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THE TREATMENT OF POLLUTED MINE WATER

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ABSTRACT

The impact of large quantities of sulphate-polluted water, by-products of various mining and mineral industries, can be disastrous on ecosystems and water resources. The social and economic benefits of reducing the salt content in the effluent to acceptable levels, to produce potable water, could be spectacular, if an economically viable solution to the problem is obtained.

Mintek, Savannah Mining and the Wren Group are developing a solution to this problem. It entails the precipitation of metal hydroxides, calcium sulphate and ettringite. The key to the viability of the new technology lies in the correct use, regeneration and recycling of the compound used to precipitate the ettringite. The water produced by this process is suitable for disposal to watercourses or for agricultural, domestic or industrial consumption. The salts in the acid mine drainage are converted to solid hydroxides, gypsum and calcium carbonate.

The technology has been tested on several waters in the laboratory, on a mini plant, and in two pilot plants. Preliminary results obtained from the mini-plant indicate that potable water can be produced (containing less than 200 mg/l sulphate and no heavy metals) as long as the monovalent ions (Na^+, Cl^-, etc.) are within limits.

In this paper, an overview of the process is presented, along with the results obtained in the laboratory, mini-plant and pilot-plant tests on specific samples of polluted mine drainage.

INTRODUCTION

South Africa is a country in which water is not available in great abundance. This means that constrains on available water supplies could limit the economy and thereby adversely affect large parts of the population. South Africa's economy is highly dependent on its mining and minerals industry, which provides hundreds of thousands of jobs - each of which supports several people. An unfortunate side-effect of the mining and minerals industry is that large volumes of polluted water (generally referred to as mine drainage) are produced. At present, this polluted water flows into local watercourses and, even if neutralised, can raise the concentration of dissolved salts in these watercourses to levels that threaten to make it unfit for human consumption, unusable for many industrial applications and inhospitable to aquatic life. Estimates of the quantities of mine drainage vary, but there is general agreement that the volumes are large. Some examples are 240 million litres per day in the Witwatersrand area, a similar amount in the Witbank area, and 120 million litres per day in the Secunda area. Purified, this could be enough to meet the basic needs of six million people. Alternatively, such water could be used to irrigate tens of thousands of hectares of currently under-utilised farmland and thus contribute significantly to the upliftment of large numbers of people.

The polluted water that is an unavoidable by-product of the mining and minerals industry, which is indispensable to the South African economy, is both a problem and an opportunity. It is threatening valuable water resources, yet if its salt content could be reduced to acceptable levels, it would be possible to make good use of this water and also significantly improve the quality of the water in the catchment areas that are currently being adversely affected. The social and economic benefits of doing this would be significant.

While this paper focuses on the South African situation, the problem of sulphate-polluted mine drainage is by no means confined to South Africa, nor is the solution that is presented.

THE SAVMIN PROCESS

Over the past two years, Mintek has been collaborating with Savannah Mining and The Wren Group on the development of new technology for treating sulphate-polluted mine water (Ramsay, (a), (b), (c)). The process contains five main stages, as described below. It produces potable water and by-products, gypsum and calcium carbonate that are pure enough to be saleable, should this be appropriate in any specific application.

Process chemistry

The Savmin process uses precipitation reactions to purify sulphate-polluted water. Figure 1 is a block diagram of the process. The main process stages are outlined in the following sections.

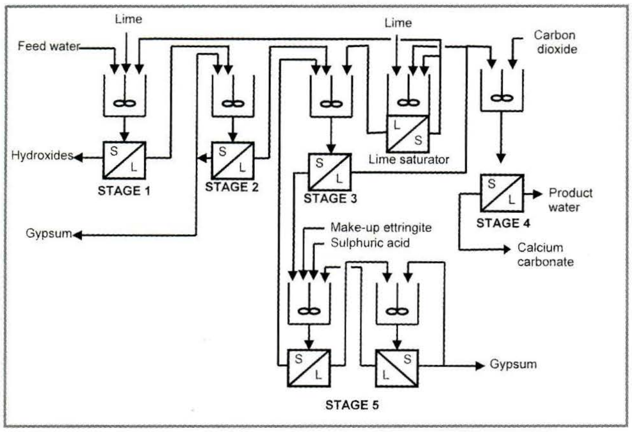

Figure 1. The Savmin Process.

