

## 8.3 Kinetic tests

## 8.3.1 Reaction rates

## CHAPTER 8

Tests were prepared with several reaction mixtures to determine the initial reaction rates and

## CONCLUSIONS

8.1 Determination and calculation of  $E_h$  values

A very good correlation was obtained between the calculated and the measured  $E_h$  values. The calculated values were determined by reaction 65:

$$E_h = E^0 - \frac{RT}{F} \ln\left(\frac{[Red]}{[Ox]}\right)$$

These values are represented in table 10

## 8.2 Leach tests

From the test work it was clear that the kinetics at 70°C are too slow for sufficient extraction of the zinc from the sphalerite.

The barium started leaching very well, just to be taken out of the reaction by a side reaction. It seems that a complex reaction was taking place and that barium was competing for the sulphate sulphur, thereby taking one of the products formed out of the reaction, and that this could have an effect the rate of the reaction. In the Pourbaix diagram presented in section 7.6 (Figure 25, Bobeck and Su (1985)) it was noticed that in the region between pH 7.5 and 2.0 and -90 to 790 mV, sulphur does exist as  $SO_4^{2-}$ . This means that the leaching of barium could be controlled by either precipitation as barium sulphate or by keeping the barium in solution (by controlling the pH).

In figure 31 the diffusion-controlled and chemically controlled models are compared on the same graph. At a value of  $R$  lower than 0.3, it

### **8.3 Kinetic tests**

#### **8.3.1 Reaction rates**

Tests were prepared with several reaction mixtures to determine the initial reaction rates under different conditions.

Two methods of data processing were compared. The MSEXcel® method to determine the initial rate of a reaction was used. The results compared very well with the differential method but were inconclusive, and it was decided to rather use the usual rate method (ln a/a-x versus t) as in equation 53 to calculate the slope for the initial part of the reaction.

A side reaction that will be interesting to investigate is the behaviour of barium in the reaction.

#### **8.3.2 Activation energy**

The activation energy of 45.81 kJ/mol was determined for the first part of the reaction that was found corresponds very well with the values reported by other researchers. Bobeck and Su (1985), reported 64.5 kJ/mol, and Mandre and Sharma (1992), reported 37.39 kJ/mol.

A value of 20.71 kJ/mol was determined for the activation energy  $E_a$  for the mixed control models showing the conversion of ZnS to Zn<sup>2+</sup> as a function of time according to equation 60 (Huang and Rowson (2002).

#### **8.3.3 Rate-controlling step**

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

In figure 31 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) and discussed in section 3.1

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 in figures 22 and 23.

The porosity of the reaction product forming on the surface of the unreacted particle seems to have a substantial influence on the rate of the reaction. As was predicted the reaction rate decreased as the reaction continues due to the dense nature of the film of the product forming around the reacting solid.

#### **8.3.4 Application of the technique**

This study can be used to evaluate the efficiency of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple in bioleaching, as this mechanism is involved in both applications. The rate-determining step will most probably also be comparable. The influence of the sulphuric acid versus the  $\text{FeCl}_3$  should, however, be investigated further.