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An Aspen Model for the Treatment of Acid Mine Water

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ABSTRACT

Although numerous methods exist to treat acid mine water they all have inherent disadvantages. A means of treating acid mine drainage is by forming a precipitate known as ettringite. Ettringite is a low solubility calcium hydrosulphoaluminate that is stable between pH values of 11.4 and 12.4. Ettringite is made up of calcium, sulphate, aluminium and a large amount of water. Decomposition of ettringite takes place by dropping the pH to about 7. A five stage process is proposed to treat acid mine drainage of which the formation of ettringite forms the cornerstone of this process. The process incorporates the formation of more than one precipitate as well as the recycling of aluminium hydroxide when ettringite is decomposed. The results obtained in this paper are as a result of modeling this process. The modeling of this process was performed on a computer simulation package known as Aspen. © 2002 SDU. All rights reserved.

Keywords: Acid mine drainage; Ettringite; Model

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1. INTRODUCTION

Mining in South Africa is a necessity, and is influential to its economy. The greenhouse effect and global warming has largely been responsible for less frequent rainfall and therefore a shortage of water. This problem has been compounded by millions of litres of water being polluted through the mining and other industries each year. Finding a cost effective solution to the pollution problem, with specific reference to acid mine drainage (AMD), is of outmost importance. The formation of AMD is as a result of a series of complex geo-chemical and microbial reactions that occur when water comes in contact with pyrite (iron disulphide minerals) in mining operations. Ore bodies commonly mined that pose AMD risk are gold, silver, copper, iron, zinc, lead (or multi-metal combinations), and coal. This water is usually high in acidity and dissolved metals.

Even though a number of methods exist to purify solutions from sulphates, such as precipitation with lime, precipitation with barium salts, co-precipitation with calcium carbonate, reverse osmosis and ion exchange, each of these has an inherent disadvantage. The addition of lime, although facilitating the removal of heavy metals, is unable to reduce the sulphate content to an acceptable level. Ion exchange technology could reduce calcium and sulphate levels considerably, but the associated costs are significantly high. A fairly low cost method of purifying AMD is based on the precipitation of SO_4^{2-} in the form of a low-solubility calcium hydrosulphoaluminate, by treating water with milk of lime and an aluminium-containing agent. This family of phases that show potential to immobilize sulphate belongs to the ettringite species, and has been investigated by numerous authors (Bambauer, 1991; Gougar *et al.*, 1996; Moore and Taylor, 1968). Ettringite in its natural form has been known for more than 100 years and was first discovered at the Ettringer Bellerberg in Eifel, Germany. It is commonly found in weathered cement, cement based solidification by-products and alkaline fly ashes (McCarthy *et al.*, 1992; Myneni *et al.*, 1997). Ettringite, as we know it today, represents a whole group of acicular calcium aluminate hydrates, which have the general composition:

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$$3CaO.Al_2O_3.3CaX_2.nH_2O$$
or
$$3CaO.Al_2O_3.3CaY.nH_2O$$
with $X = OH^-, NO_3^-, \ldots$ and $Y = SO_4^{2-}, CO_3^{2-}, \ldots$

The crystal structure of minerals of the ettringite group consists of columns, which run parallel to the c-axis (Moore and Taylor, 1970). These columns, which have the composition $[Ca_6Al_2(OH)_{12}.24H_2O]^{6+}$, contain $Al(OH)_6$ units attached to hydrated Ca^{2+} arranged in a hexagonal array. The channels in between the columns are made up of SO_4^{2-} and water molecules. Crystallization of ettringite normally takes place as prismatic needles (c-axis) of high aspect ratio and hexagonal cross section. Visible changes in morphology occur when ettringite crystals grow in the presence of organic additives, some of which are known to act as set-retarders in Portland cement (Pöllmann *et al.*, 1989).

Ettringite can withstand modest deviations in composition without a change in structure. This compositional change can occur on a crystal chemical level in the form of ionic substitution. Al^{3+} in ettringite can be substituted by Ti^{3+}, Cr^{3+}, Mn^{3+} and Fe^{3+} to form similar compounds of the type $Ca_6[M(OH)_6](SO_4)_3.26H_2O$ (Bensted and Varma,1972). According to McCarthy *et al.* (1992), SO_4^{2-} can be replaced by CrO_4^{2-}, MnO_4^-, Cl^-, OH^-, CO_3^{2-} and NO_3^-. Similarly, Sr^{2+}, Ba^{2+}, Ni^{2+} and Zn^{2+} may replace Ca^{2+}. There exists a series of related compounds, known as a mineral group or family, and they include the following minerals:

Charlesite	$Ca_6(Si,Al)_2(SO_4)_2(B[OH]_4)(OH)_{12}.26H_2O$
Sturmanite	$Ca_6Fe_2(SO_4)_2(B[OH]_4)(OH)_{12}.26H_2O$
Thaumasite	$Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}.24H_2O$
Jouravskite	$Ca_6Mn_2(SO_4)_2(CO_3)_2(OH)_{12}.24H_2O$
Bentorite	$Ca_6(Cr,Al)_2(SO_4)_2(OH)_{12}.26H_2O$

Ettringite is a stable mineral between pH values of 11.4 and 12.4 and dissolves congruently with a log K_{sp} of -43.13 (according to Reardon, 1990). Temperature, dissolved CO_2, and H_2O activity can strongly influence ettringite stability. According to Damidot and Glasser (1992), monosulphoaluminate is more stable than ettringite at high temperatures. Nishikawa *et al.* (1992), stated that at high CO_2 and low H_2O activity level, ettringite decomposed to aragonite with vaterite as an intermediate phase.