Stage 1 – Precipitation of heavy metals and magnesium

The pH of the incoming water is raised to about 12 with lime. Heavy metals and magnesium are precipitated as hydroxides, according to reactions 1 and 2. ('Me' refers to divalent heavy metals such as iron, nickel, manganese, etc.)

$$Me^{2+} + 2\ OH^{-} \longrightarrow Me(OH)_{2\downarrow} \quad (1)$$

$$Mg^{2+} + 2OH^{-} \longrightarrow Mg(OH)_{2\downarrow} \quad (2)$$

One of the characteristics of dissolved calcium sulphate is that, in the absence of suitable surfaces (such as gypsum) on which to crystallise, it can be meta-stable at concentrations that exceed its equilibrium solubility. The second stage of the Savmin process makes use of this. Depending on the sulphate content of the feed water, the solution phase may become supersaturated with respect to gypsum. Solid-liquid separation follows, and the dissolved calcium sulphate is separated from the precipitated metal hydroxides.

Stage 2 – Gypsum de-supersaturation

The solution from stage 1 is contacted with gypsum crystals. This provides active surfaces of gypsum, which catalyse the precipitation of the supersaturated gypsum. The precipitated gypsum is thickened and filtered. It leaves the process as waste or as a by-product, depending on the specific situation. Part of the precipitated gypsum is returned to the mixing tank of stage 2, to provide the seed crystals required for the rapid crystallisation of the supersaturated portion of the dissolved calcium sulphate.

The sulphate concentration of the product water is pH dependent. The higher the pH the lower the sulphate concentration in the product (Figure 2). The pH in stage 2 is, however, determined by the settling of the metal hydroxides in stage 1 (at high pH values, poor settling occur) and the required pH in the first reactor in stage 3.

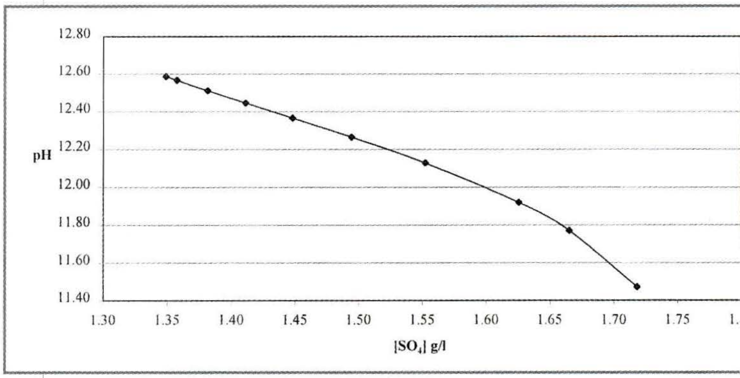

Figure 2. ASPEN output of SO_4 concentration as a function of pH in the absence of monovalent cations.

Stage 3 – Ettringite precipitation

Aluminium hydroxide is added to the solution from stage 2. This causes an insoluble salt known as ettringite ($3CaO.3CaSO_4.Al_2O_3.31H_2O$) to precipitate, thereby removing both calcium and sulphate from the solution. The stoichiometry is given by reaction 3.

$$6\ Ca^{2+} + 3\ SO_4^{2-} + 2\ Al(OH)_3 + 37\ H_2O \longrightarrow$$
$$3CaO.3CaSO_4.Al_2O_3.31H_2O + 6H_3O^{+} \quad (3)$$

The formation of ettringite is pH dependant, the optimum pH range lying between 11.6 and 12.0. The pH is kept between these two values by the addition of lime via a lime saturator. A multi-reactor stage is, however, required for efficient sulphate removal and producing ettringite that has good liquid solid separation characteristics. The precipitated ettringite is separated from the solution by thickening/filtration.

