LIMESTONE NEUTRALISATION OF ACIDIC EFLUENT, INCLUDING METAL AND PARTIAL SULPHATE REMOVAL

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ABSTRACT

This paper describes a novel process for the neutralisation of acid streams produced during coal mining and processing. The leachate from a waste coal dump was neutralised with limestone for the removal of iron, aluminium and sulphate. Specific aspects studied were the process configuration, the rates of iron(II) oxidation, limestone neutralisation and gypsum crystallisation, the chemical composition of the effluents before and after treatment, the efficiency of limestone utilisation and the sludge solids content.

The acid content is reduced from 12 000 to 300 mg/ℓ (as $CaCO_3$), sulphate from 15 000 to 2 600 mg/ℓ (as SO_4), iron from 5 000 to 10 mg/ℓ (as Fe), aluminium from 100 to 5 mg/ℓ (as Al) while the pH increases from 2,2 to 7,0. Reaction times of 2.0 and 4.5 h are required under continuous and batch operations respectively for the removal of 4 g/ℓ iron(II) (as Fe) . The iron(II) oxidation rate equation is a function of the iron(II), hydroxide, oxygen and suspended solids concentrations. The optimum suspended solids concentration for iron(II) oxidation in a fluidised-bed reactor is 190 g/ℓ. Upflow velocity has no influence on the rate of iron(II) oxidation in the range 5 to 45 m/h. Sludge with a high solids content of 55 % (m/v) is produced. This is high compared to the typical 20 % achieved with the High Density Sludge process in the case of lime neutralisation. Neutralisation cost of acid water can be reduced significantly with the integrated iron(II) oxidation and limestone neutralisation process as limestone instead of lime is used and sludge with a high solids content is produced. The alkali cost to treat discard leachate with an acidity of 10 g/ℓ (as $CaCO_3$) amounts to R5.15/m³, R2.79/m³, R1.37/m³ and R1.95/m³ for slaked lime, unslaked lime, limestone milled on-site and purchased limestone, respectively. The expected capital cost for a 1 Ml/d integrated iron(II) oxidation and neutralisation plant is R1.87 million when the alkali is purchased and R1.87 million when limestone is milled on-site.

INTRODUCTION

Coal mining and fertiliser manufacturing are examples of industrial operations which can give rise to severe acid pollution of the environment unless appropriate treatment is applied. During coal mining acid water is formed as a result of bacterial oxidation when pyrites are exposed to oxygen and water after or during the mining process.. When the pH is below 5.5, water can be toxic to plant and fish life and corrosive to pipelines and equipment. Sludge disposal resulting from neutralisation of such effluents with lime or limestone is costly. The volume of sludge to be disposed can be reduced by increasing the

solids concentration. Currently, acid water is neutralised with lime and then re-used. Apart from its dependence on lime, which is costly, this practice results in the scaling of equipment by the unstable water produced, malfunctioning of dosing equipment and settling of particles in pipelines and valves. The latter often causes blockages which may result in under-dosage, which in turn leads to acid corrosion. In contrast, limestone is relatively cheap and readily available, process control is simplified (no pH-control is required as limestone dissolution essentially occurs at pH-values below 7), and material wastage through overdosage is minimised. Also limestone is non-hazardous and easy to store. Raw material can be stockpiled in the open as $CaCO_3$ is not readily soluble in neutral water.

The fluidised-bed limestone neutralisation process has been developed to neutralise free acid and remove iron(III) and aluminium(III) concomitantly (Maree, et al., 1992; du Plessis and Maree, 1994; Maree and du Plessis, 1994; Maree, et al.,1996a; Maree, 1994; Maree 1995; Maree, et al., 1996b.). Previous studies showed that:

* Complete neutralisation of discard leachate containing (10 g/ℓ acid (as $CaCO_3$) and 4 000 mg/ℓ iron(II) (as Fe)) can be achieved in a limestone neutralisation fluidised-bed reactor, provided that the iron(II) is oxidised beforehand (Maree, et al., 1998a).
* Iron(II) can be oxidised biologically to iron(III). The rate of iron(II) oxidation is related to the surface area of the support medium. With plastic medium (specific surface area 200 m²/m³) a residence time of 18 h is required for water containing 4 g/ℓ iron(II) (as Fe) (Maree, et al., 1998b).
* When 300 mg/ℓ magnesium (as Mg) is present, sulphate can be reduced from 18 000 mg/ℓ (as SO_4) to less than 2 500 mg/ℓ by gypsum crystallisation. With a fluidised-bed contactor, a residence time of 2 h is required.

For treatment of iron(II)-rich water, a multiple-stage limestone neutralisation system is required. The expected capital cost of such a system is unacceptably high as a result of the long residence time required for iron(II) oxidation. The integrated iron(II) oxidation and limestone neutralisation process was developed to overcome this disadvantages.

An integrated neutralisation process consists of a neutralisation reactor and a clarifier. Discard leachate is treated in an aerated sludge reactor into which powder limestone (<200 µm) is dosed to a level slightly in excess of stoichiometrical requirements. Iron(II) oxidation is achieved within 2 h when the plant is operated in sequential batch mode and within 5 h under continuous conditions. Gypsum crystallises to an over-saturation index less than 1.1. The clarifier is required to return sludge to the neutralisation reactor to maintain a minimum concentration of suspended solids.

The objectives of this investigation were to determine the quality of treated water and sludge solids content when discard leachate is neutralised with the integrated iron(II) oxidation and limestone neutralisation process to determine the economic feasibility of the process and to obtain design criteria for full-scale implementation.

MATERIALS AND METHODS

Feedstock

A synthetic solution, similar to leachate from a waste coal dump, was used as feed water. The solution contained 4 000 mg/ℓ Fe(II), 40 mg/ℓ P, 20 mg/ℓ Mg, 30 mg/ℓ N, 8 900 mg/ℓ SO$_4$ and 9 200 mg/ℓ acidity (as CaCO$_3$). Limestone from Rustenburg and sodium hydroxide were used for neutralisation.

Batch studies in beakers

Batch studies were conducted in 0.5, 1.0, 2.0 and 5.0 l beakers at atmospheric pressure to determine the rate of iron(II) oxidation and neutralisation. The specific surface areas of the beakers were 58.1, 46.2, 36.8 and 27.3 m²/m³ respectively. The following steps were followed:
* Each batch test was started by mixing the treated contents from the previous batch with the synthetic feed, in a ratio varying from 1:1 to 1:4. An excess amount of CaCO$_3$ (up to 40 %) was applied over the amount required to ensure complete iron(II) oxidation to iron(III) and precipitation of the latter as Fe(OH)$_3$. NaOH additions were made as required to maintain the pH at a specific value when the influence of pH was determined.
* The reactor contents was aerated continuously. Filtered samples were taken regularly and analysed for iron(II), oxygen, acidity, sulphate and pH.
* Aeration was stopped when the iron(II) was completely oxidised to iron(III), whereafter the appropriate amount of the iron(III)-containing mixture was replaced with a fresh iron(II) solution.
* Aeration was restarted and the procedure described above repeated.

Batch and continuous studies on pilot scale

A pilot plant (Figure 1 and Table 1) consisting of a fluidised-bed reactor and a sludge separator was used for batch and continuous studies. During batch studies water was recycled through a fluidised-bed consisting of slimes/limestone/gypsum and during continuous studies through both the fluidised-bed reactor and the sludge separator. The purpose of the sludge separator during continuous operation was to prevent wash-out of support medium in an uncontrolled manner. Compressed air was used for iron(II) oxidation.
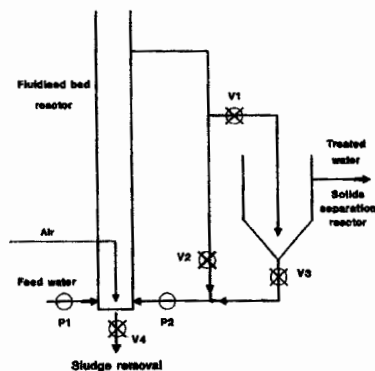
P1 - Feed pump; P2 - Recycle pump; V1, V2, V3 & V4 - Valves

Figure 1. Schematic diagram of integrated iron(II) oxidation/limestone neutralisation pilot plant (hg3:\intlsp).

Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, acidity and pH determinations were carried out manually according to procedures described in Standard Methods (APHA, 1985), and iron(II) as described in Vogel (1989). Calcium was analysed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH.

RESULTS AND DISCUSSION

Water quality

Limestone can be used in the integrated process for treatment of acid water. Table 2 shows the results when synthetic discard leachate was treated with limestone. The water was neutralised effectively and sulphate was reduced from 8 342 to 1 969 mg/ℓ (as SO_4).

Kinetics

Stumm and Lee (1961) determined the following relationship between the iron(II) oxidation rate and pH in the absence of micro-organisms for clear solutions (Equation 1).

$$-d[Fe(II)]/dt = k[Fe(II)][OH^-]^2P_{O2} \qquad (1)$$

where

$-d[Fe(II)]/dt$	-	rate of iron(II) oxidation;
k	-	reaction rate constant;
$[Fe(II)]$	-	iron(II) concentration (moles/ℓ);
$[OH^-]$	-	hydroxide concentration (moles/ℓ);
P_{O2}	-	partial pressure of oxygen (mm Hg).

It appears that iron(II) oxidation occurs either at pH levels less than 4 when catalysed by bacterial activity, or at pH values greater than 6 through chemical oxidation. Maree *et al.* (1987) showed that the rate of chemical iron(II) oxidation is also catalysed by suspended solids. The result is that the lower limit of the pH range where the rate of chemical oxidation is fast enough for practical application is reduced from 6.5 to 5.0. The integrated iron(II) oxidation and limestone neutralisation process is based on this finding as limestone can raise the pH of iron(II)-rich water to between 5 and 6. Volumetric iron(II) oxidation rates exceeding 100 g/(ℓ.d) were achieved when artificial acid mine water was treated with powdered limestone and pure oxygen in a sludge contact reactor. Neutralisation and partial sulphate removal were achieved as well.

The relative importance of various factors in terms of their influence on the rate of iron(II) oxidation was determined by a series of controlled tests in which the dependence of the rate on one variable at a time was determined. In the pH range 5 to 6, which is of importance from the point of view of limestone neutralisation, the iron(II) oxidation rate was assumed to have the following functional form:

Table 1. Dimensions of pilot plant (sc:\dat\iawq97ct).

Table 2. Chemical composition of feed and treated water (in mg/ℓ where applicable) when synthetic discard leachate was treated with limestone.

Parameter	Value	
	Fluidised-bed	Solids separation
Feed rate (ℓ/h)	24	
Recycle rate (ℓ/h)	200	
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Upflow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

Parameter	Feed (Synthetic discard leachate)	Treated (Limestone)
pH	1.8	6.6
Acidity (as $CaCO_3$)	7 300	100
Sulphate	8 342	1 969
Ortho phosphate (as P)	2.9	0.0
Chloride	27	30
Iron(II)	2 500	56
Total iron	2 500	56
Aluminium	6.8	7.3
Manganese	15.7	21.8
Magnesium	35	45
Calcium	40	682
Sodium	25.2	29.5

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{n1}.[O_2]^{n2}.[OH^-]^{n3}.[RSA]^{n4}.[SS]^{n5}.M^{n6} \qquad (2)$$

where

$-d[Fe^{2+}]/dt$ or R	=	rate of iron(II) oxidation	$[OH^-]$	=	hydroxide concentration (moles/ℓ)
k	=	reaction rate constant	RSA	=	reactor surface area (m^2/m^3)
$[Fe^{2+}]$	=	iron(II) concentration (moles/ℓ)	$[SS]$	=	suspended solids concentration (g/ℓ)
			M	=	mixing intensity (rpm)
$[O_2]$	=	oxygen concentration (moles/ℓ)			