In solution at pH values used for ettringite synthesis, aluminium exists largely as the amphoteric $Al(OH)_4^-$ species. The solubility curves for aluminium hydroxide species show that below a pH of 10.3, aluminium exists largely as insoluble amorphous aluminium hydroxide ($Al(OH)_3(am)$). The aqueous formation of ettringite should therefore not be possible below a pH of 10.3, since it is assumed that the aluminium must be present as the amphoteric species for ettringite to form. In addition to this, once the synthesis of ettringite takes place, its stability is pH dependent. Ettringite is an alkaline solid, which dissolves at a much lower pH. The stability of the mostly ettringite product is further enhanced if it contains additional alkaline components such as calcium hydroxide (portlandite), since the portlandite has additional acid-neutralizing potential. The optimum pH for ettringite decomposition takes place at a value of 6.5 (Petersen, 1998). Ettringite could also be thermally decomposed into calcium aluminate monosulphate and calcium sulphate hemi hydrate at high temperatures, which exceed 110°C (Hall *et al.*, 1996).

2. THE CHEMICAL PRECIPITATION PROCESS

2.1. Process Description

This precipitation process to remediate AMD involves the addition of lime to waste water to precipitate the metal hydroxides, and the subsequent formation of ettringite to remove the calcium and sulphates. The process consists of 5 main stages as described below and illustrated by Figure 1.

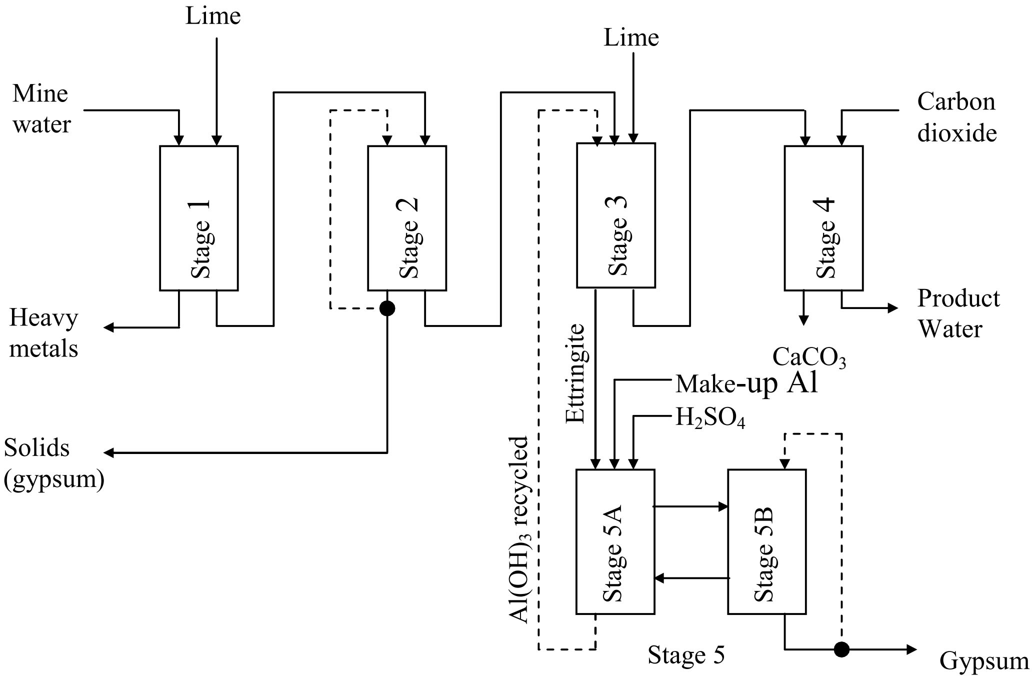

Figure 1. Ettringite process to treat AMD

Stage 1. Precipitation of heavy metals

Here the polluted mine water, at an approximate pH value of 6, is brought into contact with lime in order to raise the pH to greater than 11.5. These heavy metals are precipitated as hydroxides and although most metal hydroxide species will precipitate at relatively low pH values, a higher pH is required to precipitate magnesium. These hydroxides are sent away for land filling, as they are found to be stable.

Stage 2. Gypsum saturation

The solution from stage 1 is contacted with gypsum crystals in stage 2. One of the characteristics of dissolved calcium sulphate, is that when a suitable surface such as gypsum is not present to crystallize on it, it can be short lived or metastable at concentrations that exceed equilibrium solubility. For this reason the solution from stage 1 which is rich in calcium sulphate is brought in contact with gypsum, which results in the precipitation of the supersaturated gypsum. The precipitation of gypsum is not pH dependant, therefore the pH of the water exiting stage 2 will be the same as that entering stage 2, namely 11.5. This precipitated gypsum is thickened and filtered, and leaves the process as waste or as a by-product, depending on the specific situation. Part of the precipitated gypsum is returned to the mixing tank of stage 2 to provide the seed crystals for the rapid crystallization of the supersaturated portion of the dissolved calcium sulphate.

Stage 3. Ettringite precipitation

Stage 3 is the heart of the Ettringite process and involves the addition of aluminium hydroxide to the saturated gypsum solution from stage 2. This results in the formation of the insoluble salt known as ettringite, thereby removing both calcium and sulphate from the solution. The stoichiometry for ettringite precipitation is given by the following reaction:

$$6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O \rightarrow Ca[Al(OH)_6]_2(SO_4)_3 \,.\, 26H_2O \qquad (1)$$

The ideal conditions for ettringite formation range between pH values 11.4 and 12.4. In order to keep the pH between these limits, lime is added resulting in the maximization of ettringite precipitation. The end product of stage 3 is filtered and the solid ettringite proceeds to stage 5 while the liquid goes to stage 4.

Stage 4. Carbonation

The solution from stage 3, which is now free from all heavy metals, calcium and sulphates is treated with carbon dioxide to reduce the pH to between 6 and 8. Pure calcium carbonate is precipitated, and can be separated from the resulting product water by filtration. The pH can however also be controlled so that calcium bicarbonate is formed instead of calcium carbonate, but this however depends on certain case specific factors.

