

# AN EVALUATION OF THE SUITABILITY OF THE LIMESTONE BASED SIDESTREAM STABILISATION PROCESS FOR STABILISATION OF WATERS OF THE LESOTHO HIGHLANDS SCHEME

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## 1. INTRODUCTION

A significant proportion of the waters of South Africa and Lesotho are soft and acidic with characteristically 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 stabilisation) is conventionally achieved by the addition of lime ( $\text{Ca(OH)}_2$ ) and carbon dioxide ( $\text{CO}_2$ ). 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 stabilisation process is stabilisation via contact with limestone (solid calcium carbonate –  $\text{CaCO}_3$ ). Operation of limestone contactors in South Africa has shown limestone-mediated stabilisation to have a number of advantages over lime-mediated stabilisation (Mackintosh *et al*, 1998a). However, the use of limestone-mediated stabilisation has hitherto been limited to smaller water treatment works (less than 30 ML/day) because of the large contact tanks required. More recently, consideration of the use of limestone-mediated stabilisation for large water treatment works was made viable by the development of the CSIR's limestone mediated Sidestream Stabilisation Process (SSP).

The SSP proposes using limestone in a manner potentially suitable for large water works (Mackintosh *et al*, 1998b). With Rand Water considering water transport and treatment requirements for the Lesotho Highlands Scheme, SSP was identified as a potentially attractive alternative to conventional stabilisation using lime and  $\text{CO}_2$ . This paper provides feedback on a Water Research Commission funded project that looked at the modelling and operation of a SSP pilot plant and preliminary consideration of the financial viability of SSP for use by Rand Water for the Lesotho Highlands Scheme. As SSP requires the dosing, stripping and recovery of  $\text{CO}_2$  in a relatively complex process, a simplified version of the SSP (in which no stripping and recovery of  $\text{CO}_2$  is required) was also assessed at a desktop level. Both processes are protected by South African and International patents.

## 2. THE SIDESTREAM STABILISATION PROCESSES

SSP consists of taking a sidestream of unstabilised water, dosing high levels of gaseous  $\text{CO}_2$ , and then contacting the  $\text{CO}_2$ -acidified stream with limestone. The acidified sidestream takes up considerable amounts of  $\text{CaCO}_3$ , increasing the Alkalinity and the calcium concentration. Thereafter  $\text{CO}_2$  is stripped, recovered and reused in the process. After  $\text{CO}_2$  stripping, the sidestream is blended with the main stream in the correct proportions to allow for a fully stabilised main stream. The SSP is shown conceptually in Figure 1.

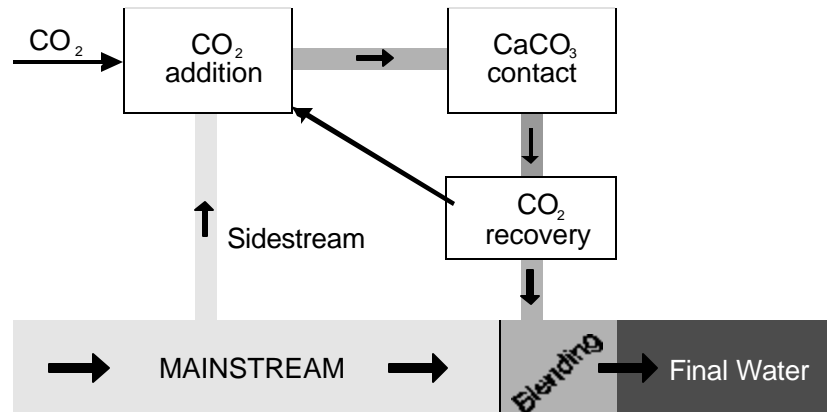


Figure 1: Conceptual description of Sidestream Stabilisation Process

With the requirement for stripping and recovery of  $\text{CO}_2$ , SSP can be seen to be a complicated process (increased process equipment requirements). A “simplified SSP” can be considered in which no  $\text{CO}_2$  stripping and/or recovery is practised.

