

## **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<sub>3</sub>). 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.

**Key words:** arsenic minerals; fluidised bed; gold mines; limestone

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### **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 has been 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; Maree et al. 1996a,b; Maree 1997). Previous studies showed that:

- Complete neutralisation of discard leachate containing (10 g/L acid (as CaCO<sub>3</sub>) 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<sup>2</sup>/m<sup>3</sup>), 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<sub>4</sub>) to about 2,700 mg/L by gypsum crystallisation and at 0 mg/L Mg to 1,500 mg/L (as SO<sub>4</sub>). 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.

The following conclusions were reached:

- The integrated iron oxidation and limestone neutralisation process can be used to remove acidity, iron, aluminium (to less than 2 mg/L, as Al) and sulphate (to a level of 2,500 mg/L, as SO<sub>4</sub>) (Maree et al. 1994). All reactions take place simultaneously.
- 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 is required when the process is operated in a sequencing batch mode; 5 h is required when it is operated on a continuous basis.

This article discusses the options for treating acid water, rich in iron, arsenic and sulphate. It is suggested that limestone can be used for neutralization instead of lime to offer the following benefits:

- Cost saving.
- Less pH control is required.

The objectives of this investigation were the following:

- To identify the most suitable limestone type and source for neutralization of arsenic rich acid water.
- To compare lime and limestone sludge for meeting Toxicity Characteristic Leaching Procedure (TCLP) specifications.

## Materials and Methods

### Feedstock

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

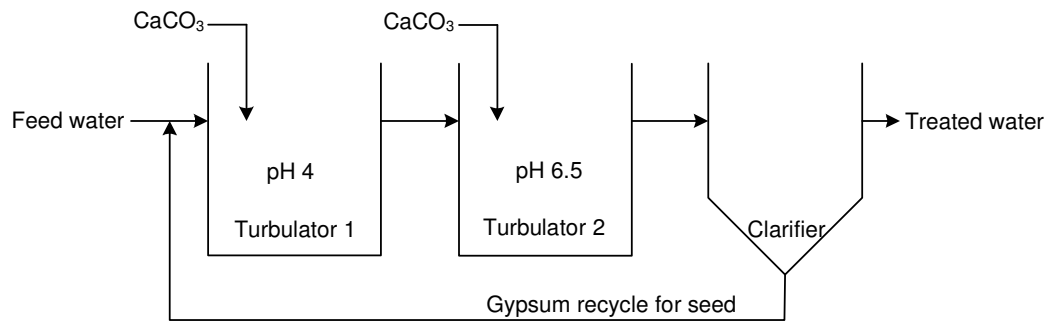
**Table 1.** Chemical composition of the arsenic-rich acid water

Parameter	Units	Quality
pH		1.5
Acidity	mg/L as CaCO <sub>3</sub>	33500
Iron(II)	mg/L as Fe	51
Sulphate	mg/L as SO <sub>4</sub>	40000
Sodium	mg/L as Na	17
Potassium	mg/L as K	19
Calcium	mg/L as Ca	346
Aluminium	mg/L as Al	9
Chromium	mg/L as Cr	6
Manganese	mg/L as Mn	45
Iron	mg/L as Fe	1366
Cobalt	mg/L as Co	49
Nickel	mg/L as Ni	317
Copper	mg/L as Cu	67
Zinc	mg/L as Zn	48
Arsenic	mg/L as As	4766
Chloride	mg/L as Cl	136
Fluoride	mg/L as F	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, feed pumps (feed water to Turbulator 1, Figure 2) and limestone slurry to turbulators 1 and 2), clarifier, recycle pump and a feed-water storage tank.



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

**Table 1.** Dimensions and flow rate characteristics of the pilot plant

Parameter	Units	Feed	Turbulator		
			1	Turbulator 2	Clarifier
Volume,	L		850	150	400
Feed rate	L/min	1.5			
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



**Figure 2.** Turbulator

The turbulator consisted of a motor, which directly drives a rotor via a hollow shaft. Due to the high speed (2000 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 and prevents 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 (Figure 1). The acid water and Ngodwana limestone slurry (20% slurry of 69% CaCO<sub>3</sub>) 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).

