# WATER RESEARCH COMMISSION PROJECT NO. 201

# THE TREATMENT OF INORGANIC BRINES AND CONCENTRATES

## APPENDIX 15

### The Removal of Sulphuric Acid from Natural and Industrial Waste Waters

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October 1990

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*Desalination*, 70 (1988) 431–442
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

# THE REMOVAL OF SULPHURIC ACID FROM NATURAL AND INDUSTRIAL WASTE WATERS

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## SUMMARY

A process is described which enables the removal of sulphuric acid from effluents without the addition of chemicals to the effluent. The technique employs an anion selective membrane which separates the acidic effluent from a lime solution.

In the case where no current is applied, facilitated transport occurs and the driving force for the demineralisation process is the difference in the chemical potential of the species on either side of the membrane. The equilibrium position may be shifted by the passage of a current through the membrane, in which instance the driving force becomes the applied electric potential.

The sulphates are removed as calcium sulphate, which precipitates in the lime solution. The specific membrane area requirements are a function of the desired degree of acid reduction. The application of low current densities (500 A/m$^2$) reduces the specific membrane area requirements for a particular duty by two orders of magnitude compared to facilitated transport.

Results of laboratory investigations are given and indicate that the sulphuric acid component can be removed from waste waters without an undesirable build-up of additional dissolved solids.

## INTRODUCTION

Because of its relative cheapness and availability, sulphuric acid is used widely in industry where acidic or anhydrous conditions are required. In addition, the weathering of sulphide bearing rock and the extraction and benefication of sulphide containing ores, leads to the production of sulphuric acid in waste streams by biological and chemical means.

The cheap nature of sulphuric acid generally precludes the economic viability of recycling effluents containing the acid. Lime neutralisation is the usual treatment method, resulting in the liquid effluent being super-saturated with calcium sulphate.

The interference of calcium sulphate precipitation is a problem in the recovery of high grade water from such wastes by techniques including soda lime softening, electrodialysis and seeded slurry evaporation and hyperfiltration.

A process has been developed (ref. 1) by the Pollution Research Group, which enables the neutralisation of sulphuric acid and the removal of sulphates without the addition of further chemicals to the effluent stream. This process is suitable for specialised applications, where it is not economically viable to recover the sulphuric acid, and where the discharge of these effluents, acidic or limed, into the environment is prohibited. The process demineralises the sulphuric acid stream and immobilises the ions, thus preventing their release into the environment.

This paper describes the laboratory evaluation of the process for the treatment of:

(i) a sulphuric acid containing waste stream from a chemicals and explosives manufacturing plant, the sulphuric acid component being mainly due to the discharge of spent ion-exchange regenerant wastes. Environmental regulations govern the discharge of such an effluent since its release into the water system prejudices the potential for reuse of the

0011-9164/88/$03.50

receiving water. At the factory concerned, the sulphuric acid effluent is combined with the effluents from explosive manufacture, limed and then discharged by spray disposal onto vast tracts of land.

(ii) acid mine waters, in which the sulphuric acid component results from the oxidation of pyritic minerals in rocks during natural weathering. This weathering is promoted in various areas as a result of mining operations and the resultant mine drainage water becomes more acidic.

Restrictive costs and limited availability of fresh water in certain mines, make it necessary to reuse mine waters wherever practical. The recycling of mine waters, however, results in a serious deterioration in the quality of the water, which increases the problems of corrosion, erosion and scale formation, often with severe practical and economic consequences (ref. 2).

Corrective action needs to be taken, for example, by improving water quality management, by the prevention of pollution at source and by treating polluted water at source to an adequate quality, appropriate to its particular use (ref. 3).

Typical compositions of streams (i) and (ii) are summarised in Table 1. Analyses are given for both the final effluent discharge from the chemical plant by spray disposal (ref. 4) and the acid ion-exchange regeneration stream. The ion-exchange regeneration stream referred to, contains small amounts of effluent from a detonator plant. This mixed stream contributes almost totally to the sulphate concentration of the final effluent, but minimally to the nitrogen concentration. The high calcium content of the final effluent results from liming prior to disposal. Liming destroys residual nitroglycerine in the final effluent. Two analyses are also given for mine drainage water (ref. 3), in both the worked and unworked areas.