By varying the value of only one parameter in a series of experiments, say $[Fe^{2+}]$, equation 2 kan be written as:

$$-\partial[Fe^{2+}]/\partial t = K.[Fe^{2+}]^{n1} \quad \text{or} \quad \log(-\partial[Fe^{2+}]/\partial t) = \log K + n_1 \log [Fe^{2+}] \qquad (3)$$

where $\quad K = k.[O_2]^{n2}.[OH^-]^{n3}.[RSA]^{n4}.[SS]^{n5}.M^{n6}$

The contribution, n_1, of iron(II), to the overall reaction rate was determined from the slope of the graph obtained by plotting log R versus log $[Fe^{2+}]$. From pH, log R was plotted against log$[OH^-]$ ($[OH^-] = 10^{pH-14}$). The data in Table 3 show that the rate of iron(II) oxidation is of order 0.42 ($\approx$ 0.5), 1.41 ($\approx$ 2), 0.51 ($\approx$ 0.5), 0.37 ($\approx$ 0.5) and 0.43 ($\approx$ 0.5) in respect of Fe^{2+}, OH^-, O_2 and SS concentrations, and mixing intensity (M), respectively. The findings suggest that the rate equation as proposed by Stumm and Lee (1961) for clear solutions, should be modified for suspensions to:

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{\frac{1}{2}}.[OH^-]^{1.5}.[O_2]^{\frac{1}{2}}.[SS]^{\frac{1}{2}}.M^{\frac{1}{2}} \qquad (4)$$

Other conclusions to be drawn from Table 3 include the following:

* The rate of iron(II) oxidation in suspensions with high concentrations of suspended solids in the pH range 4.5 to 5.5 is dominated by chemical oxidation. This was concluded from studies where experiments were carried out on sterilised and unsterilised suspensions respectively (Table 3, Experiments 1 and 2). This finding contradicts that reported by Maree *et al.* (1997). In the previous study chemical iron(II) oxidation was studied by using a clear solution (the only solids present was that which precipitated from solution during iron(II) oxidation and neutralisation) and was compared with biological iron(II) oxidation where solids were present from the start of the experiment (medium to support bacterial growth). The slower oxidation rates determined for chemical iron(II) oxidation at pH values between 5 and 5.5 should be ascribed to lower suspended solids concentrations and not to the absence of bacterial activity.

* In a previous investigation Maree *et al.* (1997) determined that the rate of iron(II) oxidation in the pH range 4.5 to 6 is influenced by the reactor surface area (RSA). It was pointed out that this behaviour is in line with the behaviour of iron(II) oxidation in the pH range 2 to 3 where the rate is directly proportional to the square root of the medium specific surface area (Maree *et al.*, 1998). The current investigation, however, shows that chemical iron(II) oxidation in the pH range 4.5 to 6 is not influenced by the medium specific surface area (RSA), but by the mixing intensity, M. In the previous investigation the values of RSA and M were varied simultaneously. This happened as beakers of different sizes were used to provide different RSA values (see Table 3, Experiment 8 for the relationship between RSA and beaker volume). Unfortunately, the mixing intensity decreases when larger beakers are used if the stirring rate is not adjusted accordingly (Table 3, Experiments 6 and 7). The iron(II) oxidation rate increases with increased mixing intensity.

The Arrhenius equation $\log k = \log A - E/(2.303RT)$ can be used to estimate the value of the reaction rate k at other temperatures. The amounts E, R and $\log A$ have the values 21.55 kcal/mole (activation energy), 13.70 (a constant) and 1.987 cal mole^{-1} degree^{-1} (gas constant) respectively (Table 3, Exp 9). A linear relationship was obtained over the range 5 to 25 ^{0}C. It is expected that the linear relationship will fail at higher temperatures as optimum reaction rates are often achieved at 37 ^{0}C.

