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DISSOLUTION KINETICS OF CHROMITE IN HYDROCHLORIC ACID SOLUTIONS

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ABSTRACT

The Leaching response of chromite in hydrochloric acid solutions was studied. The results show a 15 to 30 fold enhancement of iron over chromium extraction suggesting the feasibility of chemical beneficiation. The extraction of iron was found to be logarithmic with time. This was explained in terms of the strain-relief model involving a linear increase in the leaching activation energy as extraction proceeds.

INTRODUCTION

The Philippines ranks among the top ten chromite producing countries of the world. Unfortunately, most of the chromite exported is refractory grade characterized by low Cr/Fe ratio and consequently low dollar value. The refractory chromite market also imposes strict requirement regarding produce size which results into the non-utilization of the finer size fractions. This represents a considerable amount of material which could be converted into dollars if it could made marketable. Several pre-treatment routes have been proposed but hydrometallurgical treatment appears to be the most promising.

Studies in chromite ($FeOCr_2O_3$) leaching may be classified into two, namely a) complete dissolution of the mineral and b) chemical beneficiation. Under the first classification, the mineral is dissolved completely and chromium recovered by electrolysis. Complete dissolution is accomplished by pressure sulphuric acid leaching[1,2,3], pressure alkaline leaching[4], carbonate roasting followed by dilute hydroxide leach[5], and hydrochloric acid leach[6]. Relatively severe leaching conditions are required due to the refractory nature of the mineral.

Under the second classification, the objective is to dissolve as much of the iron present in the chromite spinel and in so doing, produce a residue with increased Cr/Fe ratio, a more desirable feed for ferrochrome smelting and commands a better selling price. Chemical beneficiation is accomplished by selective reduction of the iron oxide followed by acid leaching. Reduction may be done either with coke fines and charcoal[7], or reducing gases such as CO, H_2, and CH_4[8].

In this study, the response of discarded or unsaleable fine chromite concentrate to hydrochloric acid leaching is investigated to determine the technical feasibility of recovering values from this material.

EXPERIMENTAL METHODS AND MATERIALS

Reject chromite concentrate from the Coto Operations of Benguet Corp. in Masinloc, Zambales was used in the study. The oxide analysis is presented in the table below from which a Cr/Fe ratio of 1.576 may be calculated.

Table 1. Oxide Analysis of the Chromite Concentrate

Oxide	Per Cent
Cr_2O_3	29.65
Fe_2O_3	18.39
Al_2O_3	28.01
SiO_2	1.51
CaO	2.49
MgO	15.50

The leaching experiments were conducted in a three-piece 500 ml Pyrex erlenmeyer flask assembly. The first flask which served as the reactor was fitted with a reflux condenser and a glass sampling tube. The sampling tube emptied into the second flask which acted as the sampling flask. The third flask served as the vacuum reservoir. To obtain an aliquot sample, the vacuum line connected to the third flask is opened and this results into the aspiration of the lixiviant from the first flask to the second flask. A Robertshaw Thermostat by the Robertshaw Controls Co. was used to keep the process temperature within 1.5 ^{o}C of the desired value.

Aliquot samples taken at predetermined time intervals were analyzed for chromium and iron content using a Perkin Elmer Model 290B Atomic Absorption Spectrophotometer. Per cent extraction of chromium and iron was calculated from the sample concentrations. Corrections were made for the decrease in volume of the liquid in the reactor as well as the carry-over of values with the sample.

RESULTS AND DISCUSSIONS

Presented in Table 2 is the effect of temperature on the leaching of chromium and iron from chromite. The results show that the absolute levels of metal dissolution are relatively low, suggesting that complete dissolution is not possible. Iron, however, leaches from 15 to 25 times faster than chromium suggesting that chemical beneficiation may be feasible. Temperature increase appears to have a greater effect on chromium extraction enhancement as signified by a lowering of the ratio of amount dissolved at higher temperatures to about 15 at 85^{o}C from a value of 30 at 50^{o}C. This is further supported by the activation energies of chromium and iron extraction as presented in Arrhenius-type plots shown in Figures 1 and 2, respectively. Chromium has a leaching activation energy of 8.75 kcal/mole while iron has a leaching activation energy of 6.78 kcal/mole.

Table 3 shows the effect of particle size (which directly controls surface area) on the leaching of chromium and iron. The results show a relatively small effect when the particle size is reduced from 110 um to 74 um while a further decrease in particle size to 40 um results in a three-fold increase in chromium extraction and a two-fold increase in iron extraction. A plot of the amount of iron extracted as a function of specific surface area (see Figure 3) shows a non-linear increase in amount extracted which suggests that the enchanced leaching of the 40 um particles can not be accounted for by increased surface area alone.

