SOME ASPECTS OF THE
ACID DISSOLUTION OF HEMATITE

by

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We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA
March, 1968
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Date May 1, 1968
The dissolution of hematite ($\alpha$-Fe$_2$O$_3$) in hydrochloric acid solutions has been investigated. Sintered compacts, single crystals and particulate specimens were subjected to leaching over a range of temperatures and acid concentrations. The effects of varying the hydrogen and chloride ion concentrations independently were also investigated.

The dissolution was found to be highly anisotropic, the basal (0001) plane dissolving at a rate an order of magnitude greater than that of any of the other surfaces examined. Qualitative experiments indicated that this effect is also characteristic of dissolution in nitric, sulphuric and perchloric acids. The effect is attributed to the presence of a greater number of active dissolution sites on the basal plane, resulting from the anisotropic nature of the hematite crystal structure, and possibly also from the presence of a greater number of dislocations terminating on the basal plane.

The reaction rate was found to depend strongly on the acid concentration, increasing as the 2.5th power of the acid normality in the range 0.2-7.0N, and to vary independently with hydrogen and chloride ion concentrations. At acidities below 2N, the rate appears to vary with the product of hydrogen and chloride ion activities, while at concentrations in the range 2-7N, a linear dependence on hydrogen ion activity was observed. A tentative mechanism is proposed, in which protonation of the hydrated oxide surface is followed by adsorption of a chloride ion and desorption of a ferric-chloride complex.
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INTRODUCTION

I. GENERAL

The dissolution of oxides is of interest in several fields, including hydrometallurgy, structural ceramics and nuclear fuels technology.

In hydrometallurgy, leaching of low-grade oxide ores has long been standard practice. Many studies of the leaching of oxide minerals have been of a somewhat empirical nature, although extensive kinetic studies have been carried out on the acid dissolution of $\text{UO}_2$, $\text{Cu}_2\text{O}$ and $\text{MnO}_2$, among others.

The dissolution of oxides is also involved in the preparation of certain silicate raw materials, for example glass sands and various clays, where the treatment is usually aimed at the removal of iron oxides.

In some hydrometallurgical processes, the oxides in the ore constitute undesirable impurities rather than valuable ore minerals. In these cases it may be desirable to design process conditions so as to minimize their dissolution, in order to simplify or eliminate subsequent purification steps in the process.

The utilization of ceramic structural members in corrosive environments depends for its success on a knowledge of the dissolution characteristics of the materials. A recent paper by Dawihl and Klingler describes a study of the corrosion resistance of $\text{Al}_2\text{O}_3$ bodies to concentrated acids.

In nuclear fuels technology, the necessity for reprocessing spent fuel elements for the recovery of valuable constituents has led to the
development of leaching processes for oxide fuels. Several studies have been carried out in this context, for example those on the dissolution of $\text{UO}_2^6$ and $\text{ThO}_2^7$. BeO may be used as a moderator in certain homogeneous ceramic fuel elements, so that any study of the reprocessing of such a fuel must take into account the dissolution characteristics of BeO. Koch$^8$ has recently carried out a kinetic study of its dissolution in various acids.

Iron oxides are present in most ores in greater or lesser amounts, and in some secondary products, such as pyrite cinder, as the major constituent. Hydrometallurgical treatment of these materials may be complicated by the unwanted dissolution of iron oxides, making subsequent purification steps necessary. On the other hand, in the beneficiation of non-metallic minerals such as glass sands and clays, the maximum dissolution of iron oxides is the desired end. The mechanism by which these oxides dissolve is of interest from both these aspects.

The acid dissolution of ferric oxide has received some attention$^{9-14}$, but certain of the observed phenomena do not appear to have been fully explained. For instance, the very rapid dissolution in acids whose anions form strong complexes with the ferric ion has been noted$^9$, but not explained. The unusual S-shaped rate curves obtained by Azuma and Kametani$^{12}$ warrant further investigation, as does the fact that the activation energies for the dissolution reaction obtained by these workers are about twice the magnitude of those obtained by Furuichi et al.$^{13}$ It was with the hope of providing at least a partial answer to some of these problems that this study was undertaken.
II. REVIEW OF THE LITERATURE

Besides studies on the dissolution of ferric oxide, investigations of several other oxides are also discussed, since some of the results appear to have a bearing on the present work.

(a) Dissolution of Ferric Oxide

The most extensive previous investigations of the dissolution of ferric oxide have been by Pryor and Evans\(^9,10,11\) (1949), Azuma and Kametani\(^12\) (1964), and by Furuichi, Sato and Okamoto\(^13\) (1965). The work of Simnad\(^14\) and Smoluchowski\(^14\) on the effect of proton irradiation on the dissolution of ferric oxide, and that of Monhemius\(^15\) on the dissolution of goethite (\(\alpha\)-FeOOH), is also of interest.

Pryor and Evans carried out careful studies of both the reductive and direct dissolution of ferric oxide, as part of an extensive investigation into certain aspects of the passivity of metals. They examined the direct acid dissolution\(^8\) of chemically precipitated \(\alpha\)-Fe\(_2\)O\(_3\) after ignition at temperatures up to 1000°C. They found that \(\alpha\)-Fe\(_2\)O\(_3\) dissolves comparatively rapidly in hydrofluoric or concentrated hydrochloric acids, both of which form soluble complexes of high stability with the ferric ion. However, the bulk of their study was concerned with the dissolution of the surface layers (about 1% by weight of the oxide) in dilute solutions of hydrochloric, sulphuric or perchloric acids, which do not easily form these complexes. In these solutions the rate of dissolution was found to decrease with time, and the resulting solutions contained ferrous iron. The authors attributed the presence of this ferrous iron to preferential attack at surface defects involving oxygen deficiency. To maintain electrical neutrality, part of the iron would have to be in the ferrous state, and the lattice strain
associated with these defects would lead to the preferential removal of ferrous ions from the lattice. They attributed the fall in rate with time to the depletion of these defects at the surface, and showed that the original dissolution rate could be restored by heating the partially leached oxide to 1000°C, allowing defects to diffuse to the surface from the bulk of the oxide.

Azuma and Kametani\textsuperscript{12}, in a similar study, also noted a fall in rate with time, but only under certain conditions, namely low acid concentration and a high ratio of ferric oxide to solution volume. They attributed the decreasing rate to the fact that under the above-mentioned conditions, the solubility product of ferric hydroxide is approached as the concentration of ferric iron in solution increases. For this reason, the weight percent of dissolved oxide would be expected to vary with the particular experimental conditions i.e. solid to solution ratio and acidity, as was in fact observed by these authors.

Because of this, comparison of these two studies is difficult, but it appears that two distinct effects can operate to reduce the rate of dissolution:

(a) depletion of easily soluble defects at the oxide surface, and
(b) the saturation of the solution with Fe\textsuperscript{+++} so that the solubility product of Fe(OH)\textsubscript{3} is reached.

Depending on the particular experimental conditions, either or both of these effects may be operative.

The fall in rate observed by Pryor and Evans commenced almost immediately, being evident after only 0.05\% by weight of the oxide had been dissolved, whereas the decrease observed by Azuma and Kametani did not
begin until at least 1% dissolution had occurred. It is possible that the
difference could be explained by assuming a higher concentration of defects
in the material used by Azuma and Kametani, but as neither group of investi-
gators gave analyses for Fe$^{++}$ in their oxides, this cannot be confirmed.
The situation is further complicated by the complex rate curves obtained
by the Japanese workers.

It seems logical to conclude that two different effects were
observed by the two groups of investigators. Assuming that the decreasing
rate observed by Pryor and Evans was in fact due to depletion of surface
defects, then continued dissolution would presumably have yielded rate
curves of similar shape to those observed by Azuma and Kametani. On the
other hand, it is probable that these latter investigators did not note
this initial decrease in rate because their experiments were designed to
examine the dissolution to completion, and were not sensitive enough to
detect changes occurring in the dissolution of the first 0.1% of the oxide.
The fall in rate observed by them after the dissolution of 1% or more, was
due, as they suggested, to the approach of the system to the solubility
product of ferric hydroxide.

The initial rate of dissolution was found by Pryor and Evans to
be the same in dilute (0.01-2.0N) solutions of hydrochloric, sulphuric and
perchloric acids of equivalent concentration. They also observed that the
addition of 0.01 to 0.5N KCl to hydrochloric acid (0.01 to 0.1N) did not
influence the rate. At higher acid concentrations, the rate was found to
depend on the particular acid, decreasing in the order:

\[ HF > HCl > H_{2}SO_{4} > HClO_{4} \]

in accord with the order of decrease of the complexing affinity of the
anion for ferric ion. Azuma and Kametani, however, found that the rate of
dissolution depended on the type of acid, even at low concentrations. This difference, once again, can probably be attributed to the fact that Pryor and Evans were examining the removal of a defective surface layer, while the Japanese investigators observed the bulk dissolution.

