



An integrated limestone/lime process for partial sulphate removal

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Synopsis

This paper will focus on two topics, namely (1) an innovative process for the neutralization and partial sulphate removal of acid streams produced during coal mining and processing and (2) optimization of this integrated neutralization process by adding small amounts of synthetic organic polymers.

The integrated lime and limestone process has been developed to neutralize acid mine water and to remove sulphate (to less than 1 200 mg/l), magnesium and metals. Limestone and lime treatment is the most cost-effective technology for neutralization and partial sulphate removal of acidic/sulphate-rich water to sulphate levels of less than 1 500 mg/l due to precipitation of magnesium and removal of the associated sulphate fraction (through gypsum crystallization). Neutralized mine water of this quality may be suitable for irrigation.

The process consists of the following stages:

1. Limestone (CaCO_3) neutralization to raise the pH to 7 and CO_2 -production.
2. Lime (Ca(OH)_2) treatment to pH 12 for Mg(OH)_2 precipitation and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystallization.
3. pH adjustment with CO_2 recovered from stage 1 and CaCO_3 precipitation.

Retention times of 1 hour, 4 hours and $\frac{1}{2}$ an hour were required by stages 1, 2, and 3 respectively. The sulphate level was reduced to 1 094 mg/l, which is less than the original aim of 1 200 mg/l. Chemical costs associated with neutralization, using limestone instead of lime, are reduced by 69% in the integrated limestone/lime process.

The overflow water from the clarifier of each of the above stages generally contains a wide variety of colloidal impurities that may cause the water to appear turbid or may impart colour. This results in very slow sludge settling rates that cause overflow water with a high degree of turbidity and colour. There are a number of successive or simultaneous stages involved in the agglomeration of particles.

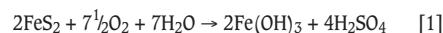
To get optimum neutralisation of the acid water and partial sulphate removal to below the saturation level of gypsum (i.e. 1 500 mg/l), maximum sludge recovery is needed. The higher the concentration of seed crystals, the larger the surface area. Therefore, effective removal of suspended and colloidal matter from the overflow of each stage is required and can be achieved by coagulation and flocculation. The polymers PAC6 and 3095 were effectively used as coagulant and flocculant respectively. The addition of these polymers resulted in a clear overflow in each of the above stages with a very low turbidity.

Introduction

By its very nature and scale, mining makes a marked and visual impact on the environment. Mining is, however, implicated as a significant contributor to water pollution, the prime reason being that most of our geological formations that are mined contain pyrites, which oxidize to form sulphuric acid when exposed to air and water. The scarcity of water in South Africa is exacerbated by pollution of the surface and groundwater resources. Typical pollutants of the aquatic environment include industrial effluents and acid mine drainage.

Mine water in the Upper Olifants River Catchment in Mpumalanga (upstream of Loskop Dam) is at times discharged into local streams, resulting in local acidification and regional salination of surface water resources. Pollution of surface water can be prevented by collecting and treating mine water to a quality where it could be re-used without restriction (Cleanwater 2020 Initiative). Although mine water in the Olifants River Catchment currently amounts to only 4.6% of the total water usage, it contributes 78.4% of the sulphate load.

Mine water in the catchment of the Witbank Dam and Middelburg Dam are rich in calcium, magnesium, sulphate and acid pH. This is due to oxidation of pyrites in the coal ore and coal waste to sulphuric acid Equation [1], followed by neutralization with dolomite, which is also present in the coal ore. When the pH is below 5.5, water can be toxic to plant and fish life and corrosive to pipelines and equipment.



Sulphate needs to be removed from effluents for the following reasons:

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An integrated limestone/lime process for partial sulphate removal

- Prevention of salination of surface water—discharge recommended concentration <500 mg/l.
- Prevention of scaling—when no Na or Mg is present, the saturation level = 1 500 mg/l SO₄
- Biocorrosion
- Acid corrosion—when acid water is neutralized with lime, scaling of the equipment by the unstable water is produced, and malfunctioning of dosing equipment and settling of particles in pipelines and valves occur. The latter often causes blockages, which may result in under-dosage, which in turn may lead to acid corrosion.

Typical sulphate removal processes are the biological sulphate removal process, RO and EDR. The integrated limestone/lime treatment process can be used for neutralization of acid water and partial sulphate removal to below the saturation level of gypsum, i.e. 1 200 mg/l. The benefits of this process are:

- Limestone treatment is the most cost-effective treatment for neutralization of acid water, and partial sulphate removal to levels of 2 000 mg/l can be achieved
- With high lime treatment (pH >11), sulphate can be reduced further to 1 200 mg/l through gypsum crystallization and magnesium precipitation
- Scaling and corrosion problems are reduced during re-use of the water in the mines
- Discharge water needs to meet certain quality requirements in accordance with environmental legislation.

Earlier investigations¹⁻³ showed that acid mine water can be neutralized effectively by limestone. Maree *et al.*⁴ also found that the sulphate concentration in acid mine water can be reduced from 15 000 to 2 000 mg/l through limestone neutralization.

Limestone and lime treatment of acid water were effectively introduced to the water reclamation field at the Navigation Colliery near Witbank. Considerable attention has been paid to the clarification of the treated water in order to remove small particles by combining them into larger aggregates by coagulation and flocculation. These particles are mainly of chemical origin as limestone and lime are added to the system, which results in the production of Mg(OH)₂, CaSO₄·2H₂O and CaCO₃.

The process of destroying the stabilizing forces and causing aggregation of clay colloids is referred to as *chemical coagulation* (Benfield *et al.*⁵). It can also be referred to as the addition of a chemical to water or sewage so as to precipitate, usually, a metal hydroxide that catches and so removes from the water most of the tiny suspended particles. The chemical lessens the surface charge of the suspended matter, unlike flocculation. Flocculation can be considered the agglomeration of destabilized particles into microfloc, and later into bulky flocules which when settled can be called floc. Flocculation can be promoted by gentle stirring (mechanical flocculation) or by adding chemicals (flocculants).

Synthetic organic polymers such as PAC6 and Type 3095 can be used effectively as coagulants and flocculants. These polymers are long-chain molecules comprised of many monomers. Polymers typically have a helical molecular

structure comprised of carbon chains with ionizing groups attached. When the groups are ionized in solution, an electrical repulsion is created, which causes the polymer to assume the shape of an extended rod. As the ionized groups become attached to colloidal particles the charges are neutralized and the polymer starts to coil and form a dense floc with favorable settling properties.

