



Flotation of oxide minerals by sulphidization—the development of a sulphidization control system for laboratory testwork

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Synopsis

Laboratory-scale testwork was undertaken to recover oxidic copper-cobalt minerals by froth flotation, which requires maintaining a certain sulphide level in the pulp. To improve control of the sulphide concentration, an electronic closed-loop system was designed that responds to the potential output of an ion-selective electrode. The PID control was improved by adding a pre-emptive control and a self-calibration feature; a data logging facility is also included. An inexpensive valve design was incorporated using locally available parts. The operating results of this control design are presented.

Introduction

Froth flotation of oxide minerals by sulphidization is a widely used technique in the metallurgical industry. Sulphidization of oxide minerals renders them amenable to recovery using a xanthate collector. Both under and over addition of sulphide have a detrimental effect on mineral recovery. Much of the sulphide is consumed through oxidation by air required in the flotation process and, therefore, it needs to be continuously replenished. The sulphide concentration is measured using an ion-selective silver/sulphide electrode. This electrode produces a potential difference in the millivolt range, according to the total sulphide ionic strength within the solution it is measuring. By maintaining the optimum potential and therefore the optimum sulphide concentration in the flotation cell, mineral recovery can be maximized.

This critical relationship between mineral recovery and sulphide concentration is the reason for the development of the control system. The system is a natural progression from less sophisticated techniques used to regulate the sulphide addition. The first of these techniques makes use of very little regulation as it is simply a slug addition at various times during the flotation process. This method is very poorly defined and the reproducibility is equally poor. The second

technique is the manual addition of the sulphide solution while monitoring the sulphide concentration. This method is better regulated and therefore a greater degree of control is achieved. The problem with manual control is that it is dependent on the operator. The third technique, reported below, makes use of an electronic closed-loop system to regulate the addition of the sulphide solution.

Methodology

The control system can be broken down into four sections, namely input, output, control algorithm and data logging. Each of these sections will be briefly discussed as to their function and effect on the system.

Input

The input to the system is the potential difference produced by an ion-selective electrode. The electrode used in this development is the Thermo Orion 96-16 silver/sulphide combination electrode, which does not require a separate reference electrode, which makes it very convenient. The electrode operation is described by the Nernst equation.

$$E = E^{\circ} + a \log[S^{2-}] \quad [1]$$

- E Measured electrode potential, mV
- E° Standard electrode potential, mV
- a Electrode slope (-28 mV/decade for sulphide)
- S^{2-} Sulphide ion concentration in solution

These electrodes are susceptible to the following factors that influence their performance.

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Temperature

Temperature affects the electrode potential slope. As can be seen in Equation [1], the slope for sulphide is around the -28 mV/decade (these figures are theoretical and the practical values may differ). Table I shows the relationship between temperature and the electrode slope:

Acidity of solution

The pH value reflects the level of acidity of the solution and determines the equilibria between the various sulphide species:



The ion-selective electrode is capable of measuring only free sulphide ions, i.e., S^{2-} , which exist in very basic solutions ($\text{pH} > 12$). In the range $\text{pH} 7-12$ the HS^- species is stable, and in acidic solutions ($\text{pH} < 7$) only undissociated H_2S . This shows that the higher the pH value, the more accurately the readings will reflect the true sulphide concentration.

Drift

When the reading slowly moves in one direction, it is known as drift. Drift is caused by the oxidation of sulphide in solution. In the present case this was caused by the compressed air blown into the flotation cell.

Noise

Noise is any electrical interference picked up by the electrode, either through the wire or by the electrode itself. This will make the readings unstable and incorrect.

Although the electrode is fairly robust and responsive, any one of these factors can have a negative effect on the proper operation of the control system and therefore need to be avoided wherever possible.

Output

The output of the system is the signal relayed to the proportional valve actuator. This regulates the quantity of sodium sulphide solution entering the flotation cell. These valves can only be imported at high cost. The high price and also time constraints resulted in the in-house design and manufacture of the proportional valve.

The design of the valve for this project made use of readily available components. The main objective was to make it inexpensive and keep it simple for future

maintenance. The valve itself consists of a standard 8 mm irrigation ball valve, which is activated by a geared motor, allowing the valve to be regulated continuously between fully closed and fully open. This is achieved by controlling the power to the motor, both in terms of polarity and duration. One important consideration with respect to the material of construction was that it had to withstand the high alkalinity of the sulphide solution to which it may be exposed from time to time. As the brass alloy composition of the ball valve is non-reactive to the relevant chemicals, this problem was averted.

