The Dissolution of Activated Titanium Slag in Dilute Sulfuric Acid

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Finely ground titanium slag (−400 mesh) dissolves slowly in dilute H_2SO_4 (2−10 mol/L) in the temperature range 70−110°C, but attrition ground slag dissolves much faster under similar conditions. The process is strongly dependent on the speed of agitation in the region 345−1035 rpm, and has an activation energy of 28 kJ/mole TiO_2, thus suggesting that the dissolution is controlled by diffusion through the boundary layer.

Les scories de titane finement moulues (−400 mailles) se dissolvent lentement dans H_2SO_4 dilué (2−10 moles par litre) à une température variant entre 70 et 110°C, mais les scories attaquées par l'attrition se dissolvent bien plus vite dans des conditions semblables. Le processus dépend fortement de la vitesse d'agitation dans la région de 345 à 1035 rpm et il possède une énergie d'activation de 28 kJ/mole de TiO_2, ce qui indique que la diffusion par la couche-limite contrôle la dissolution.

There are two methods for producing titanium oxide pigment: The sulfuric acid route and the chlorination route. In the sulfuric acid method, the feed material, usually synthetic rutile, ilmenite, or a standard titanium slag, is digested with 92% H_2SO_4 at about 200°C to get a cake composed mainly of titanyl sulfate (Barksdale, 1966; Reznichenko and Khromova, 1960; Slama, 1960). This is then dissolved in water, filtered to remove the gangue minerals, then subjected to hydrolysis to get titanium dioxide in the anatase form which is filtered, dried, and calcined to the rutile form. In the chlorination method, the feed material, usually rutile, synthetic rutile, or a high grade titanium slag is mixed with carbon and reacted with chlorine at about 800°C to get $TiCl_4$ gas which is condensed, purified by fractional distillation, then oxidized to TiO_2.

In the chlorination method, chlorine produced during the oxidation of $TiCl_4$ according to:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$
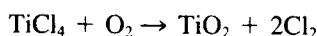
is recycled, but in the acid digestion method, the hydrolysis of titanyl sulfate solution according to:

$$TiOSO_4 + H_2O \rightarrow TiO_2 + H_2SO_4$$
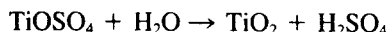
leads to the formation of a dilute H_2SO_4 (about 40%) that cannot be recycled to the digestion step unless it is concentrated back to 92%. This step is usually expensive and the industry at present prefers to dispose of this acid.

One possible route to produce the pigment without creating an acid disposal problem would be by reacting the titanium feed material with a less concentrated H_2SO_4 (about 40% concentration), then after filtering off the gangue minerals, and hydrolysing the titanyl sulfate solution, the dilute acid generated can be strengthened back to 40% either by evaporation or by adding oleum, after bleeding a certain amount to keep the impurity at a certain tolerable level (Davis, 1981; Rahm and Cole, 1981). However, the dissolution of slag is very slow in dilute H_2SO_4 (Sinha, 1979). Therefore, methods for activating the raw material should be

found. The present work was undertaken to explore this possibility, but no attempt was made to evaluate the economics of activation as compared to the cost of acid disposal as presently practiced.

Experimental

APPARATUS

Tests were conducted in open vessels (Figure 1) equipped with agitators, thermostatic temperature control, and reflux condenser.

MATERIALS

Titanium feed material was a standard grade slag having the analysis shown in Table 1. It is the commercial product of QIT Fer et Titane, Inc. in Sorel, Quebec and known under the trade name Sorelslag. It is composed mainly of iron magnesium titanate ($FeO.MgO.4TiO_2$), a silicate phase containing trivalent titanium, and some globules of metallic iron of various sizes (Toromanoff and Habashi, 1984).