Pryor and Evans concluded that the rate-determining step in the reaction was the combination of adsorbed hydrogen ions with oxygen ions in the lattice:

$$O_s^{-} + H_{ads}^+ = OH^-$$

or:

$$O_s^{-} + 2H_{ads}^+ = H_2O$$

Since the removal of one oxygen ion, as water or hydroxyl ion, does not involve the production or consumption of electrons, the reaction cannot create defects. Thus the rate of dissolution should be controlled by the number of defects originally present in the oxide surface. The transfer of an oxygen ion into solution leaves the surface positively charged. This charge can be dissipated only by the passage of iron ions into solution, since the temperature is too low to permit rapid self-diffusion. The initially rapid removal of oxide surrounding the surface defects is followed by a slower attack on the more perfect parts of the lattice, due to the stronger interionic forces associated with the defect-free lattice. It is this slower "bulk dissolution" which was probably observed by Azuma and Kametani.

Pryor and Evans\textsuperscript{10,11} coined the term "reductive dissolution" to describe the process occurring when a ferric oxide surface is continuously reduced to the ferrous state, so permitting more rapid dissolution. They used a cell in which ferric oxide powder floating on a pool of mercury constituted the cathode and a sheet of pure iron the anode. They found that both the rate and the current efficiency decreased with an increase
in the temperature of previous ignition, and with an increase in the pH of the electrolyte. They concluded that at pH values below 2.0, the rate of reductive dissolution is controlled by the surface conductivity of the oxide, and hence by the number of surface defects. The rate of reductive dissolution was found to be very much higher than that of direct dissolution.

Pryor\textsuperscript{11} proposed that the mechanism of reductive dissolution involves combination of hydrogen atoms, discharged at the ferric oxide surface, with oxygen ions belonging to the oxide lattice, to form either hydroxyl ions or water molecules which pass into the bulk of the solution. This reaction liberates electrons which reduce an equivalent number of ferric ions to the ferrous condition, thus creating a series of metal-excess type defects in the oxide surface, which then becomes particularly susceptible to direct acid attack.

Simnad and Smoluchowski\textsuperscript{14} investigated the effect of proton irradiation on the dissolution rate of \(\alpha\)-Fe\(_2\)O\(_3\) in 1.0N HCl solutions. Their specimens were prepared by oxidizing pure iron sheet, and were presumably finely polycrystalline. The irradiation treatment was found to increase significantly the rate of dissolution, presumably due to an increased concentration of lattice defects. The initial rates of dissolution of irradiated and unirradiated specimens were much the same, but after a layer approximately 6000 angstroms thick had been removed from the surface, the dissolution of the irradiated specimens was considerably accelerated.

It was suggested that the initial slow attack resulted from a lower concentration of defects in the surface layer due to their rapid outward diffusion. The apparent dissolution rate of both irradiated and unirradiated specimens increased rapidly with time. No explanation was offered for this observation.
Some comment seems necessary on the fact that while Pryor and Evans invoke the "slow" diffusion of oxygen vacancies at ordinary temperatures to explain their observed fall in rate, Simnad and Smoluchowski attribute the fact that the surface layers of irradiated and unirradiated \(\alpha\)-Fe\(_2\)O\(_3\) dissolve at the same rate, to the "rapid" diffusion of defects from the surface of the irradiated specimens. These two views appear contradictory, and it must be assumed that the nature and number of the defects in the latter investigators' specimens were very different from those in the ferric oxide studied by Pryor and Evans. It is to be expected that material subjected to proton irradiation would contain a high concentration of defects of various types, including vacancies and interstitials, which could contribute to an enhanced dissolution rate. It is also reasonable to expect that some of the defects formed in this way would be unstable and would disappear by recombination. Presumably, this would occur more easily at the surface, so accounting for the initially identical dissolution rates of irradiated and unirradiated specimens.

The work of Azuma and Kametani\(^{12}\) warrants further discussion, because of the complex shape of the rate curves they obtained. They studied the dissolution of ferric oxide powders in several inorganic acids over a wide range of concentrations and temperatures. On the basis of the shapes of the rate curves, they distinguished two types of dissolution, an "accelerated type", and a "parabolic type".

In the "accelerated type", dissolution was found to occur in three stages:

(i) an initial reaction in which the dissolved amount was nearly proportional to the cube root of time.

(ii) an accelerated region
and (iii): a final stage during which dissolution approached completion.

On a plot of log weight percent of oxide dissolved against log time, these rate curves appeared S-shaped.

In the "parabolic type", dissolution was found to proceed in four stages:

1) and 2) similar to those of the "accelerated type";
3) parabolic rate dissolution during which the dissolved amount of oxide was nearly proportional to the square root of time, and
4) a final stage.

Whether a powder dissolved according to the "parabolic type" or to the "accelerated type" appeared to depend on the method of preparation, and hence on the characteristics of the particles themselves. Extensive experiments were carried out only on powder specimens which dissolved according to the "accelerated type", and the rest of this discussion refers to this type of dissolution.

Azuma and Kametani confirmed that the dissolution rates in various acids decrease in the same order as the order of decrease of the complexing affinity of the anion for the ferric ion. They also suggested that the actual mechanism is independent of the type of acid and its concentration, since activation energies in the range $20 \pm 2$ kca\!/mole were obtained for all the acids investigated, over a wide range of concentrations.

These investigators also observed that there was a critical concentration, depending on the type of acid, below which the dissolution did not appear to go to completion. For concentrations below the critical, the shapes of the dissolution curves were no longer coincident, and the
amount of dissolved oxide increased with time to approach a finite value which was less than that for complete dissolution. The finite final concentration of Fe$^{+++}$ was found to be a function of acid concentration, suggesting an equilibrium between ferric oxide and the acid. It was concluded that the solubility product of ferric hydroxide was the controlling factor below the critical concentration. This suggested that the weight percent of oxide dissolved would vary with the ratio of the amount of oxide to volume of solution. This was confirmed by experiment. Thus the critical value should not be a constant for the acid, but dependent on the conditions of the experiment. Taking into account the limit of concentration of Fe$^{+++}$, the dissolution was found to proceed along the accelerated course even when the acidity was as low as 0.05N.

The shape of the curves obtained for dissolution in phosphoric acid appeared to be significantly different. The initial period of slow dissolution was not observed, and after about 100 hours the concentration of Fe$^{+++}$ in solution decreased abruptly due to the precipitation of an insoluble ferric phosphate.

A significant feature of this study is the similarity in shape of the curves obtained for dissolution in all acids (except phosphoric), despite wide differences in absolute rate due to type of acid, concentration and temperature. This holds true for powder prepared in a specific way - differences in preparation appear to change the shape of the curves somewhat. It is also significant that the shape of the curves cannot be explained by the assumption of uniformly dissolving, isotropic, spherical particles. The above observations suggest that the shape of the curves is not due to any "chemical" effect in the system but dependent on some physical property of the powder particles themselves.
Monhemius\textsuperscript{15}, in a study of the dissolution of natural goethite, \(\alpha\)-FeOOH, suggested that in acid solutions hydration of the oxide surface is followed by protonation and then by adsorption of an anion. This is followed by the rate-controlling desorption of the hydroxy-ferric complex. He also observed an initial accelerating region in the rate curves for dissolution in both sulphuric acid and acid sulphur dioxide solutions, similar to that obtained by Azuma and Kametani. It was suggested that this must be due to a property of the mineral itself, although no evidence was presented to support this view.

Furuichi, Sato and Okamoto\textsuperscript{13} studied the effects of ageing and roasting of ferric oxide precipitates on their subsequent dissolution in sulphuric acid solutions. They found that precipitates roasted between 350 and 400°C dissolved with average rates (over a period of 20 hours), independent of their previous ageing history, but dependent on roasting temperature, while those roasted below 350°C had average dissolution rates depending on both ageing and roasting treatments, the rate decreasing with increasing ageing time and roasting temperature. This behaviour was attributed to the change from an amorphous to a crystalline structure, and the development of a higher degree of crystallinity with higher roasting temperatures.

