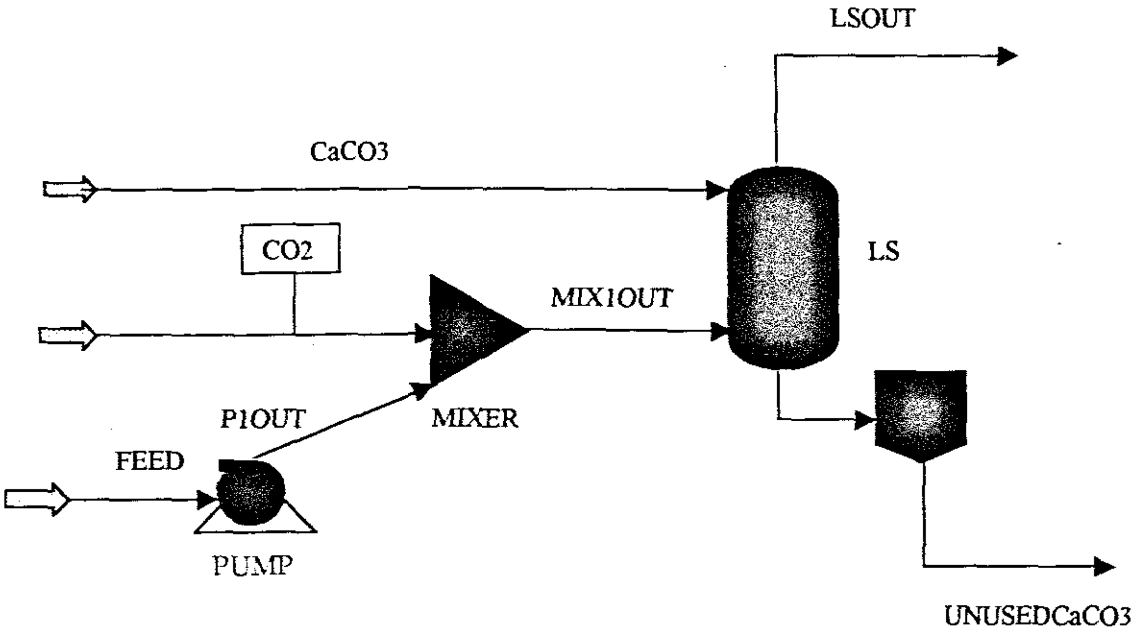


Figure 7.10: Flow diagram of model generated for $CaCO_3$ addition in *PRO/II*

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 7.9: Comparison between *STASOFT 4* and *PRO/II* model results for the stabilised 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
Alkalinity as $CaCO_3$(mg/L)	187.1	161.24
Total carbonic species as CO_2 (mg/L)	182.3	172.3
CCPP 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 7.10: Comparison between *STASOFT 4* and *PRO/II* model results for the stabilised sidestream

LIMESTONE ADDITION	***STASOFT 4***	**PRO/II MODEL**
pH	6.54	6.55
Calcium as $CaCO_3$ (mg/L)	40	40
Alkalinity as $CaCO_3$(mg/L)	100	99
Total carbonic species as CO_2 (mg/L)	144	144
CCPP as $CaCO_3$ (mg/L)	-87.1	-80.3
Electrical Conductivity (mS/m)	28	19

Concluding Remarks: $CaCO_3$ 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 $CaCO_3$) using the flash with solids unit operation. However, $CaCO_3$ 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

CO_2 Stripping and Recovery

CO_2 stripping and recovery on the SSP pilot plant is dependent on a number of factors including:

- ☐ CO_2 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 water quality, with a set CO_2 and $CaCO_3$ addition, which could accurately predict the final water quality and CO_2 recovered at specified Conditions of air flow (to aid CO_2 stripping), and CO_2 recovery vessel vacuum pressure. Once a basic model had been created investigation into the effect of varying the feed water quality, percentage sidestream, fresh CO_2 input, etc. could be undertaken. This would allow optimisation and highlight the practical limitations of the CO_2 stripping process.

Initial Investigation

In practice CO_2 is stripped from the water at pressures of ~ 50 kPa. This is achieved by spraying the water containing the entrained CO_2 through a series of spray nozzles into a column, containing a packing of Pall Rings, and other vacuum conditions. These CO_2 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 CO_2.

It was believed, and subsequently shown during preliminary pilot plant trials that the stripping of CO_2 from the water may be further enhanced by introducing an air stream into the stripping vessel, thus reducing the equilibrium partial CO_2 pressure in the vessel. In addition, preliminary pilot plant trials have also shown that the addition of a carrier gas such as air is not necessary to strip CO_2. The initial model developed therefore did not include an air stream to aid CO_2 stripping.

From the previous modelling exercise, it was evident that the stripping and recovery of CO_2 from the water was not occurring in *PRO/II* as expected from SSP pilot plant operation, and would therefore require thorough investigation. Initially, the two recovery vessels on the SSP pilot plant were modelled as a single flash unit (with no air input), with CO_2 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 CO_2 stripping was occurring even at very low operating pressures (approaching absolute zero pressure, 0 kPa).

The *SIMSCI Helpdesk* confirmed that when simulating the stripping and recovery of CO_2 in *PRO/II* a flash vessel should be used. However, as the initial investigation using this approach did not yield accurate results, following further interactions they subsequently suggested a different approach that involved the use of the stream calculator function.

CO_2 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 CO_2 required for recovery. Using this unit operation we were able to, for example, specify the amount of CO_2 to be recovered. The stream calculator then splits the stream such that the specified quantity of CO_2 reports to the overhead stream. (For example, for an 80% recovery of CO_2, one would specify that 80% of the CO_2 reports to the overhead product.) The input screens for the stream calculator unit operation and its representation in the *PRO/II* flowsheet follows.

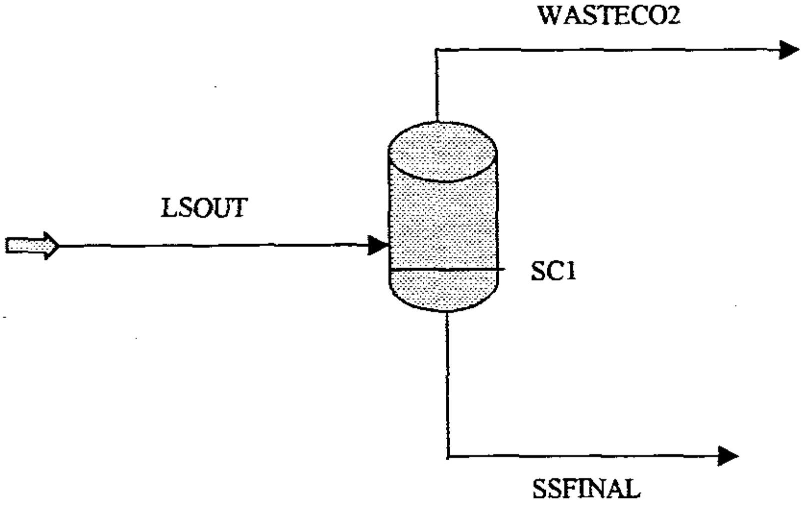


Figure 7.11: Flow diagram of model generated and input screens for stream calculator function in *PRO/II*

In the product specifications window the different specifications for the stream components are selected. In this example, it shows that 80% of the CO_2 will report to the overhead product (on a mole basis). The other components will report to the bottoms product, along with the remaining (20%) CO_2. Although this unit operation is able to strip any desired amount of CO_2, it is not practical as the amount of gas recovered is calculated according to the specific 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 N_2, O_2 and CO_2 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 recognised 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*.