Stage 4 – Carbonation

The solution from stage 3 is treated with carbon dioxide to lower the pH to a suitable level. Pure calcium carbonate is precipitated and can be separated from the resulting product water by filtration. Otherwise, depending on case-specific factors, the pH can be controlled such that dissolved calcium bicarbonate is formed instead of calcium carbonate.

Stage 5 – Recycle of aluminium hydroxide

The ettringite slurry from stage 3 is decomposed to regenerate the aluminium hydroxide for recycle. This is done by exposing the ettringite to a pH that is outside its region of stability. Sulphuric acid is used to lower the pH, and the decomposition take place in gypsum-saturated water, at a liquid to solid ratio that allows the calcium and the sulphate ions to remain in solution as supersaturated calcium sulphate. The stoichiometry is the reverse of reaction 3. The resulting aluminium hydroxide is recovered by thickening/filtration and returned to stage 3. The supersaturated solution of calcium sulphate is contacted with gypsum crystals, as in stage 2, to crystallise out the calcium sulphate, which is removed by thickening/filtration. The resulting gypsum-saturated water is returned to the ettringite decomposition stage.

Sulphuric acid is not the only reagent that can be used in stage 5 of the Savmin process. Carbon dioxide has also been found to work, except that it converts half of the calcium from the decomposed ettringite to solid calcium carbonate. This means that some of the regenerated aluminium hydroxide has to be removed from the circuit, as a bleed to control the build-up of calcium carbonate. Other acids such as hydrochloric and nitric acid could be used, but would make the process more expensive and also introduce undesirable species, that the process cannot remove, into the water.

Process equipment

The various precipitation reactions in the Savmin process are carried out in conventional stirred-tank reactors at ambient temperature and pressure. Lime is supplied to stages 1 and 3 via a conventional lime slaker and slurry pumping system. Sulphuric acid is metered into stage 5 by a conventional dosing pump. The addition of lime and the sulphuric acid is controlled by means of industrial pH probes and control systems, to maintain the appropriate pH values in the respective reactors.

In principle, the solid-liquid separations in the Savmin process can be done in various types of equipment. However, preliminary cost estimates showed that conventional thickeners would be prohibitively expensive in this application, because the settling rates of the precipitates are fairly low. The preferred equipment for solid-liquid separation in the Savmin process is the Wren parallel cone clarifier (Batson, 1997). This equipment has no internal moving parts, and is considerably less expensive and more efficient than conventional thickeners.

RESULTS ACHIEVED

Laboratory

The Savmin process has been tested extensively in the laboratory and several different samples of mine drainage have been evaluated. Tables 1 and 2 present the results achieved, in the laboratory, on two typical water samples. Sample A is from a gold mine and sample B is from a chemical plant.

Species	Feed water	Product water	Potable limits *	% Removal
		(mg/l)		
Na	289	279	200	3.5
Ca	475	51	200	89
Mg	191	0.26	30	100
Fe	226	<0.01	0.1	100
Cl	220	220	200	0
SO_4	2226	216	200	90

* Private communication

Table 1. Laboratory results – Sample A.

Species	Feed water	Product water	Potable limits *	% Removal
		(mg/l)		
Na	41	55	200	0
Ca	545	6	200	99
Mg	345	0.05	30	100
Fe	10	<0.01	0.1	100
Cl	10	26	200	0
SO_4	3000	75	200	98

Private communication

Table 2. Laboratory results – Sample B.

Univalent ions such as sodium, chloride, potassium, fluoride, etc. are not removed by the Savmin process, however these are usually not the problem in mine drainage. The heavy metals (Fe, Ni, Cu, Co, Mn, etc.) are removed to well below the limits set for potable water. (Laboratory data on heavy metals other than iron exists, but was omitted from the above tables for the sake of brevity. The other heavy metals behave very similarly to iron.)

