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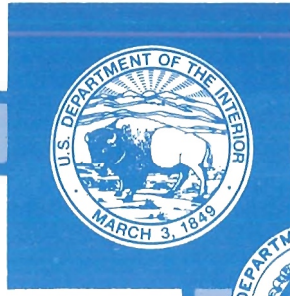
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Extraction of Titanium and Iron From Ilmenite With Fluosilicic Acid

UNITED STATES DEPARTMENT OF THE INTERIOR



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Extraction of Titanium and Iron From Ilmenite With Fluosilicic Acid

By Dennis A. Hansen, Davis E. Traut, and G. Tim Fisher II

**UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary**

**BUREAU OF MINES
Rhea Lydia Graham, Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g/L gram per liter

h hour

K kelvin

L liter

M molar concentration

min minute

mL milliliter

Mt million metric tons

wt % weight percent

μm micrometer

$^{\circ}\text{C}$ degree Celsius

EXTRACTION OF TITANIUM AND IRON FROM ILMENITE WITH FLUOSILICIC ACID

By Dennis A. Hansen,¹ Davis E. Traut,² and G. Tim Fisher II³

ABSTRACT

As part of a U.S. Bureau of Mines program to develop a more continuous titanium metal extraction process that uses domestic resources, a study was made to determine the extraction of titanium (Ti) and iron (Fe) from New York rock ilmenite using fluosilicic acid (H_2SiF_6). The effects of leach temperature, acid concentration, and particle size were investigated for the rate at which Ti and Fe are extracted from the ilmenite. Within the leach time studied, the extraction data fit a shrinking-core model; the rate-controlling step was diffusion of H_2SiF_6 through an ash layer resulting from a heterogeneous leaching reaction. The rate is linearly dependent on the H_2SiF_6 concentration and is inversely proportional to the square of the particle diameter. Using 2.6M H_2SiF_6 at 85 °C, 49% of the Ti and 53% of the Fe in 44- to 74- μm New York rock ilmenite were extracted in 3 h.

¹Chemical engineer.

²Supervisory chemical engineer.

³Metallurgist.

Albany Research Center, U.S. Bureau of Mines, Albany, OR.

INTRODUCTION

In support of its mission to help ensure that an appropriate share of the Nation's domestic resources are being used in the production of minerals, the U.S. Bureau of Mines (USBM) has investigated a fluoride leaching route to produce Ti metal starting with ilmenite (FeTiO_3) as a raw material (1-2).⁴ Part of that investigation is the study of Ti extraction by acid leaching from ilmenite. Of the major Ti-bearing ores in the United States (ilmenite, rutile, and perovskite), ilmenite represents the largest resource of Ti, an estimated 7.2 Mt of contained Ti in reserves with an additional 14.1 Mt of contained Ti in the reserve base (3). A process to manufacture pure Ti metal that would utilize lower grade, less costly, and more readily available raw materials, such as ilmenite, has long been sought.

A number of methods have been proposed for extracting Ti values from ilmenite or other Ti ores with various fluoride compounds. These fluoride compounds include

hydrofluoric acid (HF) (4-13), fluosilicic acid (H_2SiF_6) (13), HF gas (14-15), alkali fluosilicates (16-23), ammonium fluoride (NH_4F) (8, 24-25), ammonium bifluoride (NH_4HF_2) (26), alkali double fluorides (8, 16, 18, 27), calcium fluoride (CaF_2) with sulfuric acid (H_2SO_4) (18, 28), CaF_2 with ferric chloride (FeCl_3) or hydrochloric acid (HCl) (29), and ferric fluoride (FeF_3) (30). Fluosilicic acid (H_2SiF_6) was chosen for study because it is a relatively low-cost byproduct of fertilizer manufacture and thus may offer an economic advantage over other fluorides. Previous H_2SiF_6 studies (13) do not provide information concerning the effects of various leaching conditions on Ti and Fe extraction. Therefore, the objective of this research was to correlate Ti and Fe extraction data with a kinetic model such that equipment and conditions might be designed to maximize the extraction of Ti and Fe from ilmenite using H_2SiF_6 .

MATERIALS

A rock-type ilmenite from Tahawus, NY, was used for all leaching tests. About 34% (2.4 Mt of contained Ti) of the U.S. Ti reserves are of this type, and the remainder are ancient beach sand deposits (3). This material was an ilmenite concentrate obtained from a massive deposit of primary ilmenite-magnetite minerals in rock containing anorthosite and gabbro (31). A mineralogical examination indicated the presence of approximately 96% FeTiO_3 , 2% spinel, 1% garnet, and 1% miscellaneous minerals, including quartz and feldspar. The chemical analysis of the rock ilmenite is shown in table 1 and indicates 27.7 wt% Ti and 35.2 wt% Fe.

