

## A COMPARISON OF THE EFFECT OF CHEMICAL AND BIOLEACHING ON THE KINETICS OF SPHALERITE LEACHING.\*

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**Abstract** – Sphalerite concentrates were prepared from tailings dam samples obtained from Rosh Pinah Mine in Namibia. The samples were subjected to froth flotation and concentrates containing between 7% and 14% Zn were prepared.

Leaching of these froth flotation concentrates were studied in ferric chloride solutions at different  $\text{Fe}^{3+}$  concentrations for different times at different temperatures with the influence of other species on the kinetics in mind. Complementary to this research, GeoBiotics, LLC and Exxaro Resources have developed proprietary bioleaching technology for the oxidation of base metals concentrates using GEOCOAT bio heap leaching technology in a sulphate medium. The ferric chloride laboratory work was performed in a fluidising leach reactor. The studied material was obtained from flotation concentrate produced during an investigation into the recoverability of a tailings pile at Rosh Pinah mine in Namibia. The optimum conditions for the laboratory investigation were found to be a  $\text{Fe}^{3+}$  concentration of  $0.3 \text{ mol/dm}^3$  at  $80^\circ\text{C}$ . A control was performed by using synthetic zinc sulphide.

GEOCOAT evaluation tests are performed for the purpose of evaluating the bioleaching of ore and flotation concentrates by means of mesophilic bacteria, Column tests were carried out on the flotation scavenger concentrate from Rosh Pinah to assess the application of the GEOCOAT® process for the oxidation of a low grade zinc concentrate.

In this study an attempt was made to demonstrate the relationship between the Kinetic models and the experimental data by plotting the fraction of Zinc leached against time and applying the different equations to the data.

The kinetic models were applied to the data obtained from both the test regimes. Habashi (1999) proposed that if a process is controlled by a chemical reaction at the interface (phase boundary controlled reaction), the following equation applies.

$$k_c t = 1 - (1 - R)^{1/3}$$

Alternatively a process is controlled by diffusion through the product layer the following equation applies:

$$kt = 1 - \frac{2}{3}X - (1 - X)^{2/3}$$

As the anodic dissolution reaction progresses, reaction product forms either a more or less dense reaction product layer on surface

As this product layer forms, a diffusion problem develops governed by the nature of the product layer. The conclusion from the study was that the kinetics is very dependent on the type of ore processed relating to the mineral composition of the ore body.

## **INTRODUCTION**

Sphalerite concentrates were prepared from tailings dam samples obtained from Rosh Pinah Mine in Namibia. The samples were subjected to froth flotation giving concentrates of between 7% and 14% Zn.

Leaching of these froth flotation concentrates were studied in ferric chloride solutions at different  $\text{Fe}^{3+}$  concentrations for different times at different temperatures, with the influence of other species on the kinetics in mind. Complementary to this research, GeoBiotics, LLC have developed proprietary technology for the oxidation of base metal and gold concentrates using GEOCOAT® bio-heap leaching technology. As with all bio-oxidation processes, the GEOCOAT® test work was carried out in an acidic sulphate medium, typically with the pH between 1.5 and 2.0. During the GEOCOAT® process flotation concentrate is coated onto inert support rock and stacked in a heap arrangement. Acid solution containing acidophilic bacteria is applied to the column to dissolve metal species such as iron, copper, nickel and zinc. GeoBiotics and Exxaro Resources, South Africa entered into an agreement to develop GEOCOAT® leaching for zinc concentrates.