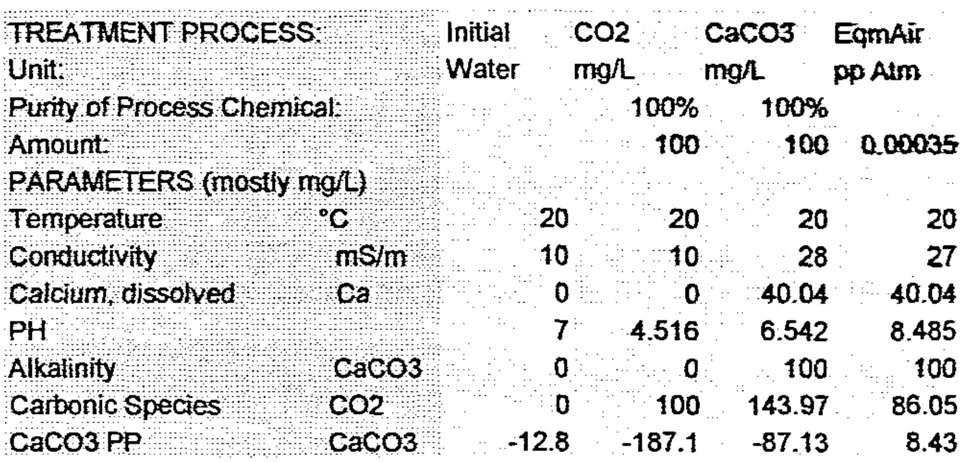
The various methodologies, functions, limitations, etc. of the *STASOFT 4* package were then conveyed to the *SIMSCI Helpdesk*. In addition, a detailed breakdown of the modelling and analysis methodology to date was presented.
During these numerous and extensive interactions it was conveyed that:
CO_2 addition/dissolution, and $CaCO_3$ addition/dissolution generally showed good correlation when compared to the same processes in *STASOFT 4*, but CO_2 stripping from the resultant water stream showed poor correlation between the two software packages. The following section highlights the main discussion points conveyed to the *SIMSCI Helpdesk* with regards to CO_2 stripping and recovery in *STASOFT 4* and *PRO/II*.

CO_2 Stripping and Recovery: *STASOFT 4*

In *STASOFT 4*, the effect of CO_2 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 thus stripping CO_2 from the water stream.*

In the *STASOFT 4* package one is required to specify the final partial CO_2 pressure of the air stream in equilibrium with the water. By varying the partial CO_2 pressure, one can strip various quantities of CO_2 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 CO_2 pressure of the equilibrated gas stream. If the size of the air stream is increased, the equilibrium partial CO_2 pressure of the air in contact with the water is expected to decrease, asymptotically approaching 0.00035 atm for relatively large air streams (partial pressure of CO_2). At this point, an increase in air flow at atmospheric pressure. We therefore expect the pH and Total Carbonic Species (Ct) values to "level out" at relatively large air flows (i.e. stay constant for all practical purpose).

In the following *STASOFT 4* example, 100 mg/L CO_2 and 100 mg/L $CaCO_3$ are added to a distilled water after which the water stream is equilibrated with air, where the CO_2 partial pressure is 0.00035 atm. The *STASOFT 4* flowsheet is shown in the following figure.



TREATMENT PROCESS:		Initial	CO2	CaCO3	EqmAir
Unit:		Water	mg/L	mg/L	pp Atm
Purity of Process Chemical:			100%	100%	
Amount:			100	100	0.00035
PARAMETERS (mostly mg/L)					
Temperature	°C	20	20	20	20
Conductivity	mS/m	10	10	28	27
Calcium, dissolved	Ca	0	0	40.04	40.04
PH		7	4.516	6.542	8.485
Alkalinity	CaCO3	0	0	100	100
Carbonic Species	CO2	0	100	143.97	86.05
CaCO3 PP	CaCO3	-12.8	-187.1	-87.13	8.43

Figure 7.12: *STASOFT 4* simulation for CO_2 and $CaCO_3$ addition 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.

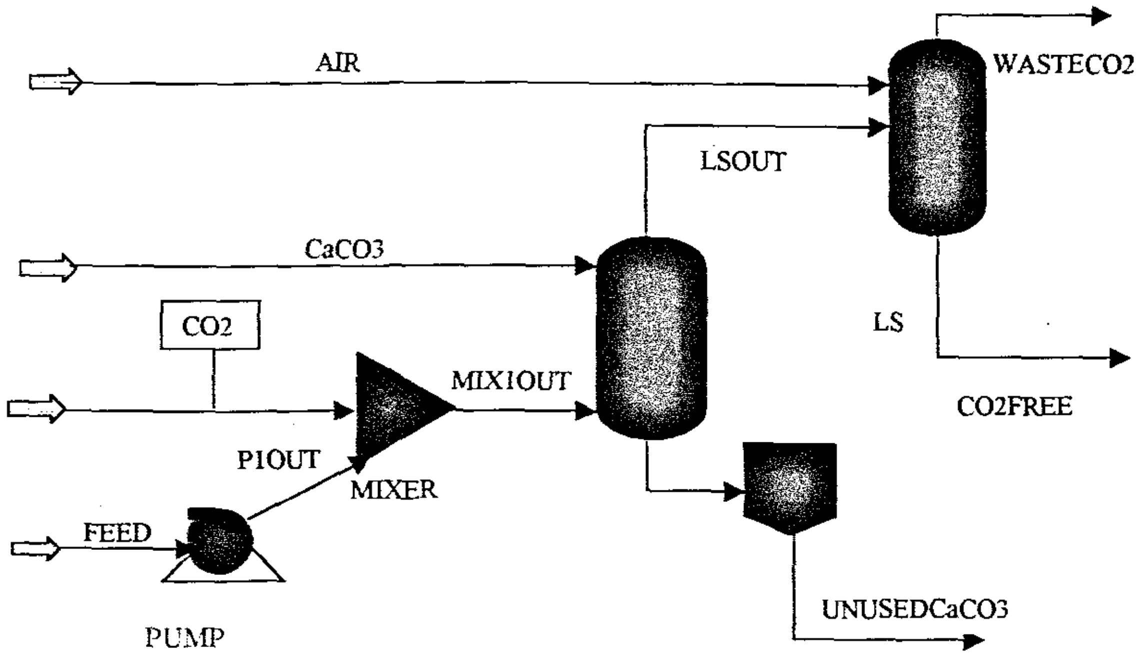


Figure 7.13: Flow diagram of model generated and input screens for stream calculator function in *PRO/II*

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 data collected graphs describing the variation in final water, pH, calcium, alkalinity and CO_2 recovered were constructed. (It must be noted that analysis/interpretation of the data collected and construction of the appropriate graphs is a time consuming exercise. Initially graphs were constructed based on a specific feed water quality, percentage sidestream, and a set of CO_2 and $CaCO_3$ 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 CO_2 stripping, 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 7.11: Comparison between *STASOFT 4* & *PRO/II* model results after CO_2 stripping

STASOFT 4

DETERMINANT	
Calcium as Ca (mg/L)	40
pH	8.485
Alkalinity as $CaCO_3$ (mg/L)	100
Carbonic species, Ct as CO_2 (mg/L)	86.05

PRO/II

DETERMINANT	**AIRFLOW (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	8.143	8.183	8.183	Error
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*, a relatively large air stream was passed through the water before the pH of the outgoing water was raised to more than 8.0. The air flow was then increased until the pH was steady, at which conditions assumption was made that the partial pressure of CO_2 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 be still ~ 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. 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 m^3/hr an error was reported (at this stage all the CO_2 in the stream is stripped).

