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A MODEL FOR THE RECOVERY OF TITANIUM FROM MIXTURES OF ILMENITE AND HEMATITE BY HYDROCHLORIC ACID LEACHING

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ABSTRACT

A partial equilibrium model has been developed to describe the leaching of $FeTiO_3$ - Fe_2O_3 mixtures by aqueous HCl. The model couples the rates of leaching of the minerals to changes in the solution species concentrations; 23 species concentrations were calculated as a function of leaching time. Solution reactions included in the model include (1) the redox reaction converting Ti(IV) and Fe(II) to Ti(III) and Fe(III); (2) formation of chloro complexes; (3) hydrolysis; and (4) dissociation of H_2O. Ilmenite is more rapidly depleted than hematite, and available data indicate that the time dependence of the leaching reactions is different. Modeling results show that the Ti/Fe concentration ratio drops steeply initially but then gradually rises as the leaching rates change. Of the two oxides, $FeTiO_3$ is consumed first, and thereafter the Ti/Fe ratio again declines. The Fe(II)/Fe(III) concentration ratio behaves similarly. The Ti/Fe and Fe(II)/Fe(III) ratios have simultaneous extrema and plots of these ratios vs. time can, with appropriate adjustments in vertical scale, virtually be superimposed. These changes are greatest when the initial molar amounts of $FeTiO_3$ and Fe_2O_3 are approximately equal. They are qualitatively the same, but of much smaller magnitude, when the initial $FeTiO_3/Fe_2O_3$ molar ratio is far from 1.0. The species distributions change in a complex way during leaching; typically, hydroxo species become more important but chloro species become less so. Implications of these results for the selective recovery of titanium will be discussed.

INTRODUCTION

Although titanium is the ninth most abundant element in igneous rock (1), titanium ores occur primarily as small or low-grade deposits. Titanium minerals are often found in association with Fe_2O_3 or Fe_3O_4. To better understand what factors influence selectivity of titanium recovery from $FeTiO_3$-Fe_2O_3 mixtures, a predictive model has been developed for leaching of mixtures of these minerals by HCl. The partial equilibrium approach was employed (2, 3, 4, 5). The variables were leaching time, HCl concentration and the $FeTiO_3/Fe_2O_3$ feed ratio; other factors such as temperature and particle size could readily be incorporated if more complete kinetic information were available. Dissolved O_2 or oxidants or reductants other than Fe and Ti species were not considered.

DATA SOURCES

Leaching of ilmenite by HCl is often represented by

$$FeTiO_3 + 4HCl \rightarrow FeCl_2 + TiOCl_2 + 2H_2O \qquad (1)$$

Although there are a number of reports on $FeTiO_3$ leaching by HCl (6, 7, 8, 9, 10, 11), a rate law has been determined in only one investigation (5). This equation is

$$X = 3.91 \times 10^9 (2.0 \times 10^{-3} a_{H+} + 0.02) \ \exp(-7954.5/T) \ t^{0.80} \qquad (2)$$

In Eq. (1), X is the ilmenite fraction leached, a_{H+} the hydrogen ion activity, T the temperature in K and t the time in hours. The data from which the rate law was developed pertain to Ti leaching; a brief period of non-congruent leaching was observed experimentally. For the purposes of the model developed here, in which long term effects are of greatest concern, Eq. (2) has been assumed to be suitable. Eq. (2) applies to -45 + 38μm particles; surface areas were not measured because $FeTiO_3$ becomes porous upon leaching and titanium hydrolyzes and precipitates extremely readily, making it impossible to dry partially leached particles and obtain accurate surface areas. Changes in overall particle dimensions and development of internal pore structure are incorporated into the $t^{0.80}$ factor.

Hematite leaching follows the equation

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \qquad (3)$$

Quantitative information on the leaching of hematite is scarce. The only rate data sufficiently detailed for modeling purposes are those of Majima et al. (12). These investigators reported leaching rates only for 328K; the HCl concentrations used ranged from 0.1 to 4.0 mol/dm^3. For 3 and 4 mol/dm^3 HCl, the rates were 7.80×10^{-8} and 1.26×10^{-7} mol/cm^2-h, respectively (Ref. (12), Fig. 5).