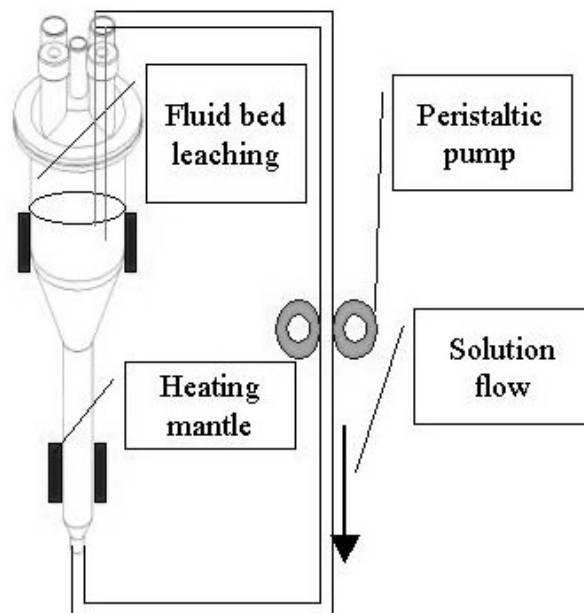
Considerable work has been done on kinetics on ferric chloride leaching of sphalerite Jin et al, (1985)<sup>1</sup>, Mandre and Sharma(1992)<sup>2</sup> and Warren et al(1985)<sup>3</sup> gave an elaborate explanation on the reaction mechanism for the chloride leaching of sphalerite in ferric chloride medium. Kolodziej and Adamski <sup>4</sup> reported on the dissolution of sphalerite in aqueous hydrochloric acid under reducing conditions.

## **EXPERIMENTAL**

An experimental routine was designed to include all the parameters to be investigated. Table 1 gives a tabled representation of the experimental parameters.

## EQUIPMENT

The equipment consists of a well-stirred 1-litre batch fluidising reactor which is thermostatically controlled (Figure 1 Schematic diagram of the fluidising leach reactor); peristaltic pump; acid resistant pump tubing; fitted with a thermocouple and a condenser. The reactor is fitted with a lid with various ports to ensure solution-sampling capabilities.



**Figure 1** Schematic diagram of the fluidising leach reactor

The bioleaching tests included a series of experiments in 6-meter high, 150mm diameter columns, equipped with peristaltic pumps for irrigation and heating mantles to conserve and control the columns at a constant temperature.

## REAGENTS

Solutions were prepared from reagent grade ferric chloride, de-ionised water and reagent grade hydrochloric acid.

## PROCEDURE

The following procedure was used:

The flotation concentrate is washed with acetone and dried.

1000 ml of a known concentration of ferric chloride solution is transferred to the one-litre fluidising leach reactor or batch reactor fitted with a multiple port lid. The one-litre fluidising reactor was connected to a peristaltic pump and tubing.

The pH of ferric chloride solution is kept below 2 by adding 20 ml of concentrated HCl per litre of solution before it is transferred to the reactor.

The reaction reactor is placed in the heating mantle or on the hotplate and heated to the desired temperature.

A desired weight (5 grams) of sample of concentrate is weighed and transferred quantitatively to the pre heated reactor and solution.

The solution is stirred at 100% of the pump capacity.

During the experiment, approximately 10 ml of solution is withdrawn with a pipette.

The time interval for sampling is about 10 to 60 minutes depending on the need.

The calculation of concentrations of the sample solution is based on the volume of solution in the reaction flask at the time of withdrawing the sample.

Table I shows the typical composition of the sample used in the investigation

**Table I :** Important elements in the head sample

Element	Zn	Cu	Pb	Fe	Ag	S <sub>(T)</sub>	S <sup>2+</sup>	S <sup>0</sup>
Head analysis %	12.7	0.67	1.19	21	0.006	27.2	26.3	<0.5

Table II shows the particle distribution of the sample used in the investigation.

**Table II:** Particle size analysis Rosh Pinah concentrate

Rosh Pinah concentrate	
µm	%
+212	2
+150	6.9
+106	11.9
+75	16.2
+53	16.5
+45	6.9
+38	6.1
-38	33.5

## SAMPLING

A 15-ml sample was extracted for analysis at the commencement of the experiment and then at intervals of 0.25, 0.5, 1, 2, 4 and 8 hours respectively. Table III shows the experimental regime followed during the investigation.

**Table III:** Experimental regime

	Temperature	Fe <sup>3+</sup> concentration (mol/dm <sup>3</sup> )	Time (min)
Test 1	90°C	0.2	120
Test 2	90°C	0.2	150
Test 3	90°C	0.2	180
Test 4	90°C	0.1	150
Test 5	90°C	0.3	150
Test 6	80°C	0.2	150
Test 7	70°C	0.2	150

### Eh and pH measurement

Before each sample an Eh measurement was made inside the reaction vessel. The pH measurement as recorded immediately after the sample was taken.