TABLE 1
Effluent characterisation

| Parameter | Chemical plant | | Mine drainage water | |
|---|---|---|---|---|
| | final waste | acidic reg. stream | worked areas | unworked areas |
| pH | 4 to 8 | 2.7 | 2.2 | 3.0 |
| Total dissolved solids | - | 4 440 | 3 475 | 400 |
| Ammonia-N | 1 550 | 320 | - | - |
| Nitrate-N | 1 450 | 430 | - | - |
| Sulphate | 2 293 | 1 600 | 1 850 | 615 |
| Sodium | 249 | 380 | - | - |
| Calcium | 807 | 200 | 50 | 60 |
| Flow (Mℓ/day) | - | 0.2 | 0.5 | 1.3 |

Note : All units in mg/ℓ except pH and flow.

## PROCESS DESCRIPTION

The process requires the use of a membrane stack of the type typically used in the chlor-alkali industry. The membrane is anion selective and separates the two electrolyte compartments. The sulphuric acid waste stream is passed through one compartment and an alkali solution is recirculated through the other compartment. The alkali solution should contain cations capable of forming an insoluble sulphate, calcium hydroxide being an obvious example.

Two process options have been developed. These options are :

(i) facilitated transport

(ii) electrolysis.

The option most suited to a particular application will depend on the availability of gas venting facilities at the particular site of installation. In the second option, involving electrolysis, hydrogen is evolved. If the process is to be applied underground in the neutralisation and demineralisation of mine drainage water, then provision must be made for the venting or the catalytic combustion of this gas.

Facilitated transport

Fig. 1 shows the first option, facilitated transport, using lime as the alkali solution. The pH differential across the membrane causes anions from the lime solution to pass through the membrane and into the compartment containing the sulphuric acid, thus neutralising the acid. At the same time, charge balance considerations require that the sulphate ions pass in the opposite direction, thus deionising the sulphuric acid steam. The sulphate ions will precipitate with the calcium in the alkali solution and may be continuously removed by filtration. Lime is continuously added to this recirculating liquor to replenish the hydroxide and calcium supplies and to maintain the pH differential across the membrane, thus providing the driving force for the demineralisation and neutralisation of the sulphuric acid stream.

