

## FACTORS AFFECTING THE CYANIDATION KINETICS OF JAROSITE PRECIPITATED IN A ZINC PLANT FOR SILVER RECOVERY

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### ABSTRACT

This work presents the most important factors affecting alkaline cyanidation of ammonium jarosite, precipitated in an electrolytic zinc plant. The overall cyanidation kinetics study was done to evaluate the effect of NaCN concentration, temperature and particle size.

In this part of the study, a nominal  $\text{Ca(OH)}_2$  concentration of  $0.81 \times 10^{-2} \text{ mol} \cdot \text{cm}^{-3}$  was used, studying the NaCN effect in the  $5.1 \times 10^{-3} \text{ mol} \cdot \text{cm}^{-3}$  to  $4.08 \times 10^{-2} \text{ mol} \cdot \text{cm}^{-3}$  NaCN range concentration and particle size of  $30.5 \pm 5.5 \mu\text{m}$ . The temperature employed varies from  $65^\circ\text{C}$  to  $85^\circ\text{C}$  because with lower temperatures several problems were detected, associated with an induction period, which increased to almost 25 h.

The cyanidation curves found, have an induction period followed by a progressive conversion period. In the progressive conversion period, the experimental results fit well to the shrinking core model with chemical control.

$$[1 - (1 - X)^{1/3}] = k_{\text{exp}} \cdot t \quad (1)$$

The reaction order found was zero ( $n \approx 0$ ), which indicates that in this case, the cyanidation process for industrial ammonium jarosite can be described as a two step process: a first step (slow) of alkaline decomposition which controls the overall process and a second step (fast) of complexation of decomposed products.

On the other hand, it was found that solid products from cyanidation process were amorphous and have zinc ferrite (Franklinite) in them, which was not affected during this process. This mineral species can act as nuclei in the jarosite precipitation during the elimination of Fe in the hydrometallurgy of zinc.

### INTRODUCTION

In the zinc industry, electrowinning of this metal can be affected by several problems and the iron contents in the calcine fed to leaching circuits is the most dangerous. These iron contents commonly are present as zinc ferrite ( $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ) formed during sulfurs roasting at high temperatures. For this reason, contents of iron join with As and/or Co in the liquors from leaching solutions lead some troubles during zinc electrowinning, because current efficiency decrease strongly, giving so a poor zinc deposition which re – dissolve in the electrolyte (1) getting so low zinc recoveries and a deficiency of process.

Because zinc ferrite is insoluble in dilute sulfuric acid (2), the process has a second leaching under strong conditions of acidity and temperature. However, under these conditions iron is also dissolved and goes to solution, then it must be eliminated or decreased before electrowinning.

Some studies (3,4) have been directed to partial or total iron elimination from leaching solution. One of them, iron precipitation as a jarosite type – compound, is the most employed because besides of helping in the iron elimination also decreases another alkaline ions or iron sulfate getting so a good balance of sulfates and alkali in system (5-8). Another advantages of process are the increasing in zinc recovery and the elimination of others impurities such as As, Pb, P, and so on. However, because neutralizing reagent used for jarosite precipitation is the calcine, some losses of Zn, Pb, Cu, and Ag are found. These metallic values can be associated to jarosite lattice or co – precipitate as sulfates. Zinc losses can be reduced with an acid leaching of these residues, but the other metallic values do not suffer variations resting in these residues and then, are discarded in the jarosite lattice as wastes.

Actually, jarosite type – compound are produced in high amounts in the zinc industry worldwide, which

means a strong environmental problem, because these residues have very fine particle sizes. On the other hand, for the disposal of these kind of residues it is necessary to have ponds where it can be discarded without problem for environmental.

For the above cited, several studies related with alkaline reactivity of these kind of compounds, have been carried out. The first ones were directed to Pb, Ag and Au recovery using some methods (9,10). By the other hand, some authors have studied the kinetics of alkaline decomposition and cyanidation of silver jarosite (11), lead jarosite (12), sodium jarosite (13) and jarosite (14).

