



ADSORPTION KINETICS OF 8-HYDROXYQUINOLINE ON SMITHSONITE

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The influence of temperature and collector concentration on its adsorption rate on mineral surface was studied as regarding the 8-hydroxyquinoline/ smithsonite system. Theoretical equations as well as experimental data may be useful to estimate the adsorption rate and kinetics connected to the conditioning stage in mineral flotation in order to optimize the selectivity and the recovery of the valuable mineral.

INTRODUCTION

In analytical chemistry reagents with chelating action are used due to their selectivity for certain metallic ions in solution.¹ The functional groups of the reagent are forming stable chelated compounds with the specific metallic ions. These reagents are used for ores containing oxide minerals when neither good recovery with classic collectors, nor selective separation of tailings minerals is achieved.^{2,3}

Among these reagents, 8-hydroxyquinoline (oxine) which is successfully used in analytical chemistry forms stable chelating complexes with many metal cations. It has been reported in mineral processing that oxinates act as collectors through chemisorption onto mineral particle surfaces during the flotation process.⁴⁻⁶ Based on the fact that smithsonite ($ZnCO_3$) contains the Zn(II) ion and 8-hydroxyquinoline forms stable chelating compounds with this ion in solution, it is possible to recover zinc from smithsonite by flotation with this chelating agents acting as collector.^{7,8}

The occurrence of chemical bonds between the chemisorbed species and the mineral surface is proved by the similitude of IR spectra of bulk Zn oxinate and the superficial compound resulted when the smithsonite surface was treated with oxine solution.⁹ It is already well acknowledged that the collector – mineral adsorption reaction is the most important factor affecting the floatability of valuable minerals.

The kinetic of this reaction varies widely depending on the mineral and the conditioning parameters during the flotation process. The rate of collector adsorption can be influenced by many factors, such as the grinding conditions, pulp pH, and collector concentration. These are key factors that determine the kinetics of the conditioning stage.

In this research theoretical estimations and experimental tests were performed in order to study the kinetics of the adsorption of 8-hydroxyquinoline on smithsonite.

The long-range goal of our research is to apply theoretical connections between conditioning and flotation kinetics in order to optimize the selectivity and recovery of the valuable mineral.

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RESULTS AND DISCUSSION

Influence of the initial oxine concentration on the adsorption kinetics of oxine on smithsonite

The experimental data obtained for the initial oxine concentrations ($4 \cdot 10^{-5}$ mol L⁻¹, $30 \cdot 10^{-5}$ mol L⁻¹ and $50 \cdot 10^{-5}$ mol L⁻¹) are presented in Table 1.

The following abbreviations are used in Table 1: c_0 – the initial oxine concentration, mol L⁻¹; c_t – the oxine concentration after t minutes of contact with smithsonite particles surface, mol L⁻¹, when equilibrium is supposed to be reached; $c_{rez, \infty}$ – the oxine concentration when adsorption equilibrium has been reached and the residual concentration becomes constant.

The adsorption density (D) of 8-hydroxyquinoline on the 40-80 μ m size fraction of smithsonite has been calculated as based on the relation (1):

$$D = \frac{(c_0 - c_t)V}{1000 \cdot m} \quad (1)$$

where: V = the volume of the oxine solution (100 mL)

m = the mass of the smithsonite in the experiment (1 g)

Fig. 1 illustrates the variation of the adsorption density of oxine on smithsonite surface as a function of time, at 25° C.

The shape of the curve is similar for all initial concentrations; the adsorption density increases logarithmically in time and tends to an equilibrium value.

The variation of the oxine concentration (c_t) in time depends on the initial concentration (c_0) and $c_{rez, \infty}$ remains constant after 8, 10 and 12 minutes, depending on the c_0 value.

It may be noticed that the equilibrium is rapidly reached at low initial concentration.

The adsorption density D and $c_{rez, \infty}$ at equilibrium for the studied c_0 values are presented in Table 2.

A first order kinetic equation was applied for the adsorption reaction.¹⁰⁻¹²

$$-\frac{dc_t}{dt} = k(c_t - c_{rez, \infty}) \quad (2)$$

$$\ln(c_t - c_{rez, \infty}) = -k \cdot t + \text{const} \quad (3)$$

In order to find the reaction rate constant k , we used the equation (3) and we plotted $\ln(c_t - c_{rez, \infty})$ as a function of time (Fig. 2). The reaction rate constants and the correlation coefficients (R^2) in Table 3 were calculated from the straight lines slopes by statistic program.