Control algorithm

The heart of the system is in the PID (proportional, integral, derivative) control algorithm. The algorithm calculates the extent of how far open or closed the valve needs to be so that the appropriate amount of sulphide solution is added to the flotation cell. The basics of a PID control algorithm work as follows: an error is calculated, which is then used to determine the three control parameters. Each of these parameters is discussed below.

Error calculation

The error represents the difference between the desired potential and the current potential obtained from the electrode. This is the traditional method for calculating the error, which is then used in the rest of the component calculations.

Proportional component

The proportional component tries to reduce the error to zero. It is calculated by multiplying the error by a proportional gain, i.e. the greater the error, the more the proportional component becomes, which in turn opens the valve more.

Integral component

In general, the integral component is there to overcome any mechanical inertia. In this particular application it is to prevent a situation of equilibrium occurring. Equilibrium will occur when the rate of addition equals the rate of consumption. The error does not change, which means that the proportional component does not change. The integral component then adds small amounts to the overall control parameter until the error is zero. In this way an equilibrium scenario cannot occur. The rate at which the integral component is increased is regulated by the integral time constant.

Derivative component

The derivative component monitors the rate of change of the error. It has the effect of dampening the system's response. For this application the derivative component is used primarily as a mechanism to prevent high overshoots when the initial error is large. It monitors the rate of change of the sulphide concentration relative to the size of the error. If the rate of change is large and the error reaches a set limit below the desired concentration, the derivative control will close the valve. If the system relied entirely on the proportional and

Table I

Electrode slope vs. temperature

Temperature °C	Electrode slope mV/decade
0	-27.1
10	-28.1
20	-29.1
25	-29.6
30	-30.1
40	-31.1
50	-32.1

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integral components the valve would still be trying to close when the desired potential was passed. By pre-empting the closure of the valve, the overshoot can be kept within acceptable limits but still have a fast recovery from low initial sulphide levels.

Pre-emptive control and self-calibration

The control system has to work in a very variable environment. The different ore samples have different sulphide consumption rates. These rates also change during the flotation process, making the control of the sulphide concentration very difficult. Many of the control parameters such as the proportional gain are dependent on the sulphide consumption rate and the concentration of the sulphide solution. If any of these factors changes, the system cannot operate correctly. What is needed is a more dynamic control algorithm. Inspiration came in the form of the second control technique mentioned in the introduction, namely manual control. The modifications to the standard PID algorithm were made to simulate a human response.

With the standard error calculation the valve will only begin to open when the sulphide concentration drops below the desired level. Because of the rapid consumption of sulphide during the flotation process and the relative slowness of the valve, this method can sometimes allow the concentration to drop too low before the system reacts. A modification to the algorithm allows for a pre-emptive control strategy. This algorithm monitors the direction of the change in potential and when it decreases to within a certain distance from the desired concentration set point, the valve will start to open. If the direction changes, that is to say that the concentration starts to increase beyond the desired level, the valve is closed. This follows the method used by an operator who is manually controlling the concentration. As the concentration nears the desired level on the way down, the operator would start adding smaller quantities of sulphide to reduce the rate of the falling concentration. As soon as the concentration starts to increase the addition would be stopped.

The self-calibration procedure enables the proportional gain to be changed during run time depending on the system's performance. If the concentration overshoots the desired level by more than a certain amount, the self-calibration procedure reduces the proportional gain in an attempt to reduce the overshoot. Conversely, if the concentration drops below the desired level, it will increase the proportional gain. As the ore becomes less amenable to sulphidization, i.e. it consumes less sulphide, the system can then adjust accordingly by reducing the proportional gain.

Data logging

An additional feature of the control system is that it can communicate with a computer. A user interface written in LabVIEW enables the potential read from the electrode to be graphically displayed against time as the flotation process is carried out. This connection also allows for remote activation and deactivation of the valve and the ability to change the reference concentration level. Probably the most important feature is its ability to save the received potential values. These values can then be accessed using a spreadsheet environment for later data analysis.

Results

The overall arrangement of the flotation test cell is illustrated in Figure 1.

In manually controlled laboratory sulphidization, sulphide solution is added during a flotation test. The potential of the solution is measured by the silver/sulphide electrode connected to a pH meter millivolt port.