The effects of the following parameters were investigated:

- Limestone source
- CaCO<sub>3</sub> slurry dosage (to pH 4.3 in Turbulator 1 and to pH 6.5 in Turbulator 2)
- The leachate potential of arsenic: Four sludge samples (2 from lime process and 2 from 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, iron(II), on site. Determinations were carried out manually according to standard procedures described in Standard Methods (APHA 1992). A composite sample was sent to SGS Lakefield Research laboratories for heavy metal determinations.

### Sludge Characteristics

Test to determine MLSS and the sludge-settling rate were carried out manually according to standard procedures (APHA 1992).

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. 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-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 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 minutes and to 7 after 60 minutes.
- Acidity decreased from 50,000 mg/L in the raw water to 50 mg/L in less than 4 hours (Figure 4).
- Sludge settling rate was found to be 0.2 m/h.

It is recommended that Sappi Ngodwana calcium carbonate be used.

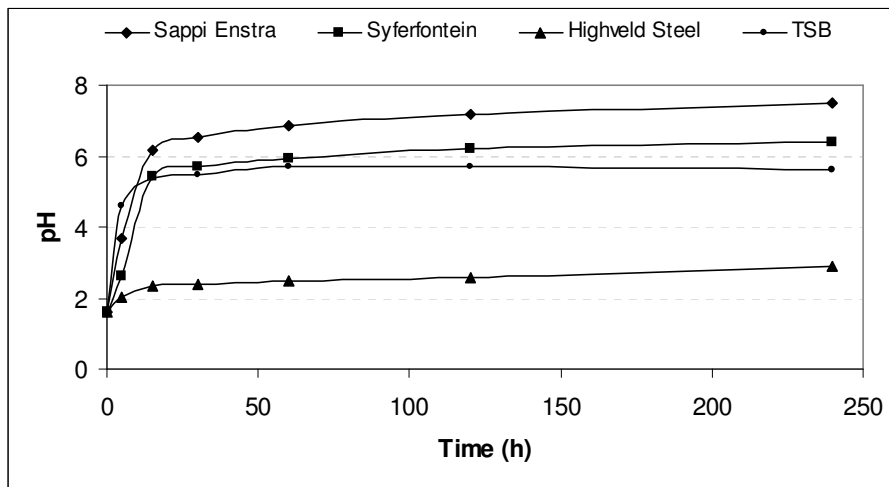


Figure 3: Effect of different limestones on pH

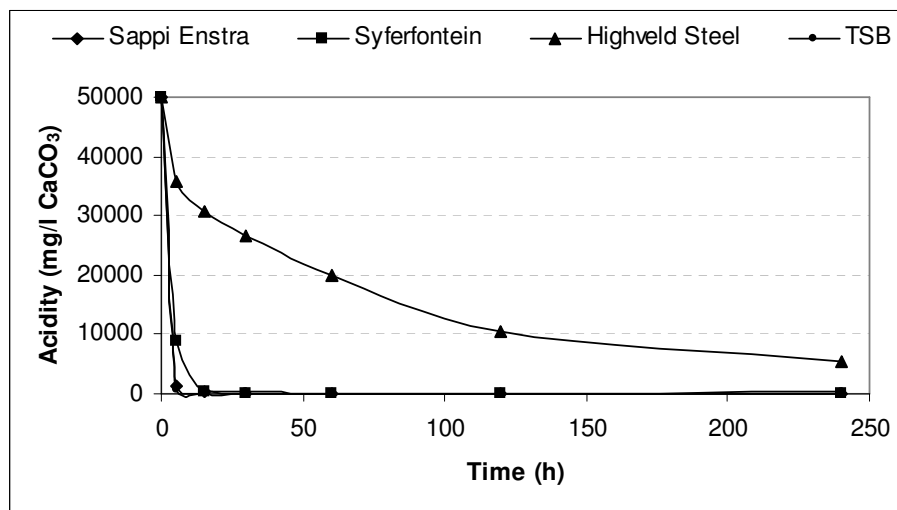


Figure 4. Effect of different limestones on acidity

## 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:

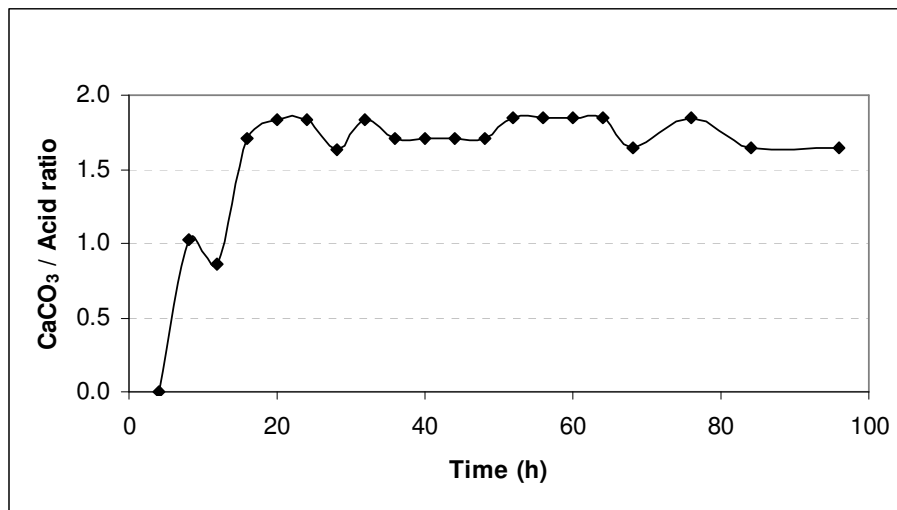
