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## EXECUTIVE SUMMARY

### Background and motivation

Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2,5. These conditions may prohibit discharge of untreated acid mine waters into public streams, as they have a detrimental effect on aquatic plant and fish life. Acid mine water drainage also causes ground water pollution. Currently, chemicals such as lime, sodium hydroxide and sodium carbonate are used for the neutralisation of acid water. Limestone can also be used which has the following advantages: low raw material cost, non-hazardous nature of material, low potential of accidental overtreatment, and production of a low-volume, high-density sludge. Disadvantages associated with limestone are the long retention time required for complete reaction and the fact that it is not completely utilised. Should these disadvantages be overcome, it will be the preferred alkali to use due to its low cost. The price (1993) of limestone is only R100/t compared to R280/t for lime.

The aim of this study was to develop a method whereby acid waters would be in contact with limestone to ensure effective neutralisation and efficient use of the limestone. A fluidised bed was proposed for this purpose. The bed is packed with small chips of limestone. The acid water together with the recycle stream enters the bottom of the column; their combined upward velocity fluidises the limestone particles ensuring good contact with the acid water. The neutralised stream passes out of the top of the column. In practise, fresh limestone is added to the top of the bed as it is consumed through dissolution in the acid water.

The main advantage of this process is that the neutralising medium, limestone, can be kept in the reactor as opposed to a rotating drum where the limestone is partially washed out with the treated stream. The fluidised bed ensures a much more efficient usage of the limestone - by controlling the feed and wastage rates of  $\text{CaCO}_3$  to and from the bed, the exact time (and hence degree of utilization) of the neutralising medium in the bed can be controlled. The degree to which the acid stream is neutralised is controlled by its retention time in the bed, i.e. the bed height. A second advantage of the fluidised bed operation is the attrition that occurs between the closely associated particles which keeps the  $\text{CaCO}_3$  surfaces clean of any  $\text{CaSO}_4$  or iron hydroxide that might inhibit the neutralisation rate.

### Objectives

The following specific aims were set for the project:

- \* Literature survey
- \* Determination of the market size for the neutralisation of acid water.
- \* Laboratory studies to determine the kinetics of limestone neutralisation.
- \* Pilot plant studies on acid water (synthetically made-up acid water and acid mine drainage) to determine the technical feasibility of limestone neutralisation in a fluidised-bed reactor.

- \* Determination of the economic feasibility of the fluidised-bed limestone neutralisation process.

All the aims set for the project were met.

### Results and conclusions

The findings from the study can be summarised as follows:

- \* Kinetics. The kinetics of acid neutralisation using  $\text{CaCO}_3$  may be represented by the rate equation:

$$-\frac{d[\text{H}_2\text{SO}_4]_b}{dt} = K S [\text{H}_2\text{SO}_4]_b$$

where  $K$  is the rate constant based on surface area,  $S$  is the total  $\text{CaCO}_3$  surface area available and  $[\text{H}_2\text{SO}_4]_b$  is the concentration of acid in the bulk liquid (as  $\text{mg CaCO}_3/\text{l}$ ). For effluents with little or no heavy metals, the value of  $K$  is  $2,45 \times 10^{-3} \text{ min}^{-1} \cdot \text{cm}^{-2}$ ; for effluents that contain significant quantities of iron, a layer of  $\text{Fe}(\text{OH})_3$  forms on the  $\text{CaCO}_3$  surfaces that causes  $K$  to decrease from the abovementioned value, depending on the thickness of the  $\text{Fe}(\text{OH})_3$  layer.

- \* Rate. It was determined that the rate of neutralisation is directly related to the dosage of  $\text{CaCO}_3$ , influenced by the particle size of limestone (the finer the particle, the higher the rate of neutralisation) and the type of metal in solution. The presence of iron(II) retards the rate dramatically while iron(III) has no influence. Aeration marginally accelerated the rate of limestone neutralisation as a result of  $\text{CO}_2$ -stripping.