The flotation tests were carried out by adding a 10 g/l solution of sodium sulphide to the agitated pulp of finely ground copper-cobalt ore and maintaining a pH value of approximately 10.5. A potential of the order of ~500 mV in the pulp was targeted.

In Figure 2 below, the design of the control valve with simple and inexpensive parts is shown.

Table II shows the accuracy of the control system's input interface. The test was conducted using five different standard solutions of sodium sulphide, ranging from 0.1 to 1 000 ppm. The potential difference produced by the electrode in each case was measured by the existing electrode meter,



Figure 1—Arrangement of flotation test cell



Figure 2—Standard irrigation ball valve operated by a geared motor

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Table II
Comparison of the electrode's potential difference readings from the existing meter, an oscilloscope and the control system

Concentration, ppm[S ²⁻]	Measured potential, mV			
	Existing meter	Oscilloscope	Control system	Ex.Met-C.Syst
0.1	-401	-401	-401	0
1	-641	-641	-641	0
10	-767	-768	-768	1
100	-818	-819	-819	1
1000	-870	-872	-872	2

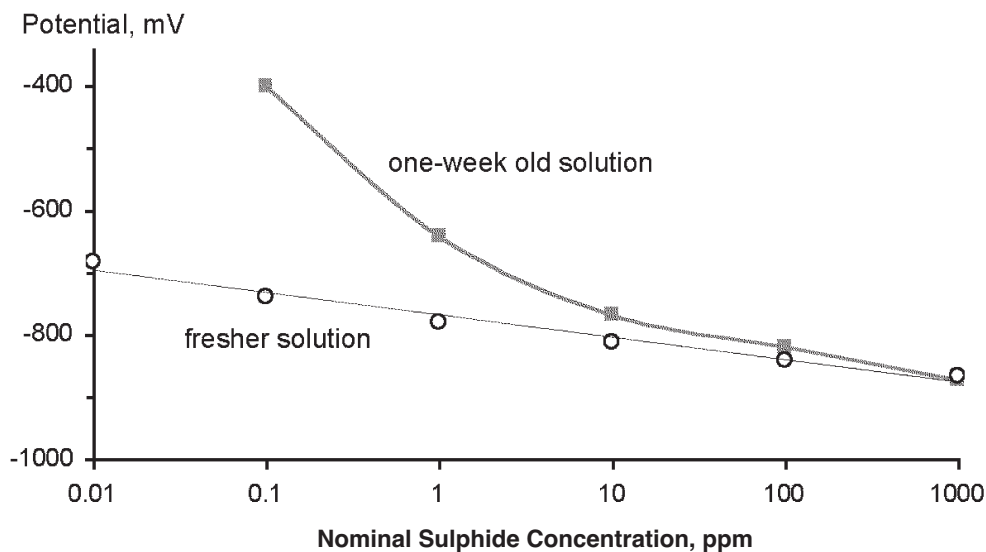


Figure 3—Relationship between nominal sulphide concentration and measured potential

an oscilloscope and the control system. It can be seen that the oscilloscope and the control system never differed from each other, while the existing meter did show a small discrepancy. The existing meter may have gone out of calibration or, in the time taken to transfer the electrode from the meter to the control system, the value may have drifted. Either way, the discrepancy is not large enough to cause any problems.

It should be noted that the absolute readings themselves are incorrect. This is attributed to the age of the standard solutions. These solutions are very unstable and begin to deteriorate very soon after they have been produced. The figures in Table II are based on a test that was conducted with 'week-old' solutions. Whether the readings are absolutely correct or not, however, is irrelevant as the objective of the experiment was to test the performance of the control system and not the accuracy of the solutions or the electrode.

In Figure 3, the results given in Table II are compared with those using a fresher solution.

The concentration in terms of free S²⁻ is indeed higher in the latter, leading to more negative potentials at nominally equivalent concentrations; also the experimental results can be analytically expressed by the least-square line $Pot = -35.8 \log [S^{2-}] - 769$, with $R^2 = 98\%$.