- The chemical composition of limestone treated water was similar to that of lime treated water. In both cases the pH was raised from 1.6 to above 6.4. Acidity was reduced from 33 g/l (as CaCO<sub>3</sub>) to less than 0.06 g/l (as CaCO<sub>3</sub>), sulphate reduced from 40 g/l to less than 7 g/l, arsenic reduced 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).

**Table 3.** Comparison between chemical compositions of lime and limestone treated water

Parameter	Units	Min detectable limit	Lime		Limestone		
			Feed	pH 4 (R1)	pH 6.5 (R2)	pH 4 (R1)	pH 6.5 (R2)
pH			1.5			4.2	6.4
Acidity	mg/L as CaCO <sub>3</sub>		33,294			438	61
Sulphate	mg/L as SO <sub>4</sub>		40,000			7,873	6,840
Iron(II)	mg/L as Fe		51			7	6
Sodium	mg/L as Na	0.05	80	69	64	440	350
Potassium	mg/L as K	0.11	52	60	59	54	32
Calcium	mg/L as Ca	0.05	590	460	450	490	250
Magnesium	mg/L as Mg	0.02	1,200	1,200	1,100	1,100	560
Aluminium	mg/L as Al	0.08	90	23	<0.08	12	<0.08
Chromium	mg/L as Cr	0.04	3.2	0.08	<0.04	0.08	<0.04
Manganese	mg/L as Mn	0.01	68	120	44	180	43
Iron	mg/L as Fe	0.02	17,000	4.1	0.59	16	0.53
Cobalt	mg/L as Co	0.12	33	27	7.3	28	4.2
Nickel	mg/L as Ni	0.05	230	170	41	190	26
Copper	mg/L as Cu	0.12	53	25	<0.02	17	0.03
Zinc	mg/L as Zn	0.17	44	34	1.9	38	1.2
Arsenic	mg/L as As	0.34	4 100	0.93	0.44	0.59	< 0.34
Chloride	mg/L as Cl	5.0	<5	33	34	46	52
Fluoride	mg/L as F	0.1	<0.1	0.19	<0.1	0.31	0.19

#### Water Quality following 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<sub>3</sub> dosage to acid concentration ratio of 1.67 (Figure 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<sub>3</sub>).



**Figure 5.** Ratio of CaCO<sub>3</sub> dosage: acid concentration of feed water in the limestone process as a function of time.