The following methods of activation were studied:
1) Grinding for 20 minutes in a tungsten carbide "Shatterbox" no. 8504 supplied by SPEX in Metuchen, N.J. It is a short steel cylindrical container 152.4 mm inner

TABLE 1
Analysis of Titanium Slag, −400 Mesh Fraction

	%
TiO_2 (total)	71.35
Ti_2O_3 (expressed as TiO_2)	10.8
Fe (total)	9.2
Fe (metallic)	0.05
Al_2O_3	5.42
SiO_2	5.26
CaO	1.12
MgO	5.24
MnO	0.26
V_2O_5	0.58
Cr_2O_3	0.18

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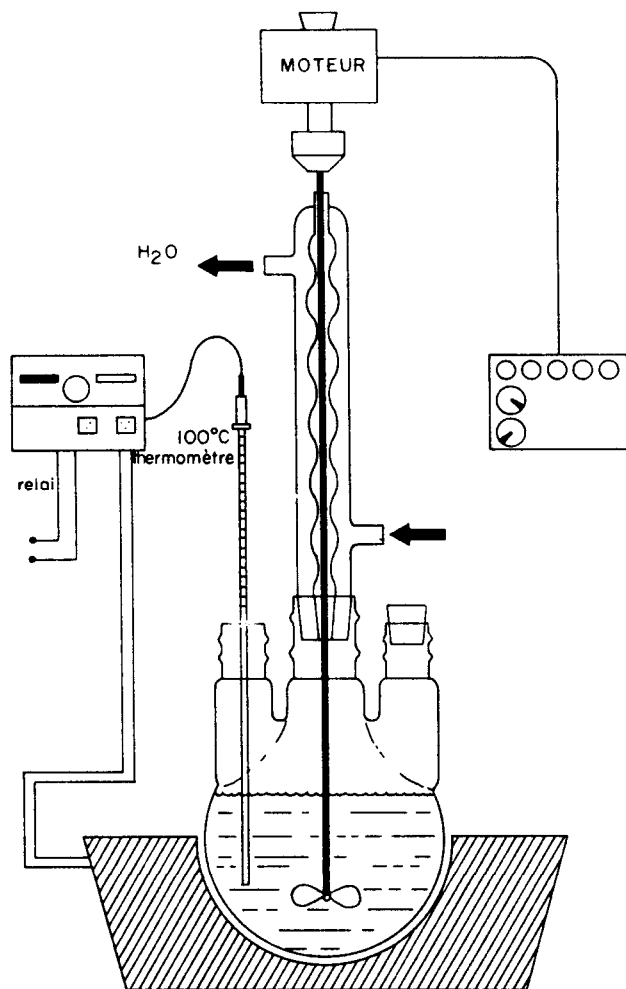
Figure 1 — Leaching reactor under ambient pressure.

Figure 2 — Scanning photomicrograph for regular slag −400 mesh.
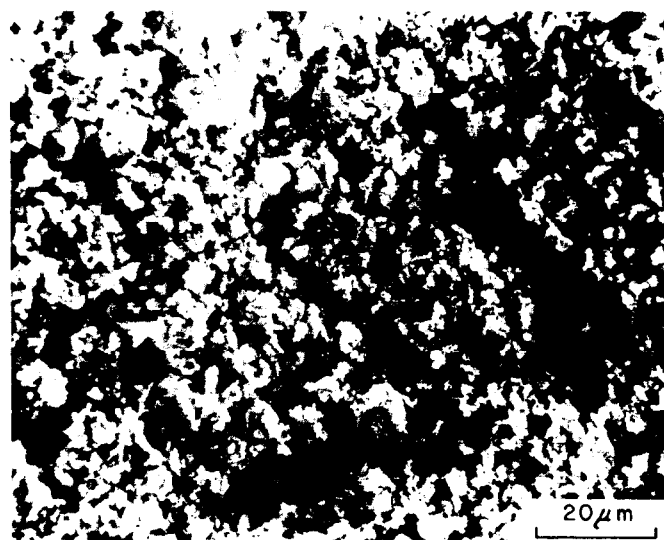
Figure 3 — Scanning photomicrograph for attrition ground slag for 5 hours.

diameter and 76.2 mm high, 100 cm^3 capacity, with a loose tungsten carbide liner, a massive loose tungsten carbide disc, and a steel cover. When the grinder is mounted on a vibrating machine, the WC disc grinds the material while bombarding the loose liner.