These authors obtained two-stage dissolution curves having an initial non-parabolic region followed by a parabolic region. For oxides roasted above 350°C, the non-parabolic region was not observed. The initial stage was considered to correspond to the dissolution of amorphous material, while the parabolic region represented the dissolution of well-crystallized oxide. The first stage was found to be fairly well described by a cubic rate equation based on a mechanism involving the adsorption of hydrogen ions.
on the surface as the rate-controlling step. Activation energies ranged from 4.8 to 12.3 kcals/mole, depending on ageing and roasting history.

In the parabolic region, i.e. the dissolution of well-crystallized material, the rate was found to be approximately proportional to acid concentration and unaffected by the addition of excess ferric ions to the solution. The activation energies calculated from the temperature dependence of the solution rate were of the order of 10-12 kcals/mole, depending somewhat on ageing and roasting treatments. Dissolution in this region was explained on the basis of a diffusion mechanism, in which diffusion of a proton into the surface of the oxide particle is the rate controlling step. The values obtained for the activation energy were compared with those for the diffusion of protons in $\alpha$-$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (12.9 kcals/mole)$^{16}$, and in $\alpha$-$\text{FeOOH}$ (16.5 kcals/mole)$^{17}$, and considered to be in good agreement.

Pryor and Evans$^9$ noted that the amorphous nature of iron oxide precipitates persisted even after roasting at temperatures up to 385°C. The maximum roasting temperature employed by Furuichi et al. was 400°C, so that it is quite possible, allowing for variations due to the conditions of precipitation, that the material they investigated was in no case a true, crystalline $\alpha$-$\text{Fe}_2\text{O}_3$. This might account, in part, for the low activation energies (10-12 kcals/mole), obtained by them, as compared with the values observed by Azuma and Kametani for $\alpha$-$\text{Fe}_2\text{O}_3$ (20 ± 2 kcals/mole), and by Monhemius$^{15}$ for $\alpha$-$\text{FeOOH}$ (18.2 kcals/mole). The very low activation energy (4.8 kcals/mole), observed for the dissolution of material roasted at low temperatures (110°C), suggests a mechanism controlled by the diffusion of an ion in the aqueous phase. This is reasonable, since the precipitate under these conditions would probably consist of a loose, porous aggregate of very fine particles. The steady increase in activation energy from 4.8
to 12.3 kcals/mole with increasing roasting temperature possibly represents a gradual transfer of control from diffusion in the aqueous phase to diffusion in the "solid" as the solid becomes less and less porous.

(b) **Dissolution of Other Corundum-Type Oxides**

\( \alpha - \text{Fe}_2\text{O}_3 \) is a member of the group of oxides having the general formula \( \text{R}_2\text{O}_3 \) and the corundum structure. This structure was first analyzed by W. H. Bragg and W. L. Bragg\(^\text{18}\), and later by Pauling and Hendricks.\(^\text{19}\) More recent work has confirmed the results of these investigators. Hematite has a rhombohedral structure, with the oxygen atoms in approximately close-packing, and the iron atoms occupying two-thirds of the octahedral holes in the oxygen lattice. Six oxygen atoms form an octahedral group around the metal atom, and each oxygen atom is surrounded by four metal atoms.

Besides \( \alpha - \text{Fe}_2\text{O}_3 \) and \( \alpha - \text{Al}_2\text{O}_3 \), the group includes \( \text{Cr}_2\text{O}_3 \), \( \text{V}_2\text{O}_3 \), \( \text{Ti}_2\text{O}_3 \), \( \alpha - \text{Ga}_2\text{O}_3 \) and \( \text{Rh}_2\text{O}_3 \).\(^\text{20}\) Because of the similarity of their structures, the dissolution of these oxides might be expected to have some features in common with the dissolution of \( \alpha - \text{Fe}_2\text{O}_3 \). However, a search of the literature failed to locate any work on the dissolution of these oxides.

Some work has been done, however, on the acid attack of \( \alpha - \text{Al}_2\text{O}_3 \). In an etch-pit study of flux-grown corundum, Champion and Clemence\(^\text{21}\) observed a marked difference in the ease with which the various crystal planes were attacked chemically. The basal planes were found to be most readily attacked, and the rhombohedral planes the least. Dawihl and Klingler\(^\text{5}\), in a study of the corrosion resistance of polycrystalline \( \alpha - \text{Al}_2\text{O}_3 \) and single crystal sapphire in hydrochloric, nitric and sulphuric acids, also noted a marked preferential attack on the basal plane. This plane appeared to dissolve at a rate approximately 40 times as great as that of the (1120) prism plane.
(c) Dissolution of Other Oxides

(i) UO$_2$ - Mackay and Wadsworth$^1$ leached sintered UO$_2$ specimens in sulphuric acid solutions under oxygen atmospheres. The rate was observed to be a function of the concentration of hydrogen ions, and to be directly proportional to the partial pressure of oxygen. The rate was also apparently independent of the particular acid used. The authors concluded that a UO$_2$ surface site reacts with a molecule of water to form a hydroxyl complex, which in turn can dissociate with the characteristics of a weak acid. A rate-determining step was proposed, involving the reaction between an oxygen molecule and the hydroxyl complex on the UO$_2$ surface.

(ii) SiO$_2$ - Most investigations into the solubility of quartz have been made in alkaline or neutral media. However, a brief discussion of some of this work is included here, since it appears that the adsorption of water on the surface is the rate-controlling step, just as it is in acids.

Siebert et al$^{22}$, in a study of the kinetics of the dissolution of the basal plane of quartz in water at high temperatures and pressures, came to the conclusion that the rate-controlling step is the reaction of water with the quartz surface, although the possibility of diffusion through a polymerized layer of silicic acid on the surface could not be excluded. These findings are in agreement with those of Hooley$^{23}$ for the dissolution of quartz in strongly alkaline solutions.

In a study of the silica-water system, Kennedy$^{24}$ quotes evidence of previous workers to the effect that the basal plane of quartz may dissolve in water or HF solutions at a rate 100 times as great as the hexagonal prism plane. Bergman et al$^{25,26}$ have studied the dissolution of
fine quartz powders in HF solutions. They found that particles with diameters greater than \(2\mu\) exhibited S-shaped dissolution curves, an upward trend in the curve appearing after the dissolution of 5-10% of the quartz. Since the possibility of an autocatalytic effect had been ruled out, as had the possibility of a change in average particle shape or size, it was concluded that the unusual dissolution curves reflected a change in the dissolving material other than one of available surface. Electron microscopy of replicas of partially dissolved particles revealed the development of distinct crystal faces, and this was taken as evidence that quartz possesses a number of preferred directions of dissolution normal to the crystal faces produced. The particles also showed surfaces on which no dissolution appeared to have occurred, evidence that the rate of etching of the preferred faces was many times that of the other surfaces. The preferred faces would accordingly tend to grow in area at the expense of the other surfaces, the proportion of fast-dissolving surface would increase rapidly, and an increase in the rate of dissolution during etching would result. This effect, coupled with the apparent decrease in rate as the dissolution neared completion, would give rise to the S-shaped rate curves.

(iii). Zinc-ferrite - In a study of the dissolution of zinc-ferrite in sulphuric acid, Nii and Hisamatsu observed that ferrite of oxygen-deficient composition dissolved more rapidly than that of stoichiometric composition. They concluded that anion vacancies or cation interstitials would be effective dissolution centres, and that the rate would be controlled by their concentrations. Additional support for this view was provided in an extension of this work to a study of the effect of reducing agents in the system. The addition of Fe metal powder, or of Fe ions, or the contact of the ferrite with a cathodically polarized electrode, all tended to increase the dissolution rate. This was ascribed to an increase in the anion vacancy concentration at the surface.
III. SCOPE OF THE PRESENT INVESTIGATION

The present investigation was originally intended to comprise the preparation of dense sintered specimens of $\alpha$-$\text{Fe}_2\text{O}_3$ and a study of their reductive dissolution using sulphur dioxide as a reducing agent. As a preliminary to the main investigation, some tests were carried out on the direct acid dissolution of hematite. The results of these tests, together with a review of the literature, suggested that there were aspects of the direct dissolution process that were not well understood, and that further work in this direction might be rewarding.

For instance, Azuma and Kametani\textsuperscript{12} offered no explanation for the S-shaped rate curves they obtained for the complete dissolution of ferric oxide powders in various acids, except to point out that they could not be explained by the assumption of uniformly-dissolving spherical particles. It was hoped that the present study might provide an explanation for this observation. Previous investigators\textsuperscript{9,12} have noted the very rapid dissolution of ferric oxide in hydrofluoric acid and concentrated hydrochloric acid, and ascribed it to the fact that the anions in these solutions form stable complexes with the ferric ion. However, the mechanism by which the dissolution rate is actually increased has not been explained, and in the present study this effect is examined by varying the anion concentration of the solutions independently of the hydrogen ion concentrations.