## RESULTS

### Determination of species in solution

The total iron and zinc concentrations were determined by ICP-OES method while potassium dichromate (VI) was used in volumetric analysis to determine the Fe<sup>2+</sup> species.

### Kinetics

Habashi (1999) states that if a process is controlled by a chemical reaction at the interface (phase boundary controlled reaction), the following equation applies.

$$k_c t = 1 - (1 - X)^{1/3} \quad [1]$$

If a process is controlled by diffusion through the product layer, then equation 2 applies:

$$k t = 1 - \frac{2}{3} X - (1 - X)^{2/3} \quad [2]$$

as indicated by Habashi (1999).

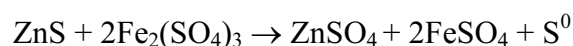
where: k =rate constant  
t = time [min]  
X =fraction leached

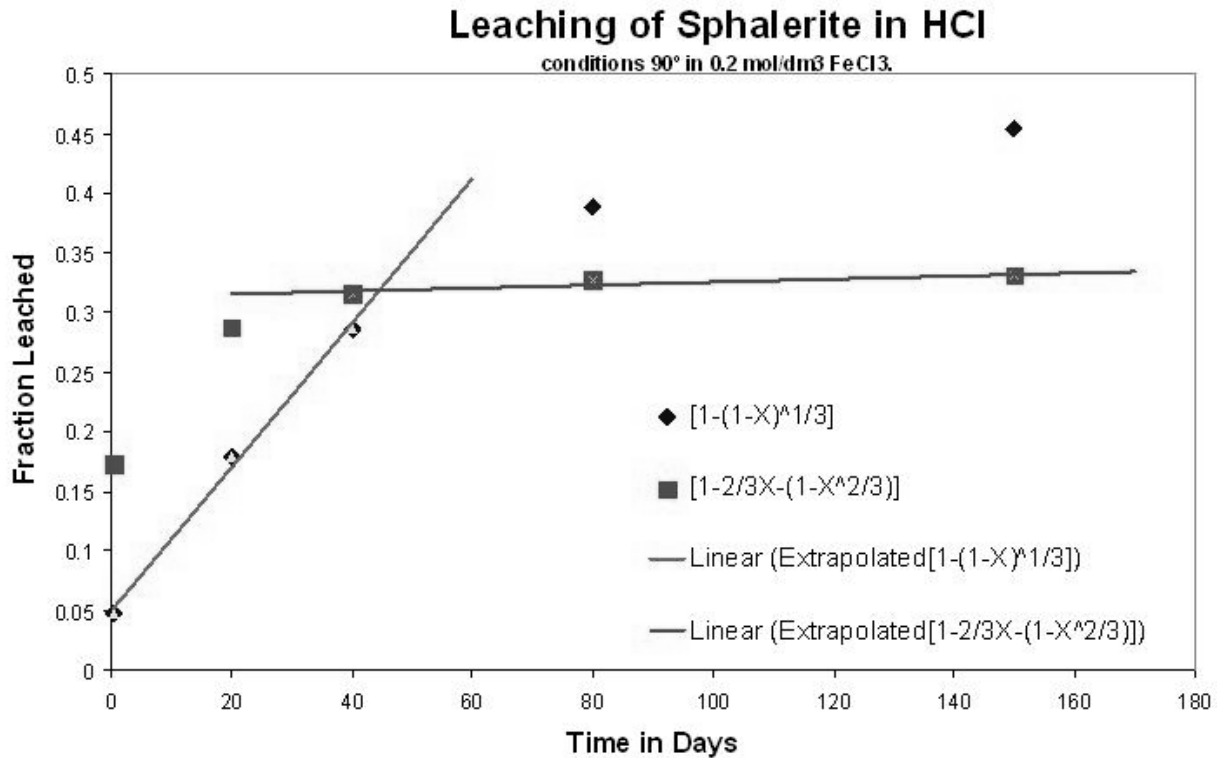
By applying the equations to the experimental data and plotting the fraction leached in relation to time, the relationship between the data and the reaction rate equations becomes apparent . Figure 2 also demonstrates the two distinct rate equations for the leached flotation concentrates.

From neither of the models a straight-line relationship could be deduced over the leaching range. At t < 45 minutes, it seems that the process is controlled by the chemical reaction at the interface. At t > 45 minutes, it seems that the process is controlled by diffusion through the product layer. These results are similar to those reported by Lochman and Pedlik (1995). The data represented in Figure 2 is from the actual study.