Design criteria for continuous operation

Oxygen versus air

The iron(II) oxidation rate increases with increased oxygen concentrations (Table 4). For a specific oxygen concentration (0.2 mg/ℓ) similar reaction rates are measured for pure oxygen and air (between 44.9 and 65.8 g Fe/(ℓ.d)). Although high iron(II) oxidation rates can be achieved by dosing pure oxygen, air is a more suitable oxidant for full-scale application due to safety reasons.

Table 3. Effect of various factors on the kinetics of iron(II) oxidation (sc23:amc97.p03).

Exp No	Variable	Value	Rate g Fe/(l.d)	Log C	log R	Reaction order
1.	pH (no bacteria)	4.50	22.56	-9.50	1.35	1.33
		5.00	90.22	-9.00	1.95	
		5.25	229.20	-8.75	2.36	
		5.50	462.44	-8.50	2.67	
2.	pH (with bacteria)	4.50	18.40	-9.50	1.26	1.41
		5.00	93.48	-9.00	1.97	
		5.25	233.24	-8.75	2.37	
		5.50	454.39	-8.50	2.66	
3.	Fe(II) (g/ℓ)	0.30	21.72	-0.52	1.34	0.42
		1.00	41.24	0.00	1.62	
		3.00	82.04	0.48	1.91	
		10.00	88.46	1.00	1.95	
4.	SS (g/ℓ)	0.00	30.36		1.48	0.37
		4.70	42.93	0.67	1.63	
		12.00	53.15	1.08	1.73	
		49.30	66.07	1.69	1.82	
		75.20	129.25	1.88	2.11	
		152.00	155.75	2.18	2.19	
		328.10	136.34	2.52	2.13	
5.	O_2 (air) (mg/ℓ)	0.10	18.16	-1.00	1.26	0.51
		0.50	30.41	-0.30	1.48	
		2.00	92.79	0.30	1.97	
		5.00	113.93	0.70	2.06	
6.	Stirring (rpm)	20	50.83	1.30	1.71	0.43
		150	120.25	2.18	2.08	
7.	Stirring (pure O_2) (rpm)	50	80.09	1.70	1.90	0.41
		150	136.92	2.18	2.14	
		300	163.73	2.48	2.21	
8.	RSA (m^2/m^3)	58.12	100.18	1.76	2.00	1.25
		46.13	94.06	1.66	1.97	
		36.61	84.64	1.56	1.93	
		26.98	37.57	1.43	1.57	
9.	Temperature (°C)			1/T		E (kcal/mole)
		5.0	13.56	0.00265	1.13	21.55
		11.0	26.99	0.00261	1.43	
		18.7	48.77	0.00256	1.69	
		25.0	81.94	0.00252	1.91	
		37.0	128.64	0.00244	2.11	
		45.0	147.30	0.00240	2.17	

Typical values for various parameters: Iron(II) = 2.8 to 4.7 g/ℓ; $CaCO_3$ = 10 g/ℓ; pH = 4.8 to 6.0; O_2 = 1 to 24 mg/ℓ; SS = 94 to 291 g/ℓ; Temperature = 23 to 28 ° C; Bacteria only present in Experiments 1 and 2; Stirring rate = 150 rpm; Reactor volume = 0.5 to 4 l.

Table 4.   Effect of oxygen concentration on the rate of iron(II) oxidation (sc23b:amc97p03).

Parameter	Oxygen concentration (mg/ℓ O₂)						
	0.11	0.20	0.20 air	0.20	0.27	5.7	10
Iron(II) oxidation rate (g Fe/(ℓ.d)	22.8	44.9	59.0	65.8	86.4	183	163
Reaction time (h)	>>4	2.25	2.00	>1.75	1.75	1.0	0.75
Order	0.37						

Note: Data collected during batch operation of pilot plant.
Conditions: pH = 5.9; Suspended solids in recycle stream = 240 to 360 g/ℓ; Initial iron(II)-concentration = 3.2 to 6.3 g/ℓ; Initial acidity = 8.8 to 12.0 g/ℓ (as CaCO₃); Temperature = 15.0 to 20.0 °C.

