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TECHNICAL COMMUNICATION

Limestone Neutralisation of Arsenic-Rich Effluent from a Gold Mine

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Abstract Traditionally acid mine water is neutralised with lime. Limestone is a cheaper alternative for such applications. A case study showed that limestone can be used effectively to replace lime for the neutralization of arsenic rich acid water. The cost of limestone treatment is 45.8% less than that of lime. The acidity can be removed from 33.5 to 0.06 g/L (as $CaCO_3$). The study also showed no significant differences in the TCLP characteristics of the resultant sludge when water is treated with lime or with limestone. Sludge from the limestone treatment process can be disposed of on a non-hazardous landfill site.

Introduction

Gold mines conventionally use lime to neutralize acid water generated during mining and processing of the ore. An alternative approach is to use limestone for the neutralization process. The fluidised-bed limestone neutralisation process was developed to neutralise free acid and remove Fe(III) and Al(III) concomitantly (du Plessis and Maree 1994; Maree and du Plessis 1994; Maree et al. 1992, 1996a, b; Maree 1997). Previous studies showed that:

- Complete neutralisation of discard leachate containing (10 g/L acid (as $CaCO_3$) 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 media (specific surface area 200 m^2/m^3), a residence time of 18 h is required for water containing 4 g/L Fe(II) (Maree et al. 1998).
- When 300 mg/L magnesium (as Mg) is present, sulphate can be reduced from 18,000 mg/L (as SO_4) to about 2,700 mg/L by gypsum crystallisation and at 0 mg/L Mg to 1,500 mg/L (as SO_4). Magnesium keeps the equivalent amount of sulphate in solution. 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 stoichiometric 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. A clarifier is required to return sludge to the neutralisation reactor to maintain a minimum concentration of suspended solids.

Maree et al. (1994) determined that an integrated iron oxidation and limestone neutralisation process can be used to

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simultaneously remove acidity, iron, aluminium (to less than 2 mg/L) and sulphate (to a level of 2,500 mg/L). They also showed that sludge with a solids content of more than 50% can be produced with the integrated process. For water containing 3 g/L Fe(II), a reaction time of 2 h was required when the process was operated in a sequencing batch mode; 5 h was required when it is operated on a continuous basis.

The objectives of this investigation were to investigate the option of using limestone to treat some extremely acidic water that is rich in iron, sulphate, and arsenic. When it appeared that limestone could be used for neutralization instead of lime to reduce costs and improve pH control, we sought to identify the most suitable type of limestone and limestone source for neutralization of the arsenic-rich acid water. Also, because there were concerns about arsenic leaching from the sludge, we also compared the lime and limestone sludge in terms of toxicity characteristic leaching procedure (TCLP) specifications.

Materials and Methods

Feedstock

Samples of acidic water were collected from a gold mine for our tests. The feed water had a pH of 1.5, and contained a high concentration of arsenic. It furthermore contained high concentrations of ions such as sodium, chloride, magnesium, calcium, manganese, and iron (II). The acidity of the raw water was 33,500 mg/L (as $CaCO_3$), and the sulphate concentration was 40,000 mg/L. Table 1 shows the chemical composition of the feed water.

Table 1 Chemical composition of the arsenic-rich, acidic water, in mg/L

Parameter	Quality
Acidity (as $CaCO_3$)	33,500
Iron(II)	51
Sulphate	40,000
Sodium	17
Potassium	19
Calcium	346
Aluminium	9
Chromium	6
Manganese	45
Iron	1,366
Cobalt	49
Nickel	317
Copper	67
Zinc	48
Arsenic	4,766
Chloride	136
Fluoride	606

Different types and qualities of calcium carbonate powder were obtained for test purposes from Aqua-lime (Sappi Enstra, Ngodwana, Syferfontein, TSB, and Highveld limestones).

Equipment

Figure 1 and Table 2 describe the flow-diagram and process parameters of the pilot plant. It consisted of two turbulators in series, pumps to feed water to Turbulator 1 (Fig. 2) and limestone slurry to Turbulators 1 and 2, a clarifier, a recycle pump, and a feed-water storage tank.

The turbulator consisted of a motor, which directly drives a rotor via a hollow shaft. Due to the high speed (2,000 rpm, 66 Hz), a partial vacuum is created by the rotor and air is sucked via the hollow shaft into the slurry. A strong vortex is created at both the upper and lower ends of the rotor. The bottom stream is pulled through the rotor and deflected upwards, forming a wave at the outside, upper end of the mixing vessel, drawing any powders and solids into the upper vortex. The stream is subsequently deflected downwards and sweeps the bottom end of the vessel, preventing any solids-settlement. The turbulator allows proper mixing between the mixture of acidic water and calcium carbonate. The advantage of using the turbulator is that it can mix/disperse slurries up to 60% solids.

