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Performance Prediction of Xanthogenate Collectors Using Flotation Kinetic Equation

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Abstract

The kinetics of flotation using xanthogen collectors - $C_2H_5OCSSNa$, $C_3H_7OCSSNa$, $C_4H_9OCSSNa$ and $C_5H_{11}OCSSK$ were studied in the flotation of lead sulphide with sodium ethyl xanthate –SEX ($C_2H_5OCSSNa$) as control. Sodium ethyl xanthates (SEX) as control gave a recovery of the mineral of interest being lead sulphide of 94% and high-grade recovery of gangue as 24% which indicated that SEX has high selectivity but low recovery. The SIPX has a flotation kinetics of gangue that are greater than for SEX, which indicates its relative greater strength than SEX. At optimum time the concentrate grades are 12.1% Pb and the separation efficiency is greater, reaching 80.5% but with lower selectivity than SEX. SIBX is a collector with much more rapid flotation kinetics for the lead sulphide but with lower recovery, being less selective than SEX. The optimum separation time for SIBX is around 7 minutes, which demonstrates its high flotation rate for the lead sulphide giving recovery of 88.9% with separation efficiencies of 76.6%, better parameters than those of SEX. PAX is a collector of great strength with recovery characteristics similar to SEX, with rapid flotation kinetics for lead sulphides but less selective. In comparison with SEX, it has lower recovery of lead sulphide but the rapid recovery percent is 91.9%. Its separation efficiency is very similar to SEX at their respective optimum times, with concentrate level of 7.4% Pb and efficiency of 73.8%

1.0 Introduction

Reagents used in flotation are collectors, frothers and modifiers. Of these, collectors are the most important and continuous efforts are made to evaluate and improve their functionalities. These collectors are organic compounds which render selected minerals water-repellent by adsorption of molecules or ions on to the mineral surface, reducing the stability of the hydrated layer separating the mineral surface from the air bubble to such a level that attachment of the particle to the bubble can be on contact (Wills, 2006). The most common collectors in use today are the alkaline collectors, known as xanthates. For successful flotation operation, addition of optimum quantities of the collectors is very essential. Too little or excess quantity of collector have either beneficial

or adverse effects on the flotation process. Therefore, extant and new reagents are constantly being evaluated with regard to their effectiveness in any particular flotation process, taking into consideration the minerals and conditions of operation in each plant. Also, for ore bodies, as the mineralogical characteristics of different zones are change, periodic reviews of the reagents used in the flotation process are carried out. (Marin and Molina, 1985).

It is the convention to evaluate the performance of flotation reagents using laboratory batch flotation tests to determine the recovery and grade of concentrates on the basis of varied dosages of the reagent under study. Small scale batch test results should be evaluated with caution due to several limitations. The most important limitations are associated with recycle streams, site water and test size (Thompson, 2002). Another method is the use of statistical approach. The use of statistical analysis in the selection of a reagent scheme is usually limited to optimizing reagent dosages after a preliminary scheme has been selected. Statistical methods are also extensively used to evaluate the relative importance of various reagents in existing reagent scheme at operating plants. The two most common types of statistical methods that are used in reagent scheme evaluation are *screening tests* and *response surface design.* The most common type of screening statistic used is the Plackett Burman (1946) analysis. This is a special two-level factorial design that is used as a preliminary screening tool to determine which reagents have a significant effect on recovery, grade, or both. Thus, it is used to reduce the number of batch tests necessary to optimize the combination of reagents, permitting the development of a more effective formula during the process. More sophisticated statistics such as response surface design are used to optimize reagent additions. These methods are based upon factorial design of experiments and may be used to evaluate several variables at several levels. This type of analysis is quite complex and software packages are used to simplify the experimental design and interpret the results. In all these cases, it is necessary to carry out intensive experimental work.

To obviate the need to carry out intensive experimental work for the evaluation of reagents in flotation processes is to consider that flotation separation can be described very simply using a kinetic equation, which not only describes the effect of the reagents, but also helps in the design and optimization of the separation process.