Table 2. The Effect of Temperature on the Leaching of Iron and Chromium.*

Time (hrs)	% Cr Extraction	% Fe Extraction
Test 1- 50°C		
1.5	0.083	4.683
3	0.123	5.242
6	0.176	6.028
9	0.203	6.274
15	0.233	6.424
20	0.234	6.512
Test 2 - 65°C		
1.5	0.154	4.748
3	0.199	6.518
6	0.276	7.096
9	0.319	7.382
15	0.330	7.552
20	0.332	7.628
Test 3 - 85 °C		
1.5	0.318	5.282
3	0.360	6.612
6	0.397	7.096
9	0.440	7.471
15	0.466	7.894
20	0.469	8.043

* particle diameter = 62 um

% Solid = 10 gm/250 ml

Acid Strength = 10 N

Fig. 1. Activation Energy of Cr Extraction

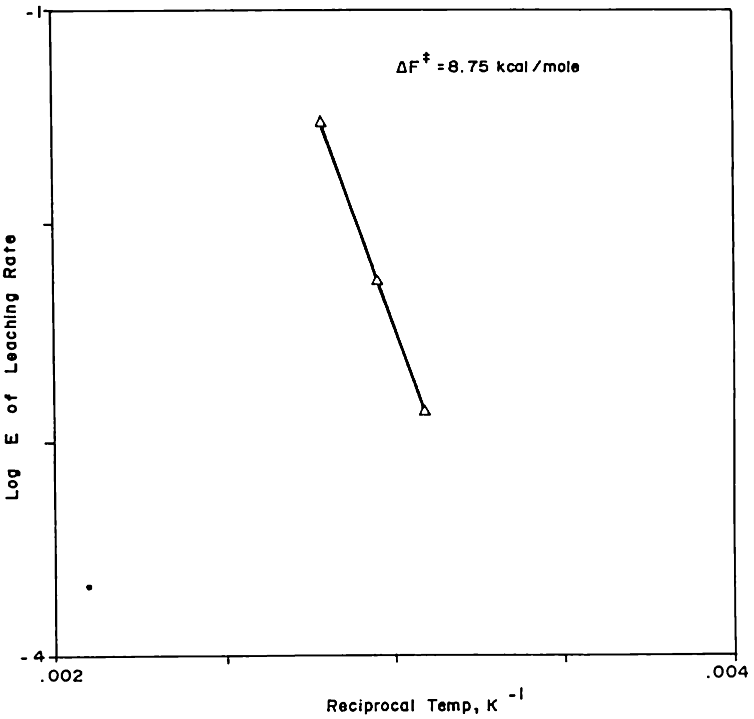


Fig. 2. Activation Energy of Fe Extraction

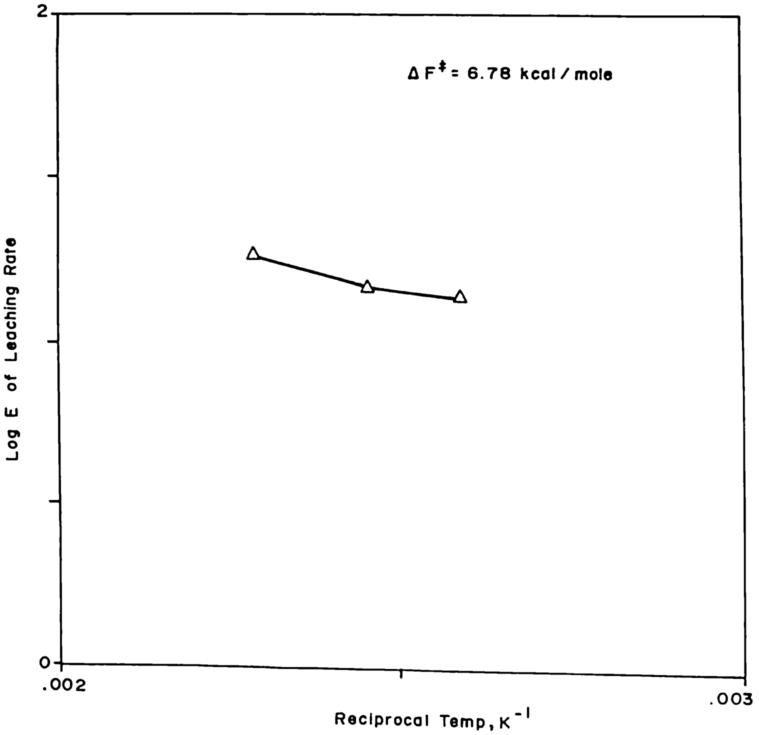


Table 3. Effect of Particle Size on the Leaching of Iron and Chromium.*

Time (hrs.)	% Cr Extraction	% Fe Extraction
Test 1 - particle size = 110 um		
1	0.099	4.349
2	0.121	4.638
3	0.142	4.830
5	0.185	4.930
10	0.227	5.336
20	0.266	5.526
Test 2 - particle size = 74 um		
1	0.099	4.434
2	0.169	5.139
3	0.189	5.445
5	0.232	5.532
10	0.272	6.001
20	0.288	6.063
Test 3 - particle size = 40 um		
1	0.197	4.392
2	0.290	5.307
3	0.355	6.345
5	0.463	7.414
10	0.522	9.124
20	0.621	12.741

* temperature = 70 C

% of Solids = 10 gm/250 ml

Acid Strength = 10 N

Figures 4 and 5 show the typical leaching curves of iron as a function of temperature and particle size, respectively. An attempt to model this behavior based on the topochemical leaching of equiaxed particles is presented in Figure 6 for chemical reaction control and Figure 7 for thickening product layer diffusion control[9]. Validity of the model is demonstrated by a straight line passing through the origin. This is obviously lacking in both figures. Furthermore, Figure 8 shows that the initial leaching rate of iron is not surface area (or particle size) dependent which precludes topochemical leaching as the possible mechanism[9].

The data presented in Figure 4 and 5 are replotted in Figures 9 and 10 but this time against the natural logarithm of time and a better linear fit is obtained. The logarithmic rate expression may be derived from consideration of the strain model proposed by Cook and Oblad[10]. In this model, the mineral lattice is assumed to be in a strained condition and as a metal, in this case iron, is leached out of the mineral, a systematic relief of strain occurs, stabilizing the mineral structure, thus making it more difficult to remove the remaining metal atoms. This results in a linear increase in the activation energy, $F^{=}$, with fraction extracted. The strain model has been used to explain the experimental results in the NTA dissolution of chrysocolla[11], the thermal decomposition of muscovite[12], and the adsorption of thoria on silica gel[13]

Consider the first order expression:

$$d\alpha/dt = A k_o \theta (1-\alpha) (kT/h) \exp(-\Delta F^{\ddagger}/RT) \qquad (1)$$

where

α = fraction extracted

θ = fraction of active surface sites

A = surface area

k_o = number of active sites

k = Boltzmann's constant

h = Planck's constant

R = gas constant

T = absolute temperature

t = time.