## 3. BACKGROUND THEORETICAL CONSIDERATIONS

For the use of SSP, understanding of the basic principles governing the carbonate system in the aqueous, gaseous and solid phases are of importance. In particular, dissolution of gaseous  $\text{CO}_2$  into a liquid phase, dissolution of solid calcium carbonate into a liquid phase, and recovery of excess dissolved  $\text{CO}_2$  from the liquid phase to the gaseous phase must be considered (Loewenthal *et al*, 1986). The following aqueous, gaseous and solid phase interactions need to be considered:

The **dissolution of carbon dioxide** into an aqueous media depends on a number of factors, *inter alia* the difference in  $\text{CO}_2$  concentration in the two phases, the surface area at the gas/liquid interface, and the mixing energy within the aqueous phase. In addition, temperature, pressure and ionic strength are important considerations. However, by using a gas phase with a  $\text{CO}_2$  partial pressure very much greater than that normally encountered by aqueous media, inordinately high concentrations of molecularly dissolved carbonate species can be attained. Such high concentrations of carbonate species and the dosing chemical type ( $\text{CO}_2$ ) lead to a water with exceptionally high total acidity and calcium carbonate dissolution potential.

The **dissolution of calcium carbonates** can only occur if the solution is undersaturated with regard to solid carbonate. Temperature and pressure of the system, calcium and carbonate species distribution and the partial pressure of  $\text{CO}_2$  influence the solubility of  $\text{CaCO}_3$ . 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 acidity and calcium carbonate dissolution potential brought into contact with solid  $\text{CaCO}_3$  minerals will take up exceptionally high levels of calcium and carbonate species.

The **stripping of carbon dioxide** from an aqueous media depend on a number of factors, *inter alia* the difference in  $\text{CO}_2$  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  $\text{CO}_2$ .

Considering the complex interaction of the abovementioned processes, it is desirable to develop models to accurately predict the behaviour and describe the aqueous, gaseous and solid phase chemistry of SSP. Such a model would be useful for developing an improved understanding of the processes, for optimisation of the process and importantly for plant control during industrial scale application.

#### 4. PROCESS MODELLING PACKAGES

For ease of process optimisation during future industrialisation, it was considered preferable to look to commercial "off-the-shelf" Chemical Engineering type process modelling packages. Following on from an initial screening procedure, the most suitable packages available at the time were the fairly similar packages *ASPEN PLUS* (manufactured and distributed by *Aspen Technology Inc.*) and *PRO/II* (manufactured and distributed by *Simulation Sciences Inc.*). Both packages have the ability to perform rigorous mass and energy balances and are widely used in industry for designing new processes, evaluating alternative process plant configurations and optimising existing process plants. Because of various factors at the time, including package development considerations and budget constraints, *PRO/II* was selected as the most suitable package.

A thorough study using *PRO/II* to model SSP showed that it was indeed possible to accurately model certain steps of SSP, namely: feed generation,  $\text{CO}_2$  addition/dissolution, and  $\text{CaCO}_3$  addition/dissolution (equilibrium conditions). However, difficulties were encountered when it was required that  $\text{CO}_2$  be stripped from the sidestream. Lengthy interactions with the manufacturers revealed that the package may have hitherto unidentified carbonate chemistry limitations (SIMSCI, 2000). Unfortunately, this significant development led to the forced abandonment of the use of *PRO/II* (it was considered probable that the *ASPEN PLUS* package would have similar limitations). During a period of growing concern as to the limitations of *PRO/II*, the project team proceeded with developing an in-house model. Considering that the failure of *PRO/II* was in the complex arena of  $\text{CO}_2$  stripping it made sense to initiate model development by looking at a Simplified SSP which excludes  $\text{CO}_2$  stripping and recovery.

## 5. PROCESS MODEL DEVELOPMENT AND PILOT PLANT ASSESSMENT

### 5.1 Modelling the Simplified SSP

The theoretical viability of the Simplified SSP was considered by the development of a model. The model included *JAVA* programming and the use of the *STASOFT 4* package. The *STASOFT 4* package is an aquatic chemistry calculation package that consists of two programs, namely *STASOFT 4*, with a user friendly Graphical User Interface and *Watchem*, a *MSDOS* version command line and input file driven program (Morrison and Lowenthal, 2000). At the time model development commenced, *STASOFT 4* development was in its final stages, and Mr Ian Morrison kindly made a preliminary test-version of the software available for the purpose of modelling the Simplified SSP.