Therefore, although the final calcium and 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 airflow. 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 airflow (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 7.12: Comparison between *STASOFT 4* & *PRO/II* model results after CO_2 stripping highlighting pH inversion

	pH		**AIR FLOW (m^3/hr)**	**pH**
STASOFT4	8.485	*PRO/II*	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 Investigation: CO_2 Stripping and Recovery in *PRO/II*

The *SIMSCI Helpdesk* was approached and the following questions were posed:

- Is the flash vessel appropriate to model the CO_2 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 occurring with an increase of airflow at high airflows?

From these interactions the *SIMSCI Helpdesk* once again confirmed that the flash vessel was indeed the appropriate unit operation to model CO_2 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 i*n 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, CO_2 is removed from the liquid with CO_2 having a partial pressure of 0.00035 atm in the stripped gas. However, as the air (modelled as N_2, O_2 and CO_2) input already had this quantity of CO_2, it was eliminated from the air input, and the controller was used to vary the air (N_2 and CO_2) inlet rate to yield the required CO_2 partial pressure in the CO_2 "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 CO_2 partial pressure = 0.00035 atm, for all practical purposes models exactly the same process as *STASOFT 4* does. Comparisons between the two models are tabulated in **Table 7.13**.

Table 7.13: Comparison of *STASOFT 4* & *PRO/II* after the introduction of the controller/calculator unit operations

SPECIES	**DETERMINANT**	**STASOFT4**	**PRO/II**
After addition of $CaCO_3$	Calcium as Ca (mg/L)	40	40
	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
	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 used, 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. [H_2CO_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 in a gas in equilibrium contact with that water by Henry's Law: $[H_2CO_3^*] = K_{CO2} * p_{CO2}$, where p is the partial pressure of CO_2 in the equilibrium gas, [H_2CO_3*] is molar concentration, and K is the Henry's Law constant, which is temperature dependant. pK_{CO2} is calculated in *STASOFT 4* from $pK_{CO2} = (-1760.0/T) + 9.619 - 0.00753 * T$ (T in Kelvin).

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 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 has 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 mainstream
- Excess CO_2 stripping and lime addition (if required)

Due to problems previously discussed, 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 minimises 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* 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 stabilised 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 blend 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*.

Concluding remarks: 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
- CO_2 addition and dissolution, and
- $CaCO_3$ addition and dissolution

Showed good correlation when compared to the same processes in *STASOFT 4*, but CO_2 stripping from the resultant water stream showed poor correlation between the two software packages. Of further importance is that the generation of a specified feed water quality, acidified stream or stabilised 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.

The separation of CO_2 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 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* were contacted, in an attempt to understand why such discrepancies exist. These interactions revealed that the package has carbonate chemistry limitations. This significant development led to the abandonment of using *PRO/II*.

7.4 DISCUSSION AND CONCLUSIONS: ASSESSMENT OF *PRO/II* PROCESS MODELING PACKAGE 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 the SSP. This would allow for both optimisation of the process, and allow 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.

Initially the investigation attempted to identify possible packages that seemed capable of modelling the SSP. From this investigation *PRO/II* (manufactured and distributed by *Simulation Sciences Inc. (SIMSCI)*) was selected.

A preliminary assessment of the capabilities and limitations of this modelling package was conducted. This investigation revealed that although problems were experienced with the preliminary assessment, it appeared capable of modelling the various unit processes of the SSP.

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, CO_2 addition and dissolution, and $CaCO_3$ addition and dissolution. However, difficulties were encountered when it was required that CO_2 be stripped from the sidestream. The *SIMSCI Helpdesk* were consulted with regards to the aforementioned problem. Various process options were assessed in *PRO/II*, but results from the models generated showed poor correlation to what is expected from simulations in *STASOFT 4*. Interactions with the model developers revealed that the package may have hitherto unidentified carbonate chemistry limitations. This significant development led to the abandonment of using *PRO/II*.

CONCLUSIONS

THE USE OF PROCESS MODELLING PACKAGES FOR PREDICTING THE BEHAVIOUR OF THE SSP

Assessment of the *PRO/II* process-modelling package showed that:

- The model developed was able to accurately simulate:
    - The incoming feed stream conditions,
    - The condition of the sidestream after CO_2 addition and dissolution, and
    - The condition of the sidestream after $CaCO_3$ addition and dissolution.
- 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 was flawed in terms of identifying 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 CO_2 stripping and recovery step is a critical step in the SSP process, the use of *PRO/II* was abandoned.

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.
- Increasing the "fresh" CO_2 added to the sidestream increases the CO_2 recovered to a maximum of ~ 70%.

- An increase in vacuum pressure within the recovery vessel increases the amount of CO_2 recovered (this relationship only holds at higher CO_2 doses).
- The addition of air decreased the final water alkalinity and the amount of CO_2 recovered because steady vacuums could not be maintained. This result indicated that the addition of air was not (using eductors) beneficial and would have to be further investigated during pilot plant trials.

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. However, during this project both eductors tested did not operate at the required design specification.
  - 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 to its optimal expectance.
  - Therefore, although considerable efforts were made to ensure that a correctly sized eductor was obtained, the eductor could not meet the required design specifications. At the end of the project, a meaningful response had not yet been received. This poor service puts the use of eductors in negative light.
- Three "Long Run" pilot plant experiments were conducted under the following conditions:
  - Low vacuum, high "fresh" CO_2 dose (Long Run 1)
  - High vacuum, low "fresh" CO_2 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" CO_2 dose – 788 mg/L) showed that even though pilot plant performance was not optimal CO_2 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" CO_2 dose – 302 mg/L

and 319 mg/L respectively) showed that CO_2 recoveries of 20 – 40% were obtained.

Due to the non-performance of the eductor, a long run incorporating high vacuum and a high "fresh" CO_2 dose could not be conducted.

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, CO_2 acidified sidestream and sidestream after $CaCO_3$ uptake.
    - The model, however, predicted a significantly lower CO_2 recovery than what had been experienced during pilot plant operation (e.g. for Long Run 1 the model predicted a CO_2 recovery of ~ 8%, while a CO_2 recovery of 35% (average) 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 CO_2 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 CO_2 recovery, and that, based on the data from Long Run 1, CO_2 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 the addition of even nominal levels of air to the recovery vessels. This result compromises the further use of eductors.