Because a partial equilibrium model couples dissolution or precipitation of solid phases to changes in solution speciation, data on the species present in the leachate are also required. For the $FeTiO_3$-Fe_2O_3-HCl-H_2O system, these include a variety of chloro and hydroxo complexes, as well as uncomplexed metal ions, H^+, Cl^- and OH^-. Dissolved O_2 was assumed to be excluded. The speciation prior to leaching must be known (see Eq. (7) and accompanying discussion) and was calculated using an algorithm previously described (5). The solution species concerned and the relevant equilibrium data are summarized in Ref. (5).

MODEL DEVELOPMENT

Although partial equilibrium models have previously been applied in hydrometallurgy (3, 4, 5), their salient features will be briefly described here. The central assumption of such a model is that the minerals dissolve slowly, gradually altering the concentrations of the solution's components. The solution quickly adjusts to these perturbations and remains internally in equilibrium. For $FeTiO_3$-Fe_2O_3 mixtures model equations can be developed that are explicit in time. There is a one-to-one correspondence between the equations needed to compute equilibrium speciations and those needed for partial equilibrium calculations of the changes in species concentrations during leaching.

The equilibrium speciation of an aqueous solution can be calculated by solving simultaneous mass action, mass balance and charge balance equations. If the ionic strength is approximately constant, the equations are

$$K_i = \prod_j m_j^{\nu_{ij}} \tag{4}$$

$$C_k = \sum_j \mu_{kj} m_j \tag{5}$$

$$0 = \sum_j \lambda_{1j} m_j \tag{6}$$

Here m_j is the molality of species j, K_i the equilibrium constant of reaction i, and C_k the analytical concentration of moiety k; ν_{ij}, μ_{kj} and λ_{1j} are stoichiometric factors. Twenty-three solution species were considered in model development; eighteen independent mass action equations may be written. Corresponding to Eq. (4)-(6), the following partial equilibrium equations can be derived

$$0 = \sum_j \frac{\nu_{ij}\bar{n}_j}{m_j} \quad \text{for reaction i} \tag{7}$$

$$\bar{C}_k = \sum_j \mu_{kj} \bar{n}_j \quad \text{for Cl, Fe, Ti, H}^+ \tag{8}$$

$$0 = \sum_j \lambda_{lj} \bar{n}_j \tag{9}$$

For an increment of time dt, $\bar{n}_j$ is

$$\bar{n}_j = \frac{dm_j}{dt} \tag{10}$$

For the redox equation, Eq. (7) is

$$0 = \frac{\bar{n}_{Fe(III)}}{m_{Fe(III)}} + \frac{\bar{n}_{Ti(III)}}{m_{Ti(III)}} - \frac{\bar{n}_{Fe(II)}}{m_{Fe(II)}} - \frac{\bar{n}_{Ti(IV)}}{m_{Ti(IV)}}$$

where, for example, $m_{Fe(III)}$ represents the sum of concentrations of all trivalent iron species.

$\bar{C}_{Cl}$ = 0 since the total chloride concentration is conserved; for Ti, Fe and H^+, $\bar{C}_k$ is determined by the leaching kinetics. For a time interval dt, using a basis of 1 kg solvent, for example,

$$\bar{C}_{Fe} = \left(R_{FeTiO_3} A_{FeTiO_3} + 2R_{Fe_2O_3} A_{Fe_2O_3}\right) = \frac{dC_{Fe}}{dt} \tag{11}$$

where the rates of mineral dissolution, R_i, are in mol/cm^2-h, and the surface areas, A_i, are in cm^2.

For $FeTiO_3$ - Fe_2O_3 mixtures, as discussed above, the available kinetic information is in the form of a rate equation for $FeTiO_3$, and numerical values of the reaction rate for Fe_2O_3. The computational procedure therefore was as follows. A time increment (Δt), acid concentration and activity (13), and initial loadings of the two minerals were specified. For the first time increment, Eqs. (4) - (6) must be solved to determine the initial m_j values required for the denominator of Eq. (7). As is customary (2), small concentrations of Ti and Fe were specified to make this possible; a value of 10^{-6} mol/kg was selected. Once Eqs. (7) - (9) were solved for the $\bar{n}_j$'s, new values of m_j were calculated, reflecting the changes in species concentration that occurred over the time increment; in this way a partial equilibrium calculation tracks the solution speciation over the course of a leaching operation. The nonlinear set Eqs. (4) - (6) must be solved once prior to the first time increment, followed by repeated solution of Eqs. (7) - (9), which are linear. Leaching kinetics were integrated with the solution phase reactions in the following way. For a dissolution time t, Eq. (2) was used to calculate X_{FeTiO_3} followed by computation of the rate of change of the Ti concentration over the current increment