The H_2SiF_6 used was reagent grade, and the chemical analysis is shown in table 2. The maximum concentration of H_2SiF_6 used in this study was 2.6M since that concentration is the commercially available reagent grade and is greater than the 2.0M H_2SiF_6 available as byproduct.

Table 1.—Chemical analysis of New York rock ilmenite

Element	Wt %
Fe	35.2
Ti	27.7
Mg	1.4
Si	0.6
F	0.3
Mn	0.3
C	0.2
Ca	0.2

Table 2.—Chemical analysis of as-received 2.6M H_2SiF_6

Element	g/L
F	261
Si	70.0
Cl	0.20
Ti	0.02
Fe	0.02

EQUIPMENT

A 400-mL tetrafluoroethylene (TFE) beaker placed in a 2-L water bath was used as the batch reactor to avoid possible problems with leaching of silica from glass by the H_2SiF_6 . The beaker was partially covered by a TFE

watchglass during the experiment. The water bath was heated by a hotplate to reach and maintain the desired temperature (± 1 °C). The temperatures of the H_2SiF_6 -ilmenite slurry and the surrounding water bath were monitored using a digital thermometer. Other equipment was either polyethylene or polypropylene to avoid corrosion and contamination problems.

⁴Italic numbers in parentheses refer to items in the list of references at the end of this report.

PROCEDURE

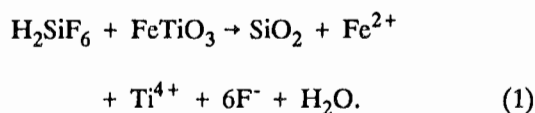
Three test series were used to independently investigate the effects of the three leach variables chosen. One series investigated temperatures of 45, 65, and 85 °C. Another series determined the effects of H₂SiF₆ concentrations using 0.65M, 1.30M, and 2.60M H₂SiF₆. The last series investigated the effect of initial ilmenite particle size using 20- to 38- μ m- and 44- to 74- μ m-diameter particles. A low pulp density (1.6%) was used during the experiments for three reasons: (1) to maintain a constant H₂SiF₆ concentration during leaching, (2) to act as a heat sink, which would minimize any temperature rise from this exothermic leach and maintain isothermal conditions, and (3) to maximize Ti and Fe extraction and solubility. The slurry was stirred vigorously throughout the test. After the

ilmenite was added, 5-mL liquid samples were taken at specified time intervals. Each test was replicated. Sampling schedules were varied for the otherwise identical tests to check the reliability of test data and to add additional data points.

Leaching progress was followed by analysis for Ti and Fe in the extracted samples. Titanium was analyzed by inductively coupled plasma spectrophotometry, and Fe was analyzed by atomic absorption spectrophotometry. Initial material and final residue analyses for both Ti and Fe were done by a volumetric method. Scanning electron microscope (SEM) photographs were obtained by first coating the cross-sectioned leached ilmenite with gold to enhance the surface deformation.

RESULTS

The reaction of ilmenite with H₂SiF₆ is a heterogeneous reaction; therefore the shrinking-core model (32) was assumed. The shrinking-core model states that the reaction rate is controlled by one of three steps that occur in series: diffusion of H₂SiF₆ through a film surrounding the particle, diffusion of H₂SiF₆ through an "ash" layer, and chemical reaction on the surface of the unreacted core. Indication of the diffusion control was provided by the SEM, which showed a rough surface on the particle after a H₂SiF₆ leach. Analysis of the rinsed particles showed an Si-containing substance, probably silica (SiO₂), present in this ash layer. A possible chemical equation for the reaction is



The ash layer slows the reaction because the diffusion-rate-controlling step is slower than the chemical reaction step. An earlier study indicated that HF leaching of ilmenite was controlled by the chemical reaction step (12). SEM photographs of those rinsed particles showed a smooth surface after an HF leach of the particles. The equation for the ash diffusion model (32, p. 51.2) is

$$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = Kt, \quad (2)$$

where α = fractional amount of element leached,

K = overall rate constant, min⁻¹,

and t = time, min.

K is linearly dependent on acid concentration and inversely dependent on the square of the particle diameter:

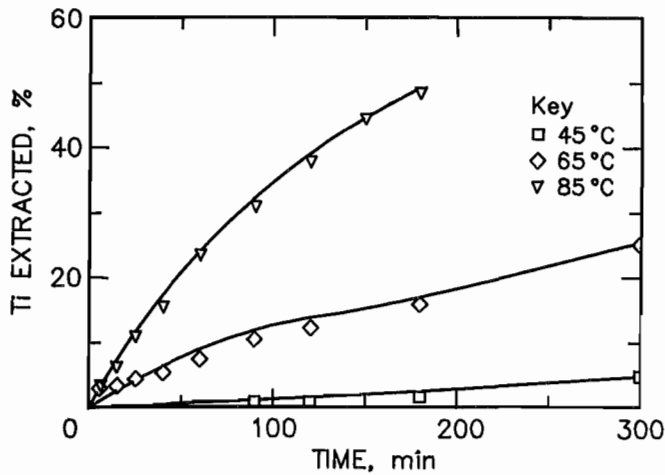
$$K \propto C/(D^2). \quad (3)$$

EFFECT OF TEMPERATURE

The effect of temperature on Ti and Fe extraction was investigated using 2.60M H₂SiF₆ solution with the 44- to 74- μ m size fraction of New York rock ilmenite. The temperatures used were 45, 65, and 85 °C. Preliminary tests showed that 25 °C was too low to obtain usable data, and at temperatures greater than 85 °C, the test results were affected by loss of H₂SiF₆ vapor.

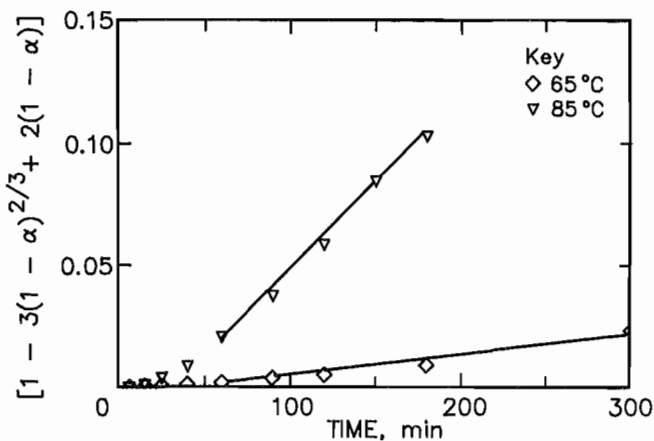
Figure 1 shows that when the concentration of extractant remains constant, the rate of leaching of Ti increases with temperature. At 45 °C, the leach took 180 min to extract 2% of the Ti. At 85 °C, the Ti extracted increased to 49%. The rates of Ti extraction are shown in figure 2 using equation 2. Similar results were observed for Fe. Within the leach time studied, the ash diffusion does not control the reaction kinetics in the beginning stages, when some other resistance or combination of resistances must be controlling. Eventually though, the controlling mechanism shifts to ash diffusion (32). The reason for this is that the particle starts with no ash layer, hence no resistance to ash diffusion. The straight lines in figure 2 were drawn from the method of least squares using the linear range of the data. The slope of the lines is K (the overall rate constant).

Figure 1



Titanium extraction as a function of time and temperature at 2.6M H_2SiF_6 concentration.

Figure 2

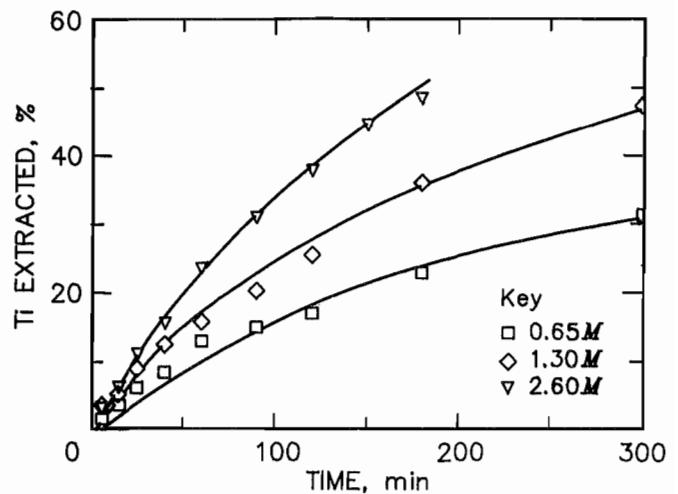


Effect of temperature on leach rate using ash diffusion model for Ti.