2) Grinding in an Attritor X Model 1S of Union Process Inc. of Akron, Ohio. This is a cylindrical water-jacketed tank equipped with three horizontal pedals mounted on a spindle driven by a variable speed motor to agitate the batch. A large number of 6 mm steel balls were added to the batch as a grinding media. Grinding was done dry but few drops of methyl alcohol were added to avoid agglomeration. One sample was ground for 2 hours and another for 5 hours. Attrition grinding is claimed by the manufacturer to consume less energy than by other grinding equipment. The effect of particle size was studied on four fractions ground in the Shatterbox as follows:

a) −325 +400 mesh (ASTM)

b) −270 +325 mesh (ASTM)

c) −200 +270 mesh (ASTM)

d) −150 +200 mesh (ASTM)

CHARACTERIZATION OF SLAG SAMPLES
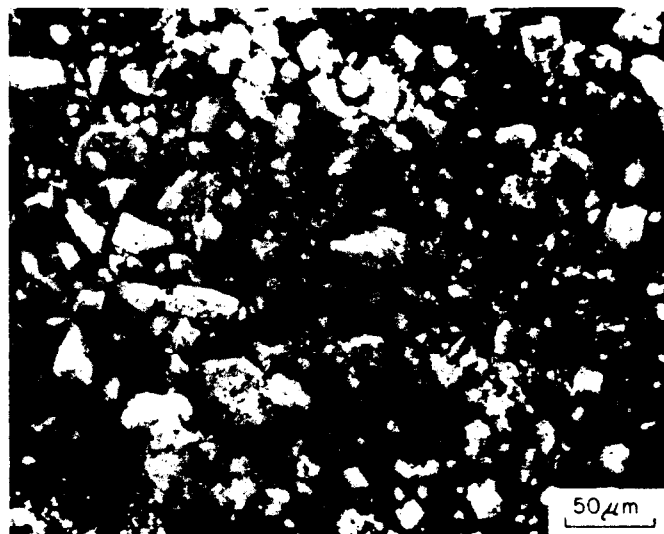
The granulometry of the ground particles was done with a Leeds and Northrop Microtrac Particle Size Monitor. This apparatus combines a laser beam with optical technology and a microcomputer to convert the light-scattering effect of particles in slurries to measured and calculated numerical values. The machine reports:

1) A 13-channel histogram. Successive channel widths vary as $\sqrt{2}$ with the smallest from 1.9 to 2.8 microns and the largest from 125 to 176 microns.

2) A 13-channel cumulative "% passing" number for 176, 125, 88, 62, 44, 31, 22, 16, 11, 7.8, 5.5, 3.9, or 2.8 microns (in volume %).

3) The average particle diameter (mean) of the volume distribution in microns.

4) The specific surface which is the scaled reciprocal of average particle diameter (mean) of the area distribution.

Table 2 shows the particle size distribution of the sieved slag. The particle size of the attrition ground slag was examined only by the scanning electron microscope because of its very small size. Scanning photomicrographs of slag ground to −400 mesh in Shatterbox and slag ground in attrition