$$\frac{\Delta C_{Ti}}{\Delta t} = \bar{C}_{Ti} \tag{12}$$

For hematite, decreasing surface area was accounted for directly. Assuming that the mineral particles are approximately spherical, the amount of Fe_2O_3 at any time is

$$n_{Fe_2O_3} = \frac{4}{3} \pi r^3 \rho N_p \tag{13}$$

where $n_{Fe_2O_3}$ is the number of moles, r the particle radius, ρ the molar density and N_p the number of particles. Then over increment Δt

$$\Delta n_{Fe_2O_3} = R_{Fe_2O_3} A_{Fe_2O_3} \Delta t = R_{Fe_2O_3} \cdot 4\pi r^2 N_p \cdot \Delta t = \rho N_p \cdot 4\pi r^2 \Delta r \tag{14}$$

where $R_{Fe_2O_3}$ is the rate of dissolution and $A_{Fe_2O_3}$ the total surface area. Δr, and new values of A and r, are calculated from $\Delta n_{Fe_2O_3}$.

RESULTS

Computations were performed for 3 and 4 mol/dm^3 HCl at 328 K. The amounts of the two minerals were varied from 10^{-4} to 10^{-2} mol/kg H_2O; the final concentrations were low enough that Ti precipitation would not occur. In all cases, the final speciations calculated using Eqs. (7) - (9) were within 5% of the equilibrium species concentrations for the came component concentrations.

Since in all simulations the metal concentrations were much lower than that of HCl, the species distributions are essentially unaffected by a change from 3 to 4 mol/dm^3 acid. The major effect of the acid concentration is on the kinetics. Of the tetravalent titanium species, by far the most important under the conditions investigated is $TiCl^{3+}$ (83%); second is $Ti(OH)_2^{2+}$ (10%). Of lesser importance are Ti^{4+} (4%), $TiOH^{3+}$ (3%), and $TiOCl^+$, $TiOCl_2^0$ and TiO^{2+} (none greater than 0.1%). $FeCl_2^0$ was the most prominant Fe(II) species (57%), and both $FeCl^+$ (33%) and Fe^{2+} (5%) were fairly important. $FeOH^+$ concentrations were negligible. The most important trivalent Fe species was $FeCl_3^0$ (41%); $FeCl_2^+$ and $FeCl^{2+}$ had virtually identical concentrations (both 29%), while 1.3% of the total Fe(III) was in the form of Fe^{3+}. $FeOH^{2+}$ and $Fe(OH)_2^+$ concentrations were negligible. The dominant Ti(III) species was $TiCl^{2+}$ (88%), followed by Ti^{3+} (12%) and $TiOH^{2+}$ (less than 0.01%). Thus, most of the major species are chloro complexes. The exception is $Ti(OH)_2^{2+}$, illustrating the tendency of Ti(IV) to hydrolyze readily. The ultimate Ti(IV) concentration is about six orders of magnitude greater than that of Ti(III); since $FeTiO_3$ is assumed to contain tetravalent Ti and divalent Fe, all Ti(III) present is produced by reduction of Ti(IV). During the leaching of pure ilmenite, therefore, the concentrations of Ti(IV) and Fe(II) should be equal and much greater than those of Ti(III) and Fe(III). Only if some other oxidant or reductant is available will the situation differ.