Hydrochloric acid was chosen for most of the test work for two reasons:

(i) conveniently measurable rates could be obtained in this system, and (ii) it provided the opportunity to examine the role of complex formation in the overall dissolution process.
In order to maintain a known, constant surface area during leaching, and to facilitate microscopic examination of leached surfaces, sintered discs of $\alpha$-$\text{Fe}_2\text{O}_3$ were used in the earlier tests, in preference to the relatively fine powders used by previous investigators. However, for reasons which will be discussed later, these gave neither linear nor reproducible dissolution curves. Qualitative results only are therefore presented for experiments on these specimens. The bulk of the experimental work was done on either single-crystal hematite specimens or on closely-sized synthetic $\alpha$-$\text{Fe}_2\text{O}_3$ powders.
EXPERIMENTAL

I. SPECIMEN MATERIALS AND REAGENTS

(a) Synthetic Polycrystalline and Powder Specimens

The sintered polycrystalline and powder specimens used in this study were prepared from reagent grade $\alpha$-Fe$_2$O$_3$ (Baker and Adams), without further purification. The maximum limits of impurities in this material are shown in Table I.

<table>
<thead>
<tr>
<th>Chemical analysis of reagent grade $\alpha$-Fe$_2$O$_3$.</th>
<th>weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble in HCl</td>
<td>0.20</td>
</tr>
<tr>
<td>sulfate (SO$_4$)</td>
<td>0.20</td>
</tr>
<tr>
<td>copper (Cu)</td>
<td>0.005</td>
</tr>
<tr>
<td>zinc (Zn)</td>
<td>0.005</td>
</tr>
<tr>
<td>Substances not precipitated by NH$_4$OH (as sulfates)</td>
<td>0.10</td>
</tr>
</tbody>
</table>

An x-ray diffraction pattern was made to confirm the identity of the material. The results agreed well with published data for $\alpha$-Fe$_2$O$_3$ (see Table BI, Appendix B).

(b) Natural Single Crystal Specimens

A group of natural hematite crystals originating in Itabira, Minas Gerais, Brazil, was obtained. These crystals showed several well-developed faces, some of which bore evidence of natural etching. The group consisted
of two large crystals partially intergrown with each other and with a polycrystalline matrix. The two large crystals were separated from each other and from the matrix by careful diamond sawing.

**X-ray diffraction:**

An x-ray diffraction pattern of some of the finely ground material showed all the major peaks for hematite, with no extraneous peaks, in agreement with published data\(^{28}\) (see Table B1, Appendix B).

**Chemical analysis:**

Portions of the single crystals were submitted to Coast Eldridge, Engineers and Chemists Ltd., for chemical analysis. Reported results are shown in Table 2(a), while Table 2(b) shows the values converted to the equivalent oxides.

**TABLE 2.**

Chemical analysis of natural hematite crystals.

(a) Values as reported

<table>
<thead>
<tr>
<th></th>
<th>weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (total)</td>
<td>69.14</td>
</tr>
<tr>
<td>Fe(^{++})</td>
<td>4.62</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.61</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1.34</td>
</tr>
</tbody>
</table>

(b) Values converted to equivalent oxides

<table>
<thead>
<tr>
<th></th>
<th>weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_2)O(_3)</td>
<td>92.10</td>
</tr>
<tr>
<td>FeO</td>
<td>5.94</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.61</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1.34</td>
</tr>
<tr>
<td>Total</td>
<td>99.99</td>
</tr>
</tbody>
</table>

The presence of a relatively large amount of ferrous iron (4.62%) is somewhat puzzling. \(\alpha\)-Fe\(_2\)O\(_3\) is known to deviate from stoichiometry,
usually exhibiting a slight metal excess, thought to be manifested as vacancies in the oxygen lattice. However, the variation from stoichiometry is small, usually barely detectable by chemical analytical methods. Microscopic examination of polished sections of the crystals failed to reveal the presence of intergrowths or precipitates of other minerals, and no explanation can be offered for the presence of such a large amount of divalent iron in the crystals. The only other impurities present in significant quantities were SiO₂ and Al₂O₃, neither of which would be expected to affect the results of the experiments.

(c) **Reagents**

Except for the natural single crystals, all materials used in this study were reagent grade. Distilled water was used for all solutions. Nitrogen was ordinary cylinder grade, supplied by Canadian Liquid Air Ltd.

II. **SPECIMEN PREPARATION**

(a) **Sintered Polycrystalline Compacts**

Although these specimens did not yield reproducible dissolution rates, their method of preparation will be described, since qualitative results are quoted.

Suitable test specimens had to satisfy the following requirements:

(a) Negligible open porosity. The presence of open or interconnected pores would lead to an uncertain solid-liquid interface area, and possibly to large changes in surface area during leaching.

(b) Freedom from cracks or flaws. Again, these imperfections would lead to uncertainties in surface area.
(c) Homogeneous and reproducible microstructure.

Initially a density of 95-96% of the theoretical value was aimed at, since it was felt that at this value, open porosity would be negligible. The theoretical density of $\alpha$-Fe$_2$O$_3$, as determined from lattice parameter measurements, is 5.25 gm/cm$^3$, so that 95% corresponds to a density of 5.00 gm/cm$^3$. In fact when satisfactory specimens were eventually produced, it was found that those with a density greater than 93% of the theoretical value had negligible open porosity.

Several methods of producing compacts were tried, including reactive hot pressing using synthetic goethite ($\alpha$-FeOOH) as starting material, conventional hot pressing, sintering of die-pressed compacts, and sintering of hydrostatically pressed compacts. Of these, only the last was fully successful. The specimens produced by the other methods were either badly cracked or showed marked inhomogeneities in polished sections.

The method finally adopted for the production of test specimens consisted in tamping 200 gm lots of reagent-grade ferric oxide powder into a thin rubber tube, which was then sealed and placed in a cylinder of oil. A hydrostatic pressure of 6000 psi was applied to the oil by means of a piston, and the pressure maintained for two minutes. The cylindrical green compacts (about 3 inches long by 1½ inches in diameter) were then sintered in air at temperatures ranging from 1000 to 1100°C, and for times ranging from 12 to 38 hours.

The sintered cylinders were sliced into 1/8 inch thick discs, using a diamond saw, and the discs ground flat on both sides with 240 mesh carborundum paste on an iron lapping wheel. A Mullard ultrasonic drilling unit, fitted with a one inch diameter thin-walled tubular cutting tool was
used to trim the discs into perfect circles. The same unit was used to
drill a 1/8 inch mounting hole in the centre of each disc. The surfaces
of the specimens were finished by conventional metallographic techniques,
0.05 µ alumina being used for the final polish.

Porosity determinations were made by rapidly weighing the shaped
specimens immediately after a two-hour immersion in boiling water. Bulk
densities were determined by drying overnight at 110°C, weighing, and
measuring thickness and diameter with a micrometer. Figure 1 shows the
relationship between sintered density and open porosity. Points on the
curve represent specimens prepared by sintering at temperatures from 1000
to 1100°C and for times from 12 to 38 hours. It is evident that specimens
with density greater than 4.9 gm/cm³ (93% theoretical), have open porosity
of less than 0.2% by volume. Microscopic examination of a polished section
showed that the discrepancy between actual and theoretical density is
accounted for by the presence of small, spherical pores within individual
grains, and occasional larger voids at grain boundaries (Figure 2).

(b) Synthetic Powder Specimens

Powder samples were prepared by crushing and grinding, in an
agate mortar, compacts which had been sintered in air at 1200°C for 60
hours. The powder was screened wet, and the plus 325 mesh, minus 270 mesh,
(44 µ - 53 µ) fraction was separated for dissolution tests. Wet screening
was employed to reduce the amount of very fine material adhering to the
larger particles. The narrow size range (44 µ - 53 µ) was chosen so as to
reduce as far as possible effects due to the change in distribution of
particle size during dissolution. Microscopic examination of the powder
showed roughly equiaxed grains, free from adhering fine dust.
Figure 1. Variation of open porosity with bulk density for sintered $\alpha$-Fe$_2$O$_3$ compacts.
Figure 2. Sintered $\alpha$-Fe$_2$O$_3$ compact, lightly etched with hot phosphoric acid to show grain boundaries (700x).
Chemical analysis, carried out by Coast Eldridge, Engineers and Chemists, Ltd., showed 70.0% total iron and 0.05% ferrous iron.