### GEOCOAT column leaching

Column test work has been carried out on a low grade zinc concentrate from Rosh Pinah to determine the amenability of the concentrate to GEOCOAT leaching. Different types of micro-organisms have been investigated, notably mesophiles that operate at 37 to 42°C. Results of the GEOCOAT leaching of the Rosh Pinah material is shown for both small and large diameter columns, and indicates both zinc and iron dissolution using the two types of microbes. The bacterial oxidation of all sulphide flotation concentrates takes place in a sulphate medium, through which sphalerite is leached to give soluble zinc as zinc sulphate. The leaching of sphalerite by ferric sulphate can be described as stated by: Fowler and Crundwell (1999)as:





**Figure 2:** Plot of chemical and diffusion control models showing the conversion of ZnS to Zn<sup>2+</sup> as a function of time according to equations 1 and 2 for establishing the rate-determining step. Leaching conditions 90° in 0.2 mol/dm<sup>3</sup> FeCl<sub>3</sub>. Actual data obtained from this study.

### Small Diameter Columns (SDC)

Columns manufactured from Perspex, fitted with thermocouples, heating elements, air supply and insulation were used in the test work.. Figure 3 shows a picture of two of the columns. The picture shows the heated, insulated columns with the on and off solution containers.

A graphical representation of the chemical and diffusion control models for the small diameter columns, showing the conversion of ZnS to Zn<sup>2+</sup> as a function of time according to equations 1 and 2 is given in Figure 4. This graph represents actual data obtained from this study.

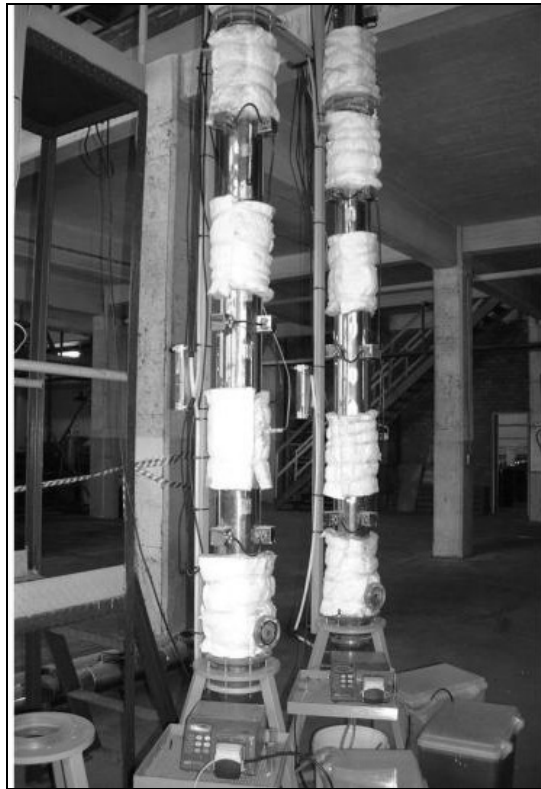


Figure 3: Photograph of the Small Diameter Columns showing the peristaltic pumps for irrigating the column and buckets for the on- and off-solutions.