In the Simplified SSP (Figure 2), the raw water stream is split into a mainstream and a sidestream. Carbon dioxide is dosed to the sidestream, after which the sidestream is contacted with solid calcium carbonate in a contactor, to take up Alkalinity and calcium. The sidestream is blended in with the mainstream again to form the final blend. Variations of the process include: different sidestream/mainstream blending ratio's, stripping  $\text{CO}_2$  to the atmosphere before or after blending or not at all, and the addition of various alkali's such as lime, sodium hydroxide or sodium carbonate.

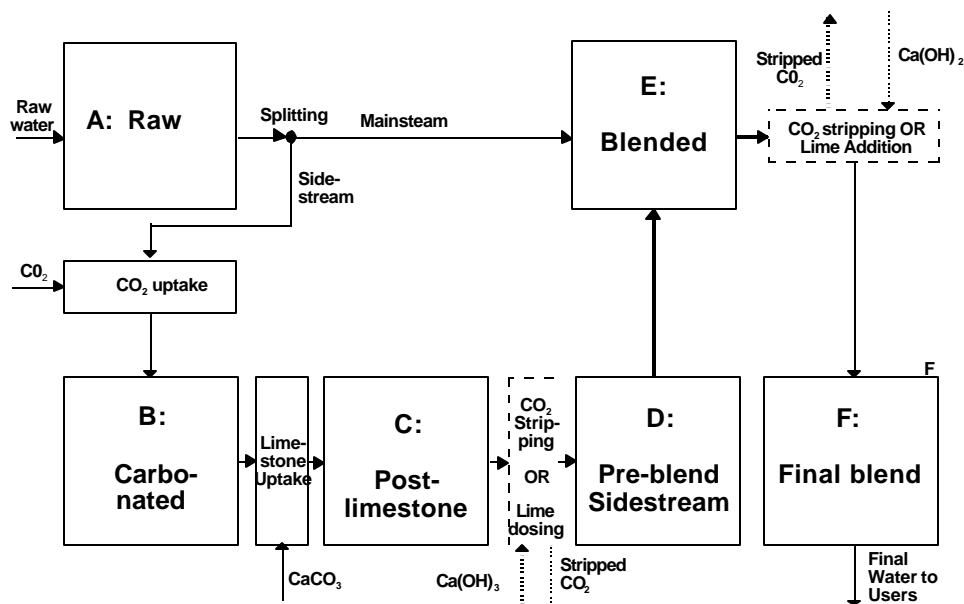


Figure 2: Possible steps in the Simplified SSP

As there is no gas recycling in the Simplified SSP, *STASOFT 4* could be used to model the Simplified SSP. However, as evaluation of the Simplified SSP required a large number of runs (to investigate the influence of varying  $\text{CO}_2$  dosage and percentage sidestream), the use of *STASOFT 4* was impractical. The *Watchem* program was therefore used to overcome this limitation. *Watchem* uses the same aquatic chemistry routines as *STASOFT 4*, but its user interface is via input-files, which makes it possible to specify the variance of input parameters over a range. Model output is made in output-files that the user can customize and import into *MSEXcel*, to obtain graphical representation of the output.

## 5.2 Modelling and Pilot Plant Operation of the SSP

The following section describes the development of a program, called “SSP-MOD”, for predicting the behaviour of the SSP. The SSP-MOD program was developed from the model developed to describe Simplified SSP. The SSP-MOD program describes the various unit processes of the SSP process including CO<sub>2</sub> stripping, recovery and subsequent recycling.

As *STASOFT 4/Watchem* does not provide a mechanism to take the feedback gas stream (recovered CO<sub>2</sub>) into account, they could not be used for SSP simulations. It was therefore necessary to incorporate computer programming to model the SSP process. *JAVA* was used as a programming language, due to its relatively user friendly object oriented style. Modules were developed to model the various unit operations and a steady state mass balance for the SSP. 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.