(c) Natural Crystal Specimens

In order to confirm that the two natural hematite crystals used in this study were in fact single crystals, Laue back-reflection x-rays were taken at several points on each. Identical patterns were obtained at the various points, and the sharp spots were taken to indicate a fairly high degree of crystalline perfection.

Test specimens of various crystallographic orientations were cut from these two crystals, conventional Laue back-reflection methods being used for the orientation. These specimens were then mounted in "Koldmount" self-curing resin with the oriented surfaces exposed, and the surfaces polished by conventional metallographic techniques. A more detailed description of the crystal orientation will be found under "Experimental Procedure".

III. APPARATUS DESIGN

Dissolution experiments were carried out in a glass reaction flask maintained at a constant temperature in a water thermostat. The main features of the apparatus are shown in Figure 3. The one-litre capacity flask was fitted with a nitrogen inlet tube and a sample tube, both having glass stopcocks. For tests on powder specimens, the lower end of the sample tube was fitted with a fritted glass filter. The solution in the vessel was stirred by means of a Teflon-covered magnet rotated by a magnetic stirrer unit below the thermostat vessel. Heat was supplied by a 100 watt immersion heater, connected to the mains supply through a variable
Figure 3. Schematic diagram of dissolution apparatus.
transformer. The temperature was controlled by a mercury-in-glass contact thermometer, connected to the heater circuit through a mercury relay. The water bath, contained in an insulated enclosure, was stirred continuously by a variable speed stirrer. Temperature was maintained within 0.2°C of the desired value by this arrangement.

Normally the vessel was open to the atmosphere, through a reflux condenser. However, in order to take a sample during a test, the appropriate stopcocks were closed, and a pressure of 5-10 psi of nitrogen was applied to the flask to force the solution out through the sample tube. Evaporation from the flask during a run was negligible.

Powder specimens were introduced into the flask by washing through the funnel (see Figure 3) with a small quantity of the test solution. Single crystal and sintered compact specimens were held in place in the solution by means of a glass rod extending to the bottom of the flask.

IV. EXPERIMENTAL PROCEDURE

(a) Orientation of Single Crystals

(1) Randomly oriented single crystal fragments.

Prior to the systematic investigation of the effect of orientation on the rate of dissolution, a number of single crystal fragments of hematite were mounted with random orientation in Bakelite mounts. The exposed surfaces were ground flat, polished, and etched for 10 minutes in boiling 5.0N HCl. Microscopic examination revealed wide variations in the degree of attack on different specimens. Back-reflection Laue x-rays were taken of those specimens showing strong attack.
(ii) Specifically oriented crystals.

In order to investigate the effect of crystal orientation on the rate of dissolution, it was necessary to prepare a series of specimens having surfaces parallel to various crystal planes. Conventional back-reflection Laue x-ray methods were used to determine the orientation of the specimens. FeK$_{α}$ radiation was used for all x-rays, with an exposure time of 20-40 minutes at 30KV and 10 mA.

The external morphology of the crystals allowed an estimate to be made of the position of the triad axis. When this had been confirmed and accurately located, a reference basal plane was cut on each crystal. Once this had been done, the positions of the other planes were easily determined. A simple two-circle goniometer was constructed to simplify this part of the work. Specimens having surfaces lying in the following crystallographic planes were cut:

(0001)
(2243)
(1010)
(1120)
(1011)

The specimens were mounted in "Koldmount" resin, and the oriented surfaces ground flat using 600 mesh alundum paste on an iron lapping wheel. The surfaces were finished by polishing with $15 \mu$ alumina, $1 \mu$ diamond paste and finally $0.05 \mu$ alumina. Where the same specimen was used for more than one test, the surface was ground and polished, as described above, before each test.

As a final check, Laue x-ray patterns were taken of all mounted
specimens, and it was confirmed that the orientation in each case was within 5° of the nominal plane. The methods available for cutting and grinding did not allow the preparation of more accurately oriented specimens, except possibly by tedious trial and error methods. However, in view of the very limited quantity of material available, it was decided not to attempt to improve on these orientations. The specimens were considered to be sufficiently accurately oriented for the purpose of the present investigation.

Since no tables of crystallographic angles or standard stereographic projections for α-Fe₂O₃ could be found in the literature, the values given by Winchell for α-Al₂O₃ were used for the orientation work. The differences in the lattice constants of these two isomorphous oxides are sufficiently small that the Laue patterns for α-Fe₂O₃ could be conveniently analyzed with the aid of the corundum data (see Table 3).

| TABLE 3 |

| Lattice constants for α-Al₂O₃ and α-Fe₂O₃ (referred to hexagonal axes). |
|-----------------|---|---|---|
| α-Al₂O₃         | 12.99 | 4.76 | 2.73 |
| α-Fe₂O₃         | 13.75 | 5.03 | 2.73 |

(b) **Dissolution Tests**

It has been shown that under conditions of low acidity and high ratio of ferric oxide to solution volume, the dissolution rate may fall with time, due to the saturation of the solution with ferric iron. In this study, experimental conditions were chosen to avoid this. Large solution volumes (500 ml) and small amounts of ferric oxide (0.1-0.2 gm) were
used.

The experimental procedure consisted of the following steps:
(i) the temperature controller was set at the required temperature.
(ii) the reaction flask, containing 500 ml of solution of the required concentration, was immersed in the thermostat, and the various connections made.
(iii) the system was allowed to come to thermal equilibrium.
(iv) the specimen was attached to the specimen holder and immersed in the solution. In the case of experiments on powder samples, a weighed quantity, usually 0.100 gm, occasionally 0.200 gm, of the material, was introduced into the flask by washing it through the funnel (see Figure 3) with a small quantity of the solution.
(v) samples were taken at intervals of 15, 30 or 60 minutes, depending on the expected rate, by applying a pressure of 5-10 psi of nitrogen to the flask to force a sample out through the sample tube. The first 10 ml of solution removed was immediately returned to the flask via the funnel, and a second sample of 6-7 ml taken. This was to ensure that the sample was not contaminated by traces of the previous sample remaining in the tube. Samples were collected in a sample bottle which was immediately stoppered to prevent vapor loss during cooling. After cooling, 1-5 ml, depending on the iron content expected, was pipetted from the sample, and the small excess returned to the flask. Runs were usually continued long enough to dissolve a minimum of 3% of the starting material. Samples were analyzed for iron as described in the following section.

At the end of each run, in the case of single crystal or compact specimens, the specimen was removed from the solution, washed with water and then alcohol, dried, and examined microscopically. Photomicrographs of the specimen surfaces were taken after many of the runs.
V. ANALYTICAL METHOD

The progress of dissolution was followed by spectrophotometric determination of the iron content of samples taken at regular intervals throughout the experiment.

Ferrous iron and 1-10 orthophenanthroline form an orange-red complex having a strong absorption peak at a wavelength of 510 μm. Absorption in dilute solutions of this complex obeys Beer’s Law and can be used for the quantitative determination of ferrous iron. Since most of the iron was expected to be in the trivalent state, hydroxylamine hydrochloride was added to each of the samples to reduce all iron to the ferrous state. Sample solutions were buffered at pH 4.5 with a sodium acetate-acetic acid buffer, since the coloured complex has been shown to be most stable in the pH range 2-9.

Procedure: A composite reagent was made up containing 0.3 gm/l. orthophenanthroline, 2.0 gm/li hydroxylamine hydrochloride and buffer. Suitable aliquots of sample solution were pipetted into 100 ml volumetric flasks, 25 ml of composite reagent added, and the volume made up with distilled water. The solutions were allowed to stand for at least 30 minutes (to ensure full development of the colour), before the optical densities were measured on a Beckman Model B spectrophotometer at 510 μm.

The concentration of iron was read from a calibration curve prepared using standard ferrous ammonium sulphate solutions, checked against a basic standard prepared from 99.9% pure iron wire.
RESULTS

For the sake of clarity, most of the results in this section are presented in the form of graphs, numerical results being grouped together in a separate appendix. This section is divided into three parts, each describing a separate phase of the work, as follows:

I. Tests on polycrystalline sintered compacts of $\alpha$-Fe$_2$O$_3$.

II. Tests on synthetic powder specimens.

III. Tests on natural hematite single crystals.
I. TESTS ON SINTERED POLYCRYSTALLINE COMPACTS

No quantitative results are presented for this phase of the investigation, since they are not considered informative enough to warrant inclusion. Reproducibility of rates in the leaching tests was poor, and non-linear rates were obtained, making interpretation difficult. The reason for both the above mentioned effects was found to be the strongly anisotropic nature of the dissolution. This is clearly demonstrated in Figure 4, which shows specimens after partial leaching in 1.0N HCl, 5.0N HClO\textsubscript{4} and 5.0N H\textsubscript{2}SO\textsubscript{4}. These micrographs show that while certain grains have been strongly attacked, others still exhibit traces of polishing scratches, indicating that virtually no dissolution has occurred. This selective attack was observed in specimens leached in HCl, HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4} and HClO\textsubscript{4}, at concentrations ranging from 1.0N to 6.0N. The rate of attack was qualitatively observed to be most rapid in HCl and slowest in HClO\textsubscript{4}, the rates in HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} being intermediate.