Experimental

Continuous studies were carried out on arsenic-rich, acid water using the set-up described above (Fig. 1). The acid water and limestone slurry were fed to turbulators 1 and 2. Samples were collected from both the lime and limestone processes and analysed for pH, acidity, sulphate, iron(II) (at 4 h intervals), and other heavy metals (daily).

We investigated the effects of using the limestone, varying the $CaCO_3$ slurry dosage (to achieve pH 4.3 in Turbulator 1 and pH 6.5 in Turbulator 2), and the leachate potential of the arsenic. For the latter, four sludge samples (two from the lime process and two from the limestone process) were subjected to TCLP tests to determine the leachate potential of arsenic.

Analytical

Water Analysis

Samples from the continuous experiments were taken at regular time intervals (4 h). The samples were filtered and analyzed for pH, acidity, sulphate, and iron(II) on site.

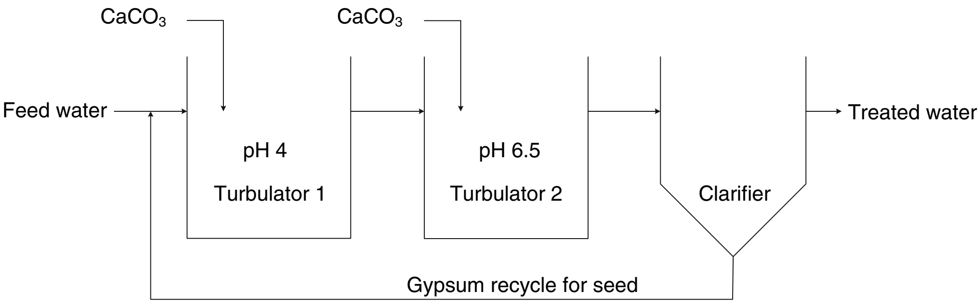

Fig. 1 Process flow diagram of on-site pilot plant for studies on an arsenic-rich acid water

Table 2 Dimensions and flow rate characteristics of the pilot plant

Parameter	Turbulator 1	Turbulator 2	Clarifier
Volume L	850	150	400
Water feed rate 1.5 L/min			
Limestone feed rate L/min	0.20	0.25	
Recycle rate L/min	2.5		
Hydraulic residence time h	7.3	1.3	3.4

Determinations were carried out manually using standard procedures (APHA 1989). A composite sample was send to SGS Lakefield Research laboratories for heavy metal determinations.

Fig. 2 Turbulator

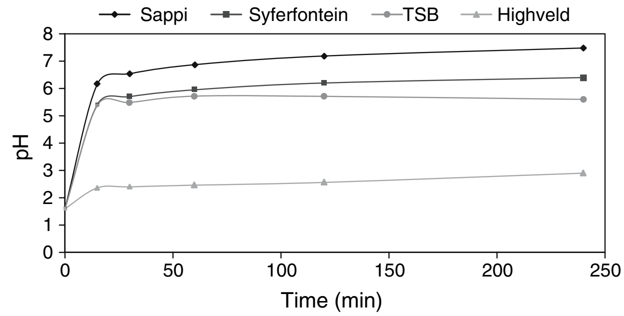

Fig. 3 Effect of different limestones on pH

Sludge Characteristics

Test to determine MLSS and the sludge-settling rate were carried out manually using standard procedures (APHA 1989). Sludge samples from both the lime and limestone processes were collected daily and dried at room temperature. Composite samples were sent to SGS Lakefield Research laboratories for TCLP tests.

TCLP Leach Testing

Leach testing was done using the TCLP test, as described by the Dept of Water Affairs and Forestry (1998). The leachates were submitted for analysis by ICP-OES and ICP-MS.

The TCLP test is designed to determine the mobility of both organic and inorganic parameters present in multi-

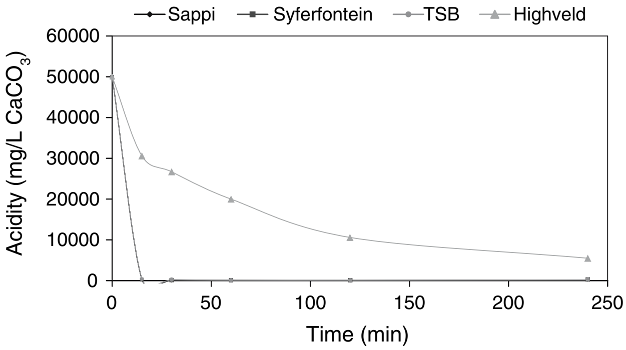

Fig. 4 Effect of different limestones on acidity

Table 3 Comparison between chemical compositions of lime and limestone treated water, in mg/L except for pH