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APPENDIX A

SHORT RUN

Pressure readings at various sections/columns of the SSP

TIME	**Motive pressure kPaG**	**Discharge pressure kPaG**	**RV1 mmHg**	**RV2 mmHg**	**RV1 kPaG**	**RV2 kPaG**
9:25	550	170	300	297	-40.0	-39.6
9:55	540	170	387	387	-44.8	-44.7
10:25	540	170	376	370	-50.8	-50.1
10:55	540	170	332	335	-45.3	-45.9
11:25	550	160	471	469	-56.3	-57.3
11:55	550	160	465	463	-62.7	-62.7
12:25	560	160	491	485	-64.1	-64.0
12:55	560	160	474	470	-64.3	-64.0
13:25	560	160	477	475	-62.7	-62.0
13:55	550	160	483	477	-64.3	-63.5
14:25	550	160	495	490	-65.9	-64.9
14:55	560	160	503	498	-67.3	-66.0
15:25	560	160	516	510	-68.4	-67.6
15:55	560	160	526	525	-69.6	-69.3

pH and CO_2 dosing using both RV1 and RV2

TIME	Feed pH	Discharge pH	DV1 pH	DV2 pH	DV3 pH	L/Stone pH	RV1 pH	RV2 pH	CO_2 dose (g/l)
9:25	8.3	8.68	8.40	8.37	8.05	8.67	8.17	8.48	
9:55	8.53	8.82	8.81	8.36	8.33	8.80	8.02	8.54	
10:25	8.53	8.80	8.78	8.43	8.41	8.89	8.32	8.54	
10:55	8.51	8.80	8.75	8.37	8.36	8.94	8.38	8.58	
11:25	8.48	8.63	8.69	8.30	8.28	8.98	8.43	8.60	
11:55	8.42	8.60	8.64	8.25	8.25	9.00	8.44	8.60	0.57
12:25	8.38	8,57	8.59	8.20	4.22	7.32	7.68	8.09	0.57
12:55	8.35	5.94	6.16	6.09	4.26	6.40	6.21	6.50	0.57
13:25	8.36	5.55	5.63	5.23	4.21	6.36	6.04	6.11	0.57
13:55	8.35	5.55	5.66	5.18	4.17	6.34	6.00	6.02	0.57
14:25	8.34	5.42	5.49	4.98	4.26	6.31	6.00	6.00	0.57
14:55	8.32	5.34	5.43	4.96	4.20	6.31	6.00	5.99	0.57
15:25	8.33	5.34	5.4	4.9	4.38	6.32	6.00	5.97	0.57
15:55	8.33	5.34	5.4	4.91	4.38	6.38	5.97	5.97	0.57

APPENDIX B

LONG RUN

Pressure and vacuum recorded during extended operation of the SSP

Time hrs	Sample ID	P_1 kPaG	V_1 kPaG	V_3 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	-61	-60
04:00	M6	550	-60	-64	-46	-63	-60
05:00	M7	550	-60	-64	-46	-61	-62
06:00	M8	550	-60	-64	-50	-61	-59
07:00	M9	550	-59	-63	-49	-59	-60
08:00	M10	550	-57	-61	-47	-61	-57
09:00	M11	550	-60	-63	-50	-61	-60
10:00	M12	550	-59	-63	-48	-58	-61
11:00	M13	550	-57	-60	-46	-61	-57
12:00	M14	550	-60	-64	-48	-62	-60
13:00	M15	550	-60	-62	-48	-34	-60
14:00	M16	550	-30	-32	-22	-52	-32
15:00	M17	550	-50	-53	-40	-52	-51
16:00	M18	550	-50	-63	-40	-61	-51
17:00	M19	550	-60	-62	-48	-61	-60
18:00	M20	550	-60	-63	48-	-63	-60
19:00	M21	550	-60	-59	-48	-61	-62
20:00	M22	550	-59	-59	-48	-62	-61
21:00	M23	550	-59	-58	-48	-63	-61

22:00	M24	550	-59	-63	-48	-60	-59
23:00	M25	550	-59	-63	-48	-58	-59
00:00	M26	550	-58	-62	-48	-58	-58
01:00	M27	550	-57	-62	-46	-58	-58
02:00	M28	550	-57	-62	-46	-62	-58
03:00	M29	550	-60	-63	-50	-58	-62
04:00	M30	550	-57	-63	-46	-57	-58
05:00	M31	550	-57	-62	-46	-61	-60
06:00	M32	550	-57	-62	-46	-62	-60
07:00	M33	550	-59	-62	-48	-62	-61
08:00	M34	550	-60	-64	-49	-62	-61
09:00	M35	550	-60	-64	-50	-62	-61
10:00	M36	550	-61	-64	-50	-61	-62
11:00	M37	550	-62	-68	-50	-63	-61
12:00	M38	550	-61	-66	-50	-62	-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	-60	-61
16:00	M42	550	-60	-64	-48	-61	-59
17:00	M43	550	-60	-64	-50	-63	-59
18:00	M44	550	-61	-58	-50	-62	-62
19:00	M45	550	-60	-58	-48	-61	-62
20:00	M46	550	-60	-59	-48	-64	-61
21:00	M47	550	-60	-59	-50	-62	-64
22:00	M48	550	-61	-64	-50	-62	-61
23:00	M49	550	-60	-64	-50	-63	-61
00:00	M50	550	-61	-65	-50	-63	-62
01:00	M51	550	-61	-65	-50	-62	-62
02:00	M52	550	-60	-64	-50	-62	-61
03:00	M53	550	-61	-64	-50	-63	-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	-64	-62
08:00	M58	550	-62	-65	-50	-63	-62

09:00	M59	550	-60	-65	-50	-61	-61
10:00	M60	550	-60	-64	-50	-61	-60
11:00	M61	550	-62	-65	-50	-62	-60
12:00	M62	550	-61	-65	-50	-62	-61
13:00	M63	550	-61	-64	-50	-61	-61
14:00	M64	550	-60	-64	-50	-64	-60
15:00	M65	550	-63	-66	-52	-59	-62
16:00	M66	550	-59	-63	-48	-61	-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	-65	-61
20:00	M70	550	-62	-61	-51	-63	-64
21:00	M71	550	-61	-60	-50	-65	-62
22:00	M72	550	-63	-66	-52	-63	-64
23:00	M73	550	-62	-65	-50	-63	-62
00:00	M74	550	-62	-65	-50	-66	-62