Fig 3. Effect of Surface Area on Extraction

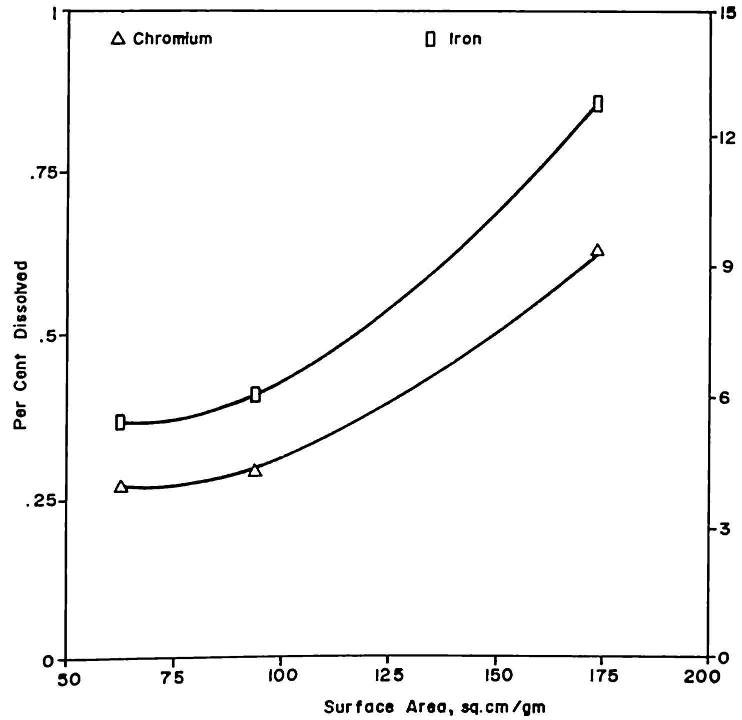


Fig 4. Effect of Temp on Fe Leaching

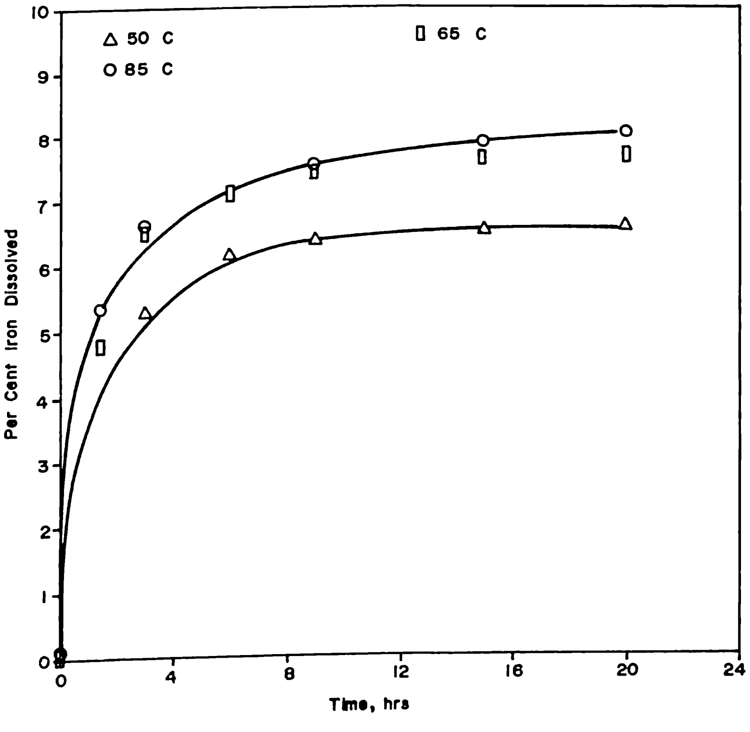


Fig 5. Effect of Particle Size

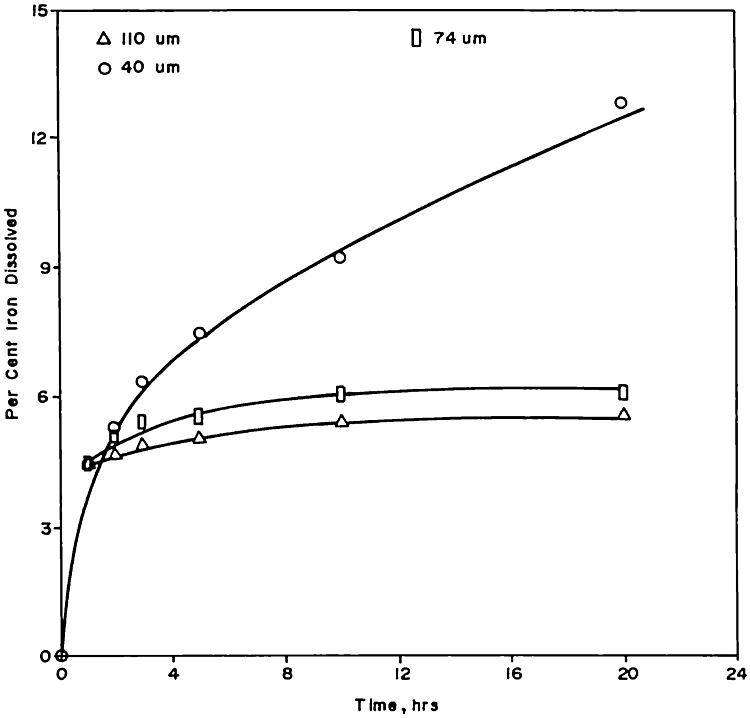