Parameter	Minimum detectable limit	Feed	Lime		Limestone	
			pH 4 (R1)	pH 6.5 (R2)	pH 4 (R1)	pH 6.5 (R2)
PH		1.5			4.2	6.4
Acidity as $CaCO_3$		33,294			438	61
Sulphate		40,000			7,873	6,840
Iron(II)		51			7	6
Sodium	0.05	80	69	64	440	350
Potassium	0.11	52	60	59	54	32
Calcium	0.05	590	460	450	490	250
Magnesium	0.02	1,200	1,200	1,100	1,100	560
Aluminium	0.08	90	23	<0.08	12	<0.08
Chromium	0.04	3.2	0.08	<0.04	0.08	<0.04
Manganese	0.01	68	120	44	180	43
Iron	0.02	17,000	4.1	0.59	16	0.53
Cobalt	0.12	33	27	7.3	28	4.2
Nickel	0.05	230	170	41	190	26
Copper	0.12	53	25	<0.02	17	0.03
Zinc	0.17	44	34	1.9	38	1.2
Arsenic	0.34	4,100	0.93	0.44	0.59	< 0.34
Chloride	5.0	<5	33	34	46	52
Fluoride	0.1	<0.1	0.19	<0.1	0.31	0.19

phase waste. The extraction fluid used is a function of the alkalinity of the solid phase of the waste material. The extraction fluids consist either of acetic acid or a blend of acetic acid and sodium hydroxide. Acetic acid is the strongest acid present in typical landfill settings and this test is typically used to define a material destined for landfill as a hazardous or non-hazardous waste.

The TCLP test was carried out as follows: 2 L of acid solution was added to 100 g of the dried solid sample. The sample was agitated end over end for 20 h and the suspension filtered prior to analysis of the filtrate.

Results and Discussion

Limestone Selection

Figures 3 and 4 depict a comparison of the performances of limestones from various sources for the treatment of the arsenic-rich process water. It was noted that:

- Sappi Enstra performed better than Syferfontein, TSB, and Highveld limestone. A product from Sappi Ngodwana was also tested. It afforded similar results to the Sappi Enstra product. With the Sappi Enstra product, the pH could be raised from 3 to 6.2 in 15 min and to 7 after 60 min.
- Acidity decreased from 50,000 mg/L in the raw water to 50 mg/L in less than 4 h (Fig. 4).
- Sludge settling rate was found to be 0.2 m/h.

It is recommended that Sappi Ngodwana calcium carbonate be used as Ngodwana is closer to the mine (100 km) than Enstra (700 km).

Limestone Versus Lime Treatment

Table 3 compares the chemical compositions after arsenic rich, acid water had been treated with lime and limestone (Sappi Ngodwana), respectively. It was noted that:

- The chemical composition of the limestone treated water was similar to that of the lime treated water. In both cases, the pH was raised from 1.6 to above 6.4.

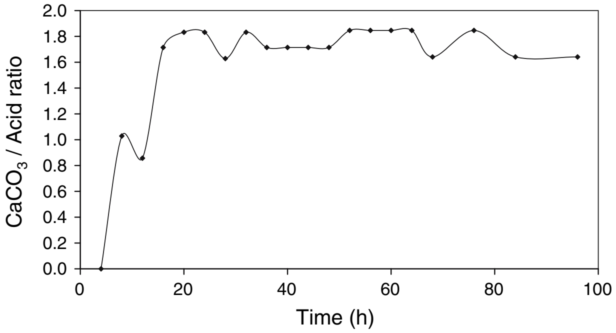

Fig. 5 Ratio of $CaCO_3$ dosage: acid concentration of feed water in the limestone process as a function of time

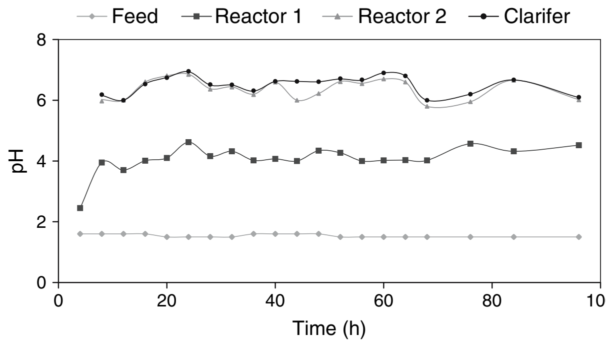

Fig. 6 Behaviour of pH when arsenic-rich acid water was treated with limestone

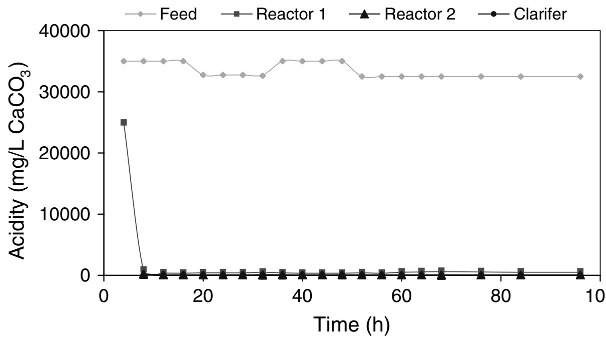

Fig. 7 Behaviour of acidity when arsenic-rich acid water was treated with limestone