TABLE 2
Particle Size Distribution of Sieved Slag

| Particle size μm | Fraction, mesh size (ASTM) | | | | | | | | | | Attrition ground Scanning microscope reading | |
| | −150 +200 | | −200 +270 | | −270 +325 | | −325 +400 | | −400 | | | |
	% cumul.	%	% cumul.	%	% cumul.	%	% cumul.	%	% cumul.	%	2 hrs	5 hrs
176	100	12.0	100		100		100		100			
125	87.9	33.4	100	5.4	100	4.9	100	0.3	100			
88	54.5	33.8	94.5	35.5	95.0	18.9	99.6	12.6	100			
62	20.6	3.0	58.9	28.2	76.1	28.2	80.9	24.8	100	3.0		
44	17.5	1.3	30.6	6.0	47.8	19.5	56.1	17.2	96.9	12.0		
31	16.2	—	24.6	8.2	28.3	5.6	38.9	13.1	84.9	17.5		
22	16.2	0.2	16.4	2.0	22.7	3.6	25.7	7.0	67.3	14.9		
16	15.9	5.1	14.3	—	19.0	3.6	18.7	6.2	52.3	12.0		
11	10.7	—	14.3	2.0	15.4	3.4	12.4	2.8	40.3	10.3		
7.8	10.7	—	12.3	8.5	11.9	2.2	9.6	1.9	30.3	7.8		
5.5	10.7	4.1	3.7	—	9.6	3.2	7.7	2.7	22.1	8.8	majority	
3.9	6.6	6.6	3.7	—	6.3	4.1	4.9	2.0	13.3	7.1	majority	
2.8	0	—	3.7	3.7	2.2	2.2	2.9	2.9	6.1	6.1		(1−2 μm) majority
Specific surface area, m^2/cm^3	0.254		0.285		0.339		0.333		0.702			
Mean diam., μm	82.2		53.1		45.2		40.3		17.4		~4.5	~1.5
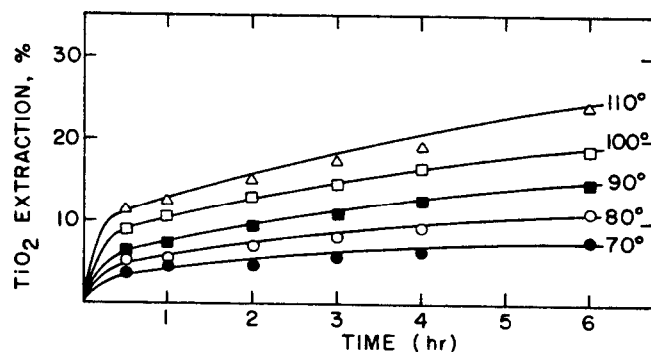
Figure 4 — Effect of temperature on TiO_2 extraction by 6 mol/L H_2SO_4.

grinder are shown in Figures 2 and 3 respectively; no obvious differences can be marked except that the attrition ground sample was much finer than that ground in a Shatterbox.

PROCEDURE

Finely ground slag sample weighing 22.4 g was introduced in the flask and mixed with 400 cm³ of H_2SO_4 of a certain concentration. The mixture was heated to a certain temperature while agitating at a certain speed.

Five cm³ of solution samples were drawn by a pipet with a sintered glass inlet at intervals. These were analyzed by atomic absorption for titanium, iron, aluminum, magnesium, and vanadium. Corrections were made for the decrease in volume due to the samples taken as follows:

weight of TiO_2 leached when 1st sample was taken
= $c_1 \times 0.400$

weight of TiO_2 leached when 2nd sample was taken
= $c_2 \times 0.395 + 0.005 \times c_1$

weight of TiO_2 leached when 3rd sample was taken
= $c_3 \times 0.390 + 0.005 (c_1 + c_2)$

weight of TiO_2 leached when nth sample was taken
= $c_n \times (0.400 - n \times 0.005) + 0.005 (c_1 + c_2 + ... c_n)$

where $c_1, c_2, c_3, ... c_n$ are the concentrations of the 1st, 2nd, 3rd, ... nth sample in g/L. No filtration problems were encountered.

Results and discussion

EFFECT OF TEMPERATURE

Figure 4 shows the effect of temperature in the range 70−110°C on leaching a −400 mesh slag with 6 mol/L H_2SO_4 at 690 rpm, and a solid-liquid ratio of 4.23%. It can be seen that the percent dissolution of Ti increases with increased temperature. In the first half hour, however, the amount dissolved was higher than afterwards. This can be due to the very small particles present that dissolve first. The rate of dissolution became relatively constant subsequently. Ignoring the first half hour period, and taking the slopes of the straight lines obtained afterwards up to 6 hours reaction time as the velocity constants, it was possible to establish an Arrhenius plot from which an activation energy of 28 kJ/mole was calculated (Figure 5). A test was conducted at 110°C for 60 hours. The percentage of titanium dissolution is shown in Figure 6.