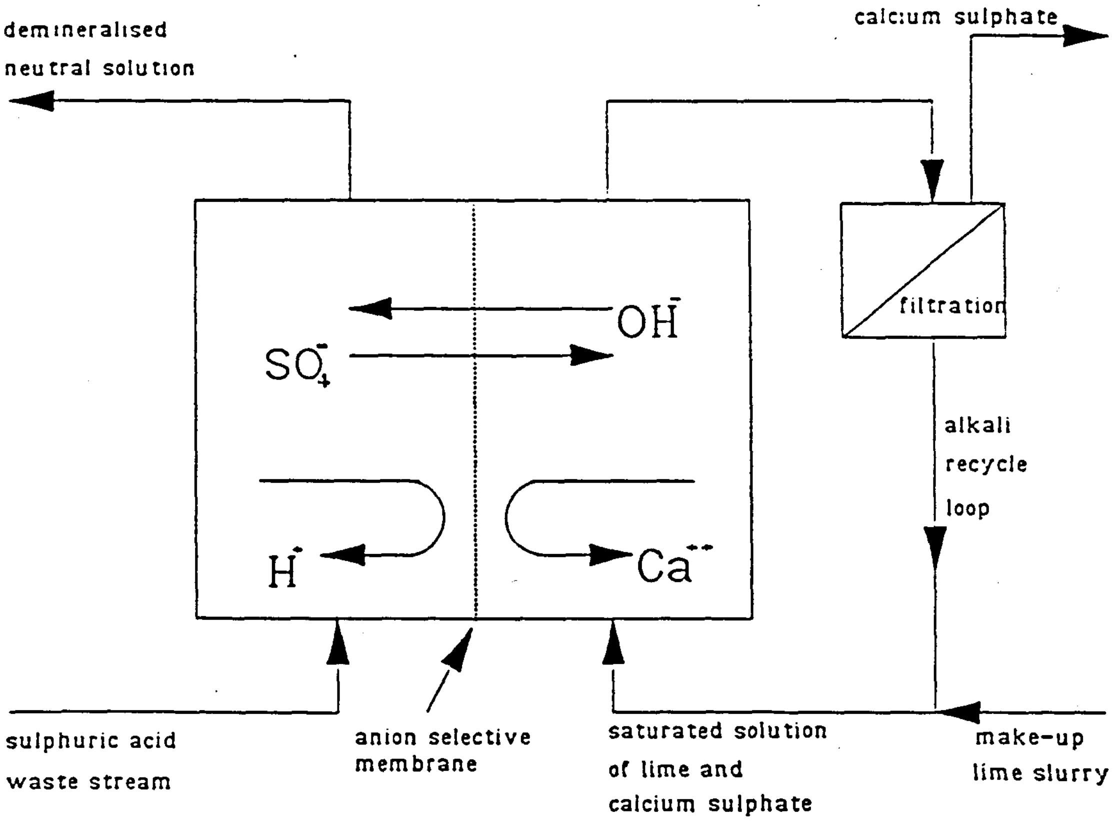

Fig. 1. Facilitated transport

### Experimental

Laboratory evaluation of the process has been conducted in a two compartment batch cell operated at ambient temperatures. The compartments of the cell were separated by a sheet of anion exchange electrodialysis membrane (Ionics 103 QZL 386) with an exposed area of 8.1 x $10^{-3}$ $m^2$. The electrolytes were stirred continuously to promote turbulence at the membrane surface. The compositions of each electrolyte were monitored for the duration of each test.

For the second process option, electrolysis, a potential was applied across two platinised titanium mesh electrodes which were placed on either side of the membrane. Relatively low current densities (60 to 400 A/$m^2$) were employed so as to extend the duration of the test to enable the collection of comprehensive data.

## RESULTS AND DISCUSSION

Typical results for the facilitated transport of acidic ion-exchange regeneration liquor and mine drainage water and for the electrolysis of acidic ion-exchange regeneration liquor are given in Tables 2, 3 and 4.

TABLE 2

Facilitated transport of acidic ion-exchange regeneration liquor

Alkali solution : initially saturated lime, no make-up
Electrolyte volumes : 820 mℓ

| Time | Effluent | | | | | Lime | | | |
|---|---|---|---|---|---|---|---|---|---|
| (h) | pH | Cond mS/cm | $SO_4^=$ mg/ℓ | $Na^+$ mg/ℓ | $Ca^{++}$ mg/ℓ | pH | Cond mS/cm | $SO_4^=$ mg/ℓ | $Na^+$ mg/ℓ |
| 0.0 | 2.8 | 6.7 | 1 280 | 322 | 278 | 12.1 | 7.0 | 20 | 9 |
| 0.7 | 3.4 | 6.2 | 1 210 | 307 | 277 | 11.9 | 6.3 | - | 22 |