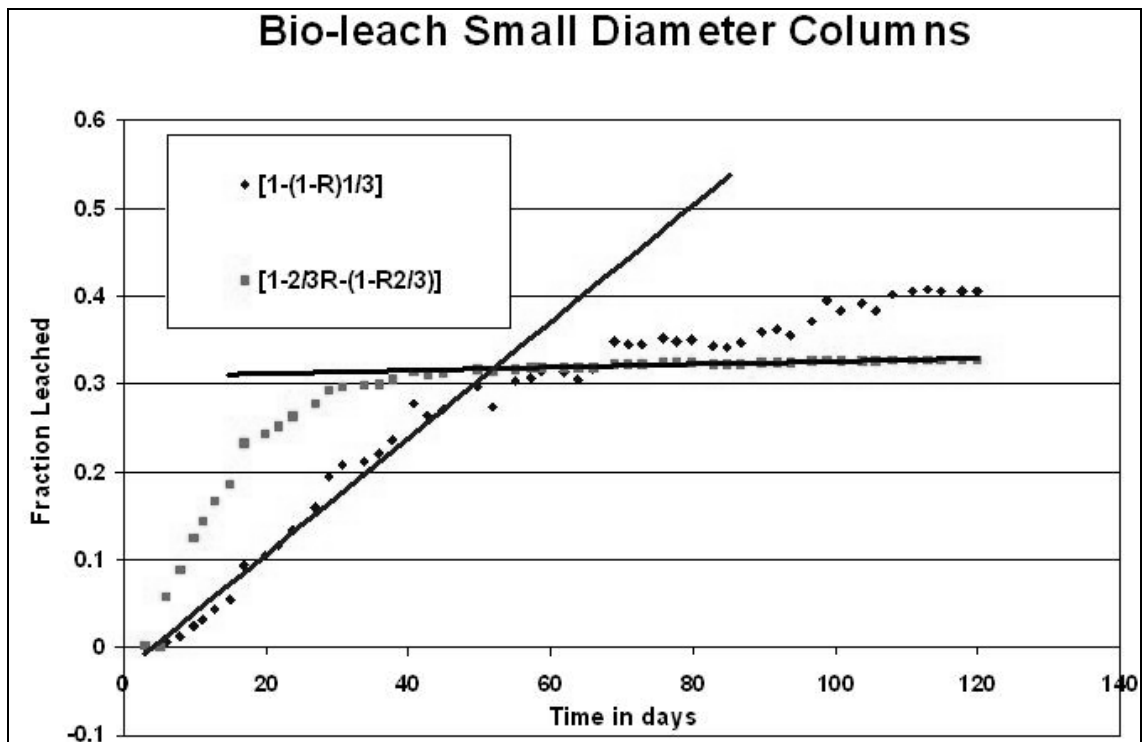
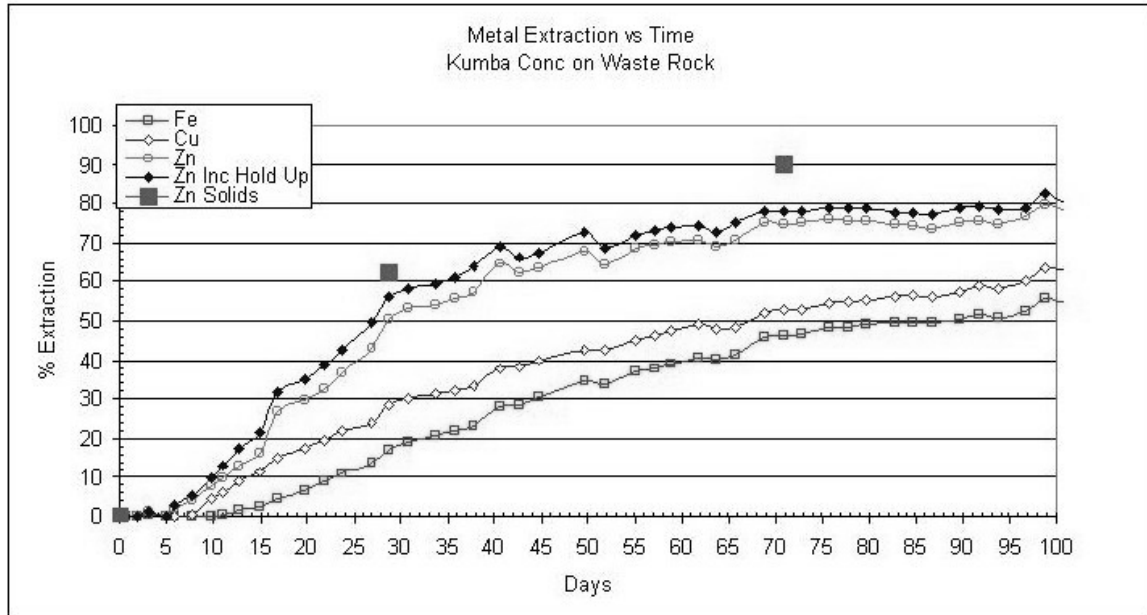


Figure 4: Plot of chemical and diffusion control models for the small diameter columns, showing the conversion of  $ZnS$  to  $Zn^{2+}$  as a function of time according to equations 1 and 2

### Large Diameter Column (LDC) leaching

The extraction of various metal species with time for the Large Diameter Column experimental work is represented in Figure 5.