Following development, the model was compared with *STASOFT 4* and found to be accurate. In parallel with verification and calibration of the SSP model, it was necessary to optimise SSP pilot plant operation. These two objectives were carried out in an iterative manner.

Assessment of the SSP process had shown that the stripping and recovery of CO<sub>2</sub> is an essential step in the SSP and that maximizing CO<sub>2</sub> recovery at economical “fresh” CO<sub>2</sub> doses was of primary importance in an attempt to optimise the process. Previous pilot plant work had shown that CO<sub>2</sub> recovery using vacuum pumps was potentially problematic, and therefore the use of an eductor was considered. Eductors have the potential advantages over vacuum pumps of low cost, simplicity and reliability, ease of installation, non-electrical, corrosion and erosion resistant. Unfortunately, during the project both eductors tested did not operate at the required design specifications. Neither the South African distributors nor the USA manufacturers could provide a meaningful reason as to why the eductors did not operate effectively at required conditions. This resulted in the project team not being able to optimise pilot plant operation. Nevertheless, non-optimised use of the eductors provided pilot plant results which revealed that:

- When a relatively low vacuum (~ 62 - 68 kPa) and relatively high “fresh” CO<sub>2</sub> dose (788 mg/L) was maintained CO<sub>2</sub> recoveries of 30 – 40% were obtained (even though pilot plant performance was not optimal due to poor performance of the eductor).
- When a relatively high vacuum (~ 40 - 45 kPa) and relatively low “fresh” CO<sub>2</sub> dose (~300 mg/L) was maintained CO<sub>2</sub> recoveries of 20 – 40% were obtained.
- Due to the non-optimal performance of the eductor, a long run incorporating high vacuum and a high “fresh” CO<sub>2</sub> dose was not possible.

Utilising results obtained from both the models developed and pilot plant operation, financial evaluations of both the Simplified SSP and SSP were conducted to assess the attractiveness of the processes for industrialisation. These financial evaluations are discussed in the following sections.

## 6. FINANCIAL ASSESSMENT OF THE VIABILITY OF A SIMPLIFIED SSP

The raw water characteristics selected as the model input was that of a typical Stellenbosch soft, raw water with temperature = 20 °C, conductivity = 6 mS/m, dissolved calcium = 2 mg/L as Ca, pH = 6.3 and Alkalinity = 5 mg/L as CaCO<sub>3</sub>. In order to determine the viability of the Simplified SSP various operating configurations were assessed including: varying sidestream/mainstream blending ratio's, stripping CO<sub>2</sub> to the atmosphere before or after blending or not at all, and the addition of various alkali's such as lime, sodium hydroxide or sodium carbonate.

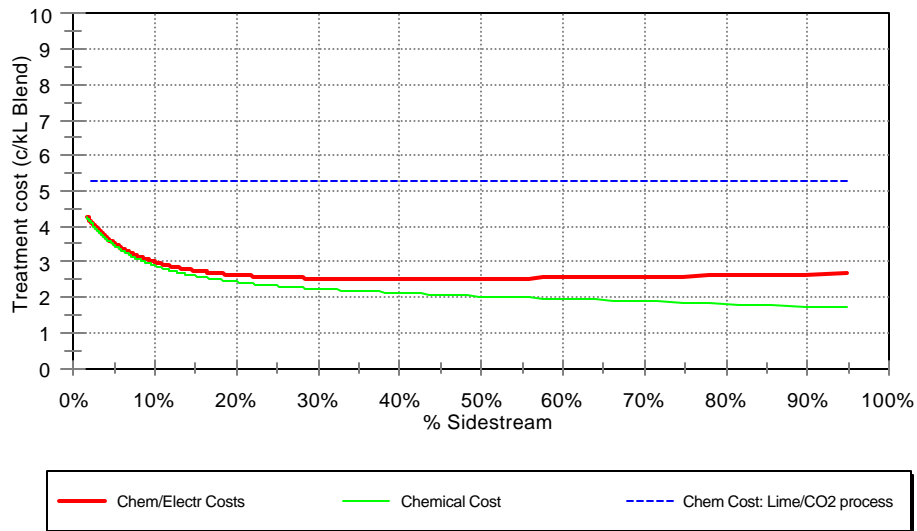
Chemical costs in Table 1 were used to compare the running costs of the Simplified SSP to conventional stabilisation using lime and carbon dioxide. The costs presented in Table 1 were valid in Stellenbosch, South Africa in November 1999. (It should be noted that the costs of chemicals used vary considerably with both the quality of the product and the region to which the product must be transported. The cost of white lime has in particular fluctuated considerably.)