| 2.5 | 4.4 | 6.0 | 1 140 | 293 | 312 | 12.0 | 5.9 | - | 24 |
| 4.5 | 5.4 | 5.9 | 1 140 | 307 | 266 | 11.8 | 5.0 | - | 24 |
| 7.0 | 7.8 | 5.5 | 1 050 | 297 | 252 | 12.0 | 4.2 | 170 | 24 |
| 22.5 | 8.8 | 5.1 | 900 | 307 | 268 | 10.9 | 1.7 | 370 | 27 |

TABLE 3

Facilitated transport of mine drainage water, worked areas

Alkali solution : Saturated lime and calcium sulphate, continuous lime addition
Electrolyte volumes : 1 000 mℓ

| Time | Effluent | | | | | | Lime | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (h) | pH | Cond mS/cm | $SO_4^=$ mg/ℓ | $Cl^-$ mg/ℓ | $Na^+$ mg/ℓ | $Ca^{++}$ mg/ℓ | pH | Cond mS/cm | $SO_4^=$ mg/ℓ | $Cl^-$ mg/ℓ | $Na^+$ mg/ℓ |
| 0.0 | 2.4 | 7.1 | 1 580 | 590 | 105 | 525 | 12.0 | 2.4 | 1 450 | 16 | 0 |
| 1.5 | 2.8 | - | - | - | - | - | 11.9 | - | - | - | - |
| 6.2 | 3.1 | 4.5 | - | - | - | - | 12.0 | 2.5 | - | - | - |
| 22.2 | 4.6 | 3.5 | - | - | 103 | 685 | 11.9 | 2.8 | - | - | - |
| 26.2 | 5.2 | 3.5 | - | - | - | - | 11.9 | - | - | - | - |
| 30.2 | 5.7 | 3.5 | - | - | - | - | 12.1 | 2.9 | - | - | - |
| 46.6 | 6.2 | 3.6 | 1 450 | 456 | 107 | 690 | 12.1 | - | 1 625 | 140 | 0 |

Initially, demineralisation and neutralisation of the effluent proceeded rapidly. As equilibrium was approached, the chemical driving force was diminished and the rate at which ions were transported through the membrane was reduced (see Fig. 4). The rate of change in the hydrogen ion concentration of the effluent has been calculated from pH measurements, since the effluent did not possess any buffering capacity.