It was determined under continuous conditions that a contact time of 4 min is sufficient for the neutralisation of acid water containing 4 g/l free acid and 580 mg/l iron(III), while a contact time of at least 40 min is required for the same water, but which contains iron(II) instead of iron(III).

- \* Water quality. The limestone neutralisation process improves the quality of the water by removing free acid and acid associated with  $\text{Fe}(\text{III})$  completely. Sulphate is removed up to the point where the water is saturated with calcium sulphate. The level to which the pH of acid water is increased depends on the metals that will remain in solution during neutralisation. If magnesium is present in the water, it co-precipitates partially with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Iron(III) and aluminium(III) are effectively removed during limestone neutralisation as metal hydroxides.
- \* Reactor type. A fluidised-bed reactor with multiple stages of increasing diameters is preferred for the limestone neutralisation process as it allows fluidisation of the bigger particles but also prevents washout of the smaller particles in the case where ungraded particle size limestone is used. The cone-shaped and pipe-shaped fluidised-bed reactors perform equally well in the limestone neutralisation process.

- \* Limestone utilisation. In the case of iron(III)-rich water, the limestone is completely utilised while the ferric hydroxide sludge which is produced is washed out together with the effluent. No bleed-off stream is therefore necessary to get rid of impurities in the limestone or produced sludge. In the case of iron(II)-rich water, gypsum and ferric hydroxide sludge and coated limestone particles accumulate in the fluidised-bed reactor. About 70% of the limestone is utilised in the case of water containing 600 mg/l iron(II). It is expected that a fraction of the trapped limestone could be recovered from the waste sludge through a backwash operation.
- \* By-products. Gypsum and CO<sub>2</sub> are produced which could be recovered as by-products.

### **Contribution and benefits from project**

The main contribution from this study is that it was demonstrated that acid water can be neutralised effectively in a fluidised-bed reactor. By using the fluidised-bed reactor for limestone neutralisation, the main weaknesses of limestone (its low reactivity and its scaling with gypsum and iron hydroxide precipitates in other systems) which prevented it from being used on a wide basis in the past, were overcome. The problem of long reaction time as a result of the low reactivity of limestone is solved in the fluidised-bed reactor because an excessive amount of limestone is in contact with the acid water. Scaling of limestone particles is prevented due to the attrition between the particles under fluidised conditions.

The comparative advantages associated with the use of limestone under practical conditions, compared to other alkalis such as lime and sodium hydroxide, are the following:

- \* More cost-effective. At prices of R100, R240, R280 and R1 500 per ton for limestone, unhydrated lime, hydrated lime and sodium hydroxide respectively (1993), the alkali cost for the neutralisation of acid water with an acid content of 2 g/l amounts to 20 c/kℓ in the case of limestone, 27 c/kℓ in the case of unhydrated lime, 41 c/kℓ in the case of hydrated lime, and 240 c/kℓ in the case of sodium hydroxide.
- \* No accurate control of dosage is required, as limestone does not dissolve at pH-values greater than 7.
- \* Sludge of a higher density is produced in the case of iron(III)-rich .
- \* It is safe to handle.
- \* It is easy to store.

Should this process be implemented on a large scale, it will lead to a significant growth in the limestone market due to the following reasons:

- \* The use of limestone is more cost-effective than other alkalis.

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- \* Industry would be willing to neutralise acid water which was previously not feasible from a cost and control point of view (e.g. seepage water from old coal mines).

Patent protection has been received in South Africa, Canada, Australia and the USA while patent protection is pending in Germany.

### **Recommendations**

It is recommended that:

- \* Design criteria be established for the pre-oxidation of iron(II) in the case of iron(II)-rich water in order to make the fluidised-bed limestone neutralisation process suitable for the treatment of any type of acid water.
- \* The benefits of the process be demonstrated to industry by the construction and operation of a demonstration plant in order to assist with the transfer of the new technology to potential users.