Table 1

Oxine concentration (c_t) during the adsorption process on smithsonite for different initial oxine concentrations at 25° C

time (minutes)	$c_0 = 4 \cdot 10^{-5}$ (mol L ⁻¹)		$c_0 = 30 \cdot 10^{-5}$ (mol L ⁻¹)		$c_0 = 50 \cdot 10^{-5}$ (mol L ⁻¹)	
	c_t 10 ⁻⁵ mol L ⁻¹	$c_t - c_{rez, \infty}$ 10 ⁻⁵ mol L ⁻¹	c_t 10 ⁻⁵ mol L ⁻¹	$c_t - c_{rez, \infty}$ 10 ⁻⁵ mol L ⁻¹	c_t 10 ⁻⁵ mol L ⁻¹	$c_t - c_{rez, \infty}$ 10 ⁻⁵ mol L ⁻¹
0	4.00	3.30	30.00	22.00	50.00	41.00
0.50	4.00	3.30	29.00	21.00	48.40	39.40
0.75	3.90	3.20	28.60	20.60	47.60	38.60
1.00	3.80	3.10	28.00	20.00	45.00	36.00
1.50	3.00	2.30	25.00	17.00	40.00	31.00
2.00	2.60	1.90	20.00	12.00	36.00	27.00
3.00	2.30	1.60	16.40	8.40	26.00	17.00
3.50	2.20	1.50	14.60	6.60	22.00	13.00
4.00	2.00	1.30	13.20	5.20	19.00	10.00
4.50	1.90	1.20	12.60	4.60	17.00	8.00
5.00	1.60	0.90	12.00	4.00	14.40	5.40
5.50	1.40	0.70	11.20	3.20	13.00	4.00
6.00	1.30	0.60	10.60	2.60	12.00	3.00
6.50	1.20	0.50	10.00	2.00	11.00	2.00
7.00	1.00	0.30	9.60	1.60	10.40	1.40
7.50	0.9	0.20	9.40	1.40	10.00	1.00
8.00	0.7	0	9,00	1.00	9.80	0.80
8.50	0.7	0	8,80	0.80	9.60	0.60
9.00	0.7	0	8.60	0.60	9.40	0.40
10.0	0.7	0	8.00	0	9.20	0.20
12.0	0.7	0	8.00	0	9.00	0
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26.0	0.7	0	8.00	0	9.00	0

