

Neutralizing Coal Mine Effluent with Limestone to Decrease Metals and Sulphate Concentrations

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Abstract. This paper describes pilot scale tests of a novel process for the neutralisation of acidic mine water. Leachate from a waste coal dump was neutralised with limestone, and iron, aluminium, and sulphate were removed. Specific aspects studied were: the process configuration; the rates of iron 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 acidity was decreased from 12,000 to 300 mg/L (as CaCO₃), sulphate from 15,000 to 2,600 mg/L, iron from 5,000 to 10 mg/L, aluminium from 100 to 5 mg/L, while the pH increased from 2.2 to 7.0. Reaction times of 2.0 and 4.5 h were required under continuous and batch operations respectively for the removal of 4 g/L Fe(II). The iron oxidation rate was found to be a function of the Fe (II), hydroxide, oxygen, and suspended solids (SS) concentrations. The optimum SS concentration for iron oxidation in a fluidised-bed reactor was 190 g/L. Up-flow velocity had no influence on the rate of iron oxidation in the range 5 to 45 m/h. Sludge with a high solids content of 55% (m/v) was produced. This is high compared to the typical 20% achieved with the high density sludge process using lime. It was determined that neutralisation costs could be reduced significantly with an integrated iron oxidation and limestone neutralisation process because limestone is less expensive than lime, and a high-solids-content sludge is produced. Full scale implementation followed this study.

Key Words: Acid mine drainage; iron oxidation; limestone neutralization

Introduction

Coal mining and fertiliser manufacturing are examples of industrial operations that can give rise to severe acid pollution of the environment unless the water is appropriately treated. Water with a pH below 5.5 can be toxic to plant and fish life and corrosive to pipelines and equipment. Disposal of sludge from neutralisation of such effluents is costly, though the volume of sludge can be reduced by increasing the solids concentration. Currently, acid water at most mine sites in arid areas 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, malfunctioning of dosing equipment, and settling of particles in pipelines and valves. The latter often causes blockages, which 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 over-dosage is minimised. Also limestone is non-hazardous and easy to store. Raw material can be stockpiled in the open as CaCO₃ is not readily soluble in neutral water.

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

- Complete neutralisation of discard leachate containing (10 g/L acid (as CaCO₃) and 4,000 mg/L Fe(II)) can be achieved in a limestone neutralisation fluidised-bed reactor, provided that the Fe is oxidised beforehand (Maree et al. 1998).
- Fe(II) can be oxidised biologically to Fe(III). The rate of iron 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 Fe(II) (Maree et al. 1998).
- Magnesium keeps the equivalent amount of sulphate in solution. When 300 mg/L magnesium (as Mg) is present, SO₄ can be reduced from 18 000 mg/L to about 2 700 mg/L by gypsum crystallisation; at 0 mg/L Mg, SO₄ can be reduced to 1 500 mg/L. With a fluidised-bed contactor, a residence time of 2 h is needed.

Treatment of Fe(II)-rich water with limestone conventionally requires a multiple-stage neutralisation system. The expected capital cost of such a system is unacceptably high due to the long residence time required for iron oxidation. An integrated iron oxidation and limestone neutralisation process was developed to overcome this disadvantage. The process consists of a neutralisation reactor and a clarifier. Discard leachate is treated in an aerated sludge reactor into which limestone powder (100% < 200 µm) is dosed to a level slightly in excess of stoichiometrical requirements. Iron

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 oxidation and limestone neutralisation process, and to obtain design criteria for full-scale implementation.

Materials and Methods

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 SO₄ and 9,200 mg/L acidity (as CaCO₃). Crushed limestone, mined near Rustenburg, South Africa, and sodium hydroxide were used for neutralisation. In later studies, calcium carbonate powder (100% < 300 µm and 80% < 75 µm), a by-product from the paper industry, was used.