In principle, the situation could be considerably more complicated when $FeTiO_3$ and Fe_2O_3 are leached simultaneously. Since the rates of reaction of the two minerals are unequal, the Ti/Fe concentration ratio changes continuously throughout the leach. As a point of comparison, it is useful to note that if the leaching rates of the two minerals were equal, the Ti/Fe ratio would be fixed by the amounts of $FeTiO_3$ and Fe_2O_3 initially present. For equimolar initial amounts of ilmenite and hematite, the Ti/Fe molar ratio would always be 1/3; deviations from this ratio indicate which mineral is reacting faster if this restriction on solid composition is obeyed. Similar criteria exist for other feed ratios. Figure 1 illustrates a case for which the initial $FeTiO_3/Fe_2O_3$ is 1/1 but the Ti/Fe ratio is greater than 1/3 until both minerals have completely reacted. Ilmenite reacts faster and is depleted first. Over the entire range of conditions investigated, Ti/Fe ratios were found to be higher than would be predicted on the assumption of equal leaching rates. Available rate data indicate that $FeTiO_3$ at first leaches faster than Fe_2O_3. The rate law for $FeTiO_3$ (5), however, has an unusual $t^{0.80}$ time dependence. This causes a minimum in the Ti/Fe ratio quite early in a leach (see Fig. 1), followed by a rise to a sharp maximum as $FeTiO_3$ is depleted. Thereafter the ratio declines smoothly until the Fe_2O_3 has also reacted completely. Since Ti(IV) and Fe(II) are supplied only by $FeTiO_3$, Fe_2O_3 is the only source of Fe(III), and formation of Ti(III) is strongly disfavored thermodynamically, changes in the Fe(II/Fe(III) ratio parallel those in the Ti/Fe ratio. (If an additional oxidant or reductant were available, e.g., dissolved oxygen, this situation would be expected to change.) Indeed, when appropriately scaled, plots of Fe(II)/Fe(III) vs. time and Ti/Fe vs. time can virtually be superimposed. The existence of the extrema in the plots suggests that a separation of Ti from Fe, e.g. by solid-liquid separation and solvent extraction of Ti, could be most easily carried out near the maximum Ti/Fe ratio and would be most difficult near the minimum. On the other hand, the leaching rates are similar, so that leaching is not highly selective. The Ti/Fe and Fe(II)/Fe(III) ratios therefore do not exhibit wide variations during the leaching. Both ratios are influenced primarily by the $FeTiO_3/Fe_2O_3$ ratio of the feed. The effect of an increased acid concentration is to decrease the times at which the maxima and minima occur. Given the variability in reaction time in batch processing, the best control strategy would likely involve monitoring changes in the Ti/Fe ratio.

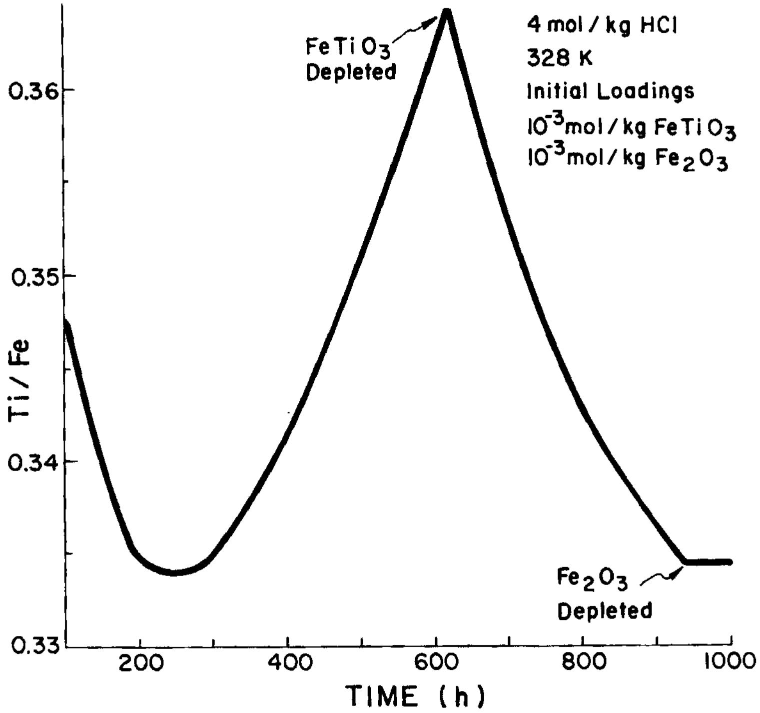

Figure 1. Ti/Fe molar ratio in solution as a function of time. Reaction conditions are 4 mol/kg HCl, 328K, and initial $FeTiO_3$ and Fe_2O_3 loadings both 10^{-3} mol in 1kg.

The relative importance of the various Ti(IV) species i.e., the fraction of the total Ti(IV) concentration comprised of a given species, is virtually the same whatever mixtures of $FeTiO_3$ and Fe_2O_3 (or $FeTi_2O_3$ alone) are leached, and the same is true of the Ti(III), Fe(II) and Fe(III) species. This is due to the large excess of chloride relative to metal and to the fact that the Ti-Fe redox reaction has only an extremely small effect. As is illustrated for Ti(IV) in Fig. 2, the concentration of each species rises quickly at the beginning of the leach, then more slowly as the $FeTiO_3$ is exhausted. Only minor changes occur late in the leach when only Fe_2O_3 is left. Similar patterns were found for Fe(II) and Fe(III). For Ti(III), the simulations indicate a slight decrease in the species concentrations after the depletion of $FeTiO_3$. During this interval only Fe(III) is being added to the solution, and it shifts the redox reaction in the direction of Fe(II) and Ti(IV). Under