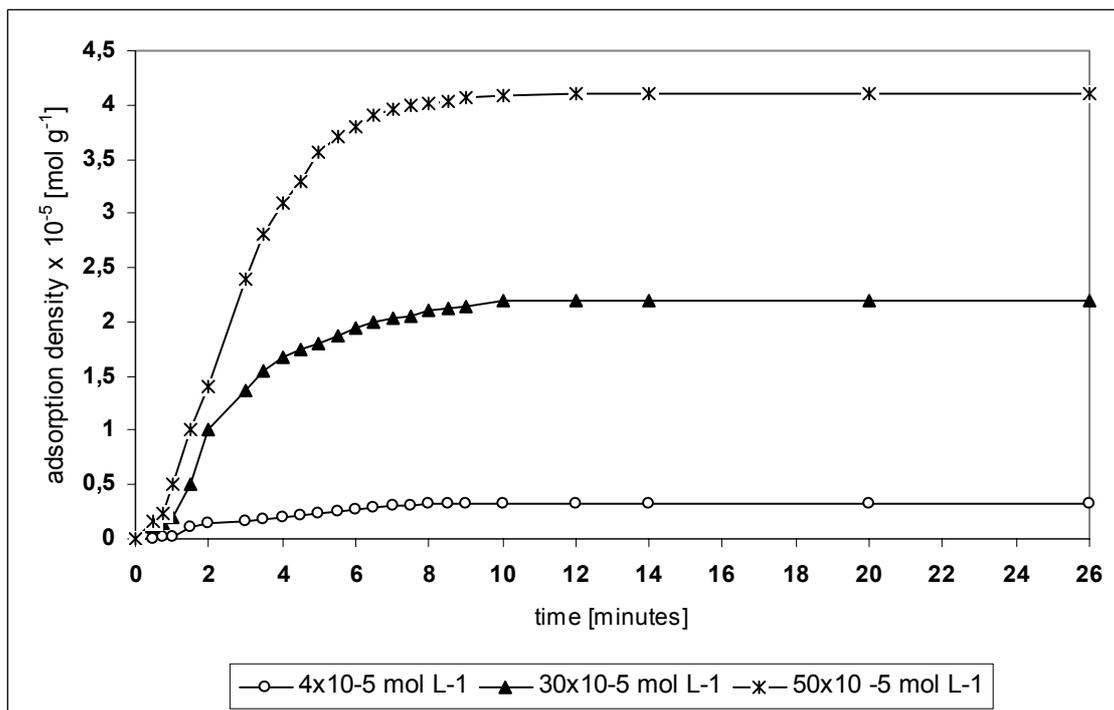


Fig. 1 – Adsorption density of oxine on smithsonite surface at 25° C.

Table 2

Adsorption density D and $c_{rez,\infty}$ at equilibrium for the studied c_0 values

c_0 (mol L ⁻¹)	$4 \cdot 10^{-5}$	$30 \cdot 10^{-5}$	$50 \cdot 10^{-5}$
D (mol g ⁻¹)	$0.32 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	$4.1 \cdot 10^{-5}$
$c_{rez,\infty}$ (mol g ⁻¹)	$0.7 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$9 \cdot 10^{-5}$

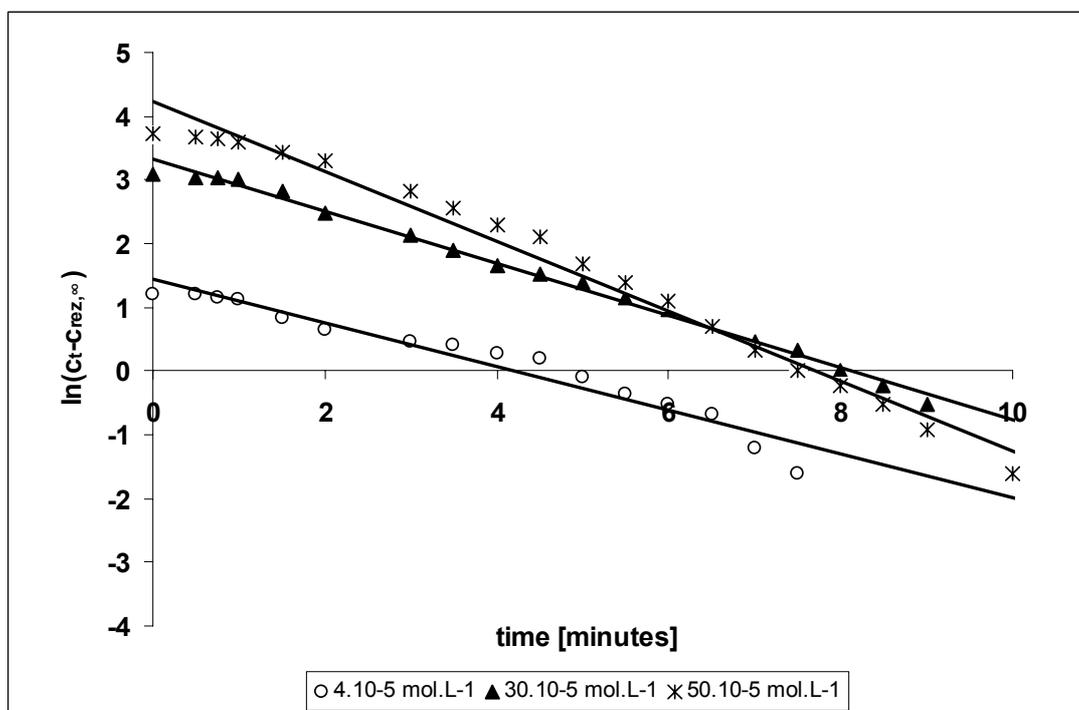


Fig. 2 – First order reaction curves for the adsorption kinetics of oxine on smithsonite surface for several initial concentrations, at 25° C.

Table 3

Reaction rate constants and correlation coefficients for oxine adsorption on smithsonite surface for several initial concentrations, at 25°C

c_0 (mol L ⁻¹)	k (min ⁻¹)	R ²
$4 \cdot 10^{-5}$	0.3175	0.9631
$30 \cdot 10^{-5}$	0.4081	0.9941
$50 \cdot 10^{-5}$	0.5494	0.9821

The reaction rate constant k was calculated for all the points plotted in Fig. 2 and for each initial concentration, as following: from 0 to 7.5 minutes for $c_0 = 4 \times 10^{-5}$ mol L⁻¹; from 0 to 9 minutes for $c_0 = 30 \times 10^{-5}$ mol L⁻¹; and from 0 to 10 minutes for $c_0 = 50 \times 10^{-5}$ mol L⁻¹.