Fig 6. Chemical Rxn Control Modeling

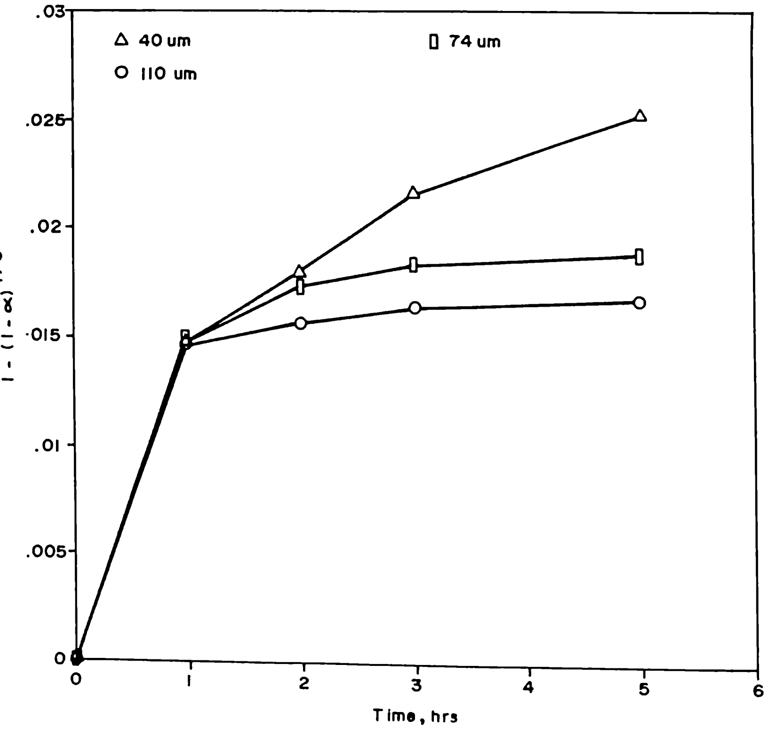


Fig 7. Product Layer Diffusion Modelling

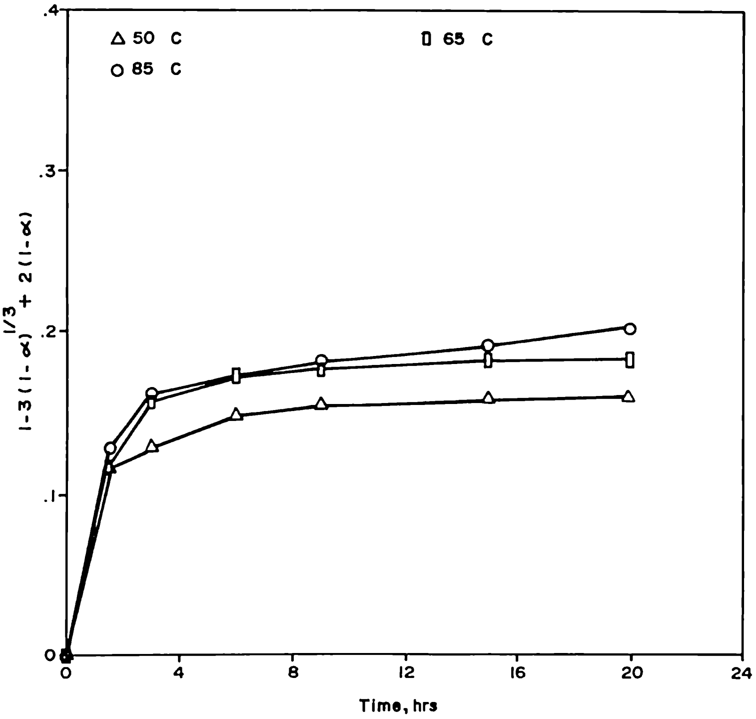
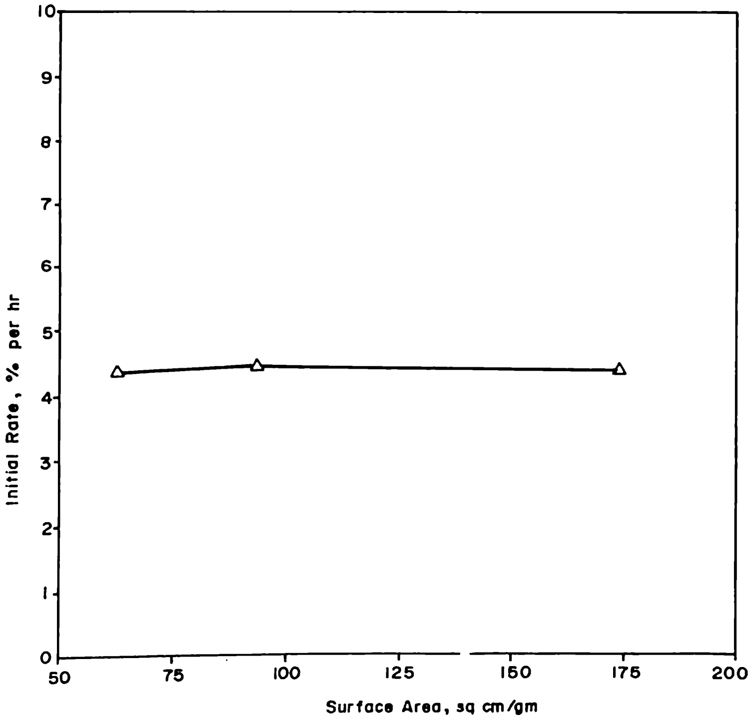