EFFECT OF H_2SiF_6 CONCENTRATION

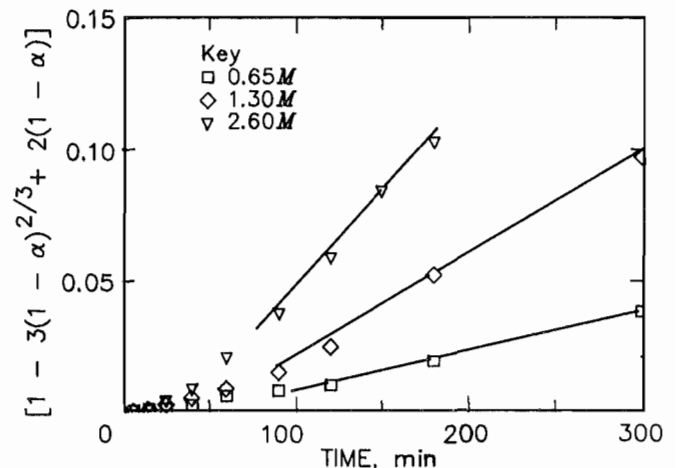
The effect of H_2SiF_6 concentration on Ti and Fe extraction was investigated using constant conditions of 85 °C with the 44- to 74- μ m size fraction New York ilmenite. The H_2SiF_6 concentrations used were 0.65M, 1.30M, and 2.60M. The percent of Ti extracted is shown in figure 3. The effect of H_2SiF_6 concentration on Ti extraction is apparent. Using 0.65M H_2SiF_6 , the leach took 180 min to extract just 23% of the Ti. Using 2.60M H_2SiF_6 , the extraction increased to 49% during the same contact time. In each of the three curves, extraction increased over time and did not level off at the end of the sampling times. Figure 4 shows the rates of Ti extraction using equation 2. Similar results were observed for Fe. Within the leach

Figure 3



Titanium extraction as a function of time and H_2SiF_6 concentration at 85 °C.

Figure 4

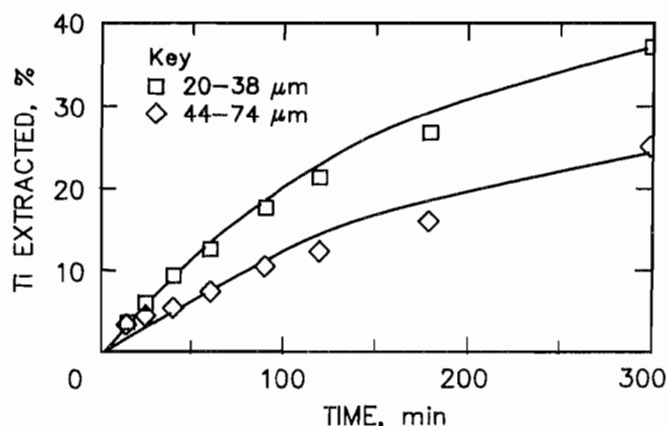


Effect of H_2SiF_6 concentration on leach rate using ash diffusion model for Ti.

EFFECT OF PARTICLE SIZE

The effect of ilmenite particle size on Ti and Fe extraction was investigated using 2.6M H_2SiF_6 solutions at 65 °C. Two discrete initial particle size ranges were used, 20 to 38 μ m and 44 to 74 μ m, as they represented most of the ilmenite material. The percent of Ti extracted is

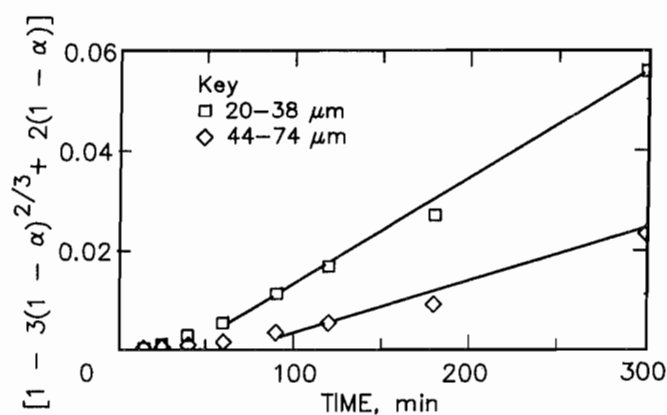
Figure 5



Titanium extraction as a function of time and particle size at 2.6M H_2SiF_6 concentration at 65 °C.

shown in figure 5. The effect of particle size on Ti extraction is apparent. With the 44- to 74- μm particle size, 25% of the Ti was extracted in 300 min, and with the smaller, 20- to 38- μm particle size, 37% of the Ti was extracted. Using equation 2, the rates of Ti extraction are shown in figure 6. Similar results were observed for Fe. Within the leach time studied, ash diffusion control did not

Figure 6



Effect of particle size on leach rate using ash diffusion model for Ti.

begin right away but the ash diffusion step did eventually control the extraction rate. The overall rate constant K should be dependent on the inverse of the square of the particle size according to equation 3. A simple plot shows this relationship to be true for both Ti and Fe using the experimental data.

CONCLUSIONS

The USBM has investigated the effects of leach temperature, acid concentration, and particle size on the extraction of Ti and Fe from New York rock ilmenite using H_2SiF_6 . Within the leach time studied, the data fit a shrinking-core model, with the rate eventually controlled by the ash diffusion step. The diffusion is a result of an ash layer developing around the unreacted core. This

diffusion control rate is slower than the chemical reaction control rate. The reaction might proceed faster, therefore, if the ash layer could be continually removed from the reacting particle by leaching in an apparatus such as an attrition mill. The rate is linearly dependent on the H_2SiF_6 concentration and is inversely proportional to the square of the particle diameter.

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