The associated environmental impact is a growing concern related to water and effluent treatment. The sludges, which result from the process and which are not recycled back to the respective stages of treatment, are inert and do not contain any toxic metals. These sludges are therefore sent through a filter press to produce a 'cake' that can be discharged. Waste sludge withdrawn from the bottom of the reactor can contain between 0 and 30% CaCO₃ (m/m dry basis), depending on the limestone excess that is applied. If the sludge contains a significant amount of CaCO₃, it might be cost effective to combine the waste sludge with acid feed water prior to discharge in order to achieve maximum utilization of the CaCO₃.

The main objectives of this investigation, where limestone instead of only lime is used to neutralize and remove sulphates partially from acid mine water, were:

- To determine the chemical composition of the coal-processing water before and after treatment
- To determine the effect of various parameters on the rate of gypsum and CaCO₃ crystallization
- To determine the sludge characteristics of the gypsum and CaCO₃ produced
- To determine the effect of the polymers (as coagulant/flocculant) on the chemical composition of the coal-processing water before and after treatment in all stages of the treatment process (settling rate of sludge and clarity of overflow water)
- To determine the optimum dosage of coagulant/flocculant for each stage of the treatment process (concentration).

Materials and methods

Feed Water

A synthetic solution (diluted sulphuric acid), similar to leachate from a waste coal dump, was used as feed water for batch studies in beakers. The solution contained 3 g/l acidity (as H₂SO₄) and 160 mg/l Mg. For batch or continuous studies on a pilot scale, acid mine water was used for treatment in all stages (limestone, lime and CO₂ treatment) of the process (see Table I for chemical composition of the feed water).

Table I

Chemical composition of acid mine water fed to the limestone/lime treatment process

Parameter	pH	SO ₄ ²⁻ mg/l	Ca mg/l	Mg mg/l	Na mg/l	Mn mg/l	Cl ⁻ mg/l	Alkalinity mg/l
Acid feed water	2.10	3 000	420	160	41	17	16	0

An integrated limestone/lime process for partial sulphate removal

Feedstock

Waste powder limestone (CaCO_3) from paper industries was used in the limestone neutralization stage of the process. For the gypsum crystallization stage, unslaked lime (Ca(OH)_2) was used. The limestone was analysed for its calcium, magnesium and alkalinity content. Calcium and magnesium were determined with EDTA, while the alkalinity content was determined by dissolving it in a stoichiometrically excessive amount of hydrochloric acid. This excess amount of hydrochloric acid was titrated with sodium hydroxide (see Tables II and III for chemical composition of powder lime and limestone respectively).

The polymers that were used as coagulant and flocculant respectively are PAC6, which is poly-aluminium-hydroxy chloride with a specific gravity of 1.3 (only available as solution) and Type 3095 (granules), poly-acrylamide which is a co-polymer of acrylamide and acrylic acid with a molecular weight of about 15 000 000 g/mole. These chemicals were supplied by Montan Chemicals, Germiston. The coagulant was used as received, while a stock solution of 2.5 g of Type 3095 flocculant per litre distilled water was made up on a weekly basis. For dissolving the flocculant in distilled water, a small amount of methanol was first added to the granules to assure effective granular dissolution.

Batch studies in beakers and batch and continuous studies on pilot scale

Neutralization studies

Batch studies (no feed water) were conducted in 1/ beakers at atmospheric pressure to study the kinetics of acid water neutralization with limestone and lime. Samples were taken regularly and analysed for pH, calcium, magnesium, sulphate, alkalinity and MLSS (mixed liquid suspended solids). The same variables as for batch studies were measured during continuous studies (constant feed water) for different hydraulic retention times.

Table II

Chemical composition of powder lime (Ca(OH)_2)

Bulk density (kg/m ³)	Available Ca(OH)_2 (min%)	Available CaO (min%)	Total CaO (min%)	MgO (max%)	$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ (max%)	SiO_2 (max%)	Acid insolubles (max%)
560	94	71	72	1	0.3	0.5	1

Particle size: fine powder, 100% passing 90 micron

Table III

Chemical composition of powder limestone (CaCO_3)

CaCO_3 (%)	Ca(OH)_2 (%)	Ca (mg/g)	Mg (mg/g)	Na (mg/g)	K (mg/g)	Moisture (%)
97.02	3.87	354.08	5.66	11.17	0.43	24

Percentages based on dried basis

Sludge settling studies

Batch studies were conducted in the laboratory in 1/ volumetric cylinders at atmospheric pressure and ambient temperature to study the efficiency of the two polymers, PAC6 and 3095 as coagulant and flocculant respectively. The polymers were added separately to the effluents of these three stages as follows:

Primary effluent (limestone neutralization): 3095 → flocculant
Secondary effluent (lime treatment for gypsum crystallization): 3095 → flocculant
Tertiary effluent (CO_2 treatment for CaCO_3 precipitation): PAC6 → coagulant
3095 → flocculant

Each effluent was stirred at a medium stirring rate for 1 minute, whereafter increasing amounts of polymer were injected into the solution (effluent). For the tertiary effluent, an additional stirring of 1 minute between the coagulant and flocculant addition was allowed. These tests enable quantification of the influence of the mentioned polymers as effective coagulants/flocculants by means of polymer concentration, settling rate and clarity. Based on the studies conducted in the laboratory, the optimum amount of polymer was used in each consecutive step of the process at pilot plant scale to demonstrate the effective settling of the various sludges and clear overflow water on a larger scale. These cylindrical tests should be used only for the evaluation of the operation, chemical dosage and removal of contaminants. They are not valid for evaluating the size of the clarifier or to simulate a reactor-clarifier, but serve merely as guidelines.

Equipment and procedure

A mobile pilot plant at Navigation Coal Mine near Witbank, with a capacity of 10m³/day was used for on-site treatment of the mine water. A CaCO_3 -handling and dosing system (see Figure 1) was designed and implemented for treating the acid mine water in the first stage of the process at the pilot plant (see Figure 2).