At last, the study of jarosite type - compounds produced in the zinc industry (15), has been of some importance in accordance of kinetics aspects related with the behavior of this kind of residues directed to evaluate the possibilities for recovery of metallic values (Pb, Cu, Zn, Ag) involved in the jarosite lattice. And for this reason, this work embraces the kinetics factors affecting alkaline cyanidation of ammonium jarosite in Ca(OH)<sub>2</sub> media, precipitated in the electrolytic zinc plant of Industrial Minera México.

## EXPERIMENTAL

**Materials:** For the kinetics study of cyanidation, a sample of ammonium jarosite precipitated in a zinc plant (Industrial Minera México) was used. The sample was collected in the press filters in the plant.

The sample was characterized by XRD, SEM and EDS and the obtained results confirms an ammonium jarosite with some contents of H<sub>3</sub>O<sup>+</sup>, Ag, Pb, Na and K in the alkaline sites; also were detected some contents of Cu and Zn in substitution by Fe. Figure 1 shows the X - ray diffractogram for this jarosite type - compound. Table 1 shows the chemical composition got for individual crystal of the jarosite (By EPMA).

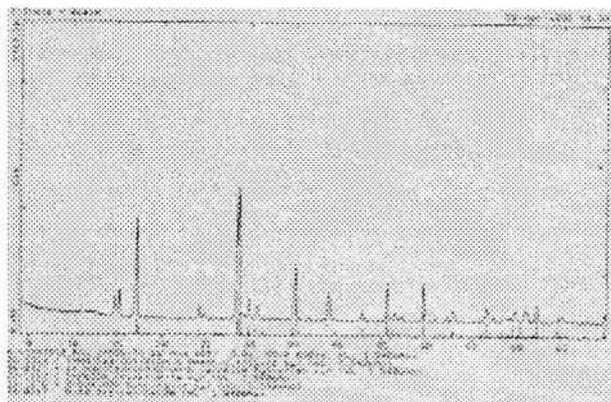


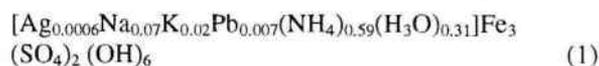
Figure 1. X - ray diffractogram of industrial ammonium jarosite.

The obtained density was of 3070 mg · cm<sup>-3</sup>, which is slightly higher than that observed for synthetic compound (5).

Table 1. Microanalysis by EPMA.

Element (% wt)	Crystals of Industrial ammonium jarosite
Fe	32.6
Cu	0.30
Zn	0.90
Na	0.32
Si	0.18
K	0.16
Cd	0.02
Ag	0.02
S	12.4
Pb	0.28
N	1.50
O	46.1

For simplicity, the formula was normalized to: SO<sub>4</sub> = 2; Fe = 3; OH = 6; the alkaline site was then normalized to 1 and it is occupied for Ag, Na, K, Pb, NH<sub>4</sub>, and H<sub>3</sub>O. Hydronium was calculated by difference and the resulting formula for industrial ammonium jarosite is:



The morphology of this jarosite consists of spherical and semi - spherical aggregates of 1.0 - 2.0 μm rhombohedral crystals forming a compact structure (Figure 2) quite similar to synthetic jarosites (11,13).

**Experimental Procedure:** Experimental procedure used in this work was similar to that employed in previous studies (11-15).



Figure 2. Morphological aspects of jarosite (SEM).

In this study in  $\text{Ca}(\text{OH})_2$  media; 1.6 g of ammonium jarosite were used in an initial volume of  $400 \text{ cm}^3$  with a stirring rate of  $900 \text{ s}^{-1}$  while pH was kept constant (pH = 10.56) with additions of  $\text{Ca}(\text{OH})_2$  concentrated solution at  $25 \text{ }^\circ\text{C}$  during the experiment. As in previous works done with synthetic jarosite type – compounds,  $\text{OH}^-$  concentration was calculated according nominal pH solution and ionization constant for water at working temperature (16).

For these experiments, the progress of the reaction was followed for silver by Atomic Absorption Spectrometry (AAS). For this, samples of solution ( $5 - 10 \text{ cm}^3$ ) were taken at pre-determined times throughout the experiment. Variation due to sampling and reagent addition was corrected by mass balance.

The obtained solids at different conversion values were characterized by XRD, SEM and EDS to observe its evolution during cyanidation of this compound.