Suspended solids concentration

The optimum suspended solids concentration for iron(II) oxidation in the fluidised-bed reactor of the integrated iron(II) oxidation and limestone neutralisation process is 190 g/ℓ (Table 5). The decrease in the iron(II) oxidation rate for suspended solid concentrations greater than 190 g/ℓ can possibly be ascribed to decreased oxygen transfer. It is expected that the optimum level of 190 g/ℓ can be increased when pure oxygen is used and/or when the mixing intensity is increased. The reaction order with respect to suspended solids (over the range 0 to 190 g/ℓ) is 0.50.

Table 5.   Effect of suspended solids on the rate of iron(II) oxidation (sc23b:amc97p03).

Parameter	Suspended solids (g/ℓ)					
	41.1	91.2	95.6	190	277	462
Iron(II) oxidation rate (g Fe/(ℓ.d)	28.7	38.6	47.7	61.9	42.3	32.3
Order	0.50					

Note: Data collected during batch operation of pilot plant.
   Conditions: pH of feed = 5.0; Excess alkali dosage = 41 %; Initial sulphate concentration = 5.7 to 12.2 g/ℓ; Initial iron(II)-concentration = 2.4 to 5.6 g/ℓ; Initial acidity = 4.2 to 9.2 g/ℓ (as CaCO₃); Temperature = 14.5 to 17.5 °C.

Upflow velocity

Upflow velocity has no influence on the rate of iron(II) oxidation in the range 5 to 45 m/h.

Residence time and mode of operation

A shorter reaction time is required during batch operation than in continuous operation. For the removal of 4 g/ℓ iron(II) (as Fe) reaction times of 2.0 and 4.5 h are required for continuous and batch operations respectively (Figure 2). The shorter reaction time required during batch operations can be explained by the iron(II) oxidation rate equation:

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{\frac{1}{4}}.[OH^-]^{1.5}.[O_2]^{\frac{1}{4}}.[SS]^{\frac{1}{4}}.M^{\frac{1}{4}} \qquad (5)$$

The values for O_2 and SS are the same for batch and continuous operations. The oxygen level is controlled at a specific concentration of say 2 mg/ℓ (as O_2) while the SS concentration is kept at a high concentration of say 150 g/ℓ. During continuous operation sludge would be withdrawn continuously to maintain a specific level. During batch operation the suspended solids will increase during the course of each batch operation. The increase would, however, be small compared to the initial concentrations. The values of Fe^{2+} and OH^- during batch operation are, except for the values at the end of the batch experiment, higher than those measured during continuous operation. As the order of the latter parameters are greater than 0, the reaction rate increases with increased values for the parameters mentioned.
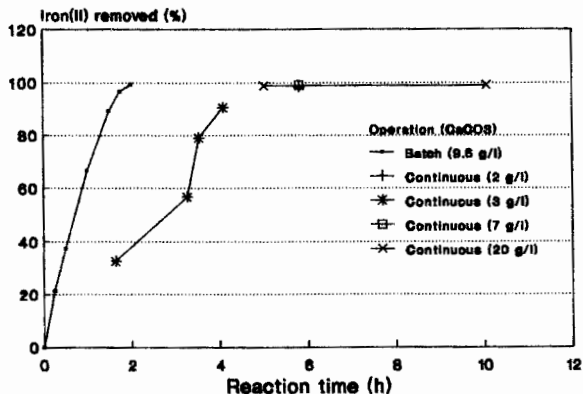

Figure 2.   Comparison between batch and continuous operation during iron(II) oxidation (hgsc23b:mode6).