EFFECT OF ACID CONCENTRATION

Figure 7 shows the effect of H_2SO_4 concentration in the range 2−10 mol/L on leaching a −400 mesh slag at 690 rpm agitation speed, at 110°C and a solid liquid ratio of 4.23%. It can be seen that the percentage extraction of titanium increases with increased acid concentration.
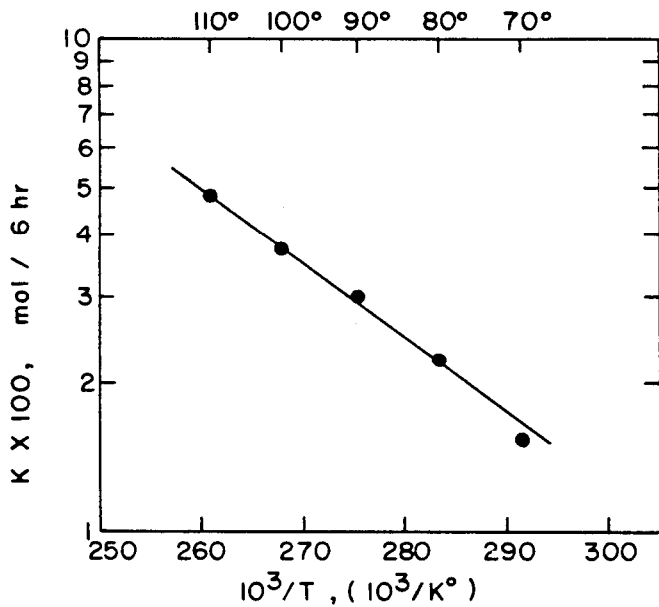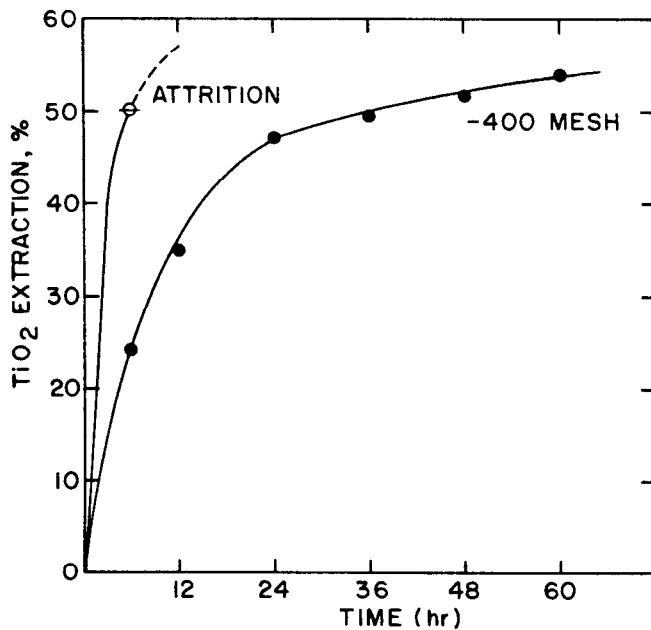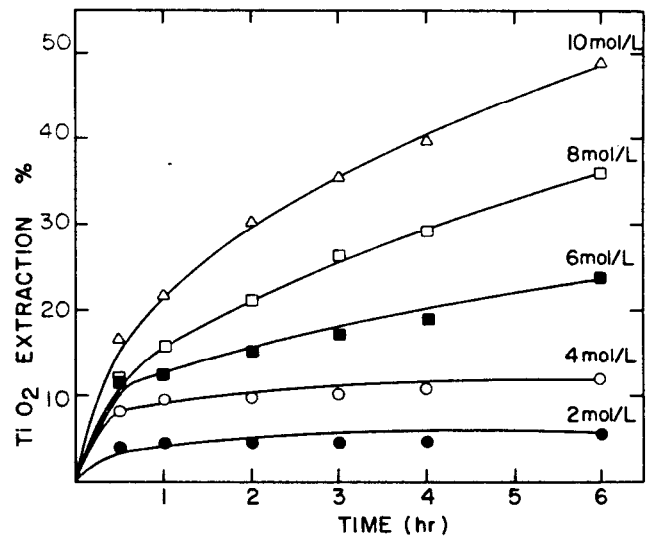
Figure 5 — Arrhenius plot.

Figure 7 — Effect of acid concentration on the dissolution of titanium from slag at 110°C.