Stage 5. Regeneration of Aluminium Hydroxide

Ettringite slurry is transported to stage 5 so that it may decompose in order to regenerate the amorphous aluminium hydroxide for recycle. The decomposition of ettringite is achieved by bringing it into contact with sulphuric acid, which in turn lowers the pH of the slurry and thereby renders it unstable. The optimum pH for ettringite decomposition is 6.5 (Petersen, 1998). The decomposition reaction stoichiometry is the reverse of that for ettringite formation. The end of this stage is characterised by thickening and filtration, which separates into an aluminium hydroxide and gypsum. The gypsum is recycled to the beginning of stage 5 while the aluminium hydroxide is recycled as feed for stage 3.

3. ASPEN MODELLING

Simulating the ettringite process on an Aspen Plus simulation package serves as a useful tool to predict the behaviour of the process. It is a cost effective means of examining how the process is affected by using certain quantities of chemicals, various grades of polluted water, varying flow rates, and altering the split fractions at separators. Simulators are often used at the laboratory and pilot plant stages of plant design, and it is no different for this process. This simulation acts as a guideline as to how this process will react under actual conditions. Aspen Plus makes it possible to determine the effects of non-ideal conditions on ettringite formation and serves as a guide for the trends that are obtained when analyzing various sensitivities.

The Aspen simulation flow sheet is illustrated in Figure 2. The feed water (stream A) enters at a flow rate of 300m^3/h and has the following composition.

Table 1
Concentration of elements in the feed water

	Element							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}	Cl^-	SO_4^{2-}
Concentration (mg/L)	14.89	154.7	578	29.7	0.1	0.23	0.42	1614

Carbon dioxide gas is inserted at stream 1 so as to increase the pH of the feed water so that less lime is required to raise the pH to the heavy metal precipitation level. A 40% lime concentration was made-up at streams 2 and 15, and enters at a flow rate of 1036kg/hr, in order to adjust the pH at stages 1 and 3 respectively. 90% Sulphuric acid is added at stream 25 at a flow rate of 558.01kg/hr in order to decompose the ettringite from stage 3.