The poor reproducibility of leaching rates of these specimens is believed to result from the loosening of grains from the surface by dissolution of neighbouring grains, resulting in an increased area available for dissolution. This would result in a steadily increasing apparent rate of dissolution, as was observed in some tests, and in poor reproducibility between runs under identical conditions.

Although these tests did not give quantitatively reproducible results, they served to indicate the strongly anisotropic nature of the dissolution, and to point out the desirability of taking this into account in subsequent work.
Figure 4. Sintered polycrystalline compacts of $\alpha$-Fe$_2$O$_3$ after leaching under various conditions (700x).
(a) 1.0N HCl, 16 minutes at 100°C.
(b) 5.0N HClO$_4$, 90 minutes at 100°C.
(c) 5.0N HClO$_4$, 90 minutes at 100°C.
(d) 5.0N H$_2$SO$_4$, 5 minutes at 100°C.
II. SYNTHETIC POWDER SPECIMENS

The effects of the following variables on the rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder (-270 mesh, +325 mesh) in hydrochloric acid solutions were investigated:

(a) temperature

(b) acid concentration

(c) varying hydrogen ion concentration at constant chloride ion concentration

(d) varying chloride ion concentration at constant hydrogen ion concentration.

Except for those designed to examine the effect of temperature, all runs were carried out at 85°C. Linear rate curves were obtained for dissolution amounting to approximately 40% of the original material. After this, the apparent rate decreased as the available surface area of the powder began to decrease significantly. In the following rate curves, the number of milligrams of iron dissolved from a 0.100 gm sample of $\alpha$-Fe$_2$O$_3$ powder is plotted against time, due allowance being made for the iron content of samples removed during a run. All rates were measured on the initial linear part of the curves.

(a) Effect of Temperature

Typical rate plots for dissolution in 5.0N HCl at various temperatures are shown in Figure 5. The rate is seen to increase markedly with temperature. The effect of temperature on the rate of dissolution in 0.5N HCl was also investigated. The results of these tests are presented in Table A1, Appendix A, while Figures 6 and 7 are Arrhenius plots for dissolution in 5.0N and 0.5N HCl respectively. Activation energies determined from the slopes of these lines are 21.6±1.0 and 19.4±1.8 kcals/mole respectively.
Fe in solution (mgms.)

Figure 5. Typical rate curves. Effect of temperature on rate of dissolution of \(\alpha\)-Fe\(_2\)O\(_3\) powder in 5.0N HCl.
Figure 6. Arrhenius plot for dissolution of $\alpha$-Fe$_2$O$_3$ powder in 5.0N HCl.

$E_a = 21.6 \pm 1.0$ kcsals/mole.
$E_a = 19.4 \pm 1.8 \text{ k} \text{cals/mole.}$

Figure 7. Arrhenius plot for dissolution of $\alpha$-Fe$_2$O$_3$ powder in 0.5N HCl.
(b) Effect of Acid Concentration

The effect on the dissolution rate of varying the hydrochloric acid concentration in the range 0.2N to 7.0N was investigated. Figures 8 and 9 show that the rate increases rapidly with acid concentration. A log-log plot of this data gives a straight line with a slope of 2.5 over the whole range of experimental conditions, indicating an apparent 2.5 th power dependency of rate on HCl concentration. However, when the rate is plotted against activity, as in Figure 10(a), the rate appears to depend on the square of the hydrogen ion activity (or the product of the hydrogen and chloride ion activities) in the range 0.2-2.0N, and directly on activity in the range 2.0N-7.0N. Figure 10(b) shows the initial part of this plot (0 - 2.0N) on a larger scale, while in Figure 10(c) the rate in the range 0 - 2.0N is plotted against the square of the hydrogen ion activity.

Appendix C describes the estimation of the activities in HCl solutions, while numerical rate data are given in Table A2, Appendix A.
Figure 8. Effect of HCl concentration on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C - typical rate curves.
Figure 9. Effect of HCl concentration on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C.
Figure 10(a) Effect of hydrogen ion activity on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C.
Figure 10 (b) Effect of hydrogen ion activity on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder in dilute HCl solutions. (Initial part of Figure 10(a) plotted on larger scale.)

Figure 10 (c) Dissolution rate of $\alpha$-Fe$_2$O$_3$ powder in dilute HCl solutions as a function of the square of hydrogen ion activity.
(c) Effect of Varying Hydrogen Ion Concentration at Constant Chloride Ion Concentration

To investigate the independent effects of hydrogen and chloride ions, tests were carried out in which part of the HCl was replaced by an equivalent amount of KCl, so allowing the hydrogen ion concentration to be varied while keeping the total chloride ion concentration constant. Three sets of experiments were performed, with total chloride ion concentrations of 5.0N, 3.0N and 2.0N respectively. In each case the rate was found to increase, apparently linearly, with increase in hydrogen ion concentration [see Figures 11(a), (b), and(c)]. It was also noted that the rate of dissolution in solutions in which part of the HCl had been replaced by an equivalent amount of KCl was less than that in solutions of HCl of the same total ionic strength. The range over which the hydrogen ion concentration could be varied by this method was limited by the rather low solubility of KCl in concentrated HCl solutions. Numerical results are given in Table A3, Appendix A.
Figure 11. Effect of hydrogen ion concentration on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C and various constant chloride ion concentrations.
(d) Effect of Varying Chloride Ion Concentration at Constant Hydrogen Ion Concentration

Since the results of the foregoing experiments appeared to indicate that the dissolution rate was dependent on the concentrations of both hydrogen and chloride ions, tests were carried out to determine the effect of varying the chloride ion concentration independently of the hydrogen ion concentration.

Dissolution rates were determined in 1.0N, 2.0N and 4.0N HCl solutions to which varying amounts of KCl had been added. Results are shown graphically in Figures 12 (a), (b), and (c), and numerical results are given in Table A4, Appendix A. The rate increases approximately linearly with chloride ion concentration at a given hydrogen ion concentration.

Unfortunately, the dissolution rates in these mixed HCl-KCl solutions cannot be represented as functions of hydrogen and chloride ion activities, since only very scanty thermodynamic data are available at 25°C, and none at all at the experimental temperature (85°C). The degree of dissociation in these solutions is also unknown. It is clear from the available activity coefficient data for HCl solutions, and for HCl-KCl solutions at 25°C, that large deviations from unity are to be expected in the more concentrated solutions. This makes it impossible even to estimate the activities in these solutions, and therefore in Figures 11 and 12, dissolution rates are plotted as functions of added chloride (or hydrogen) ion at various concentrations of added hydrogen (or chloride) ion.
Figure 12. Effect of chloride ion concentration on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C and various constant hydrogen ion concentrations.
III. SINGLE CRYSTAL SPECIMENS

To investigate further the anisotropic nature of the dissolution process, a series of experiments was performed using natural single crystal hematite.

The effects of the following variables on the rate of dissolution were investigated:

(a) crystal orientation
(b) temperature
(c) acid concentration
(d) The above experiments were all carried out on oriented surfaces of single crystal specimens. In addition, the dissolution of a single crystal sphere was investigated.

(a) Crystal Orientation

(i) Randomly oriented crystal surfaces

Microscopic examination of randomly oriented single crystal surfaces, after etching in boiling 5.0N HCl for 10 minutes, showed wide variations in the degree and nature of attack from specimen to specimen. These differences were felt to be due to orientation differences, and to confirm that one (or possibly more) crystallographic plane(s) was dissolving at a far greater rate than any of the others, the orientations of those specimens showing severe attack were determined.

Of the fifteen specimens examined, seven showed surfaces etched to a greater or lesser degree, while the others were virtually unattacked. Back-reflection Laue patterns were obtained from those specimens showing
evidence of etching. Figure 13 is a simplified (0001) stereographic projection for $\alpha$-Fe$_2$O$_3$ on which have been plotted the orientations of the seven etched specimens. The surfaces all appear to be oriented close to the basal plane, suggesting that this plane, or possibly a high index plane close to it, is being most rapidly attacked.