Fig 8. Particle Size Effect on Leaching Rate



Fig'9. Effect of Temp on Iron Leaching

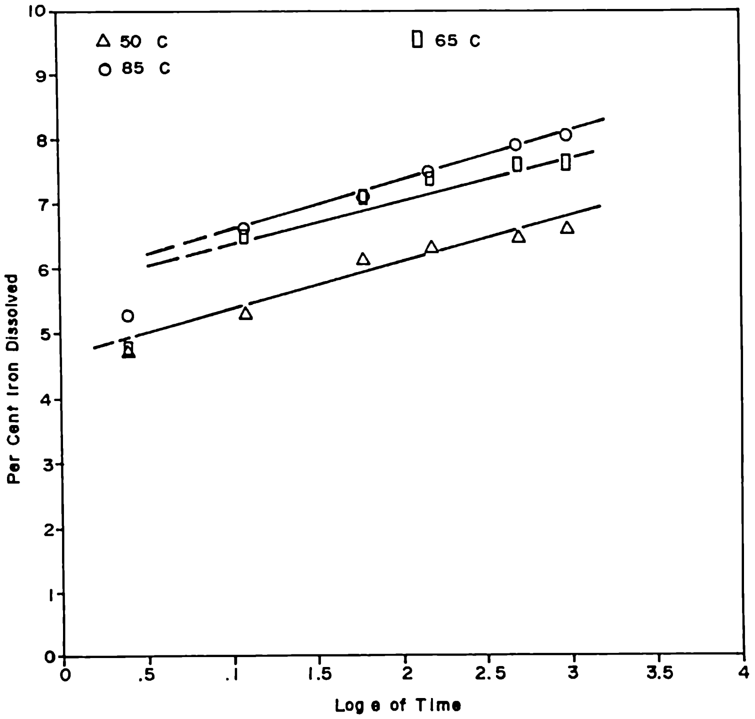
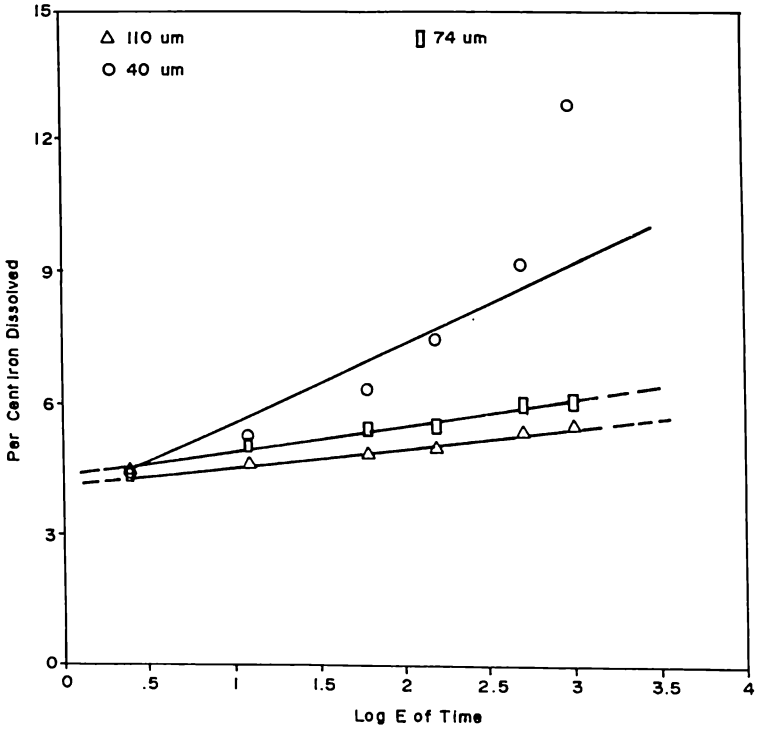