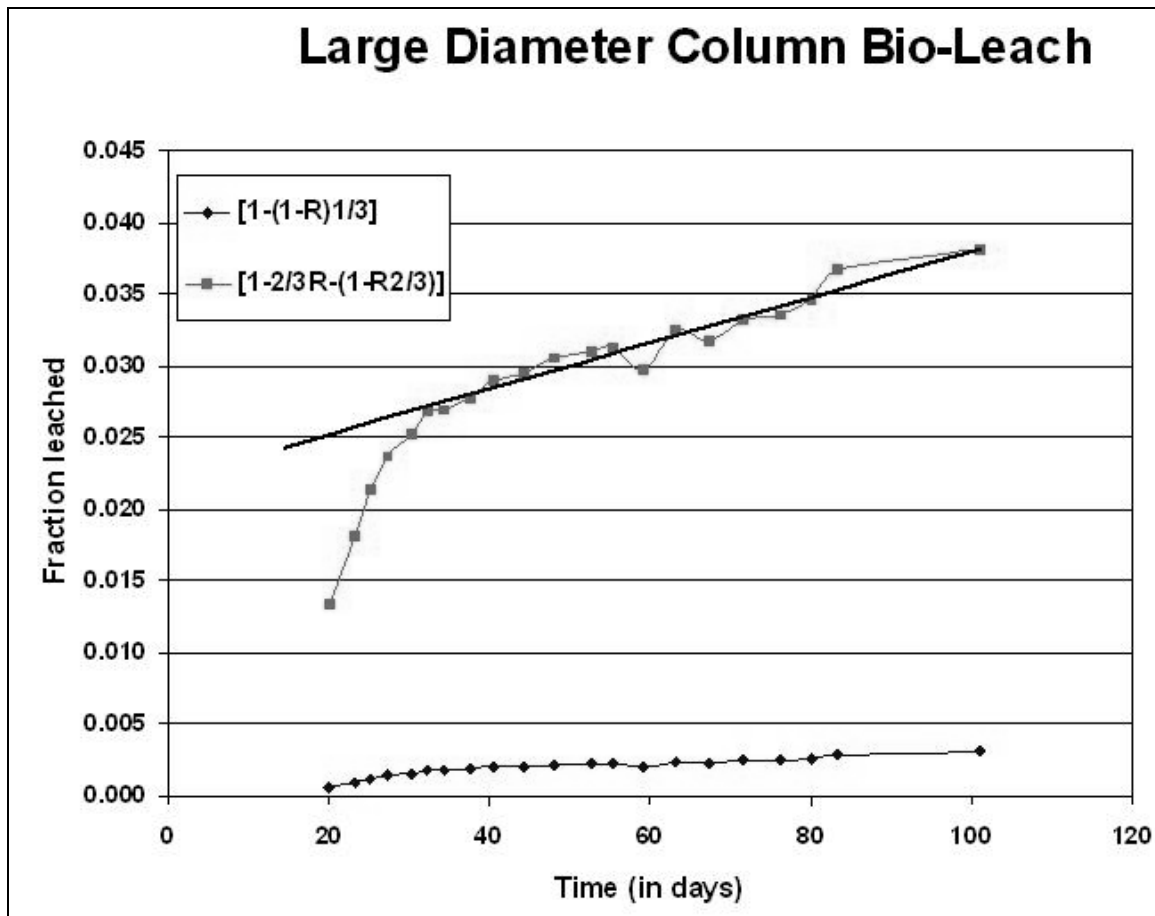


**Figure 5:** Results of the GEOCOAT leaching of the Rosh Pinah material is shown and indicates both zinc and iron dissolution using the two types of microbes.

The graph shows the bioleaching of zinc from sulphide concentrates with mesophile bacteria. The results of the bioleaching column tests indicate that a leach time of 70 days would be sufficient to ensure a zinc dissolution of 90%. During a commercial application of the GEOCOAT technology, it is anticipated that the overall leach time would be decreased to 45-50 days as the micro-organisms are more adapted to the heap environment.