In general, it was noted that those surfaces lying close to the (0001) plane appeared, after etching, to consist of pyramidal facets, with each of the three pyramidal faces approximately equally developed, while those situated further from the (0001) plane tended to have one facet developed at the expense of the others. This is illustrated in Figures 14 and 15 which show two of these surfaces, one (M8B) lying close to the (0001) plane, and the other (M6) situated some distance from it (see Figure 13).

These facets apparently correspond to particular crystallographic planes, since their orientation on any one specimen was constant over the whole surface, and was reproduced when the surface was polished and re-etched. Evidence was obtained in a later experiment to show that the facets represent the (1011) or the (1012) planes in the crystal.

(ii) Specifically oriented crystal surfaces

Figure 16 shows typical dissolution curves for single crystal specimens of five different orientations in 5.0N HCl at 85°C. Within the limits of experimental error, the plots are linear. Note that although specimen areas vary, the plots in this figure have been normalized so that each represents the dissolution of one cm$^2$ of surface. Table A5, Appendix A gives actual rates in terms of mgm.cm$^{-2}$, minute$^{-1}$. 

Figure 13. Simplified (0001) stereographic projection of $\alpha$-Fe$_2$O$_3$ with orientations of easily etched surfaces superimposed. M6 etc. represent sample numbers - see also Figures 14 and 15.
Figure 14. Specimen M8B after etching in 5.0N HCl for 10 minutes (700x). (see Figure 13).

Figure 15. Specimen M6 after etching in 5.0N HCl for 10 minutes (700x). (see Figure 13).
It is clear from these results that the rate of dissolution of the (0001) plane is very much greater than that of any of the other planes investigated, at least in strong HCl solutions. It was not possible to extend this series of experiments to other acids or to solutions of lower concentration because of the difficulty in measuring the rather low rates (due to the small available surface area). The rates on the other surfaces are all of the same order, apparently decreasing in the order:

\[(10\bar{1}0) > (1\bar{1}20) \approx (2\bar{2}4\bar{3}) > (1\bar{1}1)\]

and approximately an order of magnitude smaller than the rate on the basal plane. However, caution should probably be exercised in drawing conclusions from the relative magnitudes of these rates, as the reproducibility was not good (see Table A5, Appendix A). It is possible that the true rates on surfaces other than (0001) are in fact lower than indicated by the measured values. Due to inherent imperfections in the crystals, it was impossible to produce a flaw-free test surface by polishing. Fine cracks and pores were always present, and it is considered that dissolution of basally oriented regions exposed by these defects would contribute disproportionately to the overall dissolution rate. Microscopic examination did in fact reveal regions of severe attack, obviously initiated at surface defects, in otherwise essentially unetched surfaces. On the other hand, these defects would be of no significance in the basal specimens, since the areas exposed at cracks and pores would be of slow dissolving orientations, and would not affect the overall observed rate.

Microscopic examination of the surfaces after leaching revealed extensive etch-pit formation in the basal specimens. Figures 17(a) and (b) are optical micrographs of a basal surface after leaching in 5.0N HCl at 85°C for 3 hours. The sharp-edged triangular (or hexagonal) pits had the
Figure 16. Typical rate curves for dissolution of natural single crystal hematite - effect of orientation on dissolution in 5.0N HCl at 85°C.
Figure 17. Basal surfaces of natural hematite crystal after leaching in 5.0N HCl at 85°C for 3 hours (260x).
same orientation over the whole surface, and since they were reproduced after repolishing and etching, they are assumed to correspond to the intersection of dislocations with the surface. In some areas of the surface, these pits appeared to be concentrated within shallow, conical depressions (Figure 17(a)). These latter features were also reproduced after repolishing and etching, and therefore probably also represent dislocations. The micrographs show large areas, relatively free of pits, in which dissolution appears to have occurred by the stripping of layers parallel to (0001). No etch pits were observed in specimens other than (0001), possibly because dissolution was not continued for a sufficient length of time.

(b) Effect of Temperature

Two possible explanations were considered for the fact that dissolution of the basal plane is an order of magnitude greater than that of any of the other planes investigated:

(i) The number (or density) of "active dissolution sites" is very much greater on the basal plane.

(ii) The rate-determining step in the dissolution process is different for the basal plane.

If (i) is true, then the activation energy for dissolution should be the same for all planes, while if (ii) is the case, then a measurable difference might exist between the activation energy for dissolution of the basal plane on the one hand, and all other planes, on the other.

To test this hypothesis, the effect of temperature on the rates of dissolution of the (0001), (1010) and (2243) surfaces were measured in 5.0N HCl solutions. For each of these surfaces the rate of dissolution was determined at 75, 85 and 95°C. The results are illustrated (as Arrhenius
plots) in Figure 18, while numerical data are given in Table A6. The activation energies for dissolution determined from these data are:

\[
\begin{align*}
(0001) & : 22.6 \pm 2.2 \text{ kcals/mole} \\
(1010) & : 20 \pm 7 \text{ kcals/mole} \\
(2243) & : 24.1 \pm 2.3 \text{ kcals/mole}
\end{align*}
\]

(c) Effect of Acid Concentration

A series of tests was carried out to determine the effect of acid concentration on the rate of dissolution of the basal plane. The rate was found to increase with concentration in the range 3.0N to 6.0N, as shown in Figure 19 and in Table A7, Appendix A. The plot of log rate against log of acid concentration has a slope of approximately 3.

(d) Dissolution of Single Crystal Sphere

A small sphere, 6.5 mm in diameter, was ground from a natural single crystal of hematite and its dissolution in 6.0N HCl examined. Figure 20 shows the appearance of the sphere before dissolution and at various stages during the test. These macrographs show one of the two parallel "faces" developed on opposite sides of the sphere. Laue x-rays confirmed that these areas were centred around the poles of the c-axis. Virtually no attack was evident on the rest of the spherical surface, even after 90 hours in 6.0N HCl at 95°C. Also evident in these photographs is the pronounced faceting of the surface during the later stages of dissolution. These facets appeared to correspond to either the (1011) or to the (1012) planes in the crystal. A Laue back-reflection x-ray normal to one set of facets gave the (1012) pattern, but microscopic examination suggested the presence of two sets of facets, possibly (1011) and (1012).
Figure 18. Arrhenius plots for dissolution of (0001), (10\bar{1}0) and (22\bar{4}3) surfaces of natural hematite in 5.0N HCl.
Figure 19. Effect of HCl concentration on rate of dissolution of (0001) surface of natural hematite at 85°C.
Figure 20. Single crystal sphere of natural hematite at various stages during dissolution in 6.0N HCl at 95°C. (approx. 10x).
DISCUSSION

(a) Solution anisotropy

Many crystalline materials exhibit differences in chemical reactivity on different crystal planes. This has been ascribed to the effect of differences in atomic spacing or packing (and in some cases, composition) between different crystal planes, on the ease of adsorption of reacting ions or molecules. Since the heterogeneous reaction of a solid with its gaseous or aqueous environment necessarily includes the adsorption of an ion or molecule as one of the steps in the reaction sequence, this dependence on crystal orientation is not unexpected.

The anisotropy of surface reactivity has been observed in metals, covalent crystals and ionic crystals. The effect in metals is not very marked, the reactivity of the various surfaces (as measured by solubility in acids, for example) differing at the most by a factor of about three. The effect appears to be most pronounced in crystals of low symmetry, but is evident even in cubic metals. However, the relative magnitudes of the reaction rates on various planes also appear to depend on the experimental conditions, particularly the composition of the reactant.

Solution anisotropy appears to be more marked in non-metallic materials. For instance, evidence has been presented for the dissolution of the basal plane of quartz at a rate approximately two orders of magnitude greater than that of any other plane, while the basal surface of $\alpha$-$\text{Al}_2\text{O}_3$ (corundum) has been shown to dissolve in acids 40 times as rapidly as the $(11\bar{2}0)$ prism plane.

In the present study, the appearance of the surfaces of sintered
α-Fe$_2$O$_3$ specimens after leaching in acid solutions suggested that dissolution of this material is highly anisotropic (Figure 4). This anisotropy is thought to be the cause of the poor reproducibility and increasing rates observed for these specimens, as previously discussed. The single crystal experiments confirm that the basal plane dissolves, at least in hydrochloric acid solutions, at a rate approximately an order of magnitude greater than that of any of the other surfaces examined.