pH Readings recorded at various ~~stages within the SSP~~

Time hrs	Sample ID	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	5.83	5.59	6.07
01:00	M3	8.54	6.06	4.57	4.76	4.09	5.81	5.77	6.12
02:00	M4	8.53	5.98	4.63	4.84	4.11	5.82	5.80	6.18
03:00	M5	8.51	6.01	4.65	4.80	4.12	5.81	5.80	6.17
04:00	M6	8.49	6.19	4.66	4.86	4.14	5.81	5.83	6.19
05:00	M7	8.49	6.20	4.71	4.89	4.31	5.83	5.80	6.13
06:00	M8	8.47	6.21	5.01	5.35	4.25	5.84	5.85	6.28
07:00	M9	8.46	6.71	4.92	5.08	4.21	5.83	5.83	6.18
08:00	M10	8.46	5.17	4.86	5.05	4.21	5.81	5.82	6.16
09:00	M11	8.44	5.33	4.75	4.92	4.16	5.81	5.83	6.18
10:00	M12	8.39	5.20	4.75	4.95	4.20	5.81	5.80	6.14
11:00	M13	8.34	5.37	4.73	4.89	4.21	5.81	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	5.81	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	5.83	5.77	6.18
16:00	M18	8.21	5.26	4.75	4.89	4.20	5.83	5.77	6.14
17:00	M19	8.23	5.28	4.74	4.90	4.18	5.80	5.80	6.14
18:00	M20	8.21	5.37	4.78	4.92	4.19	5.78	5.80	6.13
19:00	M21	8.23	5.27	4.75	4.92	4.14	5.78	5.80	6.13
20:00	M22	8.23	5.25	4.71	4.92	4.14	5.83	5.78	6.10
21:00	M23	8.23	5.27	4.71	4.92	4.17	5.83	5.77	6.10
22:00	M24	8.25	5.21	4.78	4.95	4.19	5.83	5.77	6.10
23:00	M25	8.25	5.35	4.81	4.98	4.16	5.82	5.77	6.10
00:00	M26	8.26	5.42	4.81	5.01	4.16	5.80	5.76	6.10
01:00	M27	8.28	5.40	4.83	5.01	4.14	5.80	5.76	6.10
02:00	M28	8.28	5.40	4.83	5.01	4.16	5.88	5.76	6.10
03:00	M29	8.31	5.40	4.86	4.98	4.19	5.88	5.80	6.10
04:00	M30	8.31	5.49	4.86	5.03	4.21	5.88	5.77	6.10

05:00	M31	8.31	5.40	4.83	4.96	4.16	5.88	5.80	6.10
06:00	M32	8.31	5.38	4.81	4.95	4.19	5.88	5.77	6.13
07:00	M33	8.34	5.37	4.76	4.96	4.21	5.88	5.80	6.10
08:00	M34	8.34	5.29	4.74	4.98	4.21	5.85	5.77	6.12
09:00	M35	8.34	5.28	4.76	5.03	4.18	5.79	5.78	6.14
10:00	M36	8.31	5.27	4.77	5.02	4.19	5.83	5.80	6.10
11:00	M37	8.26	5.27	4.83	5.13	4.21	5.84	5.78	6.16
12:00	M38	8.21	5.30	4.83	5.00	4.29	5.84	5.78	6.22
13:00	M39	8.16	5.22	4.78	4.95	4.24	5.84	5.78	6.17
14:00	M40	8.13	5.21	4.80	4.95	4.23	5.95	5.79	6.19
15:00	M41	8.13	5.16	4.78	4.95	4.23	5.80	5.82	6.19
16:00	M42	8.14	5.18	4.77	4.95	4.19	5.84	5.80	6.19
17:00	M43	8.16	5.09	4.77	4.91	4.28	5.84	5.81	6.17
18:00	M44	8.16	5.24	4.78	4.92	4.17	5.86	5.79	6.19
19:00	M45	8.16	5.25	4.75	4.95	4.16	5.84	5.79	6.18
20:00	M46	8.19	5.30	4.77	4.95	4.13	5.83	5.79	6.16
21:00	M47	8.21	5.23	4.75	4.98	4.23	5.81	5.80	6.16
22:00	M48	8.23	5.40	4.77	4.89	4.20	5.81	5.80	6.14
23:00	M49	8.23	5.32	4.80	4.89	4.18	5.83	5.79	6.18
00:00	M50	8.24	5.28	4.73	4.90	4.23	5.81	5.79	6.16
01:00	M51	8.26	5.26	4.71	4.92	4.16	5.81	5.79	6.14
02:00	M52	8.28	5.24	4.75	4.89	4.18	5.83	5.80	6.14
03:00	M53	8.31	5.22	4.75	4.89	4.18	5.84	5.79	6.16
04:00	M54	8.31	5.25	4.73	4.88	4.16	5.84	5.77	6.16
05:00	M55	8.32	5.24	4.73	4.88	4.19	5.84	5.79	6.14
06:00	M56	8.34	5.25	4.75	4.92	4.21	5.83	5.78	6.12
07:00	M57	8.32	5.25	4.81	4.92	4.16	5.84	5.78	6.12
08:00	M58	8.31	5.60	4.76	4.91	4.18	5.84	5.80	6.14
09:00	M59	8.32	5.44	4.77	4.91	4.23	5.84	5.78	6.12
10:00	M60	8.26	5.12	4.77	5.00	4.20	5.84	5.80	6.14
11:00	M61	8.18	5.16	4.73	4.99	4.15	5.84	5.77	6.17
12:00	M62	8.09	5.17	4.82	4.99	4.23	5.87	5.77	6.17
13:00	M63	8.06	5.35	4.82	4.99	4.23	5.85	5.77	6.14
14:00	M64	8.11	5.14	4.79	4.91	4.20	5.85	5.79	6.20
15:00	M65	8.13	5.12	4.70	4.91	4.17	5.86	5.80	6.17

16:00	M66	8.14	5.10	4.75	4.90	4.14	5.84	5.81	6.17
17:00	M67	8.16	5.14	4.75	4.90	4.17	5.83	5.84	6.19
18:00	M68	8.19	5.25	4.72	4.90	4.17	5.83	5.79	6.19
19:00	M69	8.22	5.26	4.72	4.90	4.10	5.81	5.81	6.22
20:00	M70	8.24	5.27	4.79	4.25	4.09	5.81	5.81	6.19
21:00	M71	8.26	5.22	4.72	5.05	4.75	5.81	5.82	6.28
22:00	M72	8.28	5.45	4.72	4.95	4.25	5.82	5.86	6.18
23:00	M73	8.22	5.39	4.33	4.99	5.05	5.82	5.82	6.20
00:00	M74	8.24	5.30	4.90	4.99	4.95	5.88	5.84	6.22