Acidity was decreased from 33 g/L (as $CaCO_3$) to less than 0.06 g/L (as $CaCO_3$), sulphate was decreased from 40 g/L to less than 7 g/L, and arsenic was decreased from 4 g/L to less than 0.4 g/L, after sludge separation.

- The sludge-settling rate for the lime and limestone processes was the same in both cases (0.2 m/h).

Water Quality after Limestone Treatment

Figures 5, 6, and 7 show the behaviour of various parameters during continuous treatment of arsenic-rich acid water with limestone. At a $CaCO_3$ dosage to acid concentration ratio of 1.67 (Fig. 5) and higher, the pH was consistently raised from 1.5 to 6.4, and acidity was reduced from 33.5 g/L to less than 0.06 g/L (as $CaCO_3$).

TCLP Results for Lime and Limestone Sludge

The purpose of the TCLP leachate tests was to determine whether limestone has any negative effect on the concentration of leachable arsenic in the limestone sludge compared to the lime sludge.

There were no significant differences in the TCLP values of the sludge when the water was treated with lime or limestone (Table 4). This was expected, as acid water

Table 4 Toxicity Characteristic Leaching Procedure (TCLP) values of the sludge from the lime and limestone treatment processes

Parameter	Units (mg/L)	Minimum detectable limit	Lime Sludge		Limestone Sludge	
			pH 4 (R1)	pH 6.5 (R2)	pH 4 (R1)	pH 6.5 (R2)
Antimony	Sb	0.31	< 0.31	< 0.31	< 0.31	< 0.31
Arsenic - (inorg)	As	0.34	< 0.34	< 0.34	< 0.34	< 0.34
Barium	Ba	0.02	0.02	0.03	0.07	0.11
Cadmium	Cd	0.03	< 0.03	< 0.03	< 0.03	< 0.03
Cobalt	Co	0.12	2.2	5.0	1.2	4.2
Copper	Cu	0.02	1.2	0.7	1.5	0.32
Iron	Fe	0.02	0.86	0.29	2.1	0.08
Lead	Pb	0.31	4.2	2.0	4.1	3.3
Magnesium	Mg	0.02	78	99	44	74
Manganese	Mn	0.01	14	22	8.1	30
Mercury - (tot)	Hg	0.003	< 3	< 3	< 3	< 3
Nickel	Ni	0.05	15	32	6.3	25
Selenium - (inorg)	Se	0.02	< 20	< 20	< 20	< 20
Silver	Ag	0.003	< 5	< 5	< 5	< 5
Titanium	Ti	0.02	< 0.02	< 0.02	< 0.02	< 0.02
Vanadium	V	0.07	< 0.07	< 0.07	< 0.07	< 0.07
Zinc	Zn	0.17	2.5	5.1	1.8	3.5
Zirconium	Zr	0.05	< 0.05	0.08	0.05	0.06

Table 5 Comparison between the cost of lime and limestone for 17 m^3/h of mine water with an acidity of 55 g/L, an acid load of 682 t/day $CaCO_3$, and a utilization efficiency of 90%

Parameter	Unit	Lime	Limestone
Purity	%	85	70
Mol mass	Daltons	56	100
Alkali usage	t/d	499	1,083
Price	R/t	800	200
Cost	R/month	399,497	216,564
Savings	%	0	45.8

neutralized with limestone is identical to that neutralized with lime. In the case of limestone neutralization, CO_2 is evolved. CaO remains in solution as $Ca(OH)_2$.

TCLP values for arsenic of less than 5 mg/L indicate that the sludge can be disposed of in a landfill as a non-hazardous waste.

Alkali Cost Comparison

Table 5 compares the costs of lime and limestone treatment.

Conclusions

The present studies showed that:

- Limestone (Sappi Ngodwana) can be used effectively to replace lime for the neutralization of arsenic rich acid water.
- The cost of limestone treatment is 45.8% less than that of lime.
- With limestone treatment, the acidity can be decreased from 33.5 to 0.06 g/L (as $CaCO_3$).
- There is no significant difference in the TCLP characteristics of the resultant sludge when the water was treated with lime or with limestone.
- Sludge from the limestone treatment process could be disposed of in a non-hazardous landfill site.

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