2.0 Modeling Flotation Process

According to King (1982), many batch flotation tests conducted in the laboratory have indicated that the kinetic model for flotation does describe the essential nature of the flotation process at least in a well–stirred flotation environment where the solid particles are kept in suspension and are available for capture by the bubbles. Also, according to Gochin and Smith (1987), state that research has shown that flotation can generally be regarded as a first-order rate process with respect to the concentration of the floating species in the pulp. Therefore, flotation separation can be described in kinetic terms using a first order rate equation. The first order rate equation can be expressed (Lynch et al, 1981) as:

$$R = 1-\exp(-kt) \quad (1)$$

A modified first order rate equation is of this form (Wills, 2006) in equation (2) in which the parameter of maximum recovery is $R_{m.}$

$$R = R_m[1-\exp(-kt)] \quad (2)$$

Where:
R = cumulative recovery at time t,
R_m = maximum recovery that is approximately asymptotic as $t \rightarrow \infty$
K = flotation rate constant (min^{-1})
t = flotation time (min)

This equation can be applied to all the components of the flotation system, including water. Of course, some gangue will float and dilute the concentrate Gochin and Smith (1987). The longer flotation continues the more will be this dilution and cumulative concentrate grade will decrease Gochin and Smith (1987). Hence it is evident that there is an optimum flotation time beyond which the incremental increase in recovery in the unwanted minerals begins to exceed that of valuable mineral. Also, it has been shown that through the use of this equation, a continuous circuit can be simulated from batch data, and even more, the time used in the various stages can be optimized.

The premise on which this application is based is that a variation in the quantity of reagents or the introduction of reagents into the flotation system affects in some way K and R_m. This is valid for any agent in the process, whether they are collectors, frothers or modifiers.

To interpret the data kinetically, only one flotation test would be necessary. The froth bearing the concentrate is collected in concentrate launder over an increasing period of time. The unknown parameters of the rate equation can be calculated from the first order kinetic equation. A first estimate of the value of maximum recovery R_m is obtained by plotting the cumulative recovery as a function of time (Figure 1), when the curve becomes asymptotic after a long period of flotation. The initial estimate of R_m can be corrected by preparing a logarithmic plot of (R_m –R/R_m) as a function of the flotation time (Figure 2). If the estimate of the value of R_1 is too great, the line will curve downwards. The value of the constant K is obtained as a slope of that straight line.

With the parameters K and R_m determined, the first order equation can be used to calculate the optimum separation time. The optimum time is defined as the time at which the difference between the recovery of valuable mineral and the gangue ΔR is at a maximum.

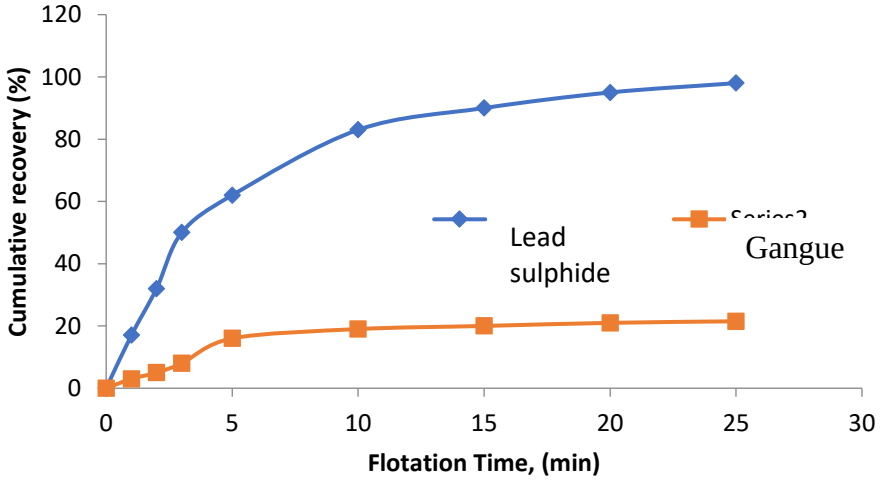

Figure 1: Kinetic flotation curve for estimating R_m (SEX)