Fig 10. Particle Size Effect on Iron Leaching



Assuming that the activation energy increases linearly with the fraction extracted as represented by the equation,

$$\Delta F^{\ddagger} = \Delta F^{\ddagger}{}_{0} + b\alpha$$

where $D\ F^{=}{}_{o}$ is the activation energy of the solid at the state of maximum strain, substitution of this equation into Equation (1) yields

$$d\alpha/dt = Ak_{o}\theta\ (1 - \alpha)(kT/h)\ \exp\ (-\Delta F^{\ddagger}{}_{o}/RT - b\ \alpha/RT) \qquad (3)$$

At low values of α, Equation (3) simplifies into:

$$d\alpha/dt = Ak_{o}\theta\ (kT/h)\ \exp\ (-\Delta F^{\ddagger}{}_{o}/RT - b\alpha/RT) \qquad (4)$$

Defining B and D as

$$B = (b/RT) \qquad (5)$$

and

$$D = Ak_{o}\theta\ (kT/h)\ \exp\ (-\Delta\ F^{\ddagger}{}_{o}/RT) \qquad (6)$$

Equation (4) may be written as

$$d\alpha/dt = D\ \exp(-B\ \alpha) \qquad (7)$$

which integrates into:

$$\alpha = (1/B)\log_{e}(BD\,t + 1) \qquad (8)$$

showing that the fraction extracted plots linearly with the natural logarithm of time. Such behavior was also observed by Schader and Hoffman[6] wherein mechanically activated chromite was observed to dissolve completely in dilute hydrochloric acid solutions. Mechanical activation was accomplished by shear grinding in which a considerable amount of the grinding energy is converted into lattice distortion. The data presented in Figure 3 supports this phenomenon. It is expected that ore particles subjected to longer grinding periods (fine grinding) would have high lattice distortion.

The Cr/Fe ratio was optimized with respect to temperature and HCl concentration using Response Surface Methodology[14]. An initial surface was fitted at a temperature range of 35 to 55 C and 1 to 5 N HCl concentration and the following equation of the line with the steepest ascent was obtained:

$$Y = 1.596 + 0.018X_1 + 0.007X_2 \qquad (9)$$

where

$$X_1 = (\text{HCl conc} - 3) / 2$$

and

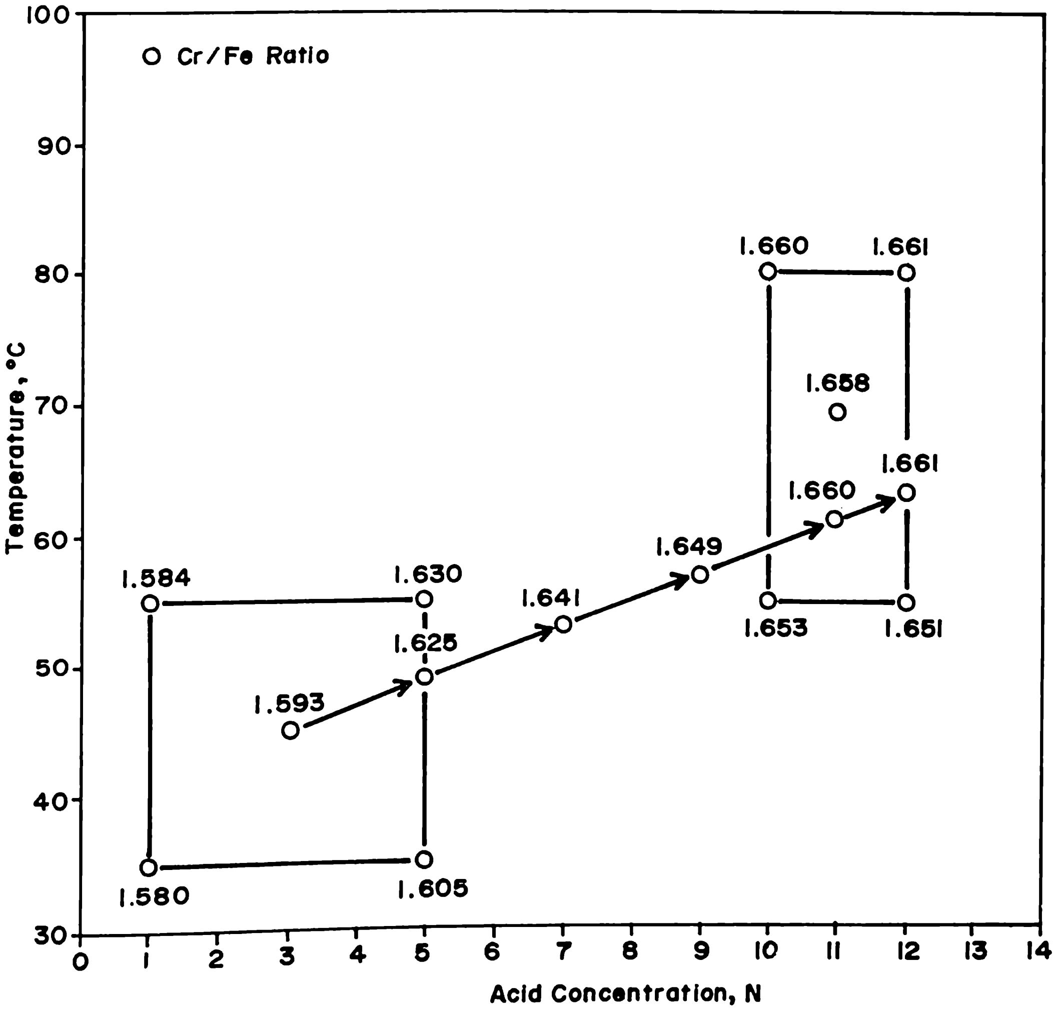
$$X_2 = (\text{Temp} - 45) / 10$$

The direction was followed until the practical limits with respect to HCl concentration was reached. A second surface was fitted in this vicinity which showed that the surface in this area is no longer flat. This means that the area is curved, which is chracteristic of the region of optimum response, as in a mountain wherein the slope decreases and virtually becomes zero at the summit.

CONCLUSION

The results show that iron dissolves from 15 to 30 times faster than chromium, making chemical beneficiation of chromite feasible. The Cr/Fe ratio is upgraded from a value to 1.576 to a final value of 1.661. The leaching of iron is logarithmic with respect to time, indicative of a dissolution reaction with a linearly increasing activation energy. This was explained in terms of the strain model wherein iron in the initially strained chromite spinel is easily leached while the residual iron in the stabilized mineral lattice becomes more difficult to extract.

Fig 11. Response Surface of Cr/Fe Ratio



REFERENCES

1. F. Habbashi (1970), Principles of Extractive Metallurgy, Vol. 2, Gordon and Breach Science Pub., N.Y.

2. R. R. Lloyd, et. al. (1946), The Electrowinning of Chromium from Trivalent Salt Solutions, Trans. Electrochemical Soc., Vol. 89, pp. 443-453.

3. R. R. Lloyd, et, al. (1948), Pilot Plant Production of Electrolytic Chromium, Trans Electrochemical Soc., Vol 94, pp. 122-138.