Figure 6 — Effect of time on titanium extraction for attrition-ground and −400 mesh slag, 110°C, 6 mol/L H_2SO_4.
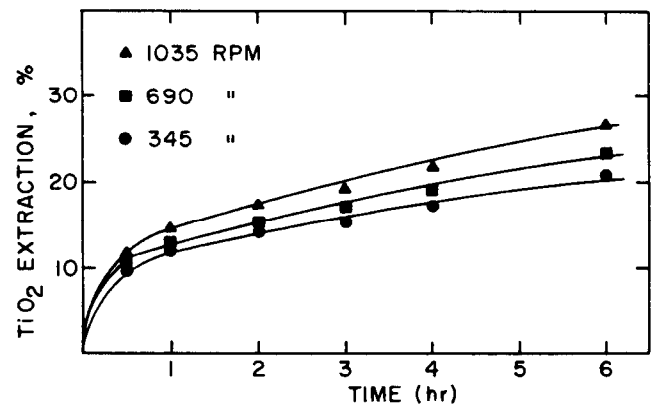

Figure 8 — Effect of speed of agitation (revolutions per minute) on titanium extraction at 110°C, 6 mol/L H_2SO_4.

EFFECT OF SPEED OF AGITATION

Figure 8 shows the effect of speed of agitation in the range 345 to 1035 rpm, in 6 mol/L H_2SO_4, solid-liquid ratio of 4.23% and 110°C. It can be seen that the rate of reaction depends on the speed of agitation. Since no precipitates are formed during leaching, the dependence can be only due to diffusion through the boundary layer. This is supported by the fact that the activation energy is 28 kJ/mole which is a value typical for such processes (Habashi, 1980). The percentage extraction in 6 hours is proportional to $\sqrt{rpm}$ as shown in Figure 9.

EFFECT OF PARTICLE SIZE

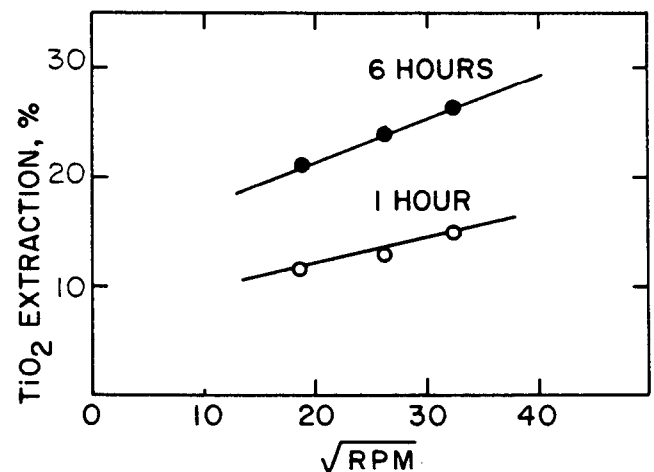The rate of dissolution of slag of different particle sizes in

Figure 9 — Effect of speed agitation (revolutions per minute) on titanium extraction at 100°C, 6 mol/L H_2SO_4, 6 hours.