## RESULTS

Alkaline cyanidation study of industrial ammonium jarosite in  $\text{Ca}(\text{OH})_2$  media, was carried out to determinate  $\text{CN}^-$  concentration effect on decomposition process, and also to evaluate the most important factors affecting cyanidation kinetics.

For this study, several experiments were realized evaluating NaCN concentration effect, under the following conditions:

- NaCN concentration:  $4.08 \times 10^{-2}$ ,  $3.06 \times 10^{-2}$ ,  $1.02 \times 10^{-2}$  and  $5.1 \times 10^{-3} \text{ mol} \cdot \text{cm}^{-3}$
- $\text{Ca}(\text{OH})_2$  nominal concentration:  $0.81 \times 10^{-2} \text{ mol} \cdot \text{cm}^{-3}$  (pH = 10.56)
- Temperature:  $75 \text{ }^\circ\text{C}$

- Particle size :  $30.5 \pm 5.5 \text{ }\mu\text{m}$

Before the design of experiments series, preliminary studies were carried out to get magnitude order of cyanidation and decomposition rates and fix so, temperatures and concentrations to be used in this work. During first preliminary experiments, it was observed that induction period was bigger than expected (from 20 to 25 h) for  $35 - 60 \text{ }^\circ\text{C}$  temperature range; due to this, the working temperature was fixed at  $75 \text{ }^\circ\text{C}$  where induction period was reasonably short.

The obtained results are in accordance with shrinking core model for spherical particles and chemical control.

$$[1 - (1 - X)^{1/3}] = k_{\text{exp}} \cdot t \quad (2)$$

$$\text{where: } k_{\text{exp}} = V_M k_q C_A^n / r_0 \quad (3)$$

and; X = reacted fraction,  $V_M$  = molar volume of solid,  $k_{\text{exp}}$  = experimental constant,  $k_q$  = chemical constant,  $C_A$  = reactant concentration, n = reaction order,  $r_0$  = initial radius for solid and t = time.

Figure 3 shows silver extraction from industrial ammonium jarosite in  $\text{Ca}(\text{OH})_2$  and figure 4 shows its representation with the shrinking core model. It can be observed that reaction exhibits an induction period followed by a progressive conversion one.

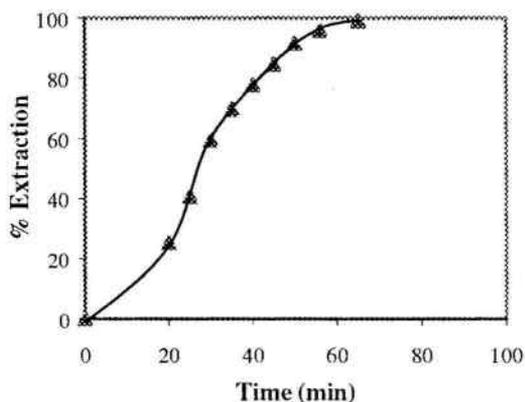


Figure 3. Alkaline cyanidation curve.  $[\text{NaCN}] = 1.02 \times 10^{-2} \text{ mol} \cdot \text{cm}^{-3}$ ,  $70 \text{ }^\circ\text{C}$  and  $4.3 \times 10^{-2} \text{ mol} \cdot \text{cm}^{-3}$   $[\text{Ca}(\text{OH})_2]$ . pH = 11.03

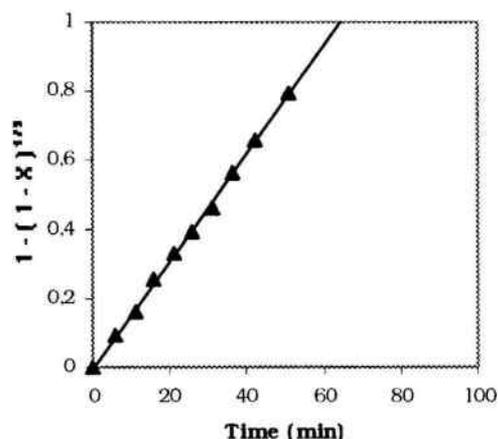


Figure 4. Representation of shrinking core model for the results shown in figure 3.