Calculated CO_2 recovery from SSP operation

Time hrs	Sample ID	CO_2 DOSAGE g/l	DV1-CO_2 Recovery (Stasoft) g/l	DV2-CO_2 Recovery (Stasoft) g/l	DV1-% Recovery (Stasoft)	DV2-% Recovery (Stasoft)
23:00	M1	0.57	1.75	1.20	75	68
00:00	M2	0.57	1.22	0.77	68	57
01:00	M3	0.57	0.98	0.60	63	47
02:00	M4	0.57	0.85	0.51	60	47
03:00	M5	0.57	0.80	0.57	58	50
04:00	M6	0.57	0.79	0.49	58	46
05:00	M7	0.57	0.70	0.45	55	44
06:00	M8	0.57	0.34	0.15	37	21
07:00	M9	0.57	0.48	0.29	42	34
08:00	M10	0.57	0.63	0.31	46	35
09:00	M11	0.57	0.63	0.42	53	42
10:00	M12	0.57	0.67	0.39	53	41
11:00	M13	0.57	0.67	0.45	54	44
12:00	M14	0.57	0.56	0.47	54	45
13:00	M15	0.57	0.70	0.45	50	44
14:00	M16	0.57	0.75	0.51	55	47
15:00	M17	0.57	0.63	0.51	57	47
16:00	M18	0.57	0.63	0.45	53	44
17:00	M19	0.57	0.59	0.45	53	44
18:00	M20	0.57	0.63	0.44	51	44
19:00	M21	0.57	0.70	0.42	53	42
20:00	M22	0.57	0.70	0.42	55	42
21:00	M23	0.57	0.59	0.42	55	42
22:00	M24	0.57	0.55	0.42	51	42
23:00	M25	0.57	0.55	0.39	49	41
00:00	M26	0.57	0.52	0.36	49	39
01:00	M27	0.57	0.52	0.34	48	37
02:00	M28	0.57	0.49	0.34	48	37
03:00	M29	0.57	0.49	0.34	46	39
04:00	M30	0.57	0.52	0.36	46	36

05:00	M31	0.57	0.54	0.32	48	36
06:00	M32	0.57	0.61	0.32	49	37
07:00	M33	0.57	0.65	0.34	52	37
08:00	M34	0.57	0.62	0.38	53	40
09:00	M35	0.57	0.60	0.38	52	40
10:00	M36	0.57	0.52	0.38	51	40
11:00	M37	0.57	0.52	0.36	48	39
12:00	M38	0.57	0.59	0.32	48	36
13:00	M39	0.57	0.56	0.33	51	37
14:00	M40	0.57	0.58	0.25	50	30
15:00	M41	0.57	0.60	0.35	50	38
16:00	M42	0.57	0.60	0.39	51	41
17:00	M43	0.57	0.59	0.39	51	41
18:00	M44	0.57	0.63	0.39	51	41
19:00	M45	0.57	0.60	0.39	53	41
20:00	M46	0.57	0.63	0.43	51	43
21:00	M47	0.57	0.60	0.42	53	42
22:00	M48	0.57	0.56	0.39	51	41
23:00	M49	0.57	0.66	0.39	50	41
00:00	M50	0.57	0.70	0.36	54	39
01:00	M51	0.57	0.63	0.45	55	44
02:00	M52	0.57	0.63	0.45	53	44
03:00	M53	0.57	0.66	0.44	53	44
04:00	M54	0.57	0.66	0.42	54	42
05:00	M55	0.57	0.63	0.45	54	44
06:00	M56	0.57	0.55	0.45	53	44
07:00	M57	0.57	0.61	0.46	49	45
08:00	M58	0.57	0.60	0.36	52	39
09:00	M59	0.57	0.60	0.42	51	42
10:00	M60	0.57	0.66	0.42	51	42
11:00	M61	0.57	0.53	0.43	54	43
12:00	M62	0.57	0.53	0.43	48	43
13:00	M63	0.57	0.57	0.34	48	37
14:00	M64	0.57	0.71	0.35	50	38
15:00	M65	0.57	0.63	0.35	55	38

16:00	M66	0.57	0.63	0.35	53	38
17:00	M67	0.57	0.68	0.43	53	43
18:00	M68	0.57	0.68	0.43	54	43
19:00	M69	0.57	0.57	0.43	54	43
20:00	M70	0.57	0.68	0.44	50	44
21:00	M71	0.57	0.16	0.44	54	44
22:00	M72	0.57	0.44	0.44	22	44
23:00	M73	0.57	0.59	0.44	44	44
00:00	M74	0.57	0.55	0.30	51	34

APPENDIX C

LONG RUN 1

Time hrs	Sample ID	Calcium Ca mg/L	Calcium $CaCO_3$ mg/L	Alkalinity $CaCO_3$ mg/L	RV1 kPa (ABS)	RV2 kPa (ABS)	CO_2 mass (kg/hr)	Dose mg/L	%CO_2 Recovery	
									A	B
00:00	M1	171	427.5	422	100	100	0.42	907	8	30
01:00	M2	168	420	409	100	100	0.38	821	7	33
02:00	M3	116	290	400	100	100	0.36	778	0	30
03:00	M4	159	397.5	396	100	100	0.38	821	1	30
04:00	M5	158	395	397	100	100	0.36	778	1	30
05:00	M6	162	405	395	100	100	0.36	778	1	30
06:00	M7	161	402.5	395	100	100	0.44	950	1	30
07:00	M8b	158	395	393	100	100	0.38	821	1	30
08:00	M9	157	392.5	386	100	100	0.36	778	4	31
09:00	M10	159	397.5	399	100	94	0.4	864	0	27
10:00	M11	157	392.5	398	100	90	0.38	821	5	30
11:00	M12	155	387.5	397	95	86	0.38	821	5	30
12:00	M13	154	385	392	91	84	0.38	821	5	30
13:00	M14	166	415	416	89	68	0.38	821	10	35
14:00	M15	164	410	414	73	65	0.36	778	15	43
15:00	M16	169	422.5	426	70	66	0.38	821	14	38
16:00	M17	164	410	424	71	65	0.38	821	14	38
17:00	M18	160	400	416	70	63	0.34	734	10	31
18:00	M19	161	402.5	417	68	62	0.38	821	5	35
19:00	M20	161	402.5	422	68	62	0.38	821	10	35
20:00	M21	160	400	423	68	62	0.4	821	10	35
21:00	M22	163	407.5	411	68	62	0.36	864	10	30
22:00	M23	164	410	417	68	64	0.4	821	2	35
23:00	M24	164	410	410	69	64	0.4	821	10	34
00:00	M25	164	410	406	70	65	0.36	821	7	32

01:00	M26	163	407.5	408	70	64	0.42	864	2	29
02:00	M27	164	410	406	71	66	0.42	778	12	36
03:00	M28	163	407.5	407	71	66	0.38	864	2	29
04:00	M29	163	407.5	406	72	66	0.38	864	2	29
05:00	M30	164	410	406	72	67	0.36	778	12	36
06:00	M31	168	420	426	72	71	0.36	907	5	32
07:00	M32	171	427.5	430	75	72	0.36	907	6	32
08:00	M33	161	402.5	398	78	65	0.36	821	2	30
09:00	M34	158	395	406	76	66	0.38	821	7	32
10:00	M35	160	400	403	72	67	0.36	778	11	35
11:00	M36	165	412.5	409	72	68	0.38	778	12	36
12:00	M37	162	405	406	70	68	0.4	778	12	36
13:00	M38	164	410	406	72	68	0.4	778	12	36
14:00	M39	166	415	412	72	69	0.38	821	10	35
15:00	M40	166	415	412	71	69	0.4	778	14	39
16:00	M41	166	415	414	73	70	0.28	821	10	35
17:00	M42	164	410	409	74	68	0.4	864	2	29
18:00	M43	167	417.5	416	77	70	0.38	864	5	31
19:00	M44	167	417.5	417	77	71	0.36	821	10	35
20:00	M45	167	417.5	421	77	72	0.36	864	7	34
21:00	M46	167	417.5	418	77	72	0.34	605	34	40
22:00	M47	164	410	416	76	72	0.4	864	5	31
23:00	M48	162	405	402	75	67	0.42	821	6	32
00:00	M49	164	410	406	75	70	0.4	778	12	36
01:00	M50	163	407.5	406	74	70	0.4	778	12	36
02:00	M51	164	410	403	76	70	0.38	734	16	29
03:00	M52	162	405	409	76	70	0.38	864	2	29
04:00	M53	164	410	401	76	70	0.38	907	0	24
05:00	M54	162	405	400	76	70	0.38	864	0	27
06:00	M55	160	400	403	76	69	0.22	864	0.7	28
07:00	M56	159	397.5	399	70	69	0.38	821	5	30
08:00	M57	164	410	405	73	69	0.36	821	6	32
09:00	M58	162	405	401	74	68	0.4	821	5	31
10:00	M59	164	410	398	73	66	0.38	821	2	30
11:00	M60	160	400	389	71	64	0.38	821	42	39