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 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:

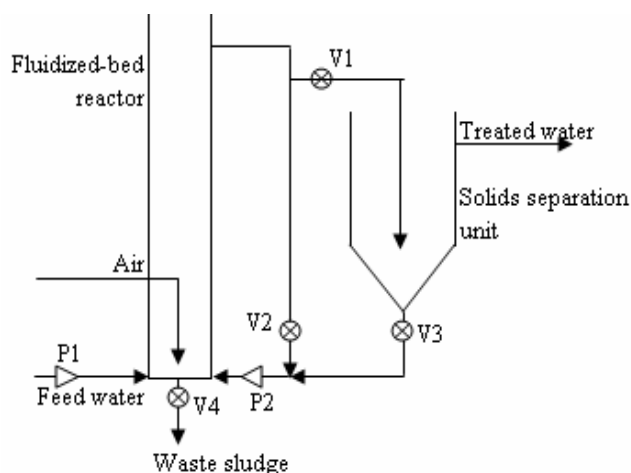
- Each batch test was started by mixing the treated contents from the previous batch with the synthetic feed, in a ratio varying from 1:1 to 1:4. An excess amount of CaCO₃ (20% to 40%) was applied over the amount required to ensure complete iron oxidation and precipitation of the iron(III) as Fe(OH)₃. NaOH additions were made as required to maintain the pH at a specific value when the influence of pH was determined.
- The reactor contents were aerated continuously. Filtered samples were taken regularly and analysed for iron(II), oxygen, acidity, sulphate and pH.
- Aeration was stopped when the iron was completely oxidised, whereafter the appropriate amount of the Fe(III)-containing mixture was replaced with a fresh Fe(II) solution. First, solids was allowed to settle, whereafter the clear water was decanted and replaced with fresh iron(II)-rich water.
- Aeration was restarted and the procedure described above repeated.

Batch and Continuous Studies on Pilot Scale

A pilot plant (Figure 1, Table 1), consisting of a fluidised-bed reactor and a sludge separator, was used for a fluidised-bed consisting of slimes/limestone/gypsum

Table 1. Dimensions of pilot plant

Parameter	Value	
	Fluidised bed	Solids separation
Feed rate (Lh)		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	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22



P1 - Feed pump; P2 - Recycle pump; V1, V2, V3 & V4 - Valves

Figure 1. Schematic diagram of integrated iron oxidation/limestone neutralisation pilot plant

during batch studies, and through both the fluidised-bed reactor and the sludge separator during continuous studies. 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 oxidation.

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 Fe (II) as described in Vogel (1989). Calcium was analysed by 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.

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

Parameter	Feed (Synthetic discard leachate)	Treated (Limestone)
pH	1.8	6.6
Acidity (as CaCO ₃)	7 300	100
Sulphate	8 342	1 969
Orthophosphate (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

Kinetics

Stumm and Lee (1961) determined the following relationship between the iron oxidation rate and pH in the absence of microorganisms for clear solutions:

$$-d[\text{Fe(II)}]/dt = k[\text{Fe(II)}][\text{OH}^-]^2 P(\text{O}_2) \quad (1)$$

where: $-d[\text{Fe(II)}]/dt$ = rate of iron oxidation; k = reaction rate constant; $[\text{Fe(II)}]$ = iron(II) concentration (moles/L); $[\text{OH}^-]$ = hydroxide concentration (moles/L); and $P(\text{O}_2)$ = partial pressure of oxygen (mm Hg).

Most iron 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. (1997) showed that the rate of chemical iron oxidation is also catalysed by suspended solids, which can lower the pH where the rate of chemical oxidation is fast enough for practical application from 6.5 to 5.0. The integrated iron oxidation and limestone neutralisation process is based on this finding, as limestone can raise the pH of Fe(II)-rich water to between 5 and 6. Volumetric iron 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 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 oxidation rate was assumed to have the following functional form:

$$-d[\text{Fe}^{2+}]/dt = k[\text{Fe}^{2+}]^{n_1}[\text{O}_2]^{n_2}[\text{OH}^-]^{n_3}[\text{RSA}]^{n_4}[\text{SS}]^{n_5}M^{n_6} \quad (2)$$

where: $-d[\text{Fe}^{2+}]/dt$ or R = rate of iron oxidation; k = reaction rate constant; $[\text{Fe}^{2+}]$ = iron(II) concentration

(moles/L); $[\text{O}_2]$ = oxygen concentration (moles/L); $[\text{OH}^-]$ = hydroxide concentration (moles/L); RSA = reactor surface area (m^2/m^3); $[\text{SS}]$ = suspended solids concentration (g/L); and M = mixing intensity (rpm).