Limestone neutralization using a CaCO_3 -handling and dosing system (Figure 1)

The CaCO_3 -handling and dosing system, which is the first technology of its kind to be built on full scale, has a capacity of 10 Ml/day and consists of the following items:

- A concrete slab with a slope of 7° onto which the CaCO_3 powder is dumped and stored. The CaCO_3 powder is slurried with a water jet and collected in a slurry tank through gravity flow.
- A slurry tank with stirrer, which acts as a mixing chamber for the acid water and CaCO_3 as well as recovery of CO_2 gas.
- A ball valve in the slurry tank to maintain the water level at a specific height by dosing tap or clarified water.
- CaCO_3 recycle slurry pump, which withdraws some of the slurried CaCO_3 of higher density from the slurry tank or clear water through a water jet onto the CaCO_3 dump to keep the CaCO_3 concentration at a constant level. The slurried CaCO_3 is returned by gravity via the sloped concrete slab back to the slurry tank. The CaCO_3 concentration is controlled by the load cells underneath the slurry tank, which activate/stop the recycle pump at preset low/high values.

An integrated limestone/lime process for partial sulphate removal

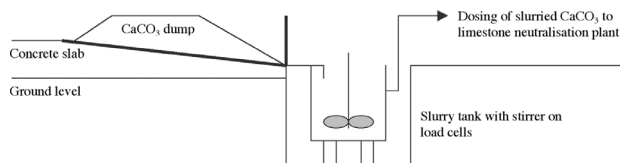


Figure 1—Schematic illustration of CaCO_3 -handling and dosing system

- A transfer pump, feeding slurried CaCO_3 into the limestone make-up tank.

Stage 1: Limestone neutralization

Acid feed water from the plant and slurried limestone from the CaCO_3 -handling and dosing system were pumped into a reactor onto which a stirrer was fixed. The overflow from the reactor went into a clarifier from where sludge was recycled back to the reactor.

Stage 2: Gypsum crystallization

Lime ($\text{Ca}(\text{OH})_2$) was fed to a second reactor, containing the neutralized water of the neutralization stage from the first reactor. Fine particles that washed out from the reactor, were allowed to settle in a clarifier and were returned to the reactor via a recycle pump.

Stage 3: CO_2 -dosing system

During this stage, CO_2 recovered from the limestone neutralization stage was bubbled through the treated water of the gypsum crystallization stage. The CaCO_3 that precipitated during this stage was recycled to the first stage where limestone was used for neutralization of the acid water.

In all three stages, the polymer(s) was added to the effluent in the overflow between the reactor and clarifier for rapid mixing to disperse the polymer(s) homogeneously and to enable good contact between the effluent and polymer(s). In each clarifier, slow speed agitation was provided by recycling a part of the sludge back to its reactor by means of a variable speed pump to enable the growth of the aggregates into voluminous flocs by collision and entrapment of the suspended matter.

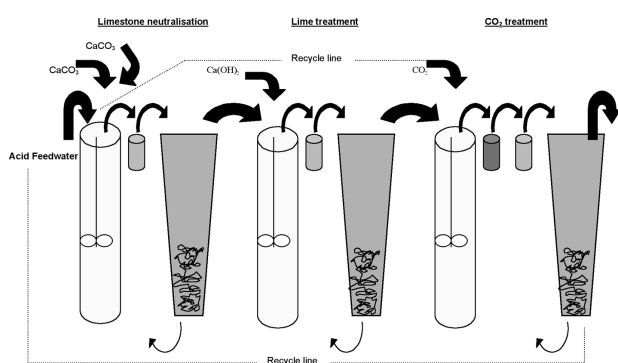


Figure 2—Schematic illustration of the limestone neutralization-, gypsum crystallization- and CO_2 -precipitation system on pilot plant scale

Programme

Neutralization studies

Batch studies on gypsum crystallization and CaCO_3 crystallization

The following parameters were varied to evaluate and optimize the rate of gypsum crystallization:

- Settling rate of sludge (200, 100, 75, 50, 30, 20 and 10%)
- Over-saturation concentration

Continuous studies on gypsum crystallization and CaCO_3 crystallization

The quality of the water from the gypsum crystallization stage was studied on a continuous basis at various hydraulic retention times (HRT), varying between 0.2 and 3.5 hours.

Sludge settling studies

Batch studies on coagulation/flocculation

The concentration of polymer added was varied to evaluate and optimize the efficiency of the polymers as coagulant/flocculant by measuring the clarity and settling rate of each trial.

Continuous studies on coagulation/flocculation

The quality of the water before and after treatment for the various stages of the process was studied at the pilot plant on a continuous basis at different hydraulic retention times.

Analysis

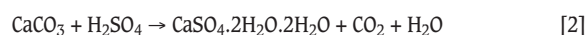
Samples were collected regularly and filtered through Whatman No. 1 filter paper. Determinations of pH and sulphate were carried out manually according to procedures described in Standard Methods⁶. Calcium and magnesium were recorded with the ICP method for metals. Alkalinity was determined by titrating with sodium hydroxide to pH 7.0. Clarity was determined with a spectrophotometer, measured in NTU (Nephelometric Turbidity Unit).

Results and discussion

Water quality

The chemical composition of the acid mine feed water and the water qualities after each of the three stages of treatment are listed in Table IV.

From Table IV, it can be noted that limestone (CaCO_3) can be used effectively in the integrated process for neutralization of acid water (HRT = 1 hour). When discard leachate was treated with limestone, the pH of the water was raised from 2.10 to 7.68 in the neutralization reactor. A decrease of 96.6% in the acidity of the water after limestone neutralization is a result of the following reaction:



When the water is under-saturated to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), acidity removal is achieved at a high rate. Once the water is saturated to gypsum, further dissolution of CaCO_3 is limited by the rate at which gypsum crystallizes out of solution.