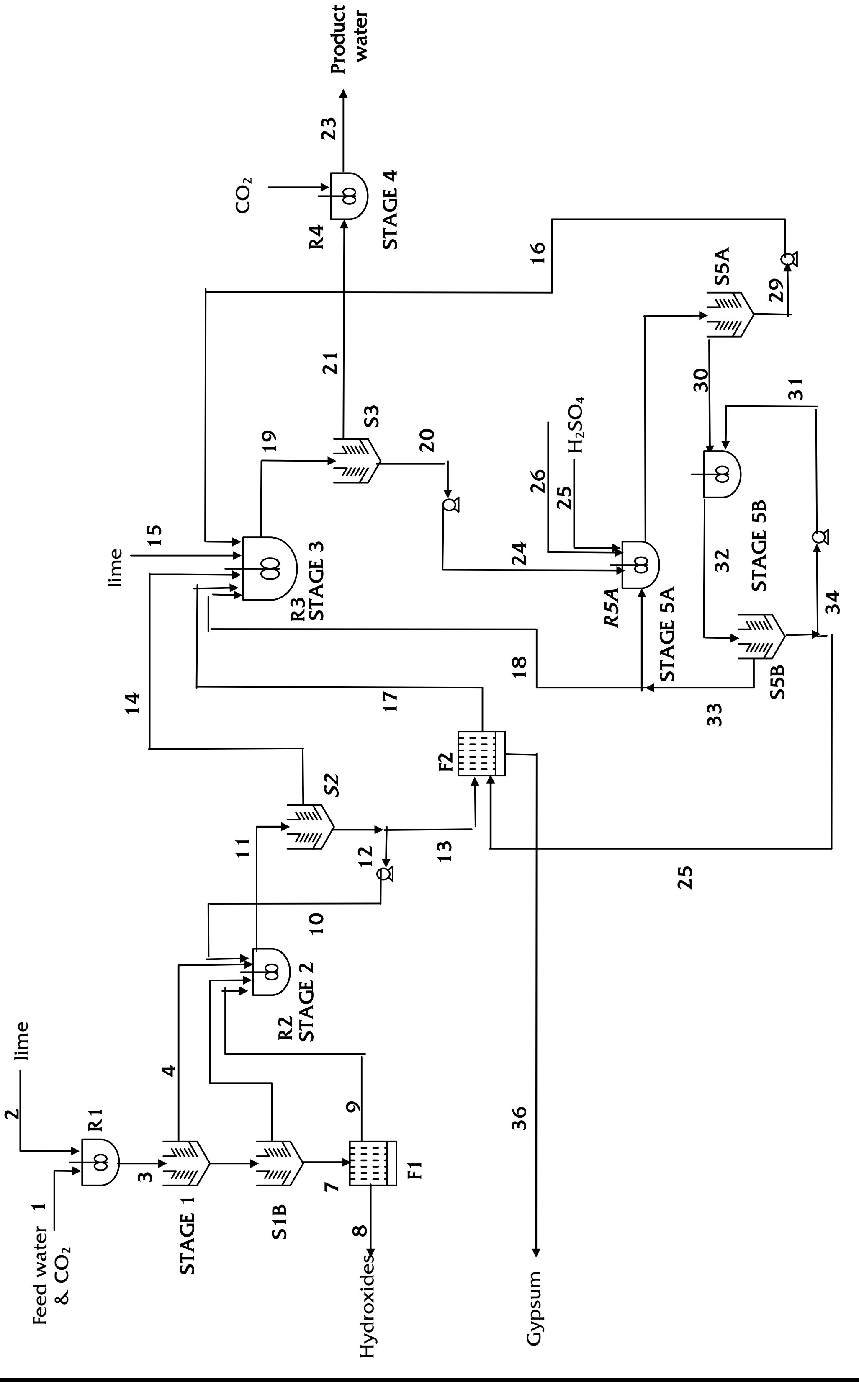

Figure 2. Aspen simulation flowsheet

The chemical reactions that take place at the various reactors (i.e. R1, R2, R3, R4, R5A, R5B) are tabulated in Table 2. To further enhance the model, certain design specifications were inserted into the system. These are tabulated in Table 3. Design specifications indicate to the program which variable needs to be changed in order to achieve a certain set point for another variable e.g. in order to keep the pH in stream 3 at 11.5, the composition of lime at stream 2 needs to be varied. This means that even though the composition and acidity of the feed water may change, the pH of stream 3 will remain constant.

Table 2
Chemical reactions at different stages of the process

Stages	Chemical reactions
Stage 1	$FeSO_4 \rightarrow Fe^{2+} + SO_4^{2-}$ $Al_2(SO4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$ $Fe_2(SO4)_3 \rightarrow 2Fe^{3+} + 3SO_4^{2-}$ $MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-}$ $Al^{3+} + 12H_2O \rightarrow Al_2(OH)_6$ (s) $+ 6H_3O^+$ $Fe^{3+} + 6H_2O \rightarrow Fe(OH)_3$ (s) $+ 3H_3O^+$ $Fe^{2+} + 4H_2O \rightarrow Fe(OH)_3$ (s) $+ 2H_3O^+$ $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$ $Ni^{2+} + Ca(OH)_2 \rightarrow Ni(OH)_2$ (s) $+ Ca^{2+}$ $Zn^{2+} + Ca(OH)_2 \rightarrow Zn(OH)_2$ (s) $+ Ca^{2+}$ $Ca^{2+} + 2F^- \rightarrow CaF_2$ (s)
Stage 2	$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow$ gypsum
Stage 3	$CaOH^+ \rightarrow Ca^{2+} + OH^-$ $Ca(OH)_2$ (s) $\rightarrow Ca^{2+} + 2OH^-$ gypsum (s) $\rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$ $6Ca^{2+} + 3SO_4^{2-} + Al_2(OH)_6$ (s) $+ 37H_2O \rightarrow$ ettringite (s) $+ 6H_3O^+$ $H_3O^+ + OH^- \rightarrow 2H_2O$
Stage 4	$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3 + H_2O$
Stage 5	
Reactor 5A	ettringite (s) $\rightarrow 3Ca(OH)_2 + Al_2(OH)_6$ (s) $+ 3CaSO_4 + 25\ H_2O$ $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$ $Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$ $H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$ $HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$ $H_3O^+ + OH^- \rightarrow 2H_2O$
Reactor 5B	$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow$ gypsum

3.1. Convergence

For Aspen to solve the unknown stream variables in the recycling loops, it uses a solution technique, which is based on tear stream guesses. In the recycle loop, a guess is taken of the variables of one of the streams (tear stream) in the loop and information is passed from unit to unit until new values of the variables in the tear stream are computed. These new values are used to repeat the calculations until the convergence tolerances are satisfied. The tolerances specified in this program are all less than 0.001. This is the principle behind the method of successive substitutions for convergence. Upon satisfying the convergence criteria, control is transferred to the unit following the recycle loop in the calculation order. This method of tearing streams is not only implemented in stream recycle loops, but it is also used to solve design specification recycle loops.

Table 3
Design specifications of the Aspen model.

Design Spec. of set point	Vary variable to achieve set point
flow rate of feed water =300 m^3/hr	mass flow of feed (stream A)
pH (stream 1) = 9.5	mass flow of CO_2 (stream AA)
pH (stream R1) = 11.7	mass flow of lime (stream B)
% solids entering reactor R2 = 5%	flow fraction of stream 12
pH (stream R3) = 11.95	mass flow of lime (stream D)
[SO_4^{2-}] at stream R3 = 200ppm	conversion of SO_4^{2-} in the ettringite formation reaction (stage 3)
pH (stream R4) = 8.5	mass flow of CO_2 (stream 22)
pH (stream R5A1) = 9	mass flow of H_2SO_4 (stream 25)
% solids entering reactor R5B = 5%	flow fraction of stream 34
ratio of SO_4^{2-} entering reactor R3 to solids entering reactor R5A = 1.59 (for every kg of SO_4^{2-} fed to stage 3, ~ 1 kg of $Al(OH)_3$ is fed to stage 5)	mass flow of stream 26
Metal hydroxides(stream 8) = 25% solids	flow fraction of stream 8
Gypsum(stream 36) = 60% solids	flow fraction of stream 36
% solids in stream 5 = 1.5%	flow fraction of stream 5
% solids in stream 7 = 5%	flow fraction of stream 7
% solids in stream S2 = 30%	flow fraction of stream S2
% solids in stream 20 = 15%	flow fraction of stream 20
% solids in stream 29 = 15%	flow fraction of stream 29
% solids in stream S5B = 30%	flow fraction of stream S5B
[Ca^{2+}] at stream R5A =1.5kg/m^3	flow fraction of stream 27

4. RESULTS AND DISCUSSION

Potable water (Ca^{2+} < 150ppm; SO_4^{2-} < 200ppm) was recovered by treating AMD using the Aspen modeling approach. Table 4 shows the removal of 97% calcium and 87.6% sulphate over the entire system. This Table also shows the removal of all the magnesium, while virtually no sodium ions were removed from the system.

Table 4
Percentage removal of species from solution as predicted by Aspen model.