Figure 5 shows dependence of  $k_{exp}$  with NaCN concentration, the reaction order found was  $n \approx 0$ . This is indicative that decomposition rate is independent of NaCN concentration. Apparently under the experimental conditions studied in this work, the cyanidation process of industrial ammonium jarosite can be described as a two step process; a first step (slow) of alkaline decomposition that controls the overall process followed by a second step (fast) of extraction of liberated silver.

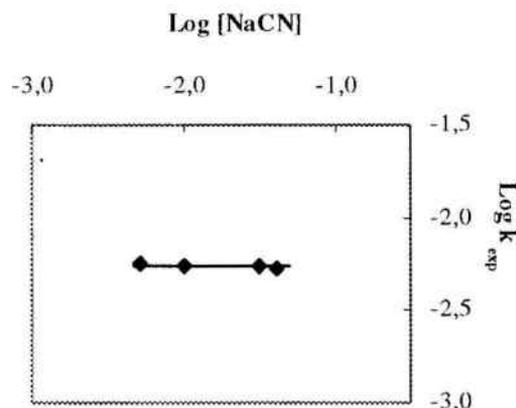


Figure 5. Dependence of NaCN on  $k_{exp}$ . Reaction order  $\approx 0$ .

Finally, the solid products from alkaline cyanidation in  $\text{Ca}(\text{OH})_2$ , were characterized by XRD (Figure 6) and EDS. These results confirm that final solid product from cyanidation leads to an amorphous product of iron hydroxide; besides, zinc ferrite is also present which means it was not affected during alkaline process of cyanidation.

The presence of this mineral species in the solids from cyanidation (Figure 7) indicates that this non-

leached species acted as nuclei during jarosite precipitation.

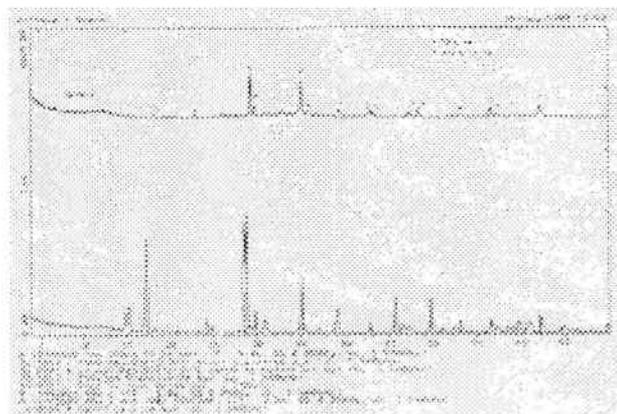


Figure 6. X - ray diffractogram of solid products from cyanidation of industrial jarosite.

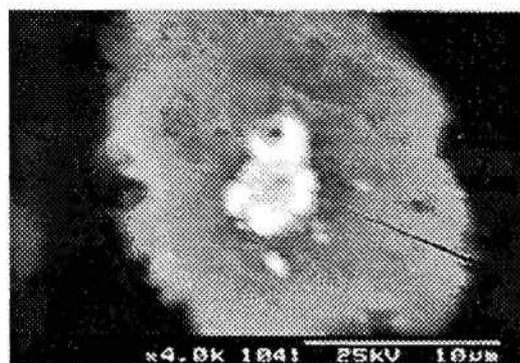


Figure 7. Cyanided jarosite particle in  $\text{Ca}(\text{OH})_2$  with zinc ferrite in its nuclei. (SEM).

## CONCLUSIONS

1. Chemical analysis by EPMA, was used to determinate chemical composition of individual crystals of industrial ammonium jarosite. According to these results, an approximate and complex formula was found:
2. Alkaline cyanidation curves present an induction period and a progressive conversion one.
3. Experimental data during progressive conversion period fit well to shrinking core model with chemical control.

$$[1 - (1 - X)^{1/3}] = k_{exp} \cdot t$$

4. Working temperature was fixed at 75 °C, because at 30 – 60 °C range big induction periods were obtained (20 – 25 h).
5. Cyanidation solid products of ammonium jarosite are amorphous (iron hydroxide) and show zinc ferrite unaffected during this process.
6. Zinc ferrite apparently acted as nuclei during jarosite precipitation.
7. Under experimental conditions used, the alkaline cyanidation process can be described as a two step process; a step (slow) of alkaline decomposition which controls the overall process followed by a second step (fast) of complexation of liberated silver.

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