**Table 1:** Chemical costs used in the Simplified SSP basic financial evaluation (Stellenbosch, November 1999)

Chemical	Notes	Cost (R/ton)	Purity (%)
Limestone	Aquastab Pebbles, Bredasdorp	140	95
Lime	Local lime with available CaO of 65%	750	85.9
Carbon dioxide	-	730	100
Sodium Hydroxide	In flake form in bags	2500	100
Soda Ash	Dense soda ash	1700	95

From the various scenarios the required chemical dosages, together with the chemical costs, were used to determine the running costs of each Simplified SSP variation. A running cost comparison was then made between the Simplified SSP and conventional stabilisation (based on achieving the same final water quality). Comparison showed that:

- Stripping excess CO<sub>2</sub> to the atmosphere before blending the sidestream and mainstream was not financially attractive.
- Stripping excess CO<sub>2</sub> to the atmosphere after blending the sidestream and mainstream, was financially attractive. The financial attractiveness varied with the both the CO<sub>2</sub> stripping efficiency and the alkali's used for final pH adjustment. Use of sodium alkali's was found to provide little or no saving relative to the use of lime, as a result of the high cost of these chemicals.
- Where partial stripping of the mainstream was accompanied by lime dosing, an attractive chemical cost saving incurred.
- Importantly, where no stripping of CO<sub>2</sub> was practised and nominal lime dosing was employed, significant chemical savings relative to conventional lime and CO<sub>2</sub> mediated stabilisation were observed.
  - For example, the following graph (Figure 3) indicates the case where, using the raw water described earlier, a final Alkalinity of 50 mg/L and a CCPP of zero is required. The graph indicates that the use of a 20% sidestream would lead to a 50% chemical cost saving of 2.63 c/kL. On a 100 ML/day treatment plant this would translate to a saving of R78 900 / month, and R959 950 / year.



**Figure 3:** Chemical and running costs for Simplified SSP configuration with nominal lime dosage after blending, for a final Alkalinity of 50 mg/L

- Considering the practical implications of CO<sub>2</sub> stripping from a main stream in a large water treatment works, it is of particular interest that the study showed that significant savings are potentially possible where no CO<sub>2</sub> stripping is required. It should, however, also be noted that the viability of the process is highly dependant on the costs of the required chemicals (CO<sub>2</sub>/white lime vs. limestone). These costs need to be carefully considered at each particular application. Furthermore, recent increases in white lime costs to approximately R2 700/ton would make the use of the more easily dosed sodium alkalis attractive.

## 7. FINANCIAL ASSESSMENT OF THE SUITABILITY OF THE SSP FOR THE LESOTHO HIGHLANDS SCHEME

In order to consider the desirability and suitability of the SSP process for the Lesotho Highlands scheme, it was necessary to compare the operational costs of SSP with those of conventional lime and CO<sub>2</sub> mediated stabilisation. The Rand Water process engineers and the CSIR project team chose to consider an operationally and financially conservative scenario (i.e. well within the performance capabilities of the pilot plant operation). The scenario chosen was a relatively large percentage sidestream (i.e. conservative in that it would reflect increased capital cost) and low percentage CO<sub>2</sub> recovery (i.e. conservative in that higher recovery had been achieved in the pilot plant operation).