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

$$-d[\text{Fe}^{2+}]/dt = K[\text{Fe}^{2+}]^{n_1} \text{ or } \log(-d[\text{Fe}^{2+}]/dt) = \log K + n_1 \log[\text{Fe}^{2+}] \quad (3)$$

where: $K = k \cdot [\text{O}_2]^{n_2} \cdot [\text{OH}^-]^{n_3} \cdot [\text{RSA}]^{n_4} \cdot [\text{SS}]^{n_5} \cdot M^{n_6}$

The contribution, n_1 , of Fe (II) to the overall reaction rate was determined from the slope of the graph obtained by plotting $\log R$ versus $\log [\text{Fe}^{2+}]$. From pH, $\log R$ was plotted against $\log[\text{OH}^-]$ ($[\text{OH}^-] = 10^{\text{pH} - 14}$). The data in Table 3 show that the rate of iron oxidation is of order 0.42 (≈ 0.5), 1.41 (≈ 1.5), 0.51 (≈ 0.5), 0.37 (≈ 0.5) and 0.43 (≈ 0.5) relative to Fe^{2+} , OH^- , O_2 and SS concentrations, and mixing intensity (M), respectively. The findings suggest that the rate equation proposed by Stumm and Lee (1961) for clear solutions should be modified for suspensions to:

$$-d[\text{Fe}^{2+}]/dt = k[\text{Fe}^{2+}]^{1/2} \cdot [\text{OH}^-]^{1.5} \cdot [\text{O}_2]^{1/2} \cdot [\text{SS}]^{1/2} \cdot M^{1/2} \quad (4)$$

The significance of this finding is that the rate of Fe (II) is not only determined by hydroxide-, Fe (II), and oxygen concentrations, but also by the SS concentration.

Table 3 also indicates that the rate of iron oxidation in suspensions with high concentrations of SS 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 Maree et al. (1997), where chemical iron oxidation was studied using a clear solution (the only solids present was that which precipitated from solution during iron oxidation and neutralisation) and was compared with biological iron oxidation where solids were present from the start of the experiment (medium to support bacterial growth). The slower oxidation rates determined for chemical iron oxidation at pH values between 5 and 5.5 should be ascribed to lower SS concentrations and not to the absence of bacterial activity.

In a previous investigation, Maree et al. (1997) determined that the rate of iron oxidation in the pH range 4.5 to 6 was influenced by the reactor surface area (RSA). It was pointed out that this behaviour is in line with the behaviour of iron 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 oxidation in the pH range 4.5 to 6 is not influenced by the medium-specific surface area, but by the mixing intensity, M . In the previous investigation,

Table 3. Effect of various factors on the kinetics of iron oxidation, as measured in nine experiments

Variable	Value	Rate g Fe/(L.d)	Log C	log R	Rxn order
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	
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	
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	
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	
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	
Stirring (rpm)	20	50.83	1.30	1.71	0.43
	150	120.25	2.18	2.08	
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	
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	
Temp. (°C)			1/T		E (kcal/mole)
	5.0	13.56	0.00265	1.13	
	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	

- the values of RSA and M were varied simultaneously, 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

Table 4. Effect of oxygen concentration on the rate of iron oxidation

Parameter	Oxygen concentration (mg/LO ₂)						
	0.11	0.20	0.20 (air)	0.20	0.27	5.7	10
Iron 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- 20.0 °C

decreases when larger beakers are used if the stirring rate is not adjusted accordingly (Table 3, Experiments 6 and 7). The iron 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 °C. It is expected that the linear relationship will fail at higher temperatures as optimum reaction rates are often achieved at 37 °C.

Design Criteria for Continuous Operation

Oxygen versus Air

The iron oxidation rate increases with increased oxygen concentrations (Table 4). For a specific oxygen concentration (0.2 mg/L), reaction rates are similar for pure oxygen and air (between 44.9 and 65.8 g Fe/(L.d)). Although high iron oxidation rates can be achieved by using pure oxygen, air is a more suitable oxidant for full-scale application due to safety reasons. Typical values for various parameters: Fe(II) = 2.8 to 4.7 g/L; CaCO₃ = 10 g/L; pH = 4.8 to 6.0; O₂ = 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.

Suspended Solids Concentration

The optimum SS concentration for iron oxidation in the fluidised-bed reactor of the integrated process was 190 g/L (Table 5). The decrease in the iron oxidation rate for SS 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.

Up-flow Velocity

Up-flow velocity has no influence on the rate of iron oxidation in the range 5 to 45 m/h.

Table 5. Effect of suspended solids on the rate of iron oxidation

Parameter	Suspended solids (g/L)					
	41.1	91.2	95.6	190	277	462
Iron 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 Fe(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.