An integrated limestone/lime process for partial sulphate removal

Table IV

Water qualities of feed water and treated water of each of the three stages of treatment

Parameter	Acid feed water	Limestone neutralization	Flocculation	Gypsum crystallization through lime treatment	Flocculation	CaCO ₃ precipitation through CO ₂ treatment	Coagulation + Flocculation
pH	2.10	7.20	7.68	11.71	12.26	9.46	8.50
SO ₄ ²⁻ (mg/l)	3 000	1 890	1 900	1 100	1 094	1 199	1 219
Alkalinity (mg/l)	-3 000	108	100	960	940	71	50
Ca (mg/l)	420	638	636	994	829	530	542
Mg (mg/l)	160.00	147.00	147.00	0.22	0.00	2.88	3.03
Al (mg/l)	556.00	0.30	0.39	0.00	0.00	0.74	1.11
Na (mg/l)	41.00	46.40	40.00	45.60	47.00	45.30	46.80
Mn (mg/l)	17.00	13.02	13.00	0.00	0.00	0.00	0.01

The stability of the treated water with respect to calcium carbonate is determined by the pH, calcium and alkalinity values of the treated water. The alkalinity of the treated water was 100 mg/l (as CaCO₃) owing to the escape of CO₂ from the solution and can be ascribed to the following reaction:



This is a benefit as the increased buffer capacity contributes to stabilizing the pH of the water (Table IV). Sulphate was reduced from 3 000 to 1 900 mg/l after neutralization with limestone. The calcium concentration increased during treatment from 420 to 636 mg/l. Only partial manganese removal (17 to 13 mg/l) was achieved, which can be expected if the pH is not raised to values higher than 7.8. Manganese removal is only achieved at pH 9.5.

The relationship between pH in the gypsum crystallization reactor and the sulphate in solution is evident from Table IV and Figures 3a and b in which the temporal behaviour of pH and SO₄²⁻ are illustrated over a period of 28 days. It can be further concluded that sulphates in the neutral water can be reduced effectively with lime treatment during gypsum crystallization to levels below the original aim of 1 200 mg/l SO₄²⁻, i.e. 300 mg/l below the saturation level of gypsum (1 500 mg/l), by raising the pH to 12.26 (HRT = 2.72 hours). Because of the removal of sulphates to this low level, no scaling of pipelines in the plant where the treated water is re-used, will occur as the treated water is well below the saturation level of gypsum. The water is also suitable for irrigation as 1 200 mg/l is a typical limit for such practice. Improved sulphate removal is achieved when magnesium is

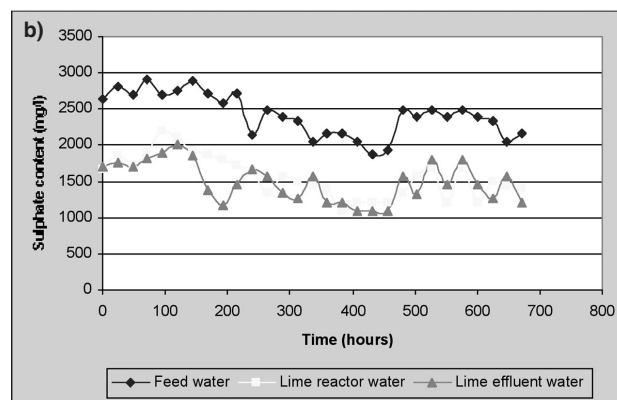
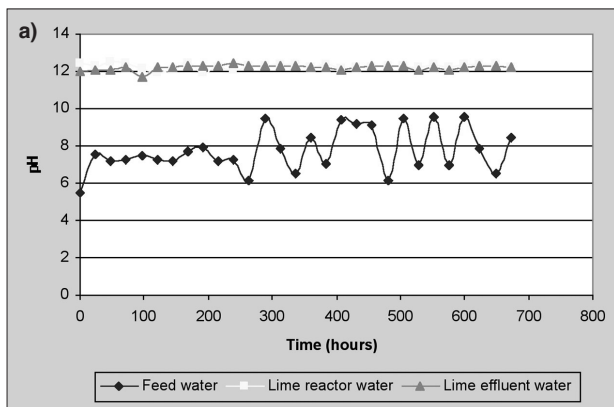
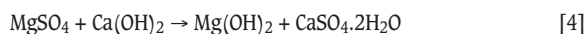


Figure 3—Levels of pH and SO₄²⁻ of the neutralized water during gypsum crystallization with lime over a period of 28 days at HRT of 2.72 hours

removed at the high pH level of 12.26 after lime treatment. The magnesium concentration at pH 7.68 was 140 mg/l while at pH 12.26, the magnesium content dropped to zero, due to magnesium hydroxide precipitation. The calcium concentration increased from 636 to 829 mg/l due to the dissolution of lime (Ca(OH)₂). This phenomenon can be explained by the following reaction:



Rate of gypsum crystallization and CaCO₃ precipitation

During limestone treatment, neutralization occurs with the soluble Ca(OH)₂ resulting in a 96.6% decrease in acidity and an increase in pH and Ca concentration in the bulk water.

It has been shown by Maree *et al.*⁴ that the above-mentioned increase in dissolved Ca concentration can result in super-saturation with respect to gypsum and concomitant precipitation with sufficient reaction time. The level to which SO₄²⁻ was removed was determined by the solubility product of gypsum, which is a function of the Ca and SO₄²⁻ concentrations as well as the ionic strength of the solution.

Maximum sulphate removal can be achieved during alkali treatment by raising the pH to 12 and higher for magnesium precipitation and removal of sulphate associated with magnesium by means of gypsum crystallization. During gypsum crystallization, the gypsum concentration was found to have a major influence on the rate of sulphate removal.

An integrated limestone/lime process for partial sulphate removal

This phenomenon, which is illustrated in Table V and Figure 4, concurs with the findings of Maree *et al.*⁴, who stated that the rate of crystallization is influenced by the concentration of gypsum seed crystals.

The rate of neutralization takes place in two stages, a fast first phase and a slow second phase. The first phase is associated with the neutralization of pure H₂SO₄ solutions. Clayton *et al.*⁷ proposed the following equation:

$$-dc/dt = K.S.C_{ab} \quad [5]$$

where $-dc/dt$ is the reaction rate, K the rate constant per unit surface area, S the total available surface area of CaCO₃ and C_{ab} the concentration of H₂SO₄.

It can therefore be concluded that the rate of gypsum crystallization is directly proportional to the surface area of the gypsum, which is illustrated in the following equation:

$$d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt = k[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)[C - C_0]^2 \quad [6]$$

where $d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt$ represents the rate of crystallization, k the reaction rate constant, $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)$ the surface area of the seed crystals, C the initial concentration of calcium sulphate in solution and C_0 the saturated concentration of calcium sulphate in solution.

Figure 5 is an illustration of the removal of sulphates through gypsum crystallization from the neutralized water, if sufficient time is provided, compared to that of the limestone neutralization process. It is evident from the decrease of the sulphate content of the water that about 2 hours are required to reduce the sulphates in the water to 1 100 mg/l during the gypsum crystallization stage with lime treatment.

