LEACHING OF ILMENITE WITH SULFURIC ACID-THIOUREA SOLUTIONS

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ABSTRACT

The dissolution of ilmenite in sulfuric acid-thiourea solutions has been examined experimentally under controlled acid concentration, particle size and temperature conditions. The temperature range of the experiments was 303 - 353 K. The reaction system was analyzed under acid concentration of 0.1, 0.5, 1.0 and 2.0 N. Particle size varied between 38 and 250 microns. Experiments have shown that the rate of dissolution increased with increasing temperature, acid concentration and specific ore surface. The arrhenius activation energy was found to be 32.3 KJ per mole. The experimental work has shown that the addition of thiourea in the leachant increases, markedly, the recovery of titanium and the rate of ilmenite dissolution as compared with sulfuric acid-ilmenite leaching systems.

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INTRODUCTION

Ilmenite is an important source of titanium in the world -- which can be treated for metal extraction and for pigmento too. Extensive studies on the dissolution of ilmenite in acid media - have been conducted to determine the behaviour of leaching sys-- tems. In general, experimental results have shown that the rate- of ilmenite dissolution in acid media is increased with increa-- sing acid concentration and temperature

It has been observed that the reactivity of ilmenite in sulfuric acid media increases as the natural weathering of the ore is in- creased (1). Experimental results have shown that the rate of - ilmenite dissolution in sulfuric acid and hydrochloric acid is - strongly affected when acid concentration increases from 0.03 to 1.0 M and temperature increases from 313 to 363 K (2).

It was observed the dissolution behaviour of ilmenite in sulfuric acid leachants where acid concentration varied between 4.7 to -- 12.5 M and temperature was varied in the range 338 to 358 K (3); it was pointed out that the reaction was indicated to be contro- led by a chemical process at the mineral surface.

The effect of temperature, particle size, stirring speed and a-- cid concentration on the rate of dissolution of ilmenite in sul- furic acid media was studied (4); it has been found that the -- leaching of ilmenite at temperature between 361 and 388 K is des cribed by a surface chemical reaction limiting.

(5); the kinetic data of the leaching of ilmenite-hematite has - been explained in terms of a complex geometrical relationship.

The leaching of powdered ilmenite ore with highly concentrated - hydrochloric acid was studied (6), where acid concentration was- varied between 11.3 to 11.6 M, over the temperature range 303 to 333K. At temperature of 303 to 323 K, the leaching of ilmenite - has been explained in terms of a surface chemical reaction. At - temperatures of 323 to 333 K, the rates were limited by difu---- ssion of dissolved metal ions through a residual layer of the -- ore.

Leaching of ilmenite was studied at temperatures between 323 to-

353 K in hydrochloric solutions (7); it was found that the rate- of dissolution was initially rapid, then declined, apparently -- due to the polymerization and transport of dissolved titanium -- within the porous solid.

The present experimental work has been intented to study the e-- ffect of addition of thiourea in the dissolution behaviour of il menite in sulfuric acid media.

EXPERIMENTAL

Materials.

the ilmenite sand used in this study was obtained from the Mi--- choacán shore (México). This sand has 11.5 wt % of TiO_2. The che micals used in this work are of analytical grade.

Apparatus and Procedure.

Sand particles less than 38 microns were prepared by grinding of the original sand. The experiments were carried out in a glass - reactor in a cosnstant temperature bath. The glass reactor was - sealed from the atmosphere by means of a glass cover which had - four openings in order to fit a vapour condenser, an air lance,- a thermometer and a sampling tube.

Leaching experiments were conducted in the temperature range 303 to 353 K.

The glass reactor was filled with 500 ml of sulfuric acid- thi- ourea solution, with the desired acid concentration, and heated- until the experimental temperature was reached; at this point 2- grams of ilmenite sand were added into the reaction system and - the experiment began. Leaching solutions contained 10 grams of - thiourea per liter.

The kinetics of the experiment was followed by taking samples of 5 ml from the experimental solution at given periods of time.

Experimental samples were analized in triplicate by both X-Ray - fluorescence analysis (KEVEX 7000-77) and atomic absorption spec trometry (Perkin-Elmer). Leaching solid residues were examined - by X-Ray diffraction techniques (Philips).

RESULTS AND CONCLUSIONS.

The dissolution of ilmenite in sulfuric acid has been represen-- ted as the equation:

$$FeTiO_3 + 4H^+ = Ti^{+2}O + Fe^{+2} + 2\ H_2O \qquad (1)$$

and the oxidation of the ferrous specie,

$$Fe^{+2} + H^+ + \tfrac{1}{4}\ O_2 = Fe^{+3} + \tfrac{1}{2}\ H_2O \qquad (2)$$

Thiourea has been used for metal extraction in the leaching of - some materials, to produce a metal-thiourea specie in solution - in acid media (8-10). Thus, the addition of thiourea in the present reaction system can be represented as follows:

$$Fe\ Ti\ O_3 + 2\ SC\ (NH_2)_2 + 4\ H^+ = Ti\ O\ (SC\ (NH_2)_2)^{+1} + Fe^{+3} + 2H_2O \quad (3)$$

Which indicates that the increase in acid concentration will increase the amount of titanium in solution.