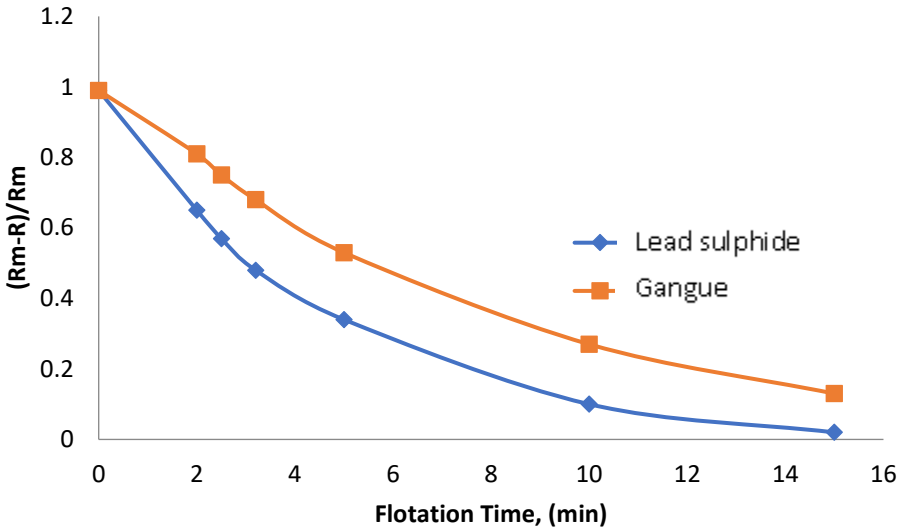

Figure 2: Adjustment of Rm in a first order equation (SEX)

$$\Delta R = Rv\text{-}Rg \quad (3)$$

Where:
R_v = recovery of valuable mineral
R_g = gangue recovery

$$\partial R/\partial t = \partial Rv/\partial t - \partial Rg/\partial t = 0 \quad (4)$$

$$\partial Rv/\partial t = \partial R_g/\partial t \quad (5)$$

$$\frac{\partial(R_{mV}[1\text{-}\exp(-K_V t)])}{\partial t} = \frac{\partial(R_{mg}[1\text{-}\exp(-Kgt)])}{\partial t} \quad (6)$$

$$t_{,optimum} = 1/K_A\text{-}K_B \ln (R_{mV} K_V/R_{mg} K_g) \quad (7)$$

The optimum time corresponds to the time when the rate of transfer of solids to the froth phase is equal for both components. When plotting the flotation rate as the slope of the kinetic curve as a function of time (Figure 3) both curves will cross at the optimum time.

Once the optimum time is determined using the rate equation, the recovery of both components is determined for that time and the difference is the optimum separation. The term ΔR is the separation efficiency and it is a measure of the fraction of the feed that can be perfectly separated. Higher flotation times than the optimum reduce the concentrate grade, due to the higher flotation of the gangue, considering that the maximum recovery of valuable mineral or mineral of interest (R_m) has already been reached.

The application of this technique, permits the evaluation of the behaviour of sulphydryl collector type of reagents.