Water, which is under-saturated with respect to gypsum, can be produced by adjusting the pH with CO₂ from the high levels of 12 and higher to a level where CaCO₃ has a low solubility. Figure 6 shows the relationship between pH and Ca concentrations in solution. It can be seen that calcium was reduced from 1 100 mg/l at pH 13.30 to 487 mg/l at pH 8.80 due to CaCO₃ crystallization.

Table V

Water qualities of feed water and treated water of each of the three stages of treatment

Sludge concentration (g/l)	1	10	50	200
Reaction rate (g/l. day)	38.02	52.70	102.53	125.76

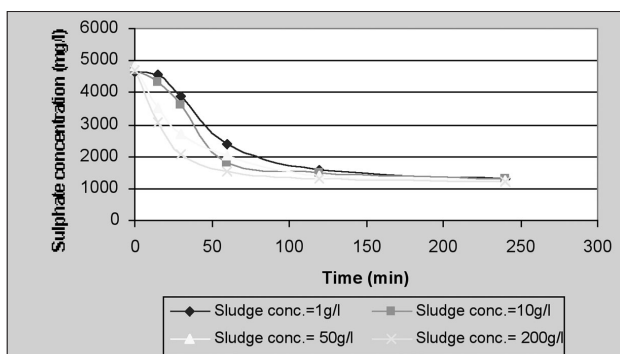


Figure 4—Effect of sludge concentration on rate of gypsum crystallization at pH 12

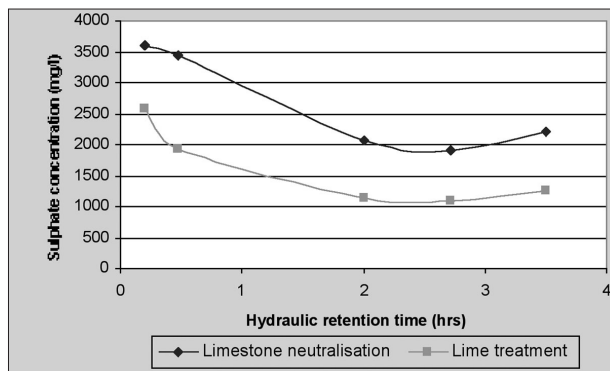


Figure 5—Effect of different retention times on rate of limestone neutralization and gypsum crystallization

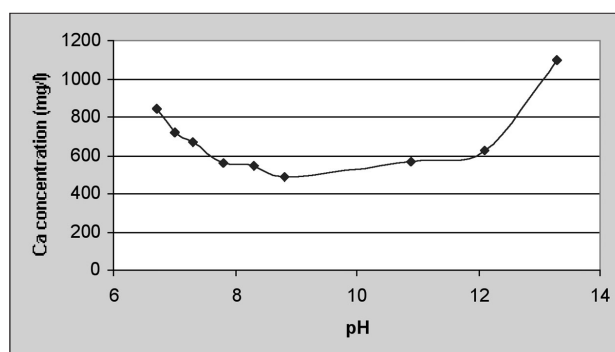


Figure 6—Relationship between pH and Ca concentration

The fact that CO₂ bubbling into the treated water of the gypsum crystallization stage resulted in an immediate decrease in pH and that it needed a very short retention time, makes it almost impossible to determine the effect of various parameters on the rate of CaCO₃ precipitation. The pH of the water was adjusted to 8.50 after CO₂-bubbling and the calcium concentration decreased from 829 to 487 mg/l as CaCO₃ crystallized out.

According to Loewenthal and Marais⁸, the saturation, under-saturation and super-saturation states of CaCO₃ are theoretically identified by the activity product of Ca²⁺ and CO₃²⁻ species that is compared with the solubility product constant k_{sp} for CaCO₃. Above the solubility product, CaCO₃ will precipitate out of the water and if below the solubility product, CaCO₃ will dissolve. The rate of precipitation or dissolution is described by the following equation:

$$-d[\text{Ca}^{2+}]/dt = kS \left\{ (\text{Ca}^{2+})^{1/2} (\text{CO}_3^{2-})^{1/2} - k_{sp}^{1/2} \right\}^2 \quad [7]$$

where k is the precipitation rate constant, S the surface area of CaCO₃ growth/dissolution sites and $()$ the activity in moles/l. Adlem⁹ further stated that this equation can be described as practical for the design of softening plants. The rate of precipitation depends on k , S and the term in brackets. Although k is affected to an unknown extent by crystal structure, S depends on size, mass and structure of the crystals. By controlling S and the degree of super-saturation (term in brackets), the rate of precipitation or dissolution of CaCO₃ can be determined.

An integrated limestone/lime process for partial sulphate removal

Table VI

Suspended solids content of the gypsum sludge at different dilutions before settling and settling rate after 24 hours

Reactor	Dilution (%)						
	200	100	75	50	30	20	10
Gypsum crystallization							
Suspended solids before settling (mg/l)	26 500	11 135	10 015	5 630	2 825	1 985	1 110
Settling rate of gypsum sludge (m/h)	0.101	0.293	0.428	0.633	0.904	1.171	2.483

Conditions: HRT in crystallization reactor: 2.72 hours

Sludge characteristics

The suspended solids content and settling rate of the gypsum sludge after 24 hours settling time are shown in Table VI at different dilutions.

For the gypsum sludge, the settling rate increased from 0.101 to 2.483 m/h as the dilution decreased from 200 to 10%. A low sludge settling rate (0.101 m/h) would therefore be expected in the gypsum crystallization reactor where the sludge solids content is high (26 500 mg/l), while a high sludge settling rate (2.483 m/h) can be expected in the sludge separation stage where the solids content is low (1 110 mg/l). The sludge concentration can be controlled by withdrawing sludge from the bottom of the reactor in which the solids content would be at a maximum.

As mentioned earlier, the CaCO_3 sludge, produced through CO_2 bubbling of the treated water of the gypsum crystallization stage, had a wide variety of particle sizes which made it almost impossible to determine settling rates. These results are supported by the conclusions made by Pontius⁶ in which he stated that individual particle behaviour is influenced or hindered by the presence of other particles and that the flow characteristics of the bulk suspension can be affected. With increased particle concentration, the free area between particles is reduced, causing greater

interparticle fluid velocities and alteration of flow patterns around particles. Consequently, the settling velocity of a suspension is generally less than that of a discrete particle. When the size, shape or density of particles in a suspension is not uniform, individual particles will have different settling velocities and smaller particles tend to be dragged down by the motion of larger particles.