12:00	M61	153	382.5	379	68	69	0.28	475	0	35
13:00	M62	158	395	398	74	70	0.1	821	8	34
14:00	M63	159	397.5	403	75	70	0.12	778	0.7	38
15:00	M64	164	410	402	75	71	0.1	864	6	32
16:00	M65	167	417.5	403	75	67	0.12	821	6	40
17:00	M66	149	372.5	367	42	38	0.12	821	15	48
18:00	M67	99	247.5	242	38	34	0.22	605	17	42
19:00	M68	87	217.5	209	38	34	0.12	216	0	39
20:00	M69	83	207.5	203	39	35	0.12	259	0	37
21:00	M70	83	207.5	202	39	35	0.12	216	0	38
22:00	M71	84	210	202	38	35	0.14	259	0	37

APPENDIX D

LONG RUN 2

Time hrs	Sample ID	Calcium Ca mg/L	Calcium $CaCO_3$ mg/L	Alkalinity $CaCO_3$ mg/L	RV1 kPa (ABS)	RV2 kPa (ABS)	CO_2 mass (kg/hr)	Dose mg/L	% CO_2 Recovery	
									A	B
00:00	M1	109	272.5	280	96	91	0.16	346	0	31
01:00	M2	92	230	236	96	91	0.14	302	0	14
02:00	M3	74	185	189	81	91	0.12	259	0	0.4
03:00	M4	93	232.5	238	81	78	0.12	259	0	26
04:00	M5	74	185	193	82	76	0.1	216	0	18
05:00	M6	88	220	228	84	80	0.12	259	0	22
06:00	M7	86	215	223	82	77	0.12	259	0	0.4
07:00	M8	97	242.5	250	80	76	0.12	259	0.4	35
08:00	M9	99	247.5	254	77	73	0.08	173	36	38
09:00	M10	100	250	256	76	73	0.12	259	4	37
10:00	M11	99	247.5	248	66	63	0.14	302	0	21
11:00	M12	105	262.5	264	59	57	0.14	302	0	31
12:00	M13	108	270	268	56	53	0.16	346	0	23
13:00	M14	107	267.5	268	53	51	0.14	302	3	33
14:00	M15	106	265	270	52	49	0.14	302	3	34
15:00	M16	109	272.5	272	52	49	0.16	346	0	26
16:00	M17	109	272.5	272	51	48	0.14	302	6	36
17:00	M18	108	270	265	51	47	0.14	302	0	31
18:00	M19	107	267.5	264	51	47	0.16	346	0	21
19:00	M20	105	262.5	264	51	47	0.16	346	0	21
20:00	M21	105	262.5	263	51	47	0.16	346	0	21
21:00	M22	106	265	264	51	47	0.16	346	0	21
22:00	M23	106	265	262	51	47	0.14	302	0	21
23:00	M24	105	262.5	261	51	47	0.16	346	0	21
00:00	M25	103	257.5	261	51	46	0.14	302	0	31

01:00	M26	105	262.5	251	49	46	0.16	346	0	20
02:00	M27	99	247.5	250	49	45	0.16	346	0	31
03:00	M28	100	250	252	49	45	0.14	302	0	14
04:00	M29	102	255	254	49	45	0.16	346	0	26
05:00	M30	102	255	253	49	46	0.14	302	0	16
06:00	M31	102	255	249	48	45	0.16	346	0	21
07:00	M32	100	250	247	48	45	0.14	302	0	9
08:00	M33	99	247.5	249	47	45	0.12	259	0	21
09:00	M34	99	247.5	256	46	44	0.14	302	4	37
10:00	M35	102	255	256	46	43	0.14	302	0	26
11:00	M36	102	255	259	46	43	0.16	346	0	27
12:00	M37	104	260	262	46	43	0.14	302	0	20
13:00	M38	104	260	264	46	43	0.16	346	0	31
14:00	M39	105	262.5	270	47	43	0.14	302	0	25
15:00	M40	107	267.5	274	47	44	0.16	346	8	38
16:00	M41	107	267.5	260	46	44	0.14	302	0	20
17:00	M42	102	255	257	45	43	0.16	346	0	30
18:00	M43	104	260	255	45	41	0.16	346	0	16
19:00	M44	105	262.5	254	45	41	0.16	346	0	16
20:00	M45	101	252.5	253	45	41	0.12	259	0	16
21:00	M46	100	250	241	45	41	0.12	259	0	22
22:00	M47	99	247.5	248	45	41	0.16	346	0	32
23:00	M48	97	242.5	247	44	41	0.14	302	0	19
00:00	M49	98	245	262	46	40	0.16	346	0	30
01:00	M50	105	262.5	251	45	40	0.16	346	0	14
02:00	M51	99	247.5	248	45	41	0.14	302	0	9
03:00	M52	99	247.5	247	44	41	0.14	302	0	21
04:00	M53	97	242.5	246	45	41	0.16	346	0	21
05:00	M54	97	242.5	245	44	41	0.14	302	0	16
06:00	M55	97	242.5	244	44	41	0.16	346	0	18
07:00	M56	97	242.5	244	44	41	0.14	302	0	16
08:00	M57	97	242.5	245	44	41	0.12	259	0	18
09:00	M58	100	250	245	44	41	0.16	346	0.4	35
10:00	M59	97	242.5	250	43	41	0.12	259	0	16
11:00	M60	97	242.5	245	44	41	0.14	302	4	37

12:00	M61	100	250	247	44	40	0.14	302	0	25
13:00	M62	100	250	251	44	41	0.14	302	0	26
14:00	M63	100	250	253	43	41	0.14	302	0	26
15:00	M64	99	247.5	254	43	41	0.16	346	0	26
16:00	M65	99	247.5	251	43	40	0.18	389	0	14
17:00	M66	97	242.5	250	43	40	0.14	302	0	16
18:00	M67	97	242.5	251	43	40	0.16	346	0	17
19:00	M68	97	242.5	251	43	40	0.16	346	0	15
20:00	M69	96	240	250	43	40	0.14	302	0	23
21:00	M70	96	240	247	43	40	0.16	346	0	25
22:00	M71	96	240	244	43	40	0.14	302	0	28
23:00	M72	97	242.5	280	96	91	0.16	346	0	31