## 7.1 Water Treatment Considerations

Rand Water monitored the Katse Dam raw water quality via on-site sample collection. The water considered was a typical As River outfall water with pH = 7.27, conductivity = 8.1 mS/m, hardness = 41.75 mg/L as CaCO<sub>3</sub>, dissolved calcium = 9.25 mg/L as Ca, Alkalinity = 35.55 mg/L as CaCO<sub>3</sub>, magnesium = 4.13 mg/L as Mg and sodium = 3.3 mg/L as Na. Furthermore, Rand Water carried out laboratory scale experiments to assess water treatment options. Both direct and indirect filtration (in which ferric chloride is used as the coagulant) and membrane micro-filtration were evaluated. Rand Water also determined their stabilisation requirements to ensure that the water is non-corrosive as being a CCPP value of 1 - 2 mg/l, an Alkalinity greater than 50 mg/l as CaCO<sub>3</sub>, and pH value of approximately 8.2.

## 7.2 Financial Model

The scenario evaluated was for stabilisation of water treated via filtration assisted by ferric chloride dosing (Rand Water's most likely treatment scenario). In this scenario a "high" percentage sidestream (10%) combined with "low" percentage CO<sub>2</sub> recovery and re-use (10%), and an airstrip of the blended stream was utilised.

The financial model took into account chemical costs, labour costs, maintenance shutdowns, capital costs recovery, inflation, required return on investment and risk. The financial model considers these and then essentially compares the ability of SSP to pay for itself based on the savings it provides. The data used in the financial model is summarised in Table 2.

**Table 2:** Cost comparison input variables (delivered to Clarens, October 2000)

	SSP		Conventional	
PLANT CAPACITY	2 000 ML/day		2 000 ML/day	
TIC COST	R77 million		R99 million	
Project Lifespan	10 years		10 years	
Operating days	350 days per year		350 days per year	
Chemicals	<i>Chemical Dose</i>	<i>Cost (R/ton)</i>	<i>Chemical Dose</i>	<i>Cost (R/ton)</i>
Carbon dioxide (CO <sub>2</sub> )	26.0 mg/L	700*	38.0	700*
Lime (Ca(OH) <sub>2</sub> )	35.0 mg/L	1400*	-	-
Limestone (CaCO <sub>3</sub> )	-	-	46.1 mg/L	370*
Chemical Wastage	5% per chemical		5% per chemical	
Plant power consumption	Electricity costs assumed to be R0.01/m <sup>3</sup> higher for the SSP than for conventional stabilisation (NOTE: This additional electricity cost is included despite the fact that in the SSP process only 10% of the main stream undergoes treatment, therefore requiring less pumping).			
Plant operation, maintenance, etc	Labour costs assumed equal for both conventional stabilisation and SSP (costs therefore cancelled in the model)			
Maintenance	5% of capital cost		5% of capital cost	



### 7.3 Financial Model Results

The financial assessment showed that payback period corrected for inflation (7%) is 2.5 years, and payback period corrected for inflation and risk (37%) is 4.3 years. Both of these are very attractive in the municipal sector, where payback periods of up to 15 years are usually the norm. Furthermore, the model calculates a Net Present Value (NPV) and an Internal Rate of Return (IRR) for the project lifespan. To infer financial feasibility, the NPV needs only to be greater than zero. The NPV was calculated to be R2,7 million with an associated IRR of 52%. These two figures confirm that the project, with the assumptions made, is financially very attractive and that a risk factor of up to 35% {52% - 7% (inflation) - 10% (required return)}, could still be applied to give an NPV of zero. A summary of the results of the detailed financial assessment is shown in Table 3.

**Table 3:** Project financial assessment summary –conventional stabilisation vs. SSP (2 000 ML/day)

	Conventional	SSP
Capital cost (R million)	77	99
Payback period (corrected for inflation and risk)		4.3 years
Discount rate		
Average inflation	7%	7%
Required real return	10%	10%
Estimated risk	0%	30%
Internal Rate of Return (IRR)		52%
Net Present Value (NPV)		R2.7 million

The detailed financial assessment therefore showed that even with a number of conservative assumptions to the detriment of SSP (lifespan of 10 years – Rand Water norm is 30 years, raised electricity costs for SSP, risk discount factor of 30% per annum, minimum required return of investment of 10% per annum, low percentage CO<sub>2</sub> recovery) the process potentially provides significant financial advantage over conventional lime/CO<sub>2</sub> stabilisation. The project team and Rand Water believes that SSP may present an opportunity for significant stabilisation cost savings and the process should now be taken through an industrialisation process.