4. A. R. Burkin (1963), The Effects and Mechanism of Oxidation Reactions at Solid Surfaces during Leaching, Unit Processes in Hydrometallurgy, Gordon and Breach Science Publishers, pp. 80-94, N.Y.

5. G. Bonnivard (1967), Research on the Upgrading of Chrome-Bearing Laterites by Alkaline Roasting, The Canadian Mining and Metallurgy Bulletin, No. 12, pp. 1424-28.

6. R. Schrader and R. Hoffman (1970), Investigation of Leaching of Mechanically Activated Chromite, Chemie-Ingenieur-Technik, Vol 42, No. 1, pp. 38-40.

7. K. W. Downes and D. W. Morgen (1951), The Utilization of Low Grade Domestic Chromite, Canada Dept. of Mines and Technical Surveys, Mem. Ser. No. 116.

8. F. S. Boericke (1946), Selective Reduction of Iron in Chromite by Methane-Hydrogen and Similar Gas Mixtures, U.S. Bu. of Mines Report of Investigation No. 3847.

9. J. Szekely (1971), Rate Phenomenon in Process Metallurgy, John Wiley and Sons, N. Y.

10. M. A. Cook and A. G. Oblad (1953), Dynamic Mechanism of Heterogeneous Catalysis, Industrial and Eng'g. Chemistry, Vol..45, pp. 1456-1461.

11. R. Scheffel (1972), The Extraction of Copper from Chrysocolla with NTA, M. S. Thesis, University of Utah.

12. J. B. Holt et. al. (1958), Rate of Thermal Dehydration of Muscovite, Journal of the Am Ceramic Soc., Vol 41, pp. 242-246.

13. J. C. Cho and M. E, Wadsworth (1963), A Kinetic Study of Silica Gel Adsorption on Thoria Surfaces, Trans Society of Mining Engineers, Vol 226, pp. 287-292.

14. R. H. Myers (1971), Response Surface Methodology, Ally and Barn, Boston, Mass.