Components	Ca^{2+}	SO_4^{2-}	K^+	Na^+	Mg^{2+}
Feed water (ppm)	578	1614	154.7	14.89	29.7
Product water (ppm)	17.2	199.8	1.44	14.83	0.01
% removal	97	87.6	99	0	100

Stage 3 produced 3997kg/hr of ettringite while 373kg/hr of gibbsite was recycled. A sensitivity analysis was performed on the model.

4.1. Calcium sulphate in the feed water

By varying the $CaSO_4$ in the feed water means that varying quantities of Ca^{2+} and SO_4^{2-} ions will be available at stage 3 to react to form ettringite. An increase in the concentration of $CaSO_4$ in the feed water will lead to a linear increase in Ca^{2+} and SO_4^{2-} in solution at stage 1. The K_{sp} of $CaSO_4$ is 2.01×10^{-4}, making it soluble in water. However, for high degrees of oversaturation, the $CaSO_4$ solution will experience rapid precipitation through spontaneous nucleation and crystal growth. $CaSO_4$ is saturated in water at 1852ppm. At this level and at fairly low degrees of oversaturation (metastable region), no noticeable precipitation will occur for long periods of time (Benefield *et al.*, 1982). $CaSO_4$ crystallizes as insoluble gypsum upon reaching a concentration of 2105ppm, since it is outside the metastable region. The Ca^{2+} and SO_4^{2-} concentrations increase until crystallizes takes place, after which it remains constant. When the Ca^{2+} and SO_4^{2-} concentration remains constant, precipitated gypsum is formed which is removed with the metal hydroxides at stream 8. The dissolved $CaSO_4$ is contacted with gypsum crystals from stage 2. This is to enable the precipitation of $CaSO_4$. Virtually no $CaSO_4$ is precipitated while the $CaSO_4$ concentration is below 1930ppm. This is in contrast to gypsum first precipitating when the $CaSO_4$ was at 2105ppm. This is because of the presence of gypsum crystals in stage 2 catalyses the precipitation of gypsum when dissolved $CaSO_4$ is saturated and metastable. After the $CaSO_4$ is at a saturated level, their exists a linear increase in the gypsum precipitated at stage 2.

A result of the precipitation of gypsum is that an increase in $CaSO_4$ in the feed water will lead to a linear increase in the Ca^{2+} and SO_4^{2-} concentration being fed to the ettringite formation stage (stage 3), until the $CaSO_4$ is at its saturation point. This is depicted in Figure 3(a), which shows that 1496ppm SO_4^{2-} and 622ppm Ca^{2+} leaves stage 2 for stage 3 once saturation of $CaSO_4$ takes place. This means that whenever AMD containing supersaturated quantities of $CaSO_4$ is fed into this process to be treated, by the time the dissolved $CaSO_4$ reaches the ettringite formation stage, it will be at its saturation level. This inevitably means that a constant amount of ettringite will be formed when supersaturated quantities of $CaSO_4$ is fed to stage 1. When undersaturated quantities of $CaSO_4$ are fed to stage 1, this leads to a linear increase in the amount of ettringite formed.

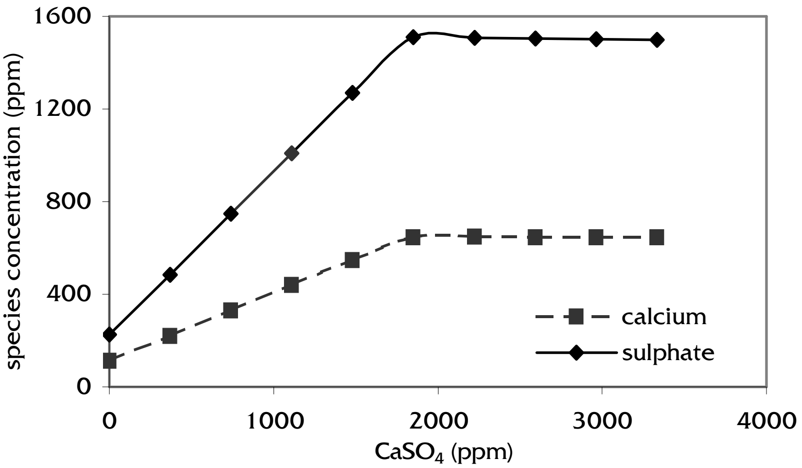

Figure 3(a). Aspen results of varying $CaSO_4$ in the feed water vs. species fed to stage 3

The program is written in such a way that the amount of ettringite formed is dependent on the amount of sulphate given off and this sulphate converted increases, as more sulphate is made available. The amount of sulphate converted to ettringite also affects the amount of calcium and gibbsite being removed at stage 3 by the formation of ettringite. Figure 3(b) shows that an increase in $CaSO_4$ into the feed water results in an increase in the amount of sulphate being converted to ettringite until it remains constant (~87%), while the calcium and aluminium hydroxide increase until saturation of $CaSO_4$ takes place. Thereafter 72% and 39% are removed from the system respectively. As more ettringite is formed, so less calcium and gibbsite is left as residue exiting stage 3. However, by decomposing more ettringite, more gibbsite will be formed, but the trend shows a decreases in the recycle of gibbsite (Figure 3(c)). This is because the amount of gibbsite entering stage 5 is more than that being formed. As with the formation of ettringite, once supersaturated $CaSO_4$ is fed to stage 1, the gibbsite recycled will remain constant at 611kg/hr.