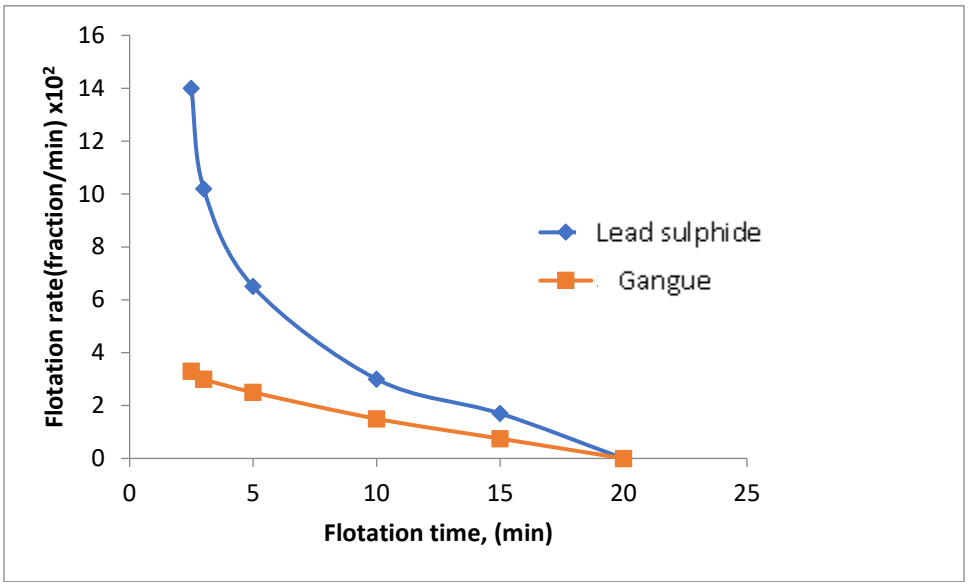

Figure 3: Flotation rate as a function of time for SEX

3.0 Experimental

Ore: the sample used in the experiment was a complex Nahuta lead sulphide ore, Bauchi State, Nigeria. Its mineralization consists principally of galena, PbS. Sample preparation was done by coning and quartering followed by rifling. Comminution of the material was by Denver laboratory jaw crusher, classifying the product through a 90µm.

Reagents: The collectors under study were synthesized through the reaction of an alkali hydroxide, an alcohol and carbon disulphide (Wills, 2006):

$ROH + CS_2 + KOH = RO.CS.SK + H_2O$

These products were purified by means of low-pressure distillation. The structure of the thiol collectors, otherwise known as xanthogenates (technically known as xanthates) was checked through the use of infrared spectrophotometry and magnetic nuclear resonance and compared with the xanthates obtained from *ALS Metallurgy* Western Australia. The results were consistent with the proposed structures. The xanthates studied were:

Sodium ethyl xanthates	SEX	$C_2H_5OCSSNa$
Sodium isopropyl xanthates	SIPX	$C_3H_7OCSSNa$
Sodium isobutyl xanthates	SIBX	$C_4H_9OCSSNa$
Potassium amyl xanthates	PAX	$C_5H_{11}OCSSK$

Other Reagents:
Frother: Pine oil; Type of water: Tap water

3.1 Techniques and Equipment

Grinding: The samples were ground in a Denver Ball Mill lined with rubber the grinding was done with 67% solids.

Flotation Tests: The flotation tests were carried out in a Denver flotation machine at 1800 rpm and with a pulp volume of 3 litres. The design of the experiments that would evaluate the xanthate collectors took into account the following variables: liberation degree, pulp pH, agitation seed, pulp density, frother type and dosage, type of water, collector dosage and its conditioning; all of which remained constant so as to study only one variable, a particular collector. The reagents dosage as follows:

a. Frother: Pine oil at 10 g/tonne of the ore
b. Collector: 50 g/tonne of ore in each case

With this collector dosage and frothers in the case of SEX, a recovery after 10 minutes of flotation of 86% was found under the prevailing conditions which left a sufficient margin of improvement. The flotation lasted 25 minutes and the launders for the concentrate were changed at the following times: 1, 2, 3, 4, 5, 10, 15 and 25 minutes. During this period, water was added to the flotation cell so as to maintain the pulp volume at 3 litres

.

At the end of the experiment, the concentrate samples that corresponded to each flotation time concentrate and final tailings were filtered and then afterwards dried and weighed. Finally, as a product of a rigorous sampling 30g were separated which were analyzed for Pb and total Pb content. The difference between them gives the percentage of insoluble Pb needed for calculations.

4.0 Results

The kinetics flotation curves for the lead sulphide and the gangue from the data in Table 2 for SEX, are shown in Figure 1. From both curves an estimation of R_m, are summarized in Fig. 2, giving for the lead sulphide minerals a value of 94.1% and for the gangue 24%. The slopes of the straight lines correspond to the first order rate constants, in the case of the sulphide minerals they are 0.233 (min^{-1}) and for the gangue 0.144 (min^{-1}).

Table 1: Kinetic parameters in the flotation of lead sulphide using different collectors.

Collector	Ore K (min-1)	Lead Sulphide R_m	K (min-1)	R_m	Optimum separation time	S.E. (%)	Conc. Grade (%) (optimum time)	Tail grade Pb % (optimum time)
SEX	0.23	0.94	0.14	0.24	20	72.6	6.4	0.15
SIPX	0.36	0.92	0.14	0.14	13	80.6	12.1	0.22
SIBX	0.56	0.89	0.13	0.21	7	76.7	11.8	0.30
PAX	0.44	0.92	0.24	0.24	10	73.8	7.4	0.19

Taking the slopes of the kinetic curves of Fig.1 at different times Fig.3 was constructed for the flotation rate, the intersection of both curves giving the optimum time of separation which gave 20 minutes. With the value for optimum time, using the kinetic curves ΔR was found to be 72.5%,

which is the value for the greatest separation efficiency. With the data in Table 2 the concentrate grades and tailings for the optimum were calculated to be 6.4% and 0.14% Pb, respectively.