Note: Data collected during batch operation of pilot plant.
       Conditions: pH of feed = 2.4; Excess alkali dosage = 2 to 20 %; Initial sulphate concentration = 6.2 to 8.3 g/ℓ; Initial iron(II)-concentration = 2.4 to 4.2 g/ℓ; Initial acidity = 6.88.7 g/ℓ (as $CaCO_3$); Oxygen = 0.2 mg/ℓ O_2; Suspended solids = 200 to 400 g/ℓ; Temperature = 15 to 22 °C.

Sequential batch mode operation

Sequential batch mode operation versus continuous operation of the integrated iron(II) oxidation and limestone neutralisation process offers the benefits of a faster reaction rate and better lime utilisation. The reaction rate is faster due to a greater driving force as a result of high iron(II) concentration in solution, except for the final period of the reaction. Limestone utilisation is better as unused limestone can be contacted with acid feed water while final treated water can be contacted with fresh limestone for maximum neutralisation.

Figure 3 shows the behaviour of the most important parameters for a typical batch operation. It is noted that iron(II) was removed during consecutive batch operations in less than 2 h at an average rate of 35 g Fe/(ℓ.d). The experimental conditions were as follows: Temperature = 24 °C and suspended solids = 250 g/ℓ. The pH was raised from 5.3 to 6.1 or higher while acidity was removed from 5.6 g/ℓ (as CaCO$_3$) to 0.3. Sulphate was removed from 6.6 to 2.2 g/ℓ (as SO$_4$) due to gypsum crystallisation.
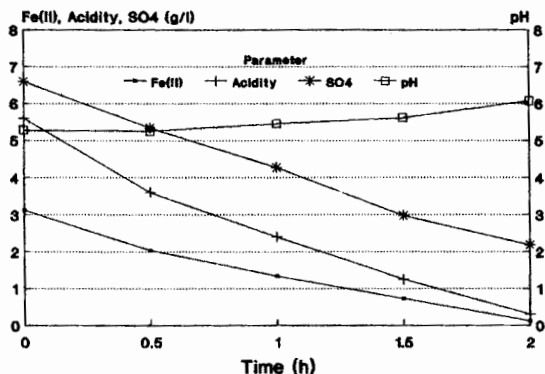

Figure 3.   Behaviour of various parameters during batch operation of the integrated iron(II) oxidation and limestone neutralisation process (Exp 13.2, c:\hg\batch132).

Sludge characteristics

Settling rate and solids content

Table 6 shows the suspended solids content of the sludge in the fluidised-bed reactor at different dilutions (1, 2, 5, 10 and 20 times) before and after settling, as well as the settling rate at each dilution. The settling rate increases from 0.07 to 2 m/h as the dilution factor increases from 1 to 20. A low sludge settling rate (0.07 m/h) would therefore be expected in the fluidised-bed reactor where the sludge solids content is high (200 to 300 g/ℓ) and a high sludge settling rate (2 m/h) in the sludge separation stage where the solids content is low (less than 10 g/ℓ). The sludge concentration can be controlled by withdrawing sludge from the bottom of the fluidised-bed reactor, where the solids content would be at a maximum. One of the major benefits of the integrated iron(II) oxidation and limestone neutralisation process is that sludge with a high solids content is produced (up to 550 g/ℓ). This compares well with the typical 200 g/ℓ solids content that can be achieved with the High Density Sludge process.

Table 6.   Suspended solids content of the sludge at different dilutions (1, 2, 5, 10 and 20 times) before and after settling, as well as the settling rate at each dilution (Exp 11.1).