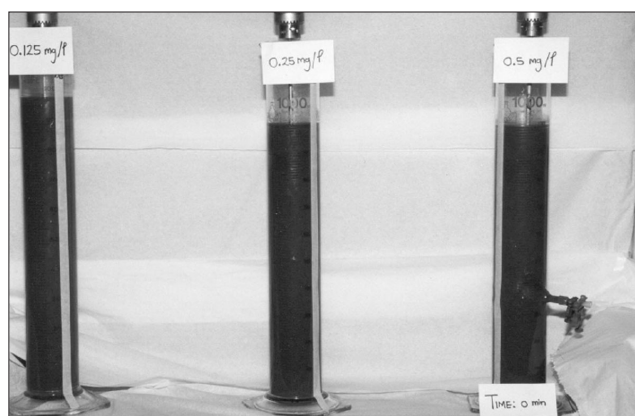
Effect of polymers for settling reasons on chemical composition of treated water

To optimize the process, settling of the various sludges in the three stages was improved by the addition of the polymers PAC6 and 3095 as coagulant and flocculant respectively to the effluents. The addition of limestone, lime, CO_2 and polymeric substances to the secondary effluents in the various pH ranges had the following effects on its inorganic composition, as illustrated in Table VI.

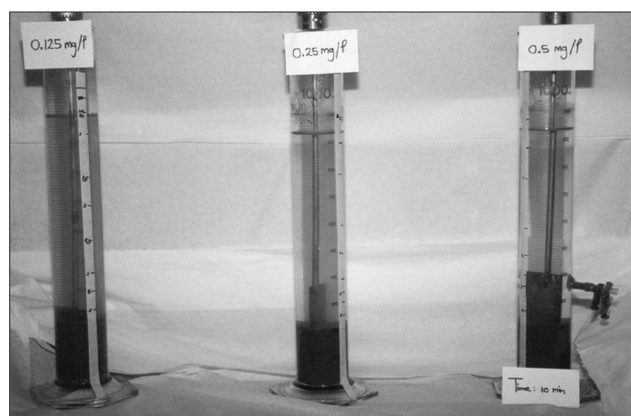
The presence of Al ions in the various secondary effluents played an important role in the achievement of optimum clarification during limestone, lime and CO_2 treatment. This is due to the formation of gelatinous Al-precipitated compounds that is illustrated in the decrease of Al concentration, from 556 mg/l to zero, in each of the three stages of the process. It can therefore be concluded that the Al content in the polymers used as coagulant or flocculant did not affect the final quality of the treated water. Al precipitated in the same way as Fe and Mn and can be treated as for inert sludge. Metal hydroxides are inert and therefore do not oxidize like metal sulphides under standard conditions to form H_2SO_4 and metals in solution.

Optimum dosage of polymeric additions for improved settling of sludges

It is known that particles in the relatively dilute solutions did not act as discrete particles but coalesced during sedimentation (Metcalf and Eddy¹⁰). As coalescence or flocculation occurs, the mass of the particle increases and it settles faster. The extent to which flocculation occurs depends on the opportunity for contact, which varies with a number of variables. One of these variables is the concentration of the particles.



Photograph 1—Effect of various concentrations of flocculant 3095 on settling rate of sludge from stage 1—time 0 min



Photograph 2—Effect of various concentrations of flocculant 3095 on settling rate of sludge from stage 1—time 10 min

An integrated limestone/lime process for partial sulphate removal

Table VII

Effect of polymer concentration on the settling rate of the sludges produced in the three consecutive stages of the treatment process (including polymer cost)

Stage 1: Limestone neutralization							
Polymer concentration (mg/l treated water)	0.000	0.125	0.250	0.500	1.000	1.250	1.500
Sludge settling rate (m/h)	1.30	4.62	5.10	5.04	5.37	5.79	5.91
Cost to treat 1m ³ water (cents)	0.00	0.28	0.55	1.10	2.20	2.75	3.30
Stage 2: Gypsum crystallization with high lime treatment							
Polymer concentration (mg/l treated water)	0.000	0.250	0.500	0.750	1.250	1.750	2.000
Settling rate (m/h)	0.21	0.67	0.84	1.64	2.58	3.44	5.61
Cost to treat 1m ³ water (cents)	0.00	0.55	1.10	1.65	2.75	3.85	4.40
Stage 3: CaCO ₃ precipitation with CO ₂ treatment							
Polymer concentration (mg/l treated water)	0.000	0.400	0.500	0.625	1.000	1.250	1.500
Settling rate (m/h)	0.00	19.98	20.04	20.10	22.08	20.34	20.16
Cost to treat 1m ³ water (cents)	0.00	4.13	4.35	4.63	5.45	6.00	6.55

A number of experiments was conducted at various polymer concentrations and the rate of settling of the sludges as well as clarity of the treated water were studied. Photographs 1 and 2 illustrate these actions. These results (including cost estimates) are also listed in Table VII.

The contacting particles tended to settle as a zone, maintaining the same relative position with respect to each other. As the particles in this region settled, a relatively clear layer of water was produced above the particles in the settling region. In the case of stages 1 and 2, an identifiable interface developed between the more or less clear upper region and the hindered settling region. The rate of settling in the hindered settling region is a function of the concentration of solids and their characteristics. As settling continued, a compressed layer of particles began to form on the bottom of each cylinder in the compression settling region. The particles in this region apparently formed a structure in which there is close physical contact between the particles. As the compression layer formed, regions containing successively lower concentrations of solids than those in the compression region extend upward in the cylinder. In the case of stage 3, such a small concentration of sludge was formed and settling of the sludge with an addition of a coagulant and flocculant was obtained within a few seconds.

Inefficient coagulation/flocculation resulted from an overdose of polymer to the system or from intense or prolonged agitation. If excessive polymer is added, the segments may saturate the surfaces of colloidal particles so that no sites are available for the formation of polymer bridges. This can restabilize the particles and may or may not be accompanied by charge reversal. A very narrow optimum

exists for the polymer and overdosing or underdosing will result in restabilization of the colloids. Intense or prolonged mixing may destroy previously formed bridges and lead to restabilization.