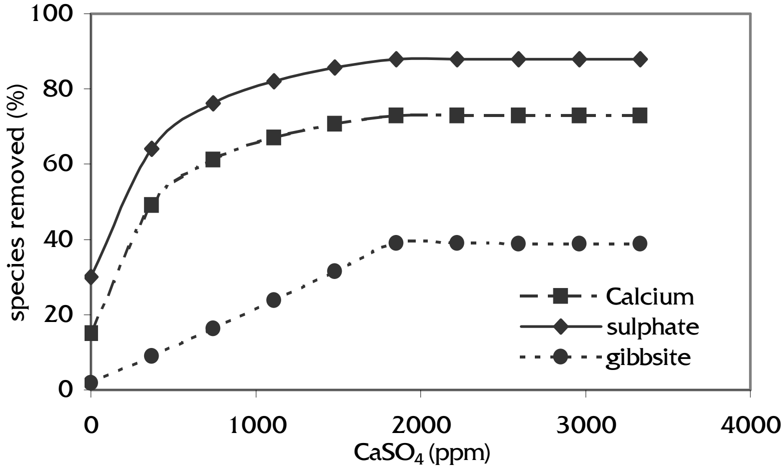

Figure 3(b). Aspen results of varying $CaSO_4$ in the feed water vs. percentage species removed at stage 3

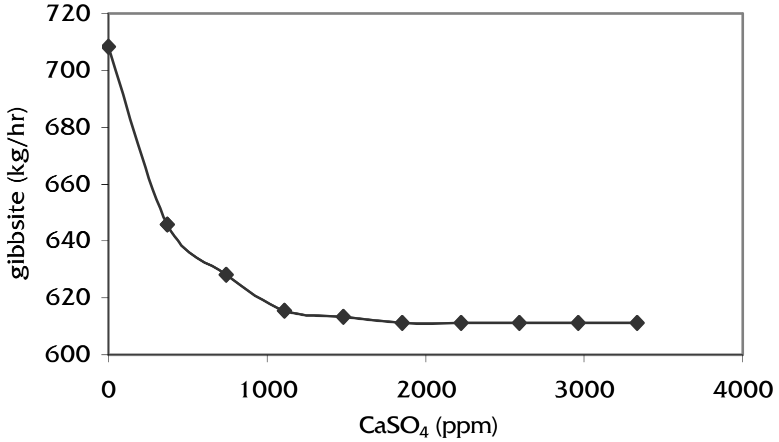

Figure 3(c). Aspen results of varying $CaSO_4$ in the feed water vs. gibbsite recycled

4.2. Mono-valent cations in feed water

The presence of Na^+ and K^+ in the feed water has the effect that alters the solubility of the sulphate in the water. The preliminary results (Table 1.) showed that the feed water contained 15ppm Na^+. At this concentration and at a pH of 9.5 in stream 1, sulphate had a solubility of 1.697g/L. As more sodium was added to the feed water, so the solubility of sulphate increased as can be seen by Figure 4. Therefore, in the presence of mono-valent cations the concentration of sulphate leaving stage 2 is substantially higher resulting in larger quantities of ettringite being formed. These cations however do not affect the formation and decomposition of ettringite nor the recycling of gibbsite.

4.3. $[Ca^{2+}]/[SO_4^{2-}]$ ratio at stage 3

At stage 3, the formation of ettringite is dependent on the conversion of sulphate in the ettringite formation reaction. This means that the mole flow of calcium taking part in this reaction is dependent on the sulphate taking part in the reaction. An increase in the $[Ca^{2+}]/[SO_4^{2-}]$ ratio entering stage 3 (ettringite formation stage) therefore results in less ettringite being formed (Figure 5). The increase in ratio is due to an increase in calcium or otherwise a decrease in the amount of sulphate at this stage. Ettringite formation first uses the mole flow of sulphate at its disposal, and then calculates how much calcium, gibbsite and water is required for this reaction. Therefore, if less sulphate reacts, then less calcium, gibbsite and water will react, and therefore less ettringite will be formed. This explains why more sulphate is always removed than calcium. All the sulphate is not removed because the ettringite formation reaction converts 90% of the mole flow of sulphate into ettringite and this model also ensures that stream R3 contains 0.2kg/m^3 of sulphate. An increase in the [Ca^{2+}]/[SO$_4$$^{2-}$] ratio results in a decrease in the amount of gibbsite produced when 95% of the ettringite is decomposed. Less gibbsite produced at this stage, means more gibbsite is recycled back to stage 3 because of the large quantity of gibbsite entering stage 5.

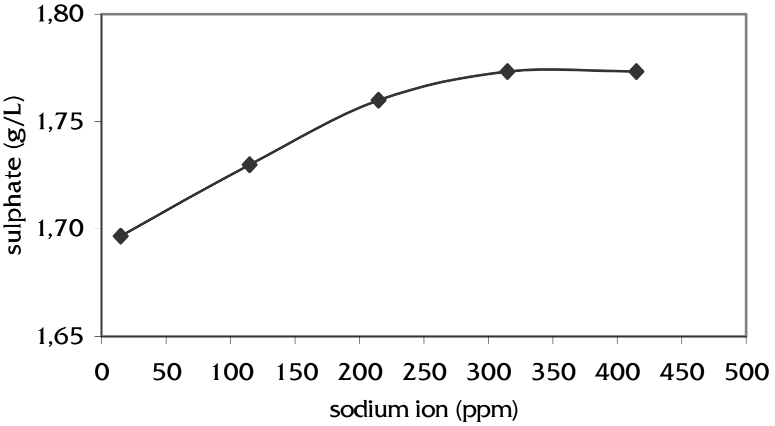

Figure 4. Aspen results showing Na$^+$ in feed water vs. the solubility of sulphate