6 mol/L H_2SO_4 at 110°C, and at a speed of agitation of 690 rpm and solid-liquid ration of 4.23% is snown in Figure 10. As expected, it was found that the finer the particles the faster the dissolution. The attrition ground slag, however,
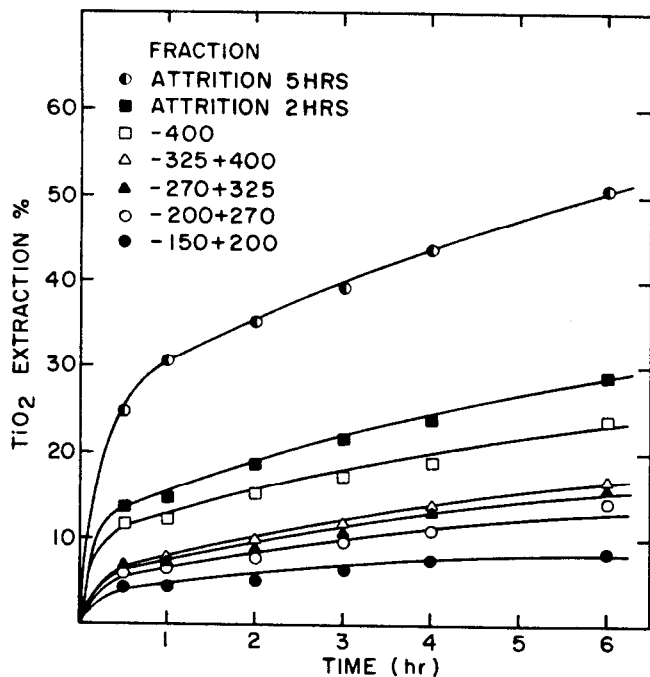
Figure 10 — Effect of particle size on the TiO₂ extraction 110°C, 6 mol/L H₂SO₄.
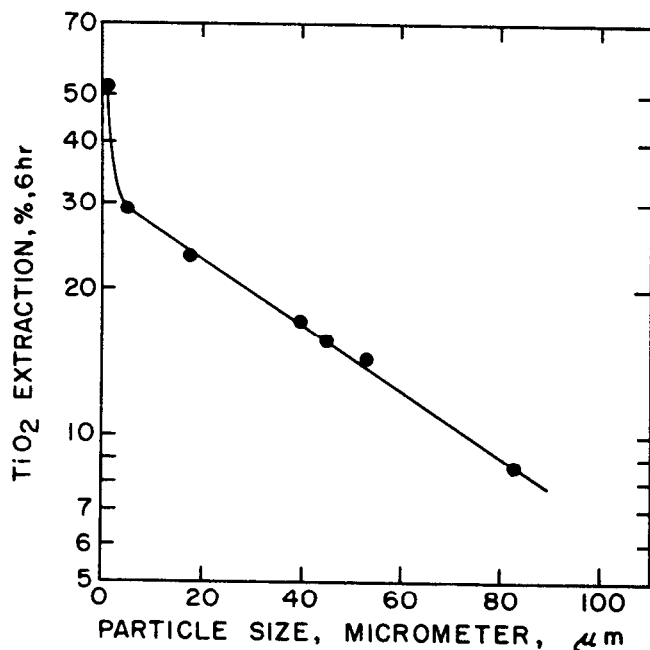

Figure 11 — Titanium extraction as a function of particle size; 110°C, 6 mol/L H₂SO₄, 6 hours.

dissolved much faster than the −400 mesh fraction. Thus, after 6 hours more than 50% dissolution took place for the attrition ground slag while under same conditions only 24% dissolution for the −400 mesh slag. It is evident that attrition grinding is a very effective method for activating the slag. Figure 11 shows the percentage dissolution as a function of the mean particle diameter of the slag.

EFFECT OF SOLID-LIQUID RATIO

Figure 12 shows the effect of solid-liquid ratio in the range 4.23 to 26.1% solids. It can be seen that the rate of
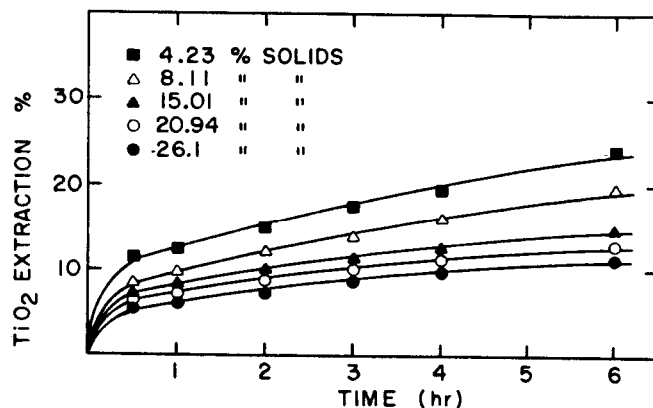

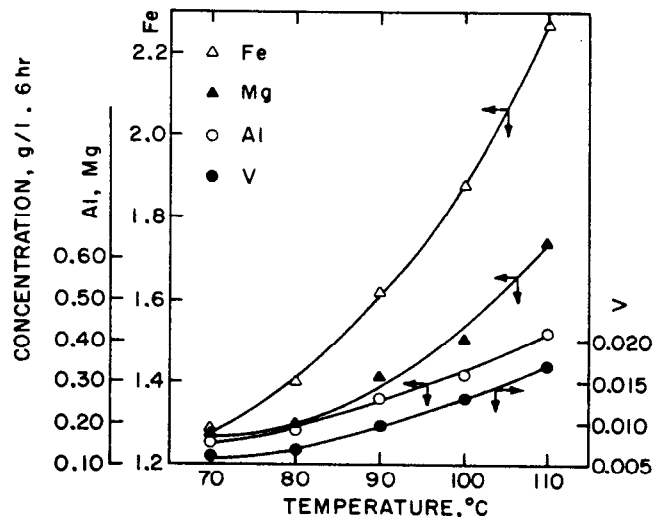Figure 12 — Effect of percent solids on titanium extraction at 110°C, 6 mol/L H₂SO₄.