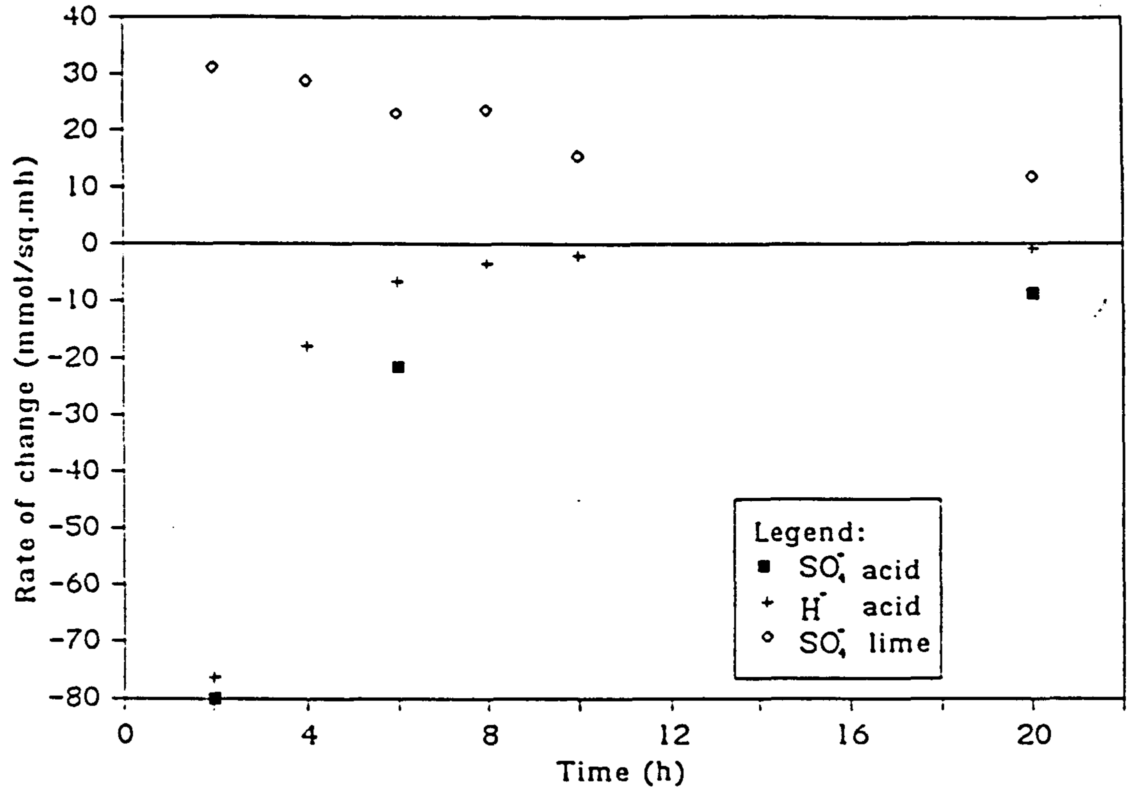

Fig. 4. Facilitated transport of ion-exchange regeneration liquor

Facilitated transport of mine drainage water produced similar trends with regard to pH change (Figs. 5 and 6). The rate of change of the sulphate ion concentrations in the electrolytes could not be determined accurately since the total change was very small.

During facilitated transport, neutralisation of both effluents occurred with a resulting decrease of 10 to 20% in sulphate concentration.

The estimated membrane duty (in *ℓ* of effluent treated per sq.m of membrane per hour) for the neutralisation of the two effluents to various pH values is given in Fig. 7. The total membrane requirements for a typical effluent flow are very high, and increase rapidly where pH values near or above neutral are required. For example, to neutralise the acidic ion-exchange regeneration liquor and the mine drainage water (worked areas), at the flows specified in Table 1, necessitates 540 and 8 300 m² of anion exchange membrane respectively.

## Electrolysis

The equilibrium reached during facilitated transport was displaced in the desired direction of sulphate removal by the application of an electric potential across the membrane. Fig. 8 shows the typical change in sulphate concentration and pH for each electrolyte during the electrolysis of acidic ion-exchange regenerant waste.