APPENDIX E

LONG RUN 3

Time hrs	Sample ID	Calcium Ca mg/L	Calcium $CaCO_3$ mg/L	Alkalinity $CaCO_3$ mg/L	RV1 kPa (ABS)	RV2 kPa (ABS)	CO_2 mass (kg/hr)	Dose mg/L	%CO_2 Recovery	
									A	B
00:00	M1									
01:00	M2				47	45	0	0		
02:00	M3				47	45	0	0		
03:00	M4	105	262.5	210	47	45	0	0		
04:00	M5	104	260	208	54	55	0.06	130	55	70
05:00	M6	111	277.5	222	57	57	0.14	302	4	36
06:00	M7	105	262.5	210	55	56	0.16	346	0	25
07:00	M8	106	265	212	55	57	0.12	259	22	47
08:00	M9	107	267.5	214	55	56	0.16	346	0	25
09:00	M10	110	275	220	54	57	0.16	346	0	29
10:00	M11	107	267.5	216	53	56	0.14	302	8	38
11:00	M12	108	270	214	53	55	0.16	346	0	29
12:00	M13	108	270	216	53	56	0.12	259	22	47
13:00	M14	108	270	216	53	56	0.14	302	8	38
14:00	M15	117	292.5	234	53	56	0.16	346	6	37
15:00	M16	117	292.5	234	54	56	0.16	346	6	37
16:00	M17	117	292.5	234	53	56	0.16	346	9	37
17:00	M18	116	290	232	53	56	0.16	346	18	38
18:00	M19	114	285	228	54	56	0.16	346	0	45
19:00	M20	105	262.5	210	54	56	0.14	302	3	25
20:00	M21	107	267.5	214	52	54	0.16	346	0	34
21:00	M22	102	255	204	51	53	0.14	302	0	30
22:00	M23	104	260	208	51	53	0.14	302	0.9	23
23:00	M24	104	260	208	51	53	0.16	346	0	33
00:00	M25	104	260	208	51	53	0.14	302	0	31
01:00	M26	104	260	208	51	53	0.14	302	0	21
02:00	M27	103	257.5	206	51	53	0.16	346	0	21

03:00	M28	103	257.5	206	51	53	0.16	346	0	31
04:00	M29	105	262.5	210	51	53	0.14	302	0	31
05:00	M30	104	260	208	51	53	0.14	302	0	21
06:00	M31	100	250	200	51	53	0.16	346	0	31
07:00	M32	101	252.5	202	50	51	0.14	302	0	31
08:00	M33	104	260	208	49	50	0.14	302	3	31
09:00	M34	102	255	204	48	50	0.14	302	3	34
10:00	M35	105	262.5	210	47	50	0.14	302	0	34
11:00	M36	105	262.5	210	47	50	0.14	302	11	31
12:00	M37	111	277.5	222	48	50	0.16	346	6	44
13:00	M38	112	280	224	48	50	0.14	302	6	37
14:00	M39	108	270	216	46	49	0.14	302	0	37
15:00	M40	110	275	220	47	50	0.16	346	0	31
16:00	M41	112	280	224	48	50	0.16	346	1	33
17:00	M42	114	285	228	48	51	0.16	346	22	36
18:00	M43	109	272.5	218	47	49	0.12	259	0	48
19:00	M44	104	260	208	45	47	0.16	346	0	20
20:00	M45	104	260	208	45	46	0.14	302	0	31
21:00	M46	99	247.5	198	44	46	0.16	346	0	20
22:00	M47	100	250	200	44	46	0.14	302	0	30
23:00	M48	100	250	200	44	46	0.16	346	0	14
00:00	M49	101	252.5	200	44	46	0.14	302	0	16
01:00	M50	101	252.5	202	44	45	0.16	346	4	14
02:00	M51	101	252.5	202	44	45	0.12	259	0	34
03:00	M52	101	252.5	202	43	45	0.16	346	6	11
04:00	M53	97	242.5	202	43	45	0.12	259	11	34
05:00	M54	97	242.5	247	42	44	0.12	259	0	40
06:00	M55	96	240	248	42	44	0.2	432	0	17
07:00	M56	98	245	246	42	43	0.16	346	0	20
08:00	M57	98	245	246	42	43	0.14	302	0	36
09:00	M58	98	245	248	41	43	0.12	259	16	46
10:00	M59	99	247.5	247	41	43	0.14	302	3	36
11:00	M60	103	257.5	246	40	43	0.12	259	0	45
12:00	M61	105	262.5	259	41	43	0.16	346	0	20
13:00	M62	105	262.5	262	41	43	0.14	302	0	23

14:00	M63	108	270	264	41	42	0.14	302	0	23
15:00	M64	108	270	270	41	41	0.16	346	0	11
16:00	M65	104	260	266	41	40	0.16	346	0	11
17:00	M66	102	255	259	40	40	0.14	302	0	23
18:00	M67	103	257.5	259	40	40	0.16	346	0	11
19:00	M68	100	250	254	39	40	0.14	302	0	23
20:00	M69	98	245	249	39	40	0.16	346	0	14
21:00	M70	99	247.5	247	39	41	0.16	346	0	14
22:00	M71	98	245	246	38	42	0.16	346	0	14

NOMENCLATURE

a - Activity in the bulk solution
b - Amount of CO_2 in the recycled product gas from the stripper
c - Concentration of dissolved mineral in solution
c_i - Concentration of species i
c_{sat} - Concentration of dissolved mineral in solution at saturation
C_T - Total carbonate species
d - Column diameter (m)
D_i - Diffusion coefficient of species i ($m^2.s^{-1}$)
$F_d.F_m$ - Activity coefficient for divalent ions which varies with strength
g - Molar amount of dissolved air in the water stream leaving the air stripper
h - Column height (m)
j - Pure CO_2 introduced to the process ("fresh" CO_2)
H_{air} - Henry's Law constant for air (7.2 x 10^4 atm/mole @ 25°C)
k - Rate constant
K_{CO2} - Henry's Law constant which is temperature dependent
K_{sp} - Thermodynamic solubility product constant for calcium carbonate
$K_{sp'}$ - Apparent solubility product constant for calcium carbonate
k_1,k_2 - Thermodynamic equilibrium constants for the carbonate system
$k_w,k_{w'}$ - Thermodynamic equilibrium constants for the water system
l - Distance across which concentration difference has been measured
p_{air} - Partial pressure of air in the gas stream
Q - volumetric flowrate (m^3/hr)
S - Surface area of calcium carbonate crystals per unit volume in solution
T - Temperature (K)

V - Actual volume of the column (m^3)
W - Moles of water leaving the stripper
X_{air} - Molar fraction of dissolved air in water
y - Molar fraction of air in the gas stream
[ ] - Molarity of species (moles/l)
( ) - Activity of species (moles/l)

Greek letters

Ω - Relative saturation index
Φ - Nominal mean granule size (mm) $3.55 \le \Phi \le 8.05$
Π - Total pressure over the air stripper
Π_{DV} - Total pressure over the CO_2 dissolution vessel