Figure 13 — Concentration of impurities in solution as function of temperature; 6 mol/L H₂SO₄, 6 hours.
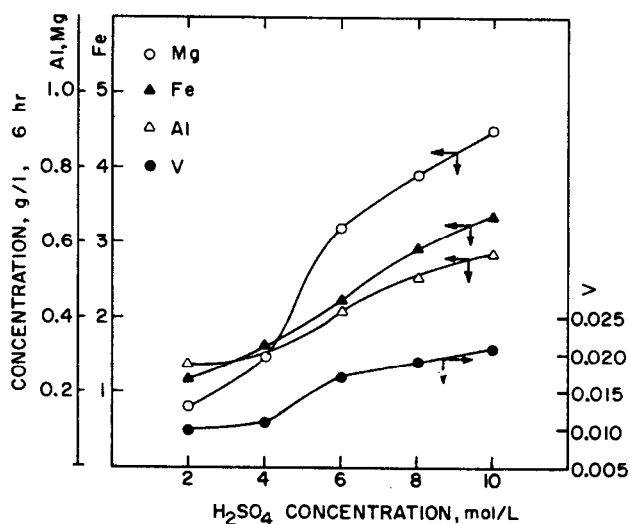

Figure 14 — Concentration of impurities in solution as function of acid concentration 110°C, 6 hours.

dissolution increases with decreased solid-liquid ratio. The concentration of titanium in the solution increases linearly with increased solid-liquid ratio. Therefore, a compromise has to be made between the concentration of titanium in the
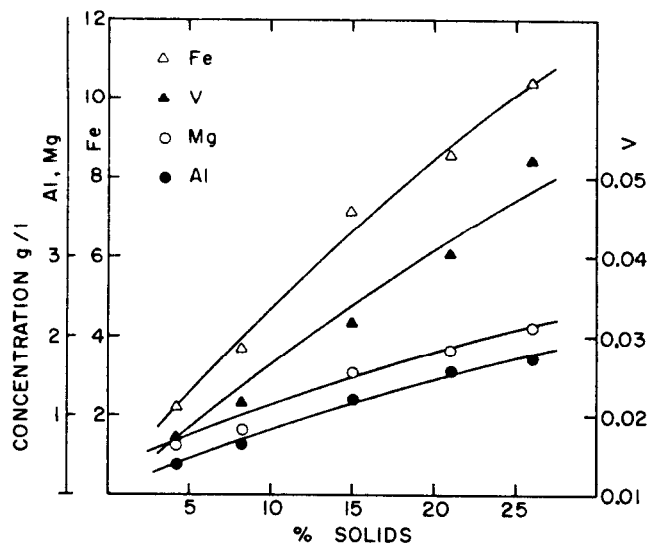
Figure 15 — Concentration of impurities in solution as function of percentage solids. 110°C, 6 mol/L H_2SO_4, 6 hours.

solution obtained and the rate of dissolution.

BEHAVIOR OF IMPURITIES

Figure 13 to 15 show the behavior of impurities Fe, Al, Mg, and V during the dissolution of the slag as a function of temperature, H_2SO_4 concentration, and percent solids, respectively. It can be seen that the concentration of impurities in solution increase with increasing temperature, acid concentration, and percent solids.

Conclusions

1) Finely ground titanium slag dissolves slowly in dilute H_2SO_4 (2−10 mol/L) in the temperature range 70−110°C.

2) Attrition ground slag dissolves nearly twice as fast as −400 mesh slag under similar conditions.

3) Dissolution of slag is governed by diffusion through the boundary layer: the more the pulp is agitated the faster the dissolution.

Acknowledgement

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