An inverse relationship exists between the optimum polymer dosage and the concentration of colloids to be removed. This can be explained as follows: at low colloid concentrations a large excess of polymer is required to produce a large amount of precipitate that will enmesh the relatively few colloidal particles as it settles. At high colloid concentrations, coagulation/flocculation will occur at a lower chemical dosage because the colloids serve as nuclei to enhance precipitate formation.

Depending on the settling rate of the sludge, the clarity of the overflow water and the cost of polymer added for sufficient sludge settling, the optimum concentration of polymer can be determined. Dosages of only 0.50 to 1.0 mg/l are needed for effective settling of the sludge in the first stage of the process with a settling rate of 5.04 to 5.37 m/h. In the second stage of the process only 0.75 to 1.25 mg/l of the polymer is needed to achieve a settling rate of 1.635 to 2.58 m/h. For the third stage, the addition of a coagulant first, followed by a flocculant, necessary to achieve good settling of the very fine CaCO₃ sludge. Only 0.005 ml/l of the coagulant PAC6 and 0.4 mg/l of flocculant 3095 were needed for effective sludge settling. A specific combination of coagulant:flocculant exists and from there the above optimum amount of this specific combination had been experimentally determined.

Economic feasibility

Neutralization and sulphate removal from water to a level where the water quality is suitable for re-use in the process, for irrigation purposes or for discharge into the sewerage network, can be achieved with limestone (CaCO₃) and slaked lime (Ca(OH)₂). For re-use in some areas of the plant, treated water may need to be under-saturated with respect to gypsum to prevent gypsum scaling of equipment. Due to the removal of magnesium, sulphate associated with magnesium and the solubility product of gypsum, which allows lower sulphate concentrations at higher calcium concentrations in solution, sulphate can be removed to lower levels with lime (pH is raised to 12.26) than with limestone (pH is raised to 7.68). Therefore, maximum benefits can be achieved by combining limestone neutralization with lime treatment for neutralizing the water, for complete magnesium removal and for sulphate removal to less than 1 200 mg/l.

The bulk of the solution can be neutralized with limestone (which is much cheaper than lime), followed by lime treatment for metal removal as well as partial sulphate removal. Further treatment of the high pH water with CO₂ (which is generated during limestone neutralization and gypsum crystallization) will not only adjust the pH of the water to neutral levels but CaCO₃ of high quality can also be produced and then recycled to the limestone neutralization stage.

A comparison between the cost associated with neutralizing 1 g/l acidity by using limestone and lime, is illustrated in Table VIII. It can be noted that acid water can be neutralized 69% more cheaply, using limestone instead of lime.

An integrated limestone/lime process for partial sulphate removal

Table VIII

Comparison between chemical costs for neutralizing 1g acid with limestone and lime

Chemical	Molecular mass (g/l)	Purity (%)	Chemical cost (R/t)	Cost of removal of 1g acid (R/M/ acid)
Limestone	100	80	150	190
Slaked lime	74	85	700	610

Table IX

Chemical cost of sulphate removal by means of limestone neutralization and gypsum crystallization

Chemical	Minimum sulphate level (mg/l)	Chemical cost (R/t)	Chemical usage(t/t sulphate)	Cost of sulphate removal (R/t sulphate)
Limestone	1 900	150	1.04	156
Slaked lime	1 200	700	0.77	539

The cost for removing of sulphate to a certain level by means of limestone and lime is listed in Table IX.

It can be noted from Table VIII that the addition of polymers to the effluents of the various stages of the process, to ensure fast enough settling of the sludges, is inevitable. Because of the higher settling rates through the usage of coagulants/flocculants, big savings will be made on capital cost, as much smaller clarifiers are needed. The quality of the treated water was also greatly improved in terms of clarity. Clarity improvement of 63, 92 and 99% can be achieved for the overflow water of the secondary settling sludges in the process by the addition of very small quantities of polymeric substances to the sludges. Settling of these sludges was improved by 74, 90 and 100% in the three consecutive stages of the process.

Conclusions

- Acid water can be neutralized effectively with limestone instead of lime. In addition, sulphate is removed to 1 900 mg/l (as SO₄)
- After limestone neutralization, the sulphate content of the treated water can be further reduced to less than the original aim of 1 200 mg/l by means of lime treatment to a pH level of 12 and higher. When pH values of 12 and higher are reached, gypsum crystallization will take place and magnesium will be fully removed from the water
- The CO₂ produced during the limestone neutralization stage can be used to reduce the high pH of the treated water after gypsum crystallization. The CaCO₃ formed during this stage is recycled to the limestone neutralization stage for re-use
- The contact time required between limestone and lime and the water depends on the surface area of the limestone and the lime. For design purposes, a contact

time of 1 hour is needed for neutralization of acid water with limestone and 2 hours for maximum sulphate removal with lime treatment

- Depending on the required level of sulphate removal, cost savings of up to 61.5% can be achieved by the integrated limestone/lime process, compared to the well-known lime neutralization process that is commonly used by acid water treatment plants
- Due to the very low concentration of Al in the treated water of the process after each stage of treatment, it can be concluded that the polymers used for coagulation/flocculation had no effect on the chemical composition of the treated water after limestone and lime treatment for neutralization and partial sulphate removal
- A contact time of 1 minute between polymer addition for coagulation/flocculation reasons was found to be sufficient for effective settling of the secondary effluents of the three consecutive stages in the process.
- The settling rates of the secondary sludges in the process were increased by 74.2, 91.9 and 100% respectively for the three stages by the addition of PAC6 as coagulant to the third stage and 3095 as flocculant to all three stages of the process. Because of higher settling rates, the clarity of the effluents was also improved greatly.
- Depending on the required level of sludge settling and effluent clarity of the treated water after each stage in the process, large cost savings can be achieved by the addition of a specific amount of polymer to each of the stages.