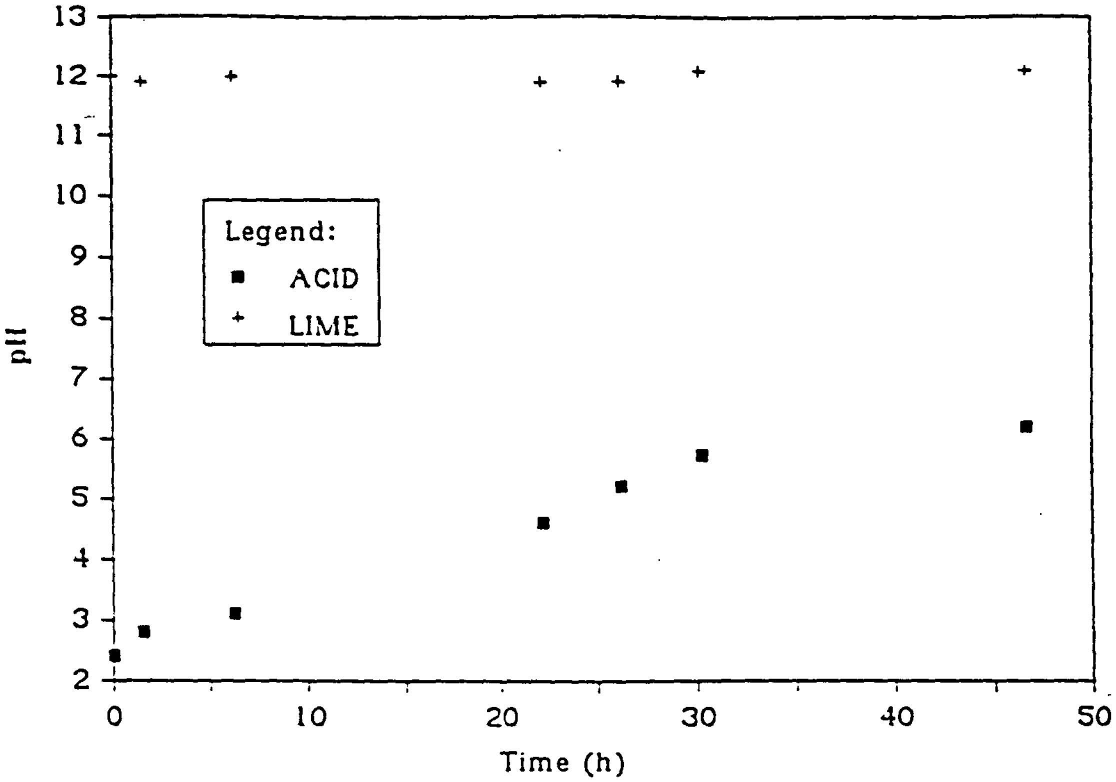

Fig. 5. Facilitated transport of mine drainage water : Electrolyte pH change

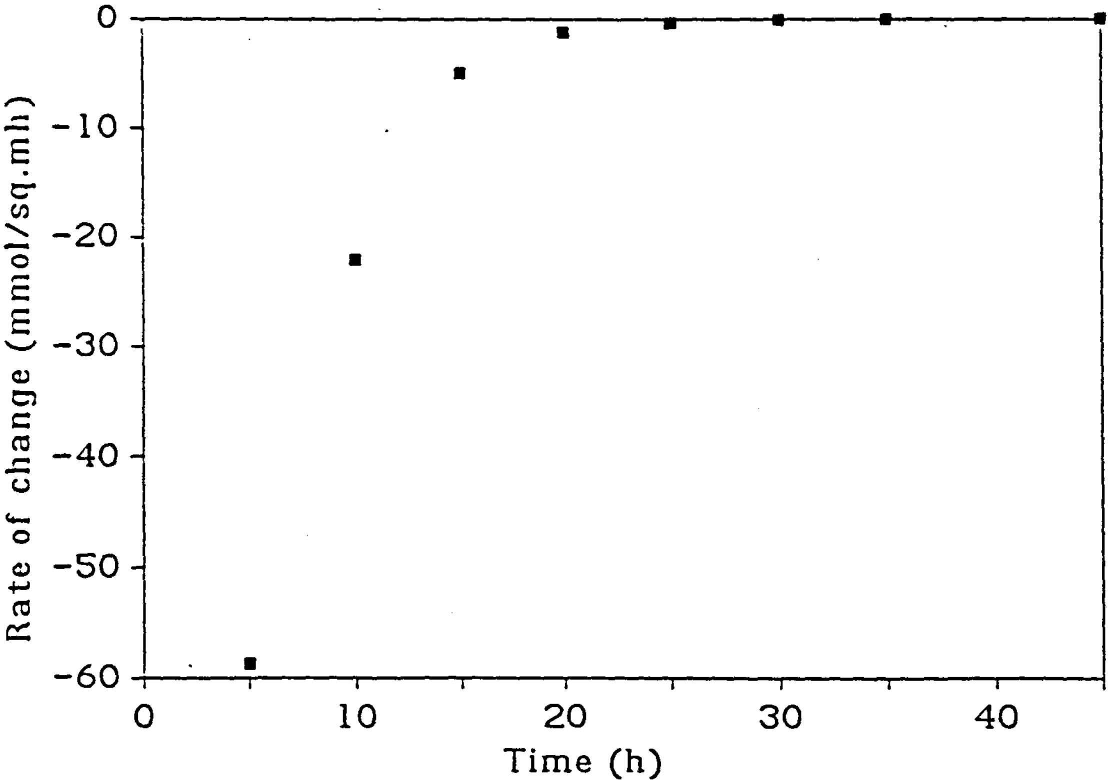

Fig. 6. Facilitated transport of mine drainage water : Rate of change in the acid hydrogen ion concentration