Figure 1 shows the fraction of leached titanium plotted as a --- function of the experimental time. As it can be noted, dissolu-- tion rate increases clearly as the concentration of sulfuric a-- cid is increased.

Figures 2(a) and 2(b), shows the rate of reaction for the ilmenite dissolution plotted as a function the acid concentration. The experimental data have shown that the dissolution rate of ilmenite in sulfuric acid-thiourea media follows an exponential pa---- ttern with respect to the change in the acid concentration. It - can be seen that the rate of dissolution remains in a relative - low value when acid concentration is low, however when acid concentration increases the rate of reaction for the ilmenite dissolution increases suddenly; this behaviour is more evident as temperature increases.

The reaction rate for the ilmenite dissolution under the present experimental conditions can be expresed as follows:

$$T = 353\ K: \ LnK = 2.5\ C - 1.03$$
$$T = 323\ K: \ LnK = 2.8\ C - 4.35 \qquad (4)$$

The most important feature in the present experimental results - is that the addition of thiourea in the leaching solution re---- sults in an increase in the ilmenite dissolution rate and high - titanium recovery in solution compared with ilmenite leaching -- systems in sulfuric acid solution (4); this effect is shown in - Figure 3.

Effect of Particle Size.

The effect of particle size on the rate of dissolution of ilmenite in sulfuric acid thiourea solution was analized at 353 K and sulfuric acid concentration 2.0 N. Figure 4 shows the experimental results for five different ilmenite particle size, 38, 100, 127, 166 and 250 microns used here. It can be seen that the rate of dissolution of ilmenite in the present experimental solutions is affected by size of the particles. The recovery of titanium in solution and the rate of dissolution of ilmenite increase as particle size decreases. Figure 5 shows the rate constant of leaching plotted as a function of particle size; it can be seen that there is an exponential behaviour of the reaction system. This fact is in according with the increase of the specific area of the mineral.

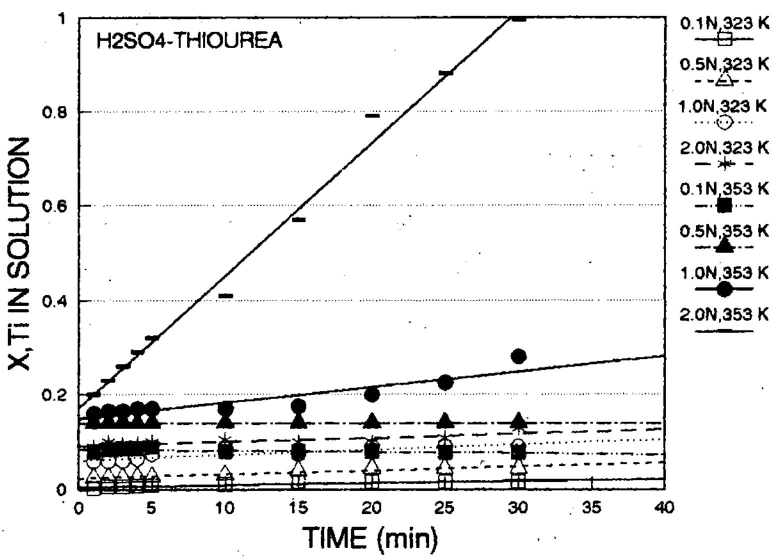

Fig.1.- Effect of acid concentration on the mole fraction of leached titanium at 323 and 353 K

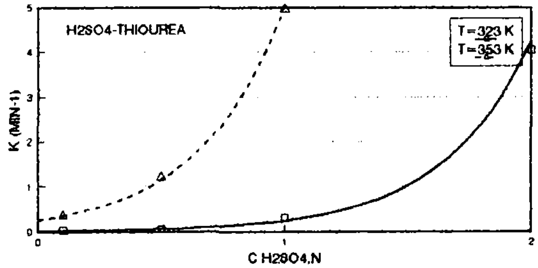

Fig.2(a).- Effect of acid concentration and leaching temperature on the reaction rate constant.

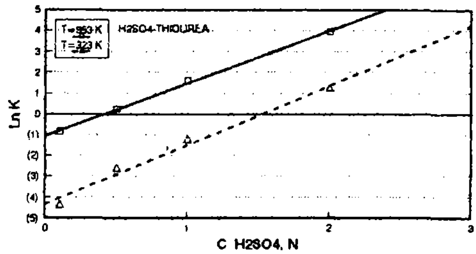

Fig.2(b).- Dependence of the reaction rate constant on the leachant acid concentration at 323 and 353 K.

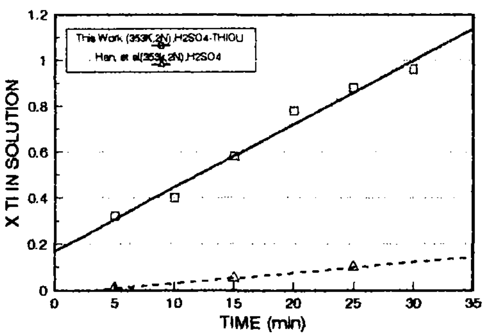

Fig.3 Comparation between the present experimental results and results from Han and coworkers.