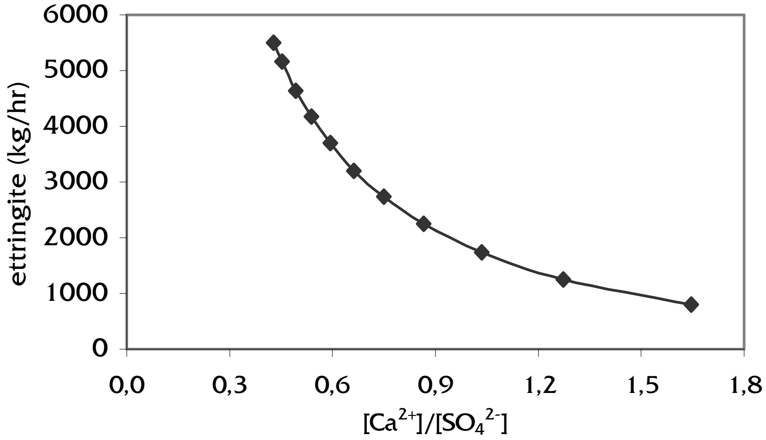

Figure 5. Aspen results showing the effect the calcium to sulphate ratio on ettringite produced

4.4. Decomposition of ettringite

The decomposition of ettringite takes place due to the stoichiometric reaction (2) at stage 5:

$$\text{ettringite (s)} \rightarrow 3Ca(OH)_2 + \text{gibbsite (s)} + 3CaSO_4 + 25\ H_2O \qquad (2)$$

As more ettringite decomposes, so more gibbsite will be formed and ultimately more gibbsite will be recycled as shown by Figure 6(a). In order to meet all the conditions of the recycle loop, a large amount of ettringite needs to be made available to be decomposed when very little decomposition of ettringite takes place. This also means that when very little ettringite is decomposed, a large amount of ettringite will be recycled (Figure 6(a)). It would therefore not make economic sense if decomposition is low. When the decomposition of ettringite is between 10% and 43%, all the gibbsite that is formed and recycled is once again used to form ettringite at stage 3. This results in a 100% removal of gibbsite when ettringite is formed. As more ettringite is decomposed between these decomposition ranges, so more sulphate and calcium is also recycled and ultimately reacts to form ettringite (Figure 6(b)).

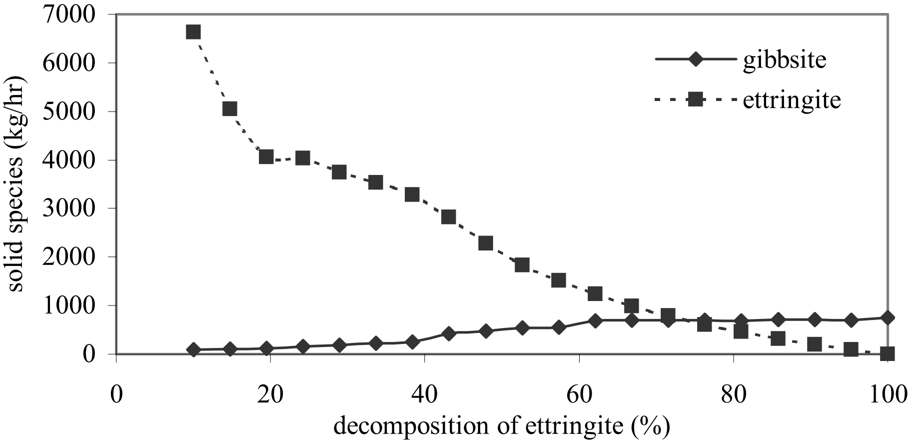

Figure 6(a). Varying the decomposition of ettringite vs. solid species recycled

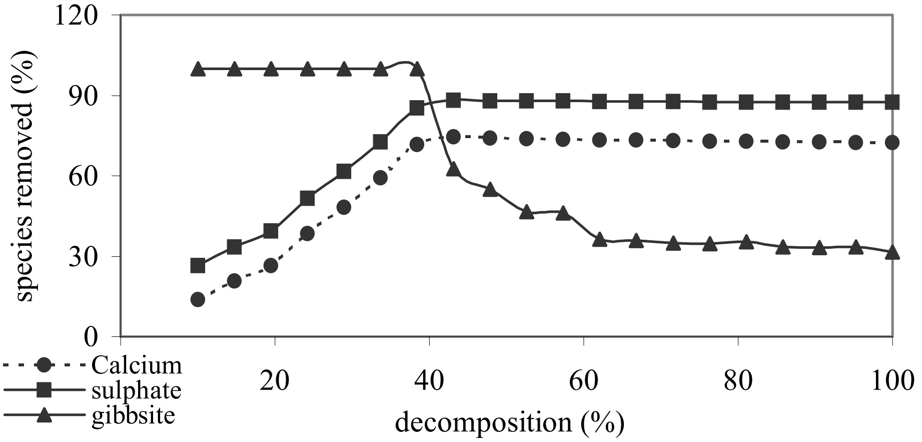

Figure 6(b). Varying the decomposition of ettringite vs. percentage species removed at stage 3

When more than 43% of ettringite is decomposed, enough gibbsite is formed and recycled in order to meet the demand set for ettringite formation. From this point onwards, the amount of sulphate entering stage 3 remains constant and therefore a constant removal of sulphate to form ettringite takes place. The increasing amount of gibbsite recycled as more ettringite is decomposed means that less of this gibbsite will react to form ettringite when the amount of sulphate reacting at stage 3 remains constant (Figure 6(b)). This results in a fairly constant formation of ettringite.

4.5. Reagent costs

The uses of reagents are of paramount importance to the treatment of wastewater in this process. The success and economic viability of the process is largely dependent on the costs incurred while running this plant. Results from the preliminary model showed that the total reagent costs amounted to R0.81 per m^3 of feed water used. These costs are calculated using slaked lime ($Ca(OH)_2$) at R313/ton, carbon dioxide at R400/ton and H_2SO_4 at R320/ton. These estimates were obtained from MINTEK, South Africa and it is interesting to notice that the amount of lime used has the greatest effect on the total reagent costs. Reagent costs will vary depending on the quality of water produced, namely agricultural water (Ca^{2+} < 300ppm, SO_4^{2-} < 500ppm), potable (Ca^{2+} < 150ppm, SO_4^{2-} < 200ppm), and high quality industrial water (Ca^{2+} < 50ppm, SO_4^{2-} < 50ppm).

