Kinetics of hydrochloric acid leaching of Gallium from zinc plant residues

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1. Introduction:

Gallium (Ga) is an important critical metal, that has been used substantially in high-tech fields, such as fiber and infrared-optics systems, and semiconductor devices including rectifiers, transistors, and diodes. Thus, the use of gallium is expected to increase more sustainably by 20-fold in 2030 (Gladyshev et al., 2015). However, Ga has not been found independently in a concentrated form, trace amounts of it are mainly found in zinc ore, zinc plant residues, bauxite ore, and coal mines (Liu et al., 2016). To address the application of Ga, its recovery from zinc ore or zinc plant residues is receiving significant attention.

In the hydrometallurgical processing of zinc ore, gallium is mainly enriched in the zinc plant residues together with iron, zinc, silicon oxide, and germanium. In that case, the recovery of gallium involves chemical leaching with inorganic acid (hydrochloric acid) leaching followed by ionic liquid-based solvent extraction of gallium from the leached solution.

To the best of our knowledge, no experimental report exists on the leaching kinetics of Ga from jarosite cake (JC) (zinc plant residues) in the relevant open literature. In this research, the results of the leaching of Ga in an HCl leaching medium. The kinetics characterizations of the leaching process were analyzed according to the shrinking core model (SCM) and the best-fitted equation to the experimental data was determined. The corresponding diffusion model was found suitable to explain the relationship between the fraction of Ga leached and the reaction time concerning the leaching medium concentration and operating temperature. Along with the apparent activation energy of the process was determined.

2. Method:

Based on open literature in related works, the leaching of JC performed (a) hydrochloric acid concentration, (b) temperature, and (c) leaching time was chosen as the three variables to be investigated. In each experiment, operating conditions were repeated twice and the arithmetic average of the results was used to plot the leaching efficiency curves.

JC was investigated for maximum leaching of Ga by using hydrochloric acid (Meark 37%). The leaching experiments were carried out in 250 ml conical flasks with a working volume of 50 ml. To maintain the desired temperature and agitation rate, experiments were carried out in a temperature-controlled incubator shaker. The effect of acid concentration (1-3 M), temperature (30-80, $\pm 5^{0}$ c), and reaction time (0-120 mins.) on Ga leaching from JC were determined. The experiments were carried out in triplicate and the average and standard deviations were reported. Leachates were collected at different time intervals and centrifuged at 10000 RPM (Eppendorf Centrifuge 5810R) to collect the supernatant of the leachates. The supernatant was acidified using 0.5% HNO3 and stored for the analyses of the metal concentrations by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900). An error in each experiment was below 5% and the uncertainties of the measurements were predicted with the regression analysis procedure. Also, the results of other metals like iron, zinc, titanium, indium, etc. dissolution will be reported in a separate paper. Still, the dissolution of other metals has been reported in a diagram at the optimum leaching conditions.

3. Results and discussion:

The reaction between gallium oxide (Ga is present as gallium oxide in JC) and hydrochloric acid can be written as follows:

 $Ga_2O_{3(\text{in JC})} + 6HCl_{(\text{aq.})} \rightarrow 2GaCl_{3(\text{aq.})} + 3H_2O_{(l)}$

Based on the above reaction, the effect of various parameters was evaluated in the following sections.

Effect of temperature:

The temperature effect was examined in the range of $30-80^{\circ}$ C under the conditions of a 1:10 solid-toliquid ratio, 2M leaching agent concentration, and 220 rpm stirring speed. As seen in Fig. 1(a), the gallium recovery increased as the temperature was increased. Also. Fig 1(b) presents the data plot according to chemical reaction control and Fig 1(c) shows the data plot according to diffusion control process.



Figure.1. (a) The effect of temperature on the dissolution of Ga at proposed experimental condition. (b) The variation of $1 - (2/3)X - (1 - X)^{2/3}$ with time at various temperatures and (c) the variation of $1 - (1 - X)^{1/3}$ with time at various temperatures.

Results reveal that the values for the correlation coefficient (R^2) in Fig. 1(c) are closer to 1 than those in Fig.1(b), so the leaching rate of Ga is controlled by diffusion through the product layer. The apparent rate constants (k_d) were calculated as the slope of the straight lines and from the Arrhenius plot ($ln k_d vs 1/T$) the activation energy was calculated as 15.85 kJ/ mol. This value confirms that this process is most likely controlled by the diffusion of ions through the product layer.

4. Conclusions:

Hydrochloric acid leaching, the first chemical step of an integrated process for recovering gallium from zinc plant residue (JC) was tested. Taking into account the parameters (temperature, solid-to-liquid ratio, leaching agent concentration, and time) used in the experiments. A kinetic model has been assigned to the dissolution of gallium present in JC within 30 min of the reaction. It was observed that the reaction rate was not sensitive to temperatures in the range of 30-80 °C. However, a minor rise in dissolution efficiency was evident due to an increase in temperature.

References:

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Key words: "Gallium", "Zinc plant residues", "Dissolution", "Kinetic model", "Diffusion control process".