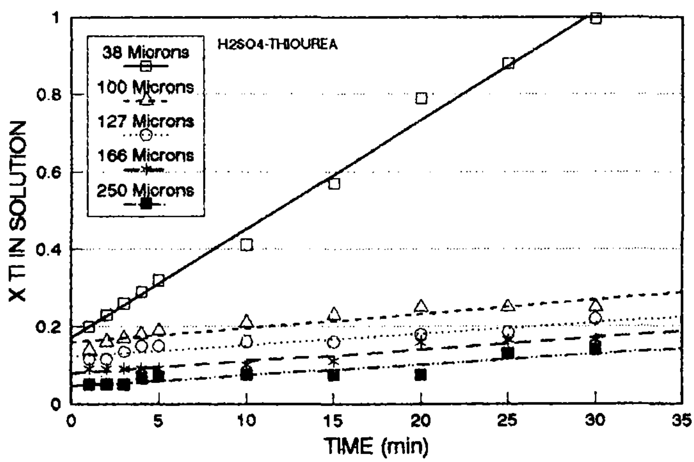

Fig. 4.- Dependence of Titanium leaching on Particle Size, at 353 K and sulfuric acid concentration 2N.

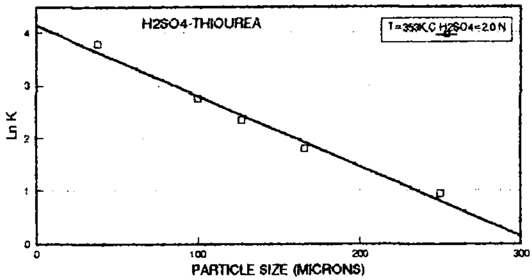

FIG.5 - Relationship between the leaching rate constant and the particle size

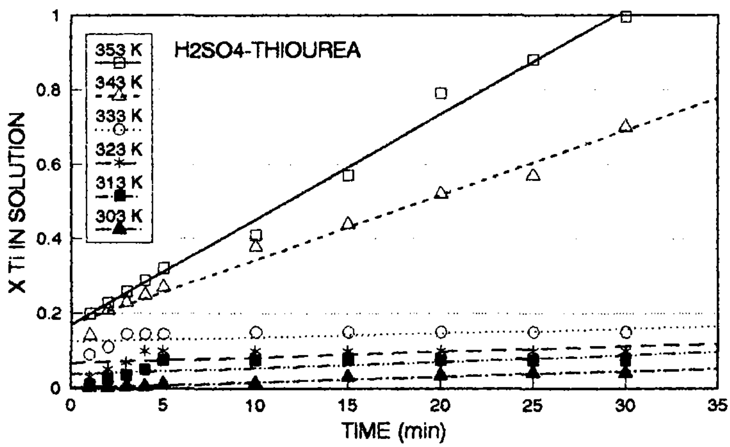

Fig. 6.- Titanium leaching dependence from experimental temperature. C H2SO4 2 N.

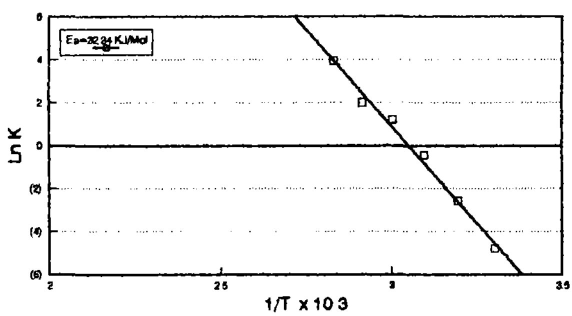

Fig. 7.- Arrhenius plot for the dissolution of Ilmenite in Sulphuric Acid-Thiourea solutions

Effect of Temperature.

Ilmenite particles, 38 microns were leached in sulfuric acid --- thiourea solutions, H_2SO_4 2.0 N, at 303, 313, 323, 333, 343 and- 353 K. It has been observed that the dissolution of ilmenite in the present leaching system is very much affected by temperature as it can be seen in Figure 6, where the fraction of dissolved - titanium is presented the experimental observations have shown - that the ilmenite rate of dissolution increases very markedly as the experimental temperature is increased.
The leaching results obtained for six different temperature are- plotted in Figure 7 as the Arrhenius relationship; the apparent- activation energy value of 32:2 KJ per mole was calculated.

CONCLUSIONS.

The leaching of ilmenite sands in sulfuric acid media containing additions of thiourea has been experimentally analized in terms- of the effect of sulfuric acid concentration, particle size and- temperature. The following conclusions can be derived based on - the experimental results.

1. The rate of dissolution of ilmenite in the experimental lea-- chants increases as temperature and acid concentration increa se and as particle size decreases.
2. The apparent activation energy is 32.2 KJ per mole.
3. The rate of dissolution of ilmenite in sulfuric acid-thiou-- rea solutions is higher than the dissolution rate of ilmeni- te in sulfuric acid solutions, as it has been compared with- recent experimental data.

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