As the quality of the water increases, so the reagent costs increase as shown by Figure 7(a). When the $CaSO_4$ in the feed water was increased (see Figure 7(b)), reagent costs increased while the calcium sulphate was unsaturated. As more ettringite is formed, so also more H_3O^+ is formed, which leads to a drop in pH. Since the pH needs to be at a certain level (i.e. 11.95), more lime needs to be added to meet this condition. The increase in the reagent costs is also due to the increasing quantities of sulphuric acid needed to break down the increasing amount of ettringite at stage 5. When ettringite decomposes, OH^- ions are given off, which increases the pH. The pH however needs to remain at 7. This requires the addition of sulphuric acid to drop the pH. Once $CaSO_4$ reaches saturation point, the reagent cost stay constant at R1.06 per m^3 of feed water used. When the flow rate of the feed water is varied the reagent costs remain fairly constant at R 0.81/m^3. (Current exchange rate: 1US $ = R 11.34, 1€ = R9.88; 2002)

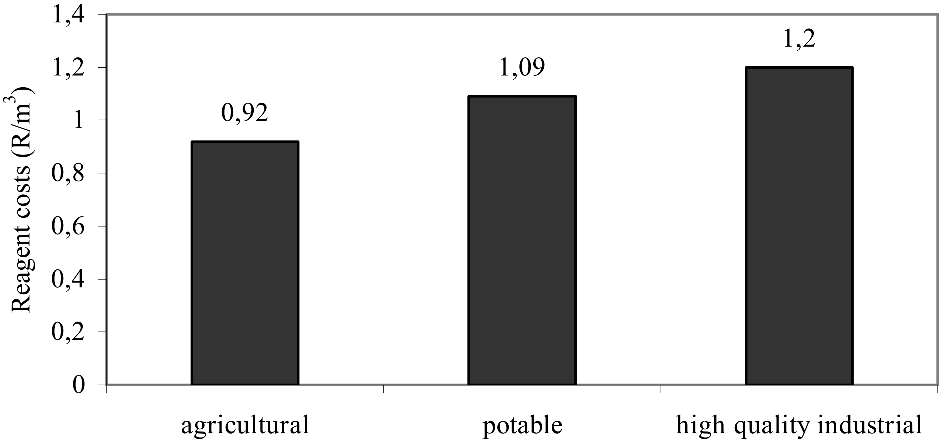

Figure 7(a). Aspen results of varying quality of water vs. total reagent costs

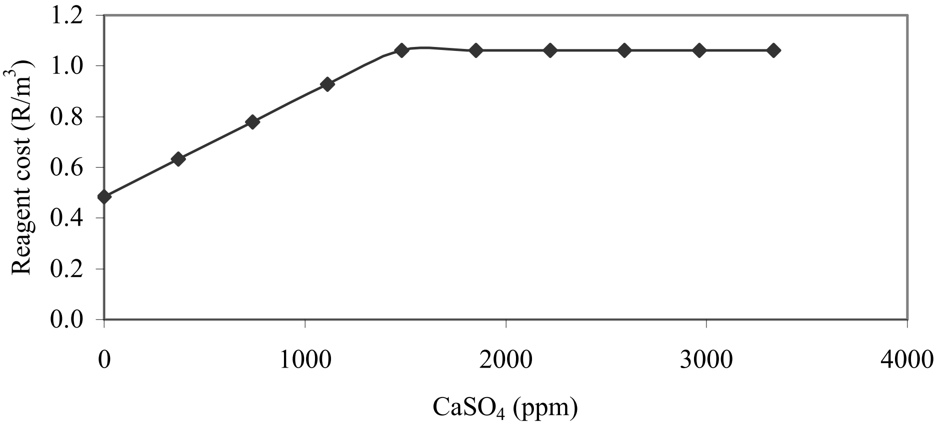

Figure 7(b). Aspen results of varying the $CaSO_4$ in the feed water vs. the total reagent costs

5. CONCLUSIONS

This process, which was modeled on an Aspen simulation package, is able to treat water that contains small as well as large quantities of $CaSO_4$. The modeling was done in such a way as to produce water of a potable quality (Ca^{2+} < 150ppm; SO_4^{2-} < 200ppm). Metal hydroxides, especially magnesium hydroxide, precipitate at high pH ranges at stage 1, and virtually all the metals are removed here. When the feed water contains a high degree supersaturated $CaSO_4$, it precipitates as an insoluble gypsum that is also removed at stage 1. Calcium and sulphate is removed from the water at stage 2 where $CaSO_4$ is contacted with gypsum. The formation of $CaSO_4$ at this stage is so that when supersaturated $CaSO_4$ is fed into the process, the Ca^{2+} and SO_4^{2-} leaving stage 2 will remain the same (i.e. Ca^{2+} = 622ppm and SO_4^{2-} = 1496ppm).

A constant supply of sulphate to stage 3 will lead to a constant formation of ettringite. An increase in the presence of mono-valent cations like Na^+ and K^+ in the feed water increases the solubility of SO_4^{2-}, which ultimately results in more ettringite being produced. None of the mono valent cations are however removed during the treatment water in this process. Decomposition takes place at about a pH a 7 and it is assumed that 95% of the ettringite is decomposed to gibbsite. An increase in the [Ca^{2+}] to [SO_4^{2-}] into stage 3 will result in less ettringite being formed as less sulphate is being made available to be converted to ettringite. Reagent costs are largely dependent on the amount of ettringite formed and decomposed. An increase in the amount of ettringite formed results in more lime being used and an increase in the amount of ettringite decomposed results in more H_2SO_4 being used.

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