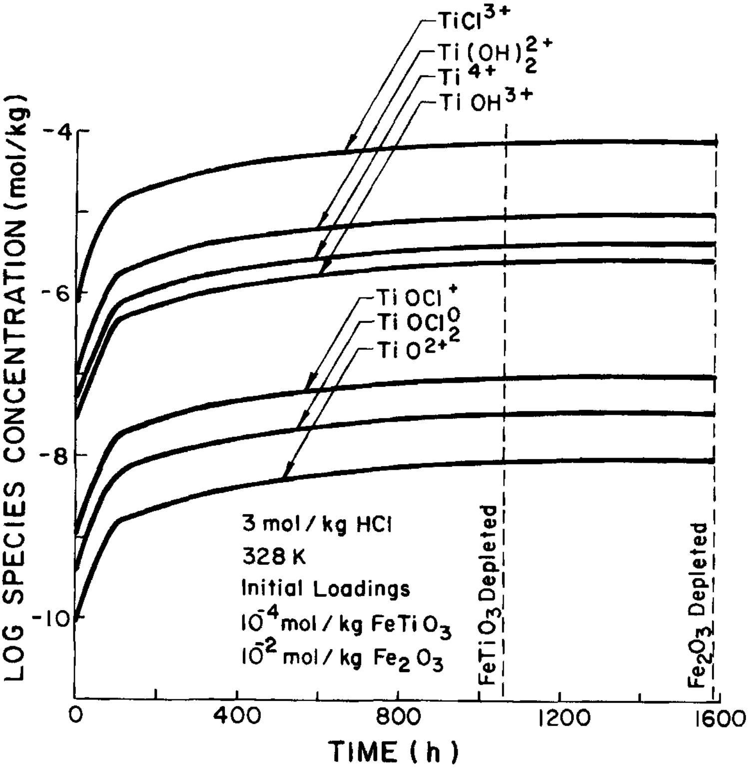

Figure 2. Concentrations of Ti(IV) species calculated using the partial equilibrium model. Reaction conditions are 3 mol/kg HCl, 328K, and initial $FeTiO_3$ and Fe_2O_3 loadings of 10^{-4} and 10^{-2} mol, respectively.

all circumstances, however, the concentrations of Ti(III) are immeasurably low. Over the course of leaching, certain species increased in importance relative to others of the same valence. While all such changes are small for the conditions of the simulations, certain patterns emerge. The species exhibiting decreases are all chloro complexes, specifically $TiCl^{3+}$, $FeCl_2^0$, $FeCl_3^0$, and $TiCl^{2+}$; these are the predominant Ti(IV), Fe(II), Fe(III) and Ti(III) species, respectively. Chloro complexes with fewer ligands, hydrolyzed species, and free metal ions all become relatively more important later in the leaching process. These changes are due to the increased metal/chloride ratio and the decreased H^+ concentration.

CONCLUSIONS

Simultaneous dissolution of ilmenite and hematite by HCl has been modeled using concepts of partial equilibrium. Available data on the rates of reaction were coupled with data on the solution species to obtain predictions of the species concentrations throughout the leaching process. Variables needed as input are the initial acid concentration and amounts of each mineral; a basis of 1 kg of H_2O, temperature of 328K, and initial particle size of -106 + 75μm were assumed.

Ti(IV), Fe(II), Fe(III) and Ti(III) species are considered, and other oxidants or reductants are assumed to be absent. Due to the fact that Ti(III) is highly unstable and can form only by reduction of Ti(IV), Ti(III) concentrations are always very low, although they are not constant. The Ti/Fe ratio drops early in a leach, then rises to a sharp maximum coinciding with the depletion of $FeTiO_3$ before dropping again. The Fe(II)/Fe(III) ratio parallels this and exhibits maxima and minima coinciding with those of the Ti/Fe ratio. Both the minima and maxima occur earlier at higher acid concentrations when the rates are faster. The magnitudes of these ratios, however, are determined primarily by the amounts of $FeTiO_3$ and Fe_2O_3 supplied. There may be opportunities to develop separation processes which exploit optimal values of these parameters. For the relatively low metal/chloride ratios investigated, the distribution of species did not shift much over the course of a leach. However, the degree of metal complexing by chloride became slightly less pronounced.

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