When the water contains higher concentrations of univalent cations like Na^+, the final sulphate level is higher than it would otherwise be. This is because charge balance requires that enough anions remain in the water to balance the cations. Increasing the final pH in stage 3, and therefore increasing the OH- concentration, can however reduce sulphate concentrations in the final product.

Mini plant

The Savmin process has been tested on a mini plant using water from a gold mine, and processing about 20 litres per hour of feed water. Figure 3 shows a Savmin pilot plant (the different stages are not so clear in the case of the mini plant) during its construction, without the aluminium recycle stage. Four of the Wren parallel-plate clarifiers are clearly visible in this picture, as are the mixing vessels ahead of each clarifier. Tables 3 and 4 show the results obtained from the mini-plant with Table 4 giving the concentration after each stage of the process.

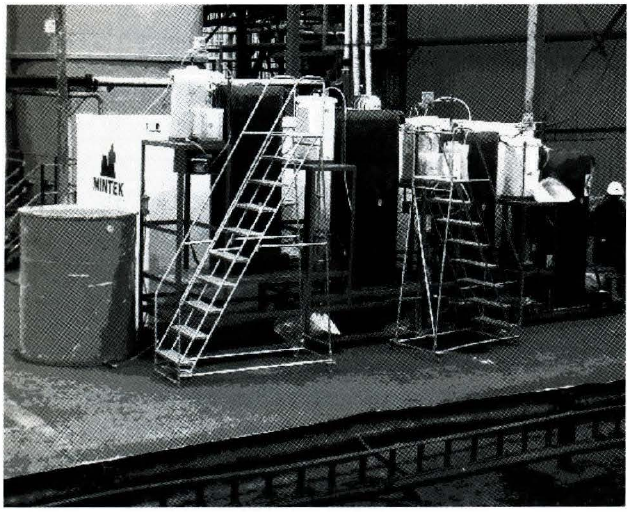

Figure 3. A Savmin pilot plant under construction.

ECONOMICS

Operating cost

The variable cost of the Savmin process depends on its reagent consumption which in turn on the level of sulphate and the level of univalent cations (Na^+, K^+, NH_3^+) in the feed water. The unit costs of the reagents are usually site-specific. Figure 4 shows the reagent costs calculated for a range of incoming sulphate levels, for a water with a low proportion of univalent cations. This range spans the 'easiest' water encountered to date to the 'worst' water, in terms of the sulphate level. The reagent costs assumed for this example are R378 per ton for lime (active calcium oxide), R340 per ton for sulphuric acid, R400 per ton for carbon dioxide gas and R250 per ton for the make-up ettringite. The variable cost ranges from R0.7 to R1.6 per cubic metre of feed water, in this example.

Figure 5 shows the total reagent costs at different sulphate levels, calculated for the water of Figure 4 and for a water containing a higher proportion of univalent cations. The overall reagent cost is dominated by the effect of the sulphate level in the feed water, but the difference between the total reagent cost in these two examples is about R0.1 per cubic metre. The higher reagent cost for the water with the higher level of univalent cations arises because of its association with sulphate, which results in a higher level of sulphate in the water leaving stage 2. This, in turn, requires more ettringite to be precipitated in stage 3, with corresponding increases in the lime required for pH control in stage 3 and the sulphuric acid required to decompose the ettringite in stage 5.