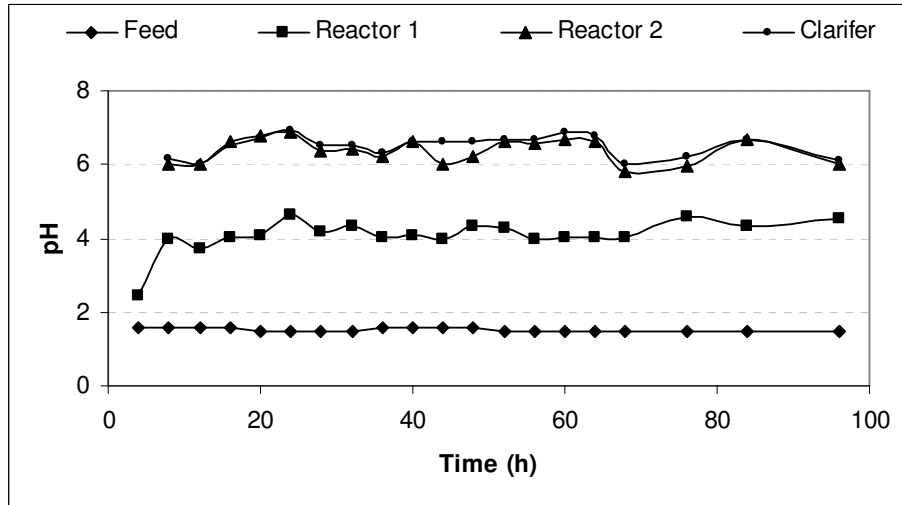


Figure 6. Behaviour of pH when arsenic-rich acid water was treated with limestone

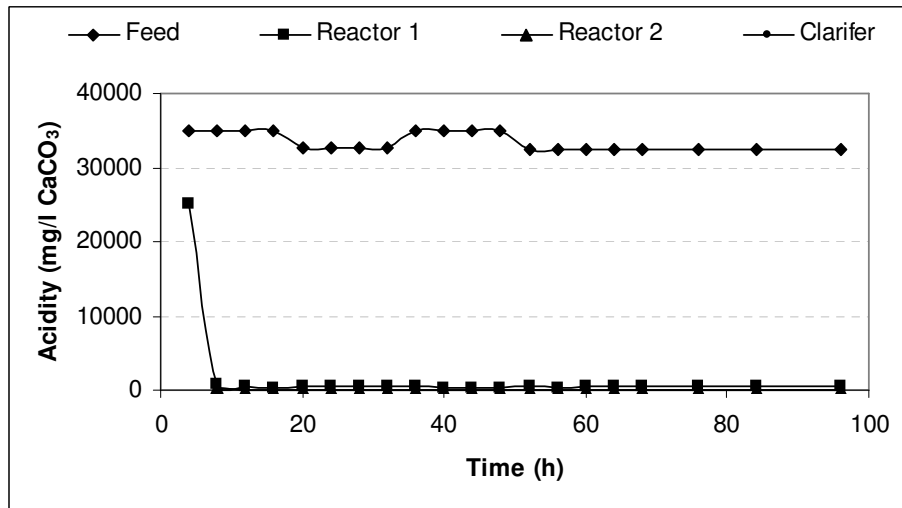


Figure 7. Behaviour of acidity when arsenic-rich acid water was treated with limestone

#### 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 neutralized with limestone is identical to that neutralized with lime. In the case of limestone neutralization, CO<sub>2</sub> is evolved. CaO remains in solution as Ca(OH)<sub>2</sub>.

Table 2. TCLP values of the sludge from the lime and limestone treatment processes

Parameter	Units	Minimum detectable limit	Lime Sludge		Limestone Sludge	
			pH 4 (R1)	pH 6.5 (R2)	pH 4 (R1)	pH 6.5 (R2)



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

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.

**Table 3.** Comparison between the cost of lime and limestone

Parameter	Unit	Lime	Limestone
Acidity	g/L	55	55
Flow	m <sup>3</sup> /h	17	17
Purity	%	85	70
Utilization efficiency	%	90	90
Mol mass	Daltons	56	100
Acid load	t/day CaCO <sub>3</sub>	682	682
Alkali usage	t/d	499	1083
Price	R/t	800	200
Cost	R/month	399,497	216,564
Saving	%	0	45.8

#### 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 removed from 33.5 to 0.06 g/L (as CaCO<sub>3</sub>).
- There is no significant difference in the TCLP characteristics of the resultant sludge when water was treated with lime or with limestone.
- Sludge from the limestone treatment process can be disposed of in a non-hazardous landfill site.

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