The correlation coefficients (R^2), in Table 3 demonstrate good linear relationships with a negative slope for each group of points. The adsorption rate increases by increasing the initial concentration from 4×10^{-5} mol L⁻¹ to 50×10^{-5} mol L⁻¹. As can be seen in Fig. 2, the reaction rate is the highest in the experiment with the initial oxine concentration of 50×10^{-5} mol L⁻¹.

Results from all experiments concluded that the adsorption mechanism of oxine on smithsonite surface is dependent to the initial concentration of the collector reagent.

The influence of temperature on the adsorption kinetics of oxine on smithsonite

Further experiments were carried out at different temperatures: 25° C, 35° C and 45° C with solutions of oxine having the same initial $30 \cdot 10^{-5}$ mol L⁻¹ concentration. The experimental data are presented in Table 4.

The adsorption densities (D) of 8-hydroxyquinoline on the surface of the 40 – 80 µm fraction of smithsonite were calculated with equation (1).

The influence of the temperature on the oxine adsorption on smithsonite is shown in Fig. 3. The increase of the adsorption density by increasing the temperature is obvious.

Table 4

Oxine concentration (c_t) during the adsorption on smithsonite at several temperatures and $c_0 = 30 \cdot 10^{-5}$ mol L⁻¹

time (minutes)	25°C		35°C		45°C	
	c_t 10 ⁻⁵ mol L ⁻¹	$c_t - c_{rez. \infty}$ 10 ⁻⁵ mol L ⁻¹	c_t 10 ⁻⁵ mol L ⁻¹	$c_t - c_{rez. \infty}$ 10 ⁻⁵ mol L ⁻¹	c_t 10 ⁻⁵ mol L ⁻¹	$c_t - c_{rez. \infty}$ 10 ⁻⁵ mol L ⁻¹
0	30.00	22.00	30,00	24,2	30.00	26.4
0.50	29.00	21.00	28,80	23	28.60	25
0.75	28.60	20.60	28,00	22.2	25.80	22.2
1.00	28.00	20.00	26,00	20.2	23.00	19.4
1.50	25.00	17.00	20,00	14.2	16.40	12.8
2.00	20.00	12.00	16,40	10.6	12.80	9.2
3.00	16.40	8.40	11,00	5.2	7.60	4
3.50	14.60	6.60	9,00	3.2	6.20	2.6
4.00	13,20	5.20	8,20	2.4	5.00	1.4
4.50	12,60	4.60	7,40	1.6	4.40	0.8
5.00	12.00	4.00	7,00	1.2	4.20	0.6
5.50	11.20	3.20	6.80	1	4.00	0.4
6.00	10.60	2.60	6.20	0.4	3.80	0.2
6.50	10.00	2.00	6,00	0.2	3.60	0
7.00	9.60	1.60	5.90	0.1	3.60	0
7.50	9.40	1.40	5.80	0	3.60	0
8.00	9,00	1.00	5.80	0	3.60	0
8.50	8,80	0.80	5.80	0	3.60	0
9.00	8.60	0.60	5.80	0	3.60	0
10.0	8.00	0	5.80	0	3.60	0
12.0	8.00	0	5.80	0	3.60	0
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26.0	8.00	0	5.80	0	3.60	0