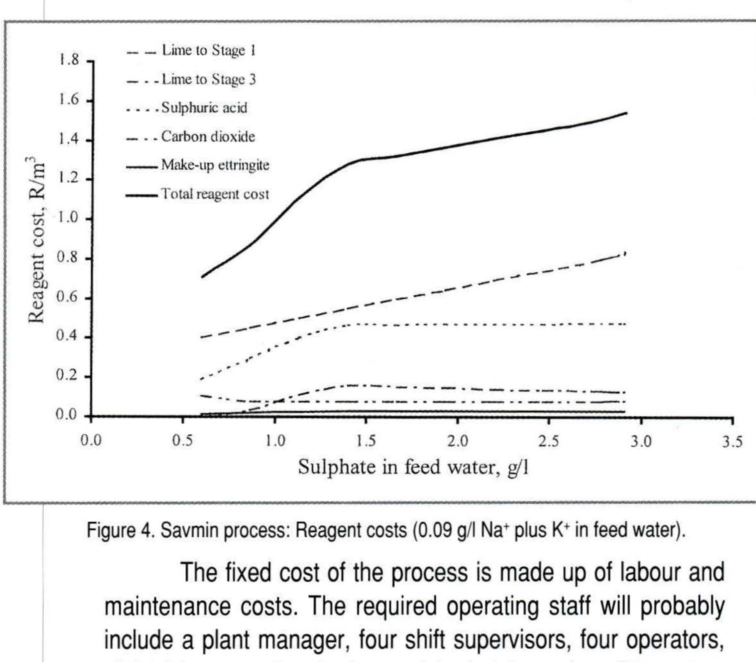

Figure 4. Savmin process: Reagent costs (0.09 g/l Na^+ plus K^+ in feed water).

The fixed cost of the process is made up of labour and maintenance costs. The required operating staff will probably include a plant manager, four shift supervisors, four operators, eight labourers, two instrument technicians, four fitters, two electricians and one clerk. At South African employment costs, this totals R2.4 million per year. For a water feed rate of 100 megalitres per day, this translates to R0.07 per cubic metre of

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cl^-	SO_4^2
Feed	289	19.0	475	191	8.40	226	0.09	0.14	0.15	220	2226
Product	274	19.7	20	0.2	0.05	0.03	0.04	0.03	0.02	232	40
% removal	5	-4	96	100	99	100	56	79	87	-5	98

Table 3. Chemical analysis of polluted mine water from Grootvlei, No 3 shaft (mg/l).

	Al^{3+}	Fe^{2+}	Ni^{2+}	Zn^{2+}	Mn^{2+}	Mg^{2+}	Ca^{2+}	K^+	Na^+	SO_4^{2-}	Cl^-
Feed	0.1	226	0.25	0.58	8.4	191	475	19	289	2213	220
Stage 1	1.9	0.31	0.01	1	0.01	0.76	865	19	288	2227	220
Stage 2	1.1	0.05	0.01	0.28	0.01	0.24	714	23	318	1900	220
Stage 3	25	0.02	0.01	0.05	0.01	0.35	80	18	278	216	220
Stage 4	0.1	0.02	0.01	0.05	0.01	0.26	50	18	278	216	220

Table 4. Results obtained in the 400 litre/hour pilot plant (mg/l).

water. Naturally, if there is an existing operation at the site in question, existing staff could be used, and the labour cost would then be lower. Maintenance and insurance costs have yet to be properly determined. Mintek usually uses estimates of 4 and 0.75 percent respectively of the capital cost of the plant for these items.