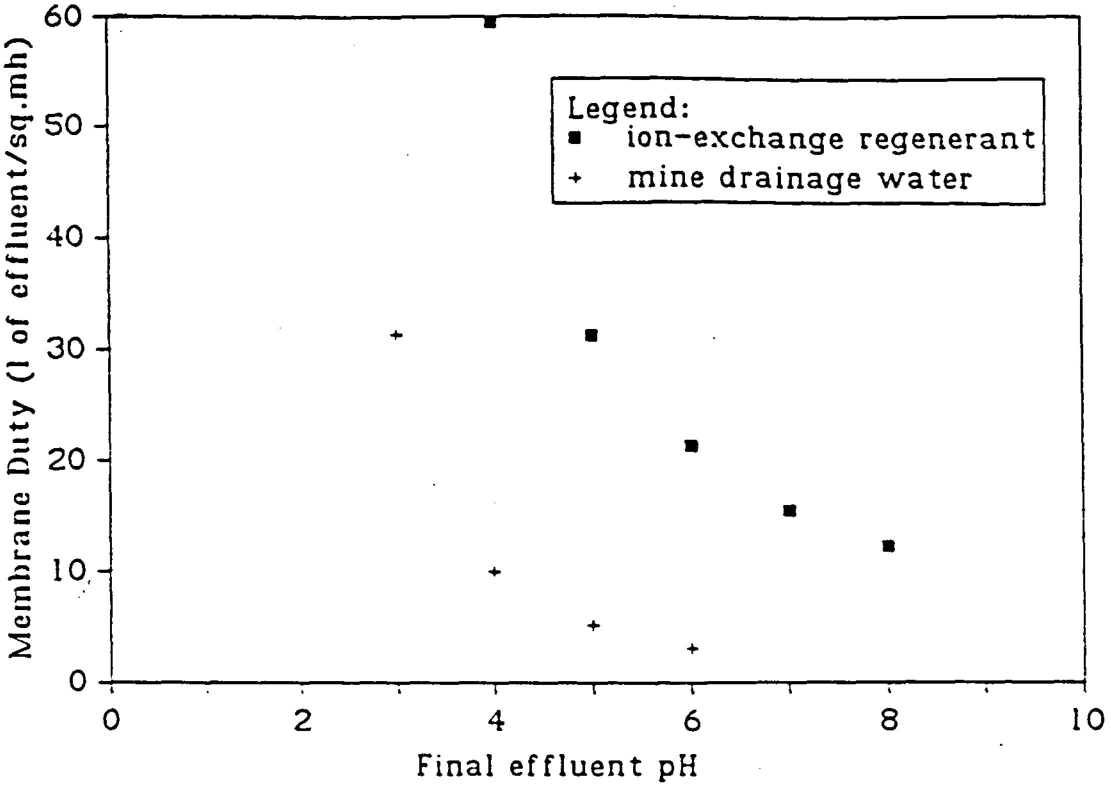

Fig. 7. Estimated membrane duty for facilitated transport

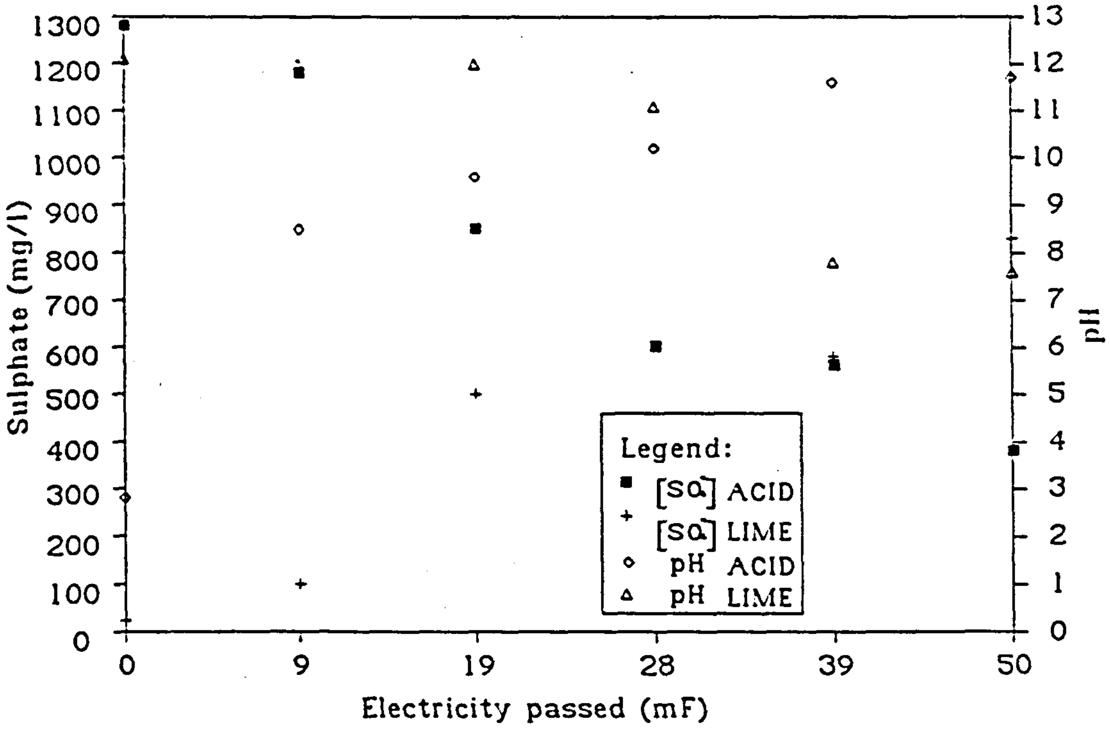

Fig. 8. Electrolysis of acidic ion-exchange regeneration liquor

Approximately 70% of the sulphate was removed from the effluent. The final effluent was alkaline. Low current densities were used in the trials so that the reactions would proceed sufficiently slowly to enable meaningful experimental data to be collected. In larger applications, the applied current may be increased to the limiting value, this value being a function of the flow and the ionic characteristics of the electrolytes.

Fig. 9 shows the change in the incremental sulphate current efficiency as a function of the difference in the total hydrogen and sulphate concentrations in the acid and lime solutions. At constant applied electric potential, the incremental current efficiency decreases as the chemical driving force decreases and electrical energy is consumed in opposing the reverse movement toward equilibrium.