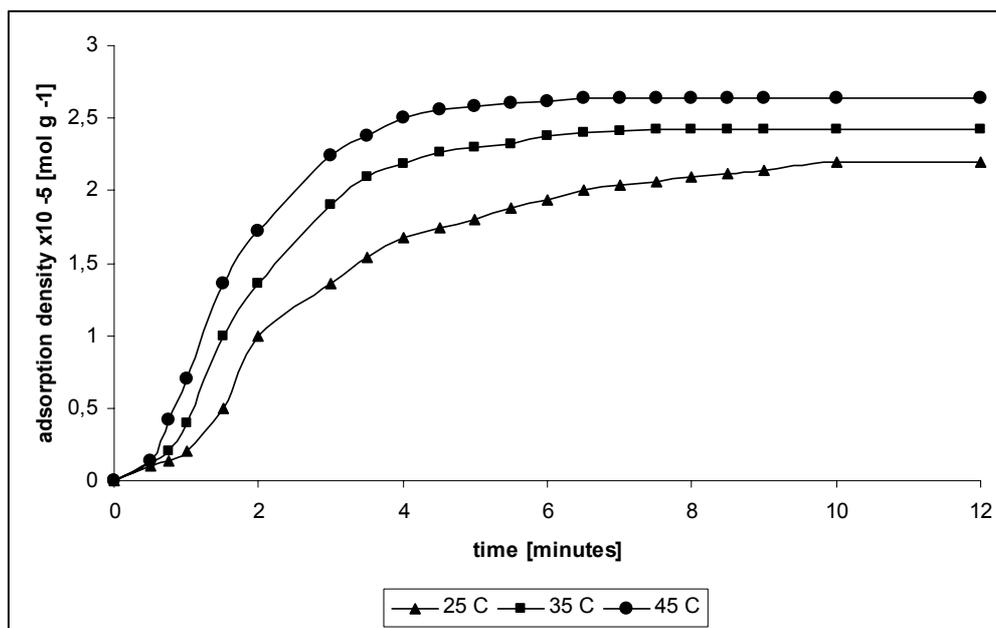


Fig. 3 – Adsorption density of oxine on smithsonite surface at different temperatures and $c_0 = 30 \cdot 10^{-5} \text{ mol L}^{-1}$.

Adsorption density D and $c_{\text{rez}, \infty}$ at equilibrium are presented in Table 5 for the experimental temperatures.

The higher the temperature, the faster the equilibrium is reached, respectively after 6.5 minutes at 45°C, after 7.5 minutes at 35°C and after 10 minutes at 25°C.

In order to find the reaction rate constant k , we used again the equation (3) and we plotted $\ln(c_t - c_{\text{rez}, \infty})$ as a function of time for the three studied temperatures (Fig. 4). The reaction rate constants were calculated from the straight lines slopes with statistic program. Table 6 shows the reaction rate constants and correlation coefficients (R^2) from the statistic data analysis of the experimental values.

Values for k were statistically calculated related again to all the points plotted in Fig. 4, respectively for the time period from 0 to 9 minutes for

experiments carried out at 25°C; 0 to 7 minutes for experiments at 35°C and 0 to 6 minutes for experiments at 45°C.

The activating energy for the oxine adsorption process on smithsonite was determined with the Arrhenius' equation:

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad (4)$$

And in its logarithmic form:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

Based on the reaction rate constant k at all the studied temperatures (see Table 6), the activating energy was calculated from the straight line slope with the statistic program.

Table 5

Adsorption density D and $c_{\text{rez}, \infty}$ at equilibrium

t (°C)	25	35	45
D (mol g ⁻¹)	$2.2 \cdot 10^{-5}$	$2.42 \cdot 10^{-5}$	$2.64 \cdot 10^{-5}$
$c_{\text{rez}, \infty}$ (mol L ⁻¹)	$8 \cdot 10^{-5}$	$5.8 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$

Table 6

Reaction rate constants and correlation coefficients (R^2) for the adsorption of oxine on smithsonite surface at $c_0 = 30 \cdot 10^{-5} \text{ mol L}^{-1}$

Temperature (°C)	k (min ⁻¹)	R^2
25	0.4081	0.9941
35	0.7634	0.9693
45	0.8432	0.9952