5.0 Discussion

The primary role of a collector is to adsorb selectively and impart hydrophobicity to particles of the mineral to be floated (Fuerstenau and Somersudaran, 2003). SEX as a collector has moderate rate of recovery of the mineral of interest in the first four minutes and begins to slow down. From five minutes upward the rate of flotation is slow and it was observed that recovery of gangue minerals became constant following the trend of the mineral of interest. Its application would be principally in rougher and scavenger flotation circuits where these metallurgical objectives are required.

Table 2: Flotation kinetic data for SEX

Flotation time (min)	Conc. Weight (g)	Grade of Pb (%)	Cumulative Recovery Sulphide (%)	Cum. Recovery gangue (%)
0	38.7	10.3	3.4	0.5
1	51.4	9.6	14.5	2.4
2	70.0	8.4	31.8	5.6
3	74.1	8.0	49.2	9.1
5	77.0	7.0	64.9	12.7
10	114.3	5.6	83.9	18.2
15	60.9	4.0	91.0	21.2
20	71.3	3.3	92.7	23.4
25	82.0	2.1	96.1	25.3

Table 3: Flotation kinetic data for SIPX

Flotation time	Concentrate Weight (g)	Grade Pb (%)	Cum. Recovery of lead sulphide (%)	Cumulative recovery gangue (%)
0	36.21	19.14	14.69	0.78
1	39.82	18.90	22.09	1.59
2	50.21	17.40	47.78	3.81
3	30.69	14.47	60.89	5.11
5	43.78	10.88	74.91	7.09
10	50.81	6.49	84.68	9.48
15	60.51	3.48	91.40	12.78
20	62.81	3.51	93.59	13.47
25	65.28	3.41	97.88	15.68

In Figures 4, 5 and 6, the kinetic flotation curves can be seen, obtained from data in Tables 3, 4, and 5 for SIPX, SIBX and PAX respectively. Those which have been drawn are those obtained for SEX (dotted line) in order to demonstrate their differences. The data for the kinetic parameters of the first order expressions for these reagents are presented in Table 1. For the collector SIPX, a K of 0.360 (min^{-1}) and a R_m of 14.3%. The optimum time value was 13 minutes, which gives a

separation efficiency (S.E) with grades of 12.1% and 0.21% Pb in the concentrate and tailings respectively.

For the collector SEX, a K of 0.562 (min^{-1}) and a R_m of 88.9% was obtained and for the gangue there was a K of 0.127 (min^{-1}) and a R_m of 20.7%. The optimum time was 7 minutes which gives a separation efficiency (S.E) of 76.6% with grades of 11.8% and 0.29% Pb in concentrate and tailings respectively.

Table 4: Flotation kinetic data for SIBX

Flotation time (min)	Concentrate weight (g)	Pb grade (%)	Cumulative recovery sulphide mineral (%)	Cumulative recovery gangue (%)
0	38.59	17.22	18.58	1.81
1	54.69	16.51	26.62	2.32
2	60.51	15.31	53.79	4.89
3	40.51	14.87	71.58	6.67
5	60.68	6.01	82.30	9.61
10	80.88	2.52	83.21	13.62
15	75.68	1.13	90.61	17.40
20	78.31	0.85	91.51	19.50
25	79.01	0.71	92.31	21.39

Table 5: Table Flotation kinetic data for PAX

Flotation time (min)	Concentrate weight (g)	Pb grade (%)	Cumulative recovery sulphide mineral (%)	Cumulative recovery gangue (%)
0	131.4	12.41	36.71	3.79
1	128.01	11.31	42.58	5.88
2	66.71	8.30	60.0	8.92
3	52.96	7.68	70.21	11.47
5	81.31	5.39	83.81	15.38
10	88.59	2.58	90.58	19.77
15	60.70	1.10	92.47	23.00
20	56.21	0.85	91.87	23.81
25	45.97	0.61	93.29	25.21