**Figure 6:** Photographs of the Large Diameter Column with peripherals at the Exxaro Pilot Plant showing the sample ports on the left, electronics and manhole right top and on- and off-solutions right bottom.



**Figure 7:** Plot of chemical and diffusion control models for the large diameter column, showing the conversion of ZnS to Zn<sup>2+</sup> as a function of time according to equations 1 and 2. Actual data obtained from this study.

A graphical representation of the diffusion control model for the large diameter columns, relating to the experimental data showing the conversion of ZnS to Zn<sup>2+</sup> as a function of time according to is given in Figure 7.

It is thus evident that the chloride and sulphate systems for the same material compares very favourable.

### INTERPRETATION

As the anodic dissolution reaction progresses, the sulphur forms a more or less dense reaction product layer on the mineral sulphide.

In Figure 3 the diffusion-controlled and chemically controlled models are compared on the same graph. At a value of R lower than 0.3, it seems that the process is controlled by the chemical reaction at the interface. At a value of R higher than 0.3, it seems that the process is controlled by diffusion through the product layer. It seems that a mixed model phenomenon is taking place. As the more inert, less easily penetrable product layer forms by chemical action, a diffusion problem develops that is governed by the

nature of the product layer. It seems that the nature of the solid reaction product is rate determining, as was predicted by Habashi (1999)<sup>6</sup>.

The assumption is made that passivation properties of the reaction product layer can be attributed mainly to its density or passivity; the reaction product layer seems to be so dense or inert that it does not dissolve in the overpotential applied. The other fair assumption that can be made is that the reaction product layer restricts the mobility of dissolving metal species.

Fowler and Crundwell (1999)<sup>6</sup> showed that during the chemical leaching of zinc sulphide, the presence of a porous layer of elemental sulphur limited the diffusion of ferrous ions through the sulphur layer, which hindered the leaching rate and zinc dissolution. However, during tests with the addition of the mesophilic bacteria *Thiobacillus ferrooxidans*, no elemental sulphur layer was detected on the mineral surfaces and there was an increase in the leaching rate of zinc sulphide. This suggested that the action of the bacteria in being able to oxidise the sulphur formed on the mineral particles removed the barrier for ferrous ions to diffuse. The investigation showed that the bacteria enhance the rate of dissolution of sphalerite only under conditions in which diffusion through the sulphur layer controls the overall rate of chemical leaching. This is achieved by the oxidation of the sulphur by the bacteria.

As the leach reactors move from stirred bench scale to small column to large column it seems that the reaction control shifts to more diffusion control. This could be because the column starts reacting as a large permeable particle.

## **DISCUSSION**

As the anodic dissolution reaction progresses, the reaction product forms a more or less dense reaction product layer on the mineral sulphide.

As the more inert, less easily penetrable product layer forms by chemical action, a diffusion problem develops that is governed by the nature of the product layer. It seems that the nature of the solid reaction product is rate determining, as was predicted by Habashi (1999)<sup>5</sup>.

The assumption is made that passivation properties of the reaction product layer can be attributed mainly to its density or passivity; the reaction product layer seems to be so dense or inert that it does not dissolve in the overpotential applied. The other fair assumption that can be made is that the reaction product layer restricts the mobility of dissolving metal species, as is verified by SEM-EDS instrumentation.

It can also be noted that during the bioleaching of chalcopyrite, passivation occurs with mesophiles and moderate thermophiles but not with the extreme thermophiles that operate at lower redox potentials (400-450mV) while the mesophiles operate at around 600-650mV.

The conclusions from the study are:

- that the kinetics is very dependent on the type of ore processed relating to the mineral composition of the ore body.

- Any of these steps may control the rate; - depending on its speed relative to the other steps.
- The leaching Fe<sup>2+</sup>/Fe<sup>3+</sup> couple is prevalent in both the Atmospheric and Bio-leaching of Sphalerite.
- It seems that the influence of the Product Layer Diffusion Control step increases in bio-leaching.
- Although the conditions were completely different:
  - HCl vs. H<sub>2</sub>SO<sub>4</sub>
  - 80°C vs 37° C
  - Stirred vs. “heap”

It seems that the mechanism and rate determining steps were similar

### ACKNOWLEDGEMENTS

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Exxaro Resources.

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