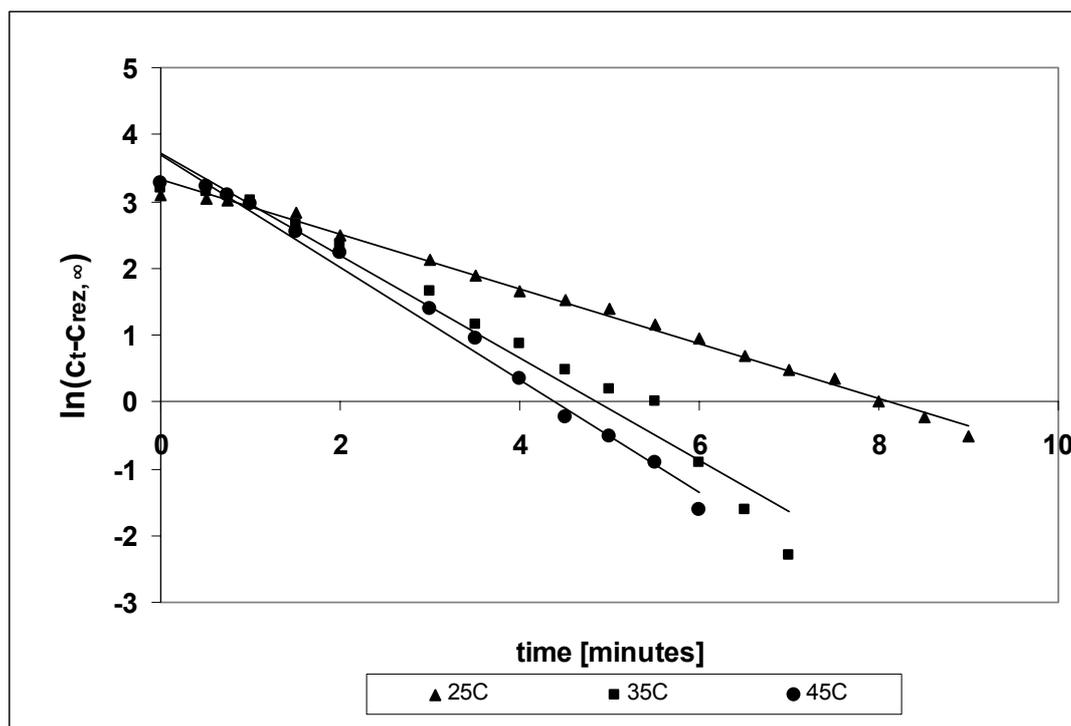


Fig. 4 – First order reaction curves for the adsorption kinetics of oxine on smithsonite at different temperatures and $c_0 = 30 \cdot 10^{-5} \text{ mol L}^{-1}$.

The activating energy calculated for the adsorption of oxine on smithsonite surface is

$$E_a = 28.8022 \text{ kJ mol}^{-1}$$

EXPERIMENTAL

Solutions of 8-hydroxyquinoline in 10% acetic acid with concentration between $4 \cdot 10^{-5} \text{ mol L}^{-1}$ and $50 \cdot 10^{-5} \text{ mol L}^{-1}$ were used in the experiments. Pure smithsonite was dry crushed by hand and sieved to get a particle size fraction of 40 – 80 μm .

In order to study the adsorption kinetics, 1 g of mineral was suspended in 100 mL solution in closed bottles at pH=8. The suspension was continuously gently shaken using the IKA HS 260 basic shaker.

Measurements of the oxine concentration at different time periods were performed by UV-VIS molecular absorption spectrometry at 319 nm wavelengths. Before starting the experiments, the adsorption spectra of the 8-hydroxyquinoline in 10% acetic acid solution were scanned from 200 to 400 nm in order to detect the wavelength of the adsorption peak. We used an UV-VIS CECIL 8000 spectrometer with 1 cm deep quartz cells.

In the first series of experiments, the influence of the initial concentration of the reagent on the adsorption kinetics at constant temperature of 25°C was studied. The following initial concentrations of oxine were used: $4 \cdot 10^{-5} \text{ mol L}^{-1}$, $30 \cdot 10^{-5} \text{ mol L}^{-1}$ and $50 \cdot 10^{-5} \text{ mol L}^{-1}$. During each test, solution sampling was performed each 0.5 minute within the first 9 minutes, then at each 2 or 3 minutes, until the residual concentration of oxine in solution remained constant.

Another series of experiments were carried out keeping constant the initial $30 \cdot 10^{-5} \text{ mol L}^{-1}$ oxine concentration and

increasing the temperature from 25°C to 35°C and then to 45°C. The residual oxine concentration was determined in each case at the same time periods, till the concentration remained constant.

CONCLUSIONS

The kinetics and equilibrium adsorption experiments were conducted in order to evaluate the adsorption characteristics of a chelating agent, namely 8-hydroxyquinoline (oxine) on smithsonite.

The rate of oxine consumption can be expected to measure the amount of adsorbed oxine or of the degree of conditioning.

The reaction rate constant is independent of the collector concentration; the k values are almost the same for the different experimental concentrations. The effect of the temperature on the reaction rate is not very significant.

The activating energy for oxine adsorption on smithsonite suggests that the reactions occur at the limit of the diffusion layer.

The experimental kinetics data could predict the floatability of smithsonite; furthermore some connections shall be made between the parameters and performances during the conditioning stage in flotation and the adsorption kinetics in order to optimise the selectivity and the recovery of the desired mineral.

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