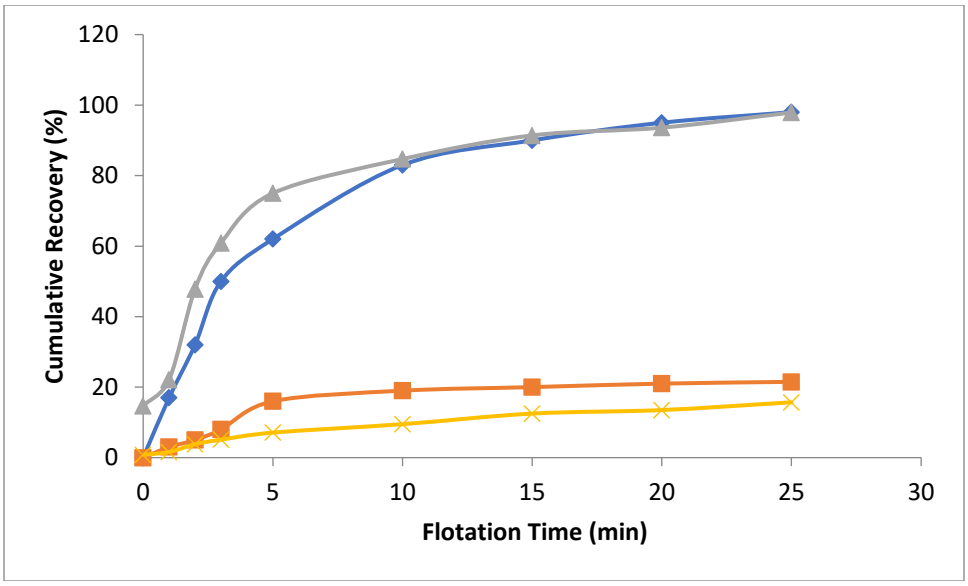

Figure 4: Flotation kinetics for SIPX

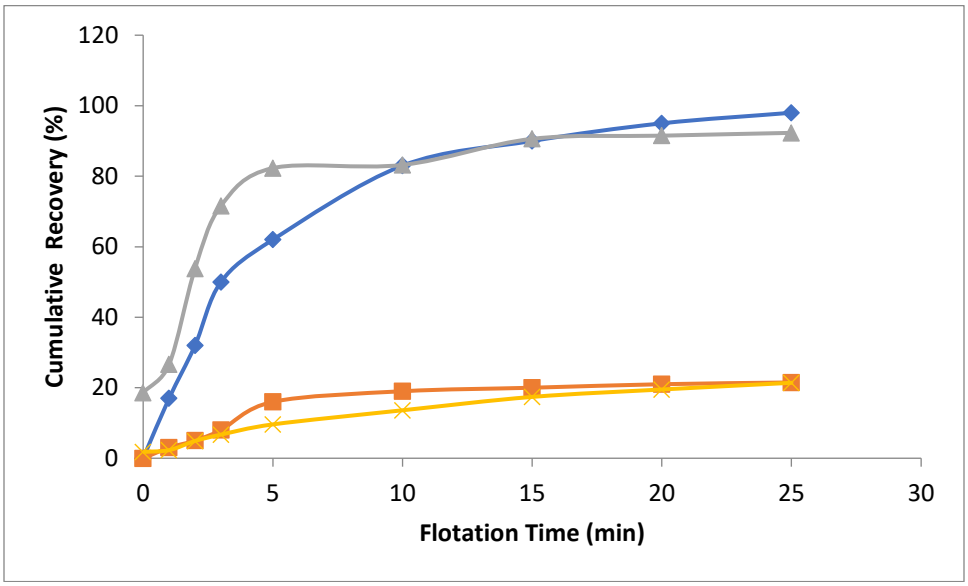

Figure 5: Flotation kinetics for SIBX

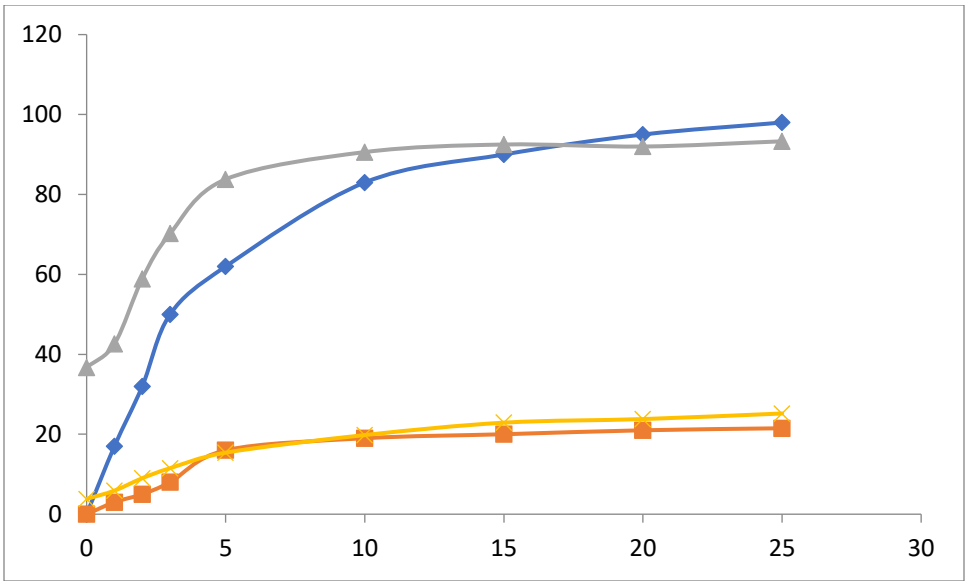

Figure 6: Flotation kinetics for PAX

The collection of lead sulphide which was the mineral of interest took place over a relatively long period of time of about 20 minutes, with a maximum efficiency of 72. 5%. The concentrate grades are low with fairly clean tailings, with recovery of 94%. As SEX is very selective, the recovery of the gangue is high, around 24%, which is reflected in a lowering of the grades.

The SIPX has very high flotation kinetics rate than SEX and with greater collecting power for lead sulphide. The rate constant K for sulphide mineral is greater for SEX, which gave, in only 13 minutes, a recovery of 92%. The SIPX has flotation kinetics of gangue that are greater than for SEX, which indicates its relative greater strength than SEX. At optimum time the concentrate grades are 12.1% and the separation efficiency is greater, reaching 80.5% but with lower selectivity.

SIBX is a collector with much more rapid flotation kinetics for the lead sulphide but with lower recovery, being less selective than SEX. The optimum separation time for SIBX is around 7 minutes, which demonstrates its high flotation rate for the lead sulphide giving recovery of 88.9% with separation efficiencies of 76.6%, better parameters than those of SEX.

PAX is a collector of great strength with recovery characteristics similar to SEX, with rapid flotation kinetics for lead sulphides but less selective. In comparison with SEX, it has lower recovery of lead sulphide but the rapid recovery percent is 91.9%. Its separation efficiency is very