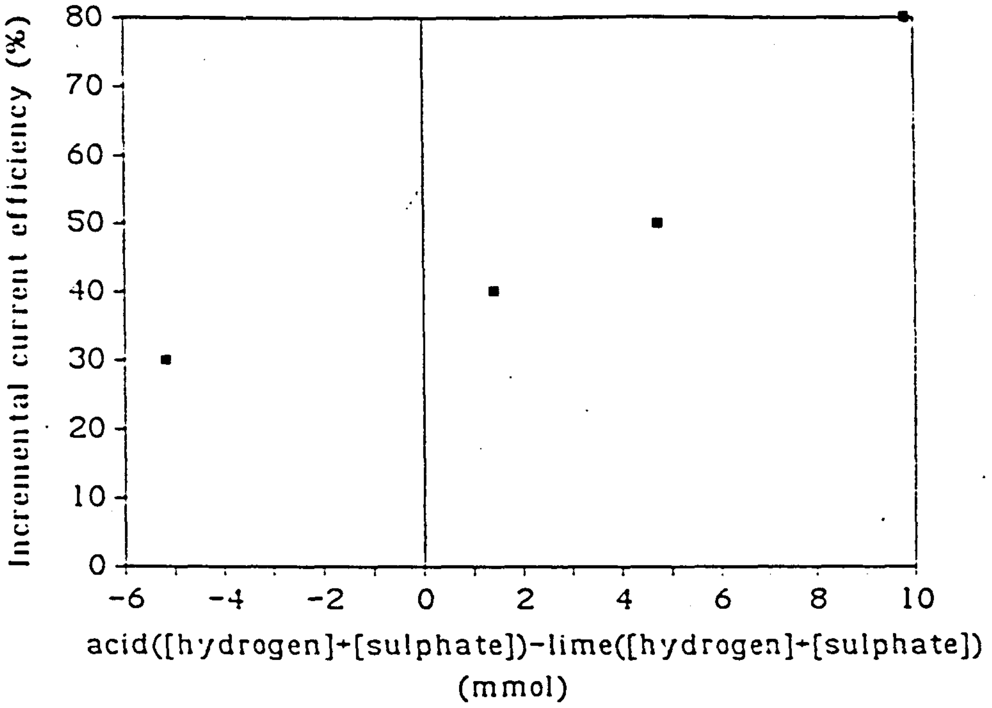

Fig. 9. Electrolysis of acidic ion-exchange regeneration liquor : Incremental sulphate current efficiencies

The estimated membrane duty (in k$\ell$ of effluent treated per sq.m of membrane per hour) for the neutralisation and demineralisation of this effluent is shown in Fig. 10. An operating current density of 500 A/m$^2$ and an average current efficiency of 60% have been assumed. Thus the application of small potentials across the membrane can substantially increase the membrane duty. In the present example, membrane duty is increased by two orders of magnitude above the membrane duty observed under facilitated transport applications. In order to neutralise the effluent (with a 20% sulphate removal) the anion exchange membrane area requirements are estimated from Fig. 10 to be 5,5 m$^2$. Higher sulphate removal would necessitate larger membrane areas. Membrane area requirements, suitable for typical effluent flows are therefore small in the case of electrolysis.

## CONCLUSIONS

Laboratory results have indicated that the proposed membrane process is effective in removing the sulphuric acid from industrial and mining waste streams containing the acid. The proposed method has the advantage over conventional treatment methods in that the acid stream is neutralised and demineralised without the addition of further salts to the main effluent stream. The sulphate ions are removed from the effluent and immobilised by precipitation as calcium sulphate in a low volume recirculating saturated lime solution.

Where suitable facilities exist for handling oxygen and, in particularly hydrogen gas streams, the use of the electrolysis option is advantageous over the facilitated transport option, since membrane area requirements may be reduced by at least two orders of magnitude.

## FUTURE DEVELOPMENTS

A pilot plant study is to be conducted to assess the feasibility of the process to large scale applications and to obtain suitable data for the design of a full scale plant.

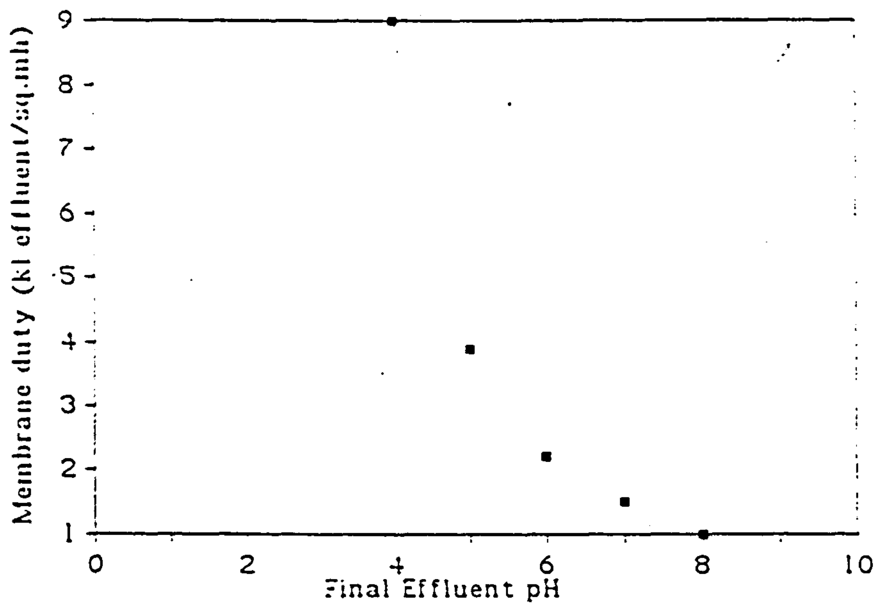

Fig. 10. Estimated membrane duty for electrolysis : (500 A/sq.m and 60% current efficiency)

## ACKNOWLEDGEMENTS

This work was performed under contract to the Water Research Commission, to whom the patent has been assigned.

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