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 oxidation rate equation:

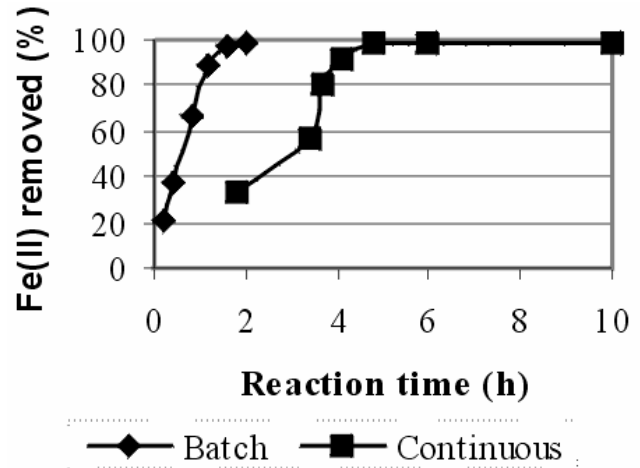
$$-d[\text{Fe}^{2+}]/dt = k \cdot [\text{Fe}^{2+}]^{1/2} \cdot [\text{OH}^-]^{1.5} \cdot [\text{O}_2]^{1/2} \cdot [\text{SS}]^{1/2} \cdot M^{1/2} \quad (5)$$

The values for O₂ and SS are the same for batch and continuous operations. The O₂ level is controlled at a specific concentration (e.g., 2 mg/L) while the SS concentration is kept high (e.g., 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 Fe²⁺ 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.

Sequential Batch Mode Operation

Sequential batch mode operation versus continuous operation of the integrated iron 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 Fe (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. Note that Fe (II) was removed during consecutive batch operations in less than 2 h at an average rate of 35 g Fe/(L.d) at a temperature = 24 °C and SS = 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 CaCO₃) to 0.3. Sulphate was removed from 6.6 to 2.2 g/L (as SO₄) due to gypsum crystallisation.



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 Fe(II) concentration = 2.4 to 4.2 g/L; initial acidity = 6.89 g/L (as CaCO₃); oxygen = 0.2 mg/L O₂; suspended solids = 200 to 400 g/L; temperature = 15 to 22 °C.

Figure 2. Comparison between batch and continuous operation during iron oxidation

Sludge Characteristics

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 oxidation and limestone neutralisation process is that a high-solids-content sludge is produced (up to 550 g/L). The high solids concentration was possible due to the column reactor which supports gypsum crystallization onto existing gypsum particles. This compares well with the typical 200 g/L solids content that can be achieved with the high density sludge process.

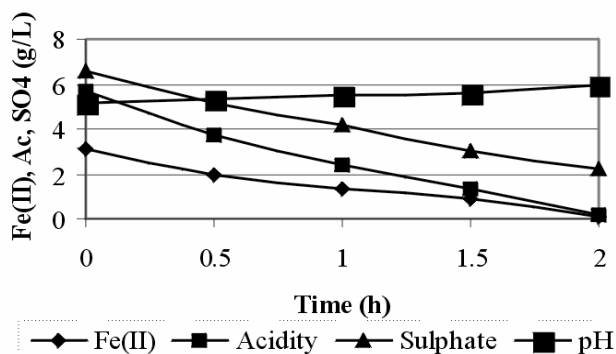


Figure 3. Behaviour of various parameters during batch operation of the integrated iron oxidation and limestone neutralisation process

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

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

General

In this process, powdered CaCO_3 is used as alkali to allow iron oxidation, neutralization of free acid, and gypsum crystallization to take place in the same reactor. It was shown that Fe (II) can be oxidised at pH 6, using only CaCO_3 and not lime; this aspect has been patented (Maree 1997). Previously, lime was used to raise the pH to 7.2, at which pH the iron-oxidation rate is fast. The results of this pilot plant study led to its full-scale application; full-scale plants using calcium carbonate powder for neutralization of acidic streams have now been constructed at the following sites in southern Africa: Ticor (Empangeni), BCL (Botswana), S A Coal Estates (Witbank) and Zincor (Springs).

Conclusions

The following conclusions were reached:

1. The integrated iron oxidation and limestone neutralisation process can be used for the removal of acidity, iron, 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.
2. Sludge with a solids content of more than 50% can be produced with the integrated process.
3. For water containing 3 g/L Fe (II), a reaction time of 2 h is required when the process is operated in a sequencing batch mode; 5 h is required when it is operated on a continuous basis.

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