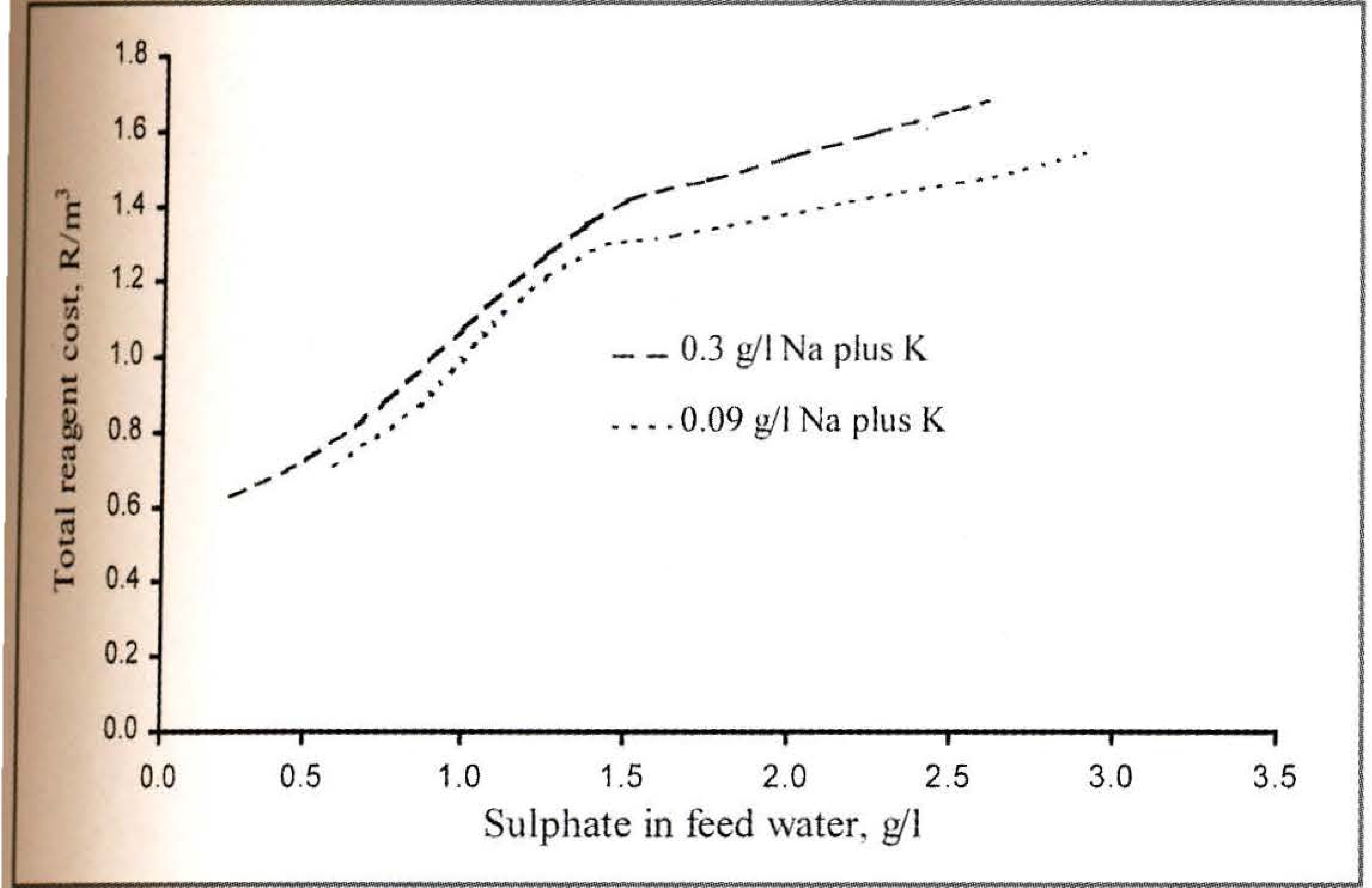

Figure 5. Reagent cost for different feed waters.

Capital cost

The capital cost associated with the Savmin process depends on the amount of polluted water to be processed. Table 5 lists the capital costs estimated to date for various throughputs of water. These values include estimates for detailed engineering design, the delivered cost of the process equipment and associated piping, the required electrical and control systems, steel structures, erection and construction. The costs of foundations and buildings are excluded.

Throughput, of feed water, m^3/hour	Estimated capital cost R million
42	3.7
1250	78.1
4167	297.0

Table 5. Estimated capital costs for the Savmin process.

CONCLUSION

The Savmin process offers a viable solution to the problem of mine drainage. Sulphate salts are removed from the polluted water by precipitation as hydroxides, pure gypsum and pure calcium carbonate. The process is able to produce water of potable quality from mine drainage. The reagents consumed are lime, sulphuric acid and carbon dioxide, and conventional equipment is used.

REFERENCES

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