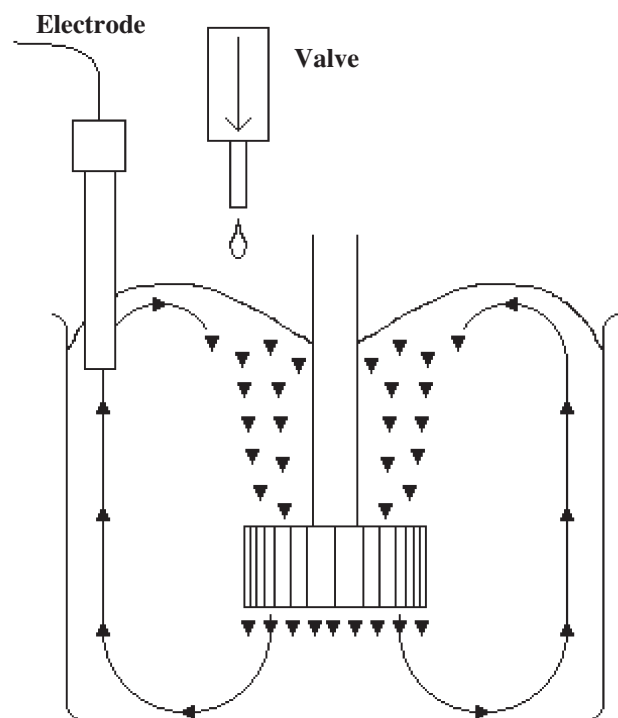


Figure 4—The circulation pattern of the solution within the flotation cell

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The position of the electrode within the cell and in relation to the input of the sulphide solution is one of the most important variables. Adequate circulation within the laboratory flotation cell is imperative to ensure that the added solution is sufficiently mixed and that the electrode's measurements are representative of the entire cell. Figure 4 shows the circulation pattern of the solution in the cell as well as the relative position of the electrode to the sulphide solution input. It can be seen that the liquid in the cell is circulated from the centre agitator outwards towards the perimeter and then forced upwards. The sulphide solution enters where the solution is drawn down and the electrode is positioned in the upward path.

There are three parameters that were examined to measure how effectively the system was working.

- *Overshoot* is defined as the maximum value the concentration reaches after the system is turned on from an initial point well below the reference value
- *Accuracy* is defined as the amount that the value varied around the reference point while it was controlling
- *Spike* is defined as the maximum value reached on sporadic overshoots.

The initial algorithm without the pre-emptive control and self-calibration was not fully successful. The system could be made to work for a specific test set-up but this is not ideal as each ore sample reacts differently. The system would not be very practical if it needed to be calibrated each time a new ore was tested. However, when the system was set up correctly and working, fairly good results were obtained. These can be seen in Table III. Every five to six cycles the concentration would spike to a value of 45 to 50 mV above the desired value. A single cycle is defined by the valve turning on and off again, that is to say the concentration has gone below the desired value and then above it again.

The improved algorithm with the pre-emptive control and self-calibration had far better results. The system was tested with a fresh ore that had not been in contact with any sulphide solution at all and initially the system laboured to reach the set-point potential as sulphide was rapidly depleted in the flotation cell. However, the system worked better than expected and after approximately eight cycles the system had calibrated itself and was regulating to within 15 mV of the desired level. A few spikes occurred due to the irregular circulation within the flotation cell. These results are shown in Table III.

Conclusion

The control system allows fairly accurate regulation of the sulphide concentration, thus eliminating one of the many variables in the flotation process and facilitating experimentation with different sulphide concentrations in attempts to optimize mineral recoveries of an ore being tested.

The ability to record and display the concentration changes in the flotation cell enables the effects of the different sulphide concentrations to be compared against the copper and cobalt recovery to concentrate. The system can be upgraded to display other important parameters such as the pH value and temperature.

Table III

Comparison of the two algorithms

Algorithm	Potential, mV			
	Desired	Overshoot	Accuracy	Spikes
Standard PID	-500	200	50	50
Pre-emptive control and self calibration	-500	150	15	20

Note: These results were obtained using a sodium sulphide concentration of 1500 ppm

Although the agitation of the sample in a laboratory flotation cell is fairly vigorous, there is a delay in the entire flotation cell contents reaching the same sulphide concentration level. This is clearly noticeable if the position of the electrode is changed relative to the sulphide solution point of addition. An additional silver/sulphide electrode located at the opposite side of the cell would improve any concentration differential within the cell. An average of the two electrode potentials would better represent the actual concentration in the flotation cell. However, the differential in a flotation cell used in laboratory research is not large enough to justify the expense of another electrode, but for larger cells this should be contemplated.

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