References

1. MAREE, J.P. and DU PLESSIS, P. Neutralisation of acid mine water with calcium carbonate, *Wat. Sci. Tech.*, 26(9), 1994. pp. 285-196.
2. MAREE, J.P., DU PLESSIS, P. and VAN DER WALT, C.J. Treatment of acidic effluents with limestone instead of lime, *Wat. Sci. Tech.*, 26(1-2), 1992. pp. 345-355.
3. MAREE, J.P., VAN TONDER, G.J., MILLARD, P. and ERASMUS, T.C. Pilot-scale neutralisation of underground mine water, *Wat. Sci. Tech.*, 34(10), 1996. pp. 141-149.
4. MAREE, J.P., DE BEER, M., STRYDOM, W.F. and CHRISTIE, A.D.M. Limestone neutralisation of acidic effluent, including metal and partial sulphate removal, *IMWA. Proceedings of the 1998 Symposium of IMWA*, 1998. Johannesburg, South Africa.
5. BENEFIELD, L.D., JUDKINS, J.F. and WEAND, B.L. *Process Chemistry for water and wastewater treatment*. United States. Prentice-Hall, Engelwood Cliffs, N.J. 1982. p. 510.
6. APHA, *Standard methods for the examination of water and wastewater treatment. 12th ed.* American Public Health Association. New York, McGraw-Hill, 1985.
7. CLAYTON, J.A., DE VILLIERS, M.G., MAREE, J.P. and PIENAAR, G. Calcium carbonate neutralization of acidic effluents in a fluidised bed, *Proceedings of The 1998 Southern Africa Industrial Water Symposium*, 1990. Johannesburg, South Africa.
8. LOEWENTHAL, R.E. and MARAIS, G.V.R. *Carbonate chemistry of aquatic systems: theory and application*. United States. Ann Arbor Science Publishers, 1976. p. 433.
9. ADLEM, C.J.L. *Treatment of sulphate-rich effluents with the barium sulphide process*, M-Dissertation, 1997. p. 107.
10. PONTIUS, F.W. *Water quality and treatment*. United States. McGraw-Hill, 4th ed. 1990. p. 1195.
11. METCALF and EDDY. *Wastewater Engineering: Treatment, disposal and re-use*. United States. McGraw-Hill, 3rd edition. 1991. p. 1334. ♦

CSIR technology implemented at Kromdraai mine*

An opencast coal mine in Witbank, Mpumalanga, is the latest recipient of exciting CSIR-patented technology that is showing great promise in the coal and metals processing industry.

The treatment of acid effluent from mining processes is an ongoing challenge in the mining industry. Neutralization of acid water is essential for maintaining watercourses in good condition, should the treated effluent be discharged to the environment. The CSIR has patented technology for the neutralization of acid leachates and acidic process water to levels that allow for the water's re-use or release into the environment. Thuthuka Project Managers is a licenseholder of this CSIR patent and has implemented the technology across a number of different industries at a number of different sites.

The most recent application of this technology was at Landau Colliery's Kromdraai Mine. This project has special significance for Thuthuka Project Managers as the very first application of the CSIR-patented technology was at Landau Colliery's Navigation Section. The mine was so impressed with the innovative approach to treating acid water that, two-and-a-half years later, it asked Thuthuka Project Managers to build another plant, albeit on a much larger scale than the Navigation pilot plant.

The project at Kromdraai Mine was for the design and construction of a limestone slurry make-up and dosing plant to process and treat acid effluent generated by the coal mining process. This plant replaces the existing lime-dosing system that the mine has been using for years.

Thuthuka Project Manager's process engineer, Francois le Roux, managed the project from the design and construction stages, through to commissioning and hand-over of the plant to the client.

Le Roux says, 'We began work on the project in October last year and the hand-over took place mid-January. We were somewhat hampered by the mine's closure over the Christmas period, but we're pleased that everything has run smoothly since the plant was commissioned at the beginning of January.'

He adds, 'The use of limestone to treat acid effluent offers the mines a financially attractive alternative to lime-dosing technology. The CSIR's limestone process offers a substantial cost saving and does exactly the same job.'

Le Roux points out that the only difference between the two systems is that the limestone process has a pH ceiling, whereas lime treatment processes can attain pH values beyond 10. Effluent that is to be released back into the environment must ideally have a pH close to neutrality. Should a more alkaline effluent be required, a lime treatment step can be incorporated at the tail end of the limestone plant, still at a considerable cost-saving to the customer. When you consider that neutralization with limestone is up to five times more cost-effective than with lime, it makes sense for the large portion of the acid water neutralization to be carried out by the CSIR's limestone technology.

The CSIR-patented process involves slurring moist limestone to a predetermined consistency, keeping the slurry in storage and dosing it into the process as required.

Effluents are treated to acceptable standards, either for recycling as process water back to the plant, or for returning to the environment.

In comparison to the use of lime, the use of powder limestone or granular limestone allows for a substantial operating cost reduction, mainly because of the cost of the raw material. An interesting further development is that clients are increasingly using this technology in conjunction with normal hydrated lime to achieve more cost-effective neutralization in their plant circuits, as opposed to only using limestone for effluent neutralization.

To date, Thuthuka Project Managers has successfully completed four commercial sites implementing the CSIR's technology: Landau Colliery in Witbank's Navigation Section; Ticor South Africa's Empangeni Plant; BCL Limited in Botswana; and Landau Colliery's Kromdraai Mine, also in Witbank.

Each of these sites demonstrates a slightly different application of the CSIR technology:

- Landau Colliery is the coal mine that successfully pioneered the use of this technology at its Navigation Section.
- Ticor is a heavy minerals recovery plant where the technology was used to neutralize process-driven acidity, employing lime, sulphuric acid, caustic soda and limestone.
- BCL Limited is a copper/nickel mining complex that has to be treated for re-use.
- Landau Colliery's Kromdraai Mine is a coal mine that by the nature of its operation, produces acid water, which has to be treated before release into the environment.

Le Roux points out that the CSIR has a vested interest in seeing its technology succeed and, as such, has been closely involved in all of the projects to date. 'For instance, at the pioneering site at Navigation, the CSIR had personnel on site for about 12 months to assist with operational matters and oversee a smooth hand-over to the client. Eventually the client takes over operation completely, but only once the process has settled and the operators have a keen understanding of how the plant is supposed to work.'

Thuthuka Project Managers is seeing an increasing demand for the CSIR-patented technology from all types of industry as the process keeps on proving itself and as end-users realise the potentially huge cost-savings inherent in the process.

Thuthuka's managing director Bill Pullen concludes: 'This technology was developed in its entirety in this country by South African companies for local application, thereby providing a cost-effective local solution to the problem of acid water drainage.'

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