similar to SEX at their respective optimum times, with concentrate level of 7.4% Pb and efficiency of 73.8%. At high level of flotation time, PAX showed tendency to recover more of the gangue and in this case it is advisable to find the optimum time of flotation to avoid more gangue recovery when the time exceeds 15 minutes in the course of the flotation process. It is evident that this time recovery of the valuable mineral (lead sulphide) starts to decrease.

6.0 Conclusion

As a general approach, the above is a good approximation of what happens with a simple two component ore where one is the valuable mineral and the other species is the gangue. Of course,

most ores have several waste minerals that have significant and different values rate constant. In this case, the k for the waste materials can be taken as a weighted average of the individual rate constants. With this it can be taken that the determination of kinetics flotation parameters, associated with a first order rate expression is valid for characterizing collectors in the flotation process.

The SIPX is a collector similar to SEX, but with a greater flotation rate and less selective for lead sulphides than SEX. SIBX is a collector of lower selectivity than SEX and fewer recovery properties than SEX. It has a greater flotation rate for the lead sulphide, reaching a very high separation efficiency in a very short flotation time.

The PAX has a lower selectivity than SEX with a greater flotation rate for sulphides and lower recovery at longer times, reaching very similar separation efficiency with SEX at about 16th minute of the flotation process and tendency to diminish in recovery properties than SEX afterwards.

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