Parameter	Dilution				
	1x	2x	5x	10x	20x
Suspended solids before settling (g/ℓ)	619	595	165	59	16
Settling rate (m/h)	0.07	0.10	0.37	0.88	2.00

Utilisation of excess CaCO₃ in the waste sludge

Waste sludge withdrawn from the bottom of the fluidised-bed reactor can contain between 0 and 30 % $CaCO_3$ (m/m dry basis), depending on the limestone excess that is applied. If the sludge contains a significant amount of $CaCO_3$, it might be cost-effective to contact the waste sludge with acid feed water prior to discharge in order to achieve maximum utilisation of the $CaCO_3$. Table 7 shows that 70.8 % of the $CaCO_3$ content of the waste sludge that was dosed to discard leachate was utilised for neutralisation of acid. The amount of acidity removed was 4.83 g/ℓ (as $CaCO_3$) as a result of $CaCO_3$ dissolution from the waste sludge and 4.75 g/ℓ (as $CaCO_3$) as a result of acidity removed from the discard leachate.

Table 7.   Partial neutralisation of discard leachate with $CaCO_3$-rich waste sludge (sc23b:amc97p03.wb2).

Parameter	Feed	Treated
$CaCO_3$-rich waste sludge:		
Dosage (ml/ℓ)	50.00	
Suspended solids (g/ℓ)	44.02	36.62
$CaCO_3$-content (%)	13.77	4.83
$CaCO_3$-content (g/ℓ)	6.06	1.77
$CaCO_3$-utilised (g/ℓ)		4.29
$CaCO_3$-utilised (%)		70.82
Water composition:		
Acidity (g/ℓ $CaCO_3$)	7.75	3.00
Acidity removed (g/ℓ $CaCO_3$)		4.75
pH	2.28	6.06
Iron(II) (g/ℓ Fe)	3.02	1.59
Sulphate (g/ℓ SO4)	8.27	4.84

Economic feasibility

The cost figures for the treatment of 1 Mℓ/d of discard leachate with an acidity of 10 g/ℓ (as $CaCO_3$) are as follows:

*   The estimated alkali cost to treat discard leachate with an acidity of 10 g/ℓ (as $CaCO_3$) is R5.15/m³, R2.79/m³, R1.37/m³ and R1.95/m³ for slaked lime, unslaked lime, limestone (milled on-site) and limestone (purchased) respectively. The corresponding cost ratios with respect to unslaked lime are 1.84, 1.00, 0.49 and 0.70. The alkali cost per ton (purity and alkali utilisation are shown in brackets) was based on delivery prices of R500 (90 %, 80 %), R360 (90 %, 80 %), R99.84 (85 %, 85 %) and R140 (85 %, 85 %) respectively. The electricity cost for milling of limestone was calculated to be R9.84/t (30 kW/h x R0.20/kW / 0.61 t/h).

*   The capital cost for 1 Ml/d plant amounts to R1.87 million when the alkali is purchased and R1.87 million when limestone is milled on-site.

General discussion

By using chemical composition of treated water, sludge characteristics (solids content and chemical composition), delivered cost of alkali and capital cost of plant, the order of preference is neutralisation with limestone in the integrated process (6 points), neutralisation with unslaked lime in the high density sludge (HDS) process (8.5 points), and neutralisation with slaked lime in the high density sludge (HDS) process (9.5 points).

CONCLUSIONS

The following conclusions were reached:

1.   The integrated iron(II) oxidation and limestone neutralisation process can be used for the removal of acidity, iron(II), iron(III), aluminium (to less than 2 mg/ℓ (as Al) and sulphate (to a level of 2 500 mg/ℓ (as SO$_4$)). All reactions take place simultaneously. For water containing 3 g/ℓ iron(II) (as Fe), a reaction time of 2 h is required when operated in sequencing batch mode and 5 h when operated on a continuous basis.

2.   Sludge with a solids content of more than 50 % can be produced with the integrated process.

3.   The estimated alkali cost to treat discard leachate with an acidity of 10 g/ℓ (as CaCO$_3$) is to R5.15/m^3, R2.79/m^3, R1.37/m^3 and R1.95/m^3 for slaked lime, unslaked lime, limestone (milled on-site) and limestone (purchased) respectively.

4.   The estimated capital cost for a 1 Ml/d plant is R1.87 million when the alkali is purchased and R1.87 million when limestone is milled on-site.

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