## 8. SUMMARY AND CONCLUSIONS

This paper provides feedback on the assessment of limestone-based alternatives for the stabilisation of soft, acidic water for large water treatment works. As a basis for this assessment, equilibrium based aquatic chemistry modelling tools were developed and two alternate forms of limestone-mediated stabilisation were investigated. The alternatives assessed were the Simplified SSP process (raw water split into a mainstream and a sidestream → dose CO<sub>2</sub> to sidestream → contact sidestream with limestone → strip CO<sub>2</sub>, with no recovery or blend sidestream and mainstream without stripping, etc) and the SSP (same as Simplified SSP but includes CO<sub>2</sub> stripping and recovery). Furthermore, pilot plant operation of the SSP was used to confirm and calibrate the accuracy of the process model. Thereafter, financial evaluation of both the Simplified SSP and SSP were carried out.

Financial evaluation of the Simplified SSP, relative to lime and carbon dioxide mediated stabilisation (using Stellenbosch water and chemical prices, November 1999), revealed that where a water with a final Alkalinity of 50 mg/L and a CCPP of zero was required, the use of a 20% sidestream would lead to a 50% chemical cost saving of 2.63 c/kL. Financial evaluation of SSP for use at Clarens for Lesotho Highlands Scheme water, again relative to lime and carbon dioxide mediated stabilisation (using Katse Dam water after filtration and chemical prices, October 2000), revealed that even with a number of conservative assumptions to the detriment of SSP, the process potentially provides significant financial advantage over conventional lime/CO<sub>2</sub> stabilisation with a project payback period of 4.3 years, NPV of R2,7 million and IRR of 52%.

Of obvious consideration for these financial assessments are the costs of the required chemicals (CO<sub>2</sub>/white lime vs. limestone). The prices for both limestone and white lime vary geographically with transport costs. In recent years the price of high quality white lime has risen dramatically (depending on quality, the Rand exchange rate, and the region to which the product must be transported). Individual assessment of the relevant process therefore needs to be considered on a case-by-case basis. Due to these variations a direct comparison between the Simplified SSP and the SSP cannot be made from the information presented in this paper. Nevertheless, a number of important conclusions can be made and these are summarised below.

In conclusion,

- The low risk Simplified SSP was shown via desktop based equilibrium chemistry modelling to be a viable alternative for the full stabilisation of soft, acidic waters.
- The Simplified SSP provides significant financial savings over conventional lime and carbon dioxide stabilisation. For example, on a 100 ML/day treatment plant treating a typical Stellenbosch raw water, and requiring a final Alkalinity of 50 mg/L and a CCPP of zero, the use of a 20% sidestream would result in a saving of R78 900 / month, and R959 950 / year.
- Although optimisation of SSP pilot plant operation could not be achieved, results from operation with sub-standard eductors revealed that CO<sub>2</sub> recoveries of 20 – 40% were obtained. It can therefore be assumed that higher CO<sub>2</sub> recoveries could be obtained if pilot plant operation was optimal.
- Conservative financial assessment of SSP for use at Clarens (Lesotho Highlands Scheme), in which CO<sub>2</sub> recovery and re-use assumptions were well within pilot plant performance, indicates that SSP provides significant financial savings over conventional lime and CO<sub>2</sub> stabilisation with a project payback period of 4.3 years, NPV of R2,7 million and IRR of 52%.
- The trend of chemical costs is that raw, graded limestone will always be significantly less expensive than use of beneficiated lime and CO<sub>2</sub> (with the latter two requiring considerable energy inputs). This cost difference is exaggerated by the present South African need to import high quality white lime. Hence, whilst use of the Simplified SSP and SSP needs to be considered on a case-by-case basis, these processes should always offer significant chemical cost savings over the use of lime and CO<sub>2</sub> based stabilisation.

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

## 9. ACKNOWLEDGEMENTS

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