It has been postulated that some materials dissolve by different mechanisms on different crystal surfaces, e.g. germanium in the HF-H$_2$O$_2$-H$_2$O system is thought to dissolve as Ge$^{++}$ on the (100) and (111) surfaces, and as GeOF$_2$ on the (110) surface. In an attempt to detect a possible difference in the reactions occurring on the various surfaces of α-Fe$_2$O$_3$, activation energies were measured for the dissolution of (1000), (1010) and (2243) surfaces (Figure 18). Although the experimental errors are relatively large, the activation energies for the dissolution of the various surfaces are comparable. On the basis of this evidence, it is concluded that the relatively high rate of dissolution of the (0001) surface of α-Fe$_2$O$_3$ results from the presence of a greater density of "active dissolution sites" as compared with other surfaces, rather than from a difference in the reactions occurring.

In the present study, etch-pits, presumably representing the points of emergence of dislocations, were observed on the basal surfaces of α-Fe$_2$O$_3$ crystals after partial dissolution in HCl solutions (Figure 17). No etch-pits were observed on any of the other surfaces, possibly because dissolution was not continued long enough. It is assumed that dislocations emerging on the basal plane are revealed as etch-pits because of the more rapid dissolution normal to this plane. However, the possibility also
exists that this plane dissolves most rapidly precisely because of the presence of a greater density of dislocations. Evidence to the contrary is presented in Figure 17(a), in which large areas, apparently free of etch-pits, are evident. Dissolution has certainly occurred on these areas, as evidenced by the step-like layers revealed on the previously smooth-polished surface. These steps presumably correspond to the crystal planes parallel to the basal plane, rendered visible because of a slight deviation (up to 5°) of the surface from the true basal orientation. However, the fact that rapid dissolution appears to occur even in the absence of dislocations does not preclude the possibility that a higher density of dislocations emerging on the basal plane may contribute to a higher dissolution rate. It is suggested that the two effects may to some extent be complementary, the dislocations providing points at which the removal of a layer parallel to (0001) can begin. This hypothesis is supported by the results of Sunagawa who has made extensive studies of the surfaces of naturally grown and etched hematite crystals, using phase contrast microscopy. He has concluded that growth occurs mainly by the two-dimensional spreading of layers parallel to (0001), and that etching occurs by the reverse of this process, starting at steps in the surface, or at screw dislocations which terminate at the surface, and removing layers parallel to the basal plane.

The anisotropy of dissolution of $\alpha$-Fe$_2$O$_3$ observed in this study can be invoked to suggest a possible explanation for the experimental results of Azuma and Kametani, who obtained S-shaped rate curves for the dissolution of $\alpha$-Fe$_2$O$_3$ powders in acids. If the powder particles can be considered approximately spherical, then as dissolution proceeds they will tend to develop "crystal faces" normal to the direction of most rapid
dissolution. As dissolution continues on these "faces", they will grow at the expense of the slower-dissolving regions of the surface, and in so doing will provide a continuously increasing area for rapid dissolution. This results in an accelerating apparent rate of dissolution, which continues until the decrease in the total available surface begins to outweigh the increase in rapidly dissolving surface, and the apparent rate decreases. The net result is an S-shaped dissolution curve. This mechanism has been suggested by Bergman\textsuperscript{26} to account for the S-shaped dissolution curves obtained in a study of the dissolution of fine quartz particles in HF solutions. Since $\alpha$-$\text{Fe}_2\text{O}_3$ has been shown to dissolve anisotropically, the above is considered to be a reasonable explanation for Azuma and Kametani's results. It is probable that the increasing rate observed by Monhemius\textsuperscript{15} in the initial stages of dissolution of goethite ($\alpha$-$\text{FeOOH}$) results from the same effect. Goethite has a structure similar to that of hematite, and might be expected to dissolve anisotropically. In a recent study of the dissolution of covellite (CuS) in sulphuric acid-ferric sulphate solutions, Thomas and Ingraham\textsuperscript{41} observed an initial slow dissolution period followed by a linear rate period. They also noted that the material dissolved anisotropically. It is suggested that these two observations can be connected on the basis of the above mechanism. In general, fine particles of any material which has a strongly preferred direction of dissolution would be expected to give rate curves of this type. However, the precise shape of the curves would obviously depend on the degree of anisotropy, particle size and size distribution, and particle shape. Bergman noted that the effect in the dissolution of quartz was most marked within a certain particle size range, becoming less pronounced as the particle size was increased or decreased. This is suggested as an explanation for the absence of the effect in the present series of tests on powdered $\alpha$-$\text{Fe}_2\text{O}_3$.\textsuperscript{42}
The facets developed on single crystal surfaces oriented close to the basal plane (Figures 14, 15 and 20) appear to correspond to either the (10\(\overline{1}1\)) or (10\(\overline{1}2\)) planes in the crystal. These would appear to be the most stable surfaces in acid solutions. Further evidence for this is provided by the fact that of all the surfaces examined, the (10\(\overline{1}1\)) dissolved at the slowest rate (Table A5).

(b) Reaction mechanism

The results of the experiments on particulate \(\alpha\)-Fe\(_2\)O\(_3\) indicate that:

(i) The rate of dissolution in HCl solutions increases with temperature, the observed activation energies being \(19.4^{+1.8}_{-1.8}\) and \(21.6^{+1.0}_{-1.0}\) kcals/mole in 0.5 and 5.0N solutions respectively.

(ii) The rate of dissolution increases with acid concentration, the apparent order of the increase depending on whether normality or hydrogen ion activity is used as the measure of concentration (see discussion below).

(iii) The dissolution rate increases approximately linearly with hydrogen ion concentration at constant chloride ion concentration.

(iv) The rate increases approximately linearly with chloride ion concentration at constant hydrogen ion concentration.

The activation energy observed for dissolution in 0.5 and 5.0N HCl solutions agrees reasonably well with the value \(20^{+2}_{-2}\) kcals/mole obtained by Azuma and Kametani\(^{12}\) for the dissolution of ferric oxide particles in various inorganic acids. It is also high enough to indicate that the rate is controlled by a surface reaction, rather than by diffusion in the aqueous phase. It compares with values of \(13.7\) kcals/mole for the dissolution of BeO in HCl\(^{8}\), 18 kcals/mole for goethite (\(\alpha\)-FeOOH) in H\(_2\)SO\(_4\)\(^{15}\), and
+ 22-1 keals/mole for covellite in ferric sulphate-sulphuric acid.\(^{41}\) All of these reactions are considered to be chemically controlled. It is concluded that diffusion in the aqueous phase plays no rate-controlling role in the reaction examined in this study. This is in contrast to the work of Furuichi et al., on the dissolution of aged and calcined ferric oxide precipitates, in which diffusion in the aqueous phase appeared to be an important factor. This difference is probably due to the relatively much larger particle size employed in the present study.

The marked dependence of rate on HCl concentration was noted by Pryor and Evans, who suggested that it was the result of the high complexing affinity of the chloride ion for ferric iron. In the present investigation, the rate appears to depend on the 2.5\(^{th}\) power of the HCl normality (or molarity) in the range 0.2-7N. However, if hydrogen ion activity is taken as the measure of concentration, it appears that at lower acidities (0.2-2N), the rate varies with the square of the hydrogen ion activity (or with the product of hydrogen and chloride ion activities). While at higher concentrations (2-7N), the rate depends directly on the hydrogen ion activity. The rate data of Azuma and Kametani were replotted as a function of hydrogen ion activity, and a similar dependence was noted. It should however be noted that there is some uncertainty in the activity values used (see Appendix C).

The effects on the rate of independently varying the hydrogen and chloride ion concentrations in mixed HCl-KCl solutions unfortunately cannot be considered in terms of the activities of these ions. Only very scanty activity data are available for HCl-KCl solutions at 25°C, and apparently none at all at higher temperatures. However some qualitative conclusions may be drawn from the results of the tests in mixed solutions.
Figures 11 and 12 show the effects of varying the hydrogen (chloride) ion concentration at constant chloride (hydrogen) ion concentration. Changes in both hydrogen and chloride ion concentrations appear to affect the rate. This suggests that chloride as well as hydrogen ions take part in the reaction. However, it seems more likely that, at least at concentrations above 2N, the observed effect of chloride ion (Figure 12) is due to changes in the hydrogen ion activity in the solutions, rather than to a direct dependence of the rate on chloride ion activity.

The available data (at 25°C) on activities in HCl-KCl solutions indicate that the activity coefficient of HCl (and therefore also of H⁺) is increased by the addition of KCl to concentrated HCl solutions.

In addition, the evidence of Figure 10(a), showing rates in pure HCl solutions, indicates that, at least at concentrations above 2N, the reaction is first order in hydrogen ion.

The second-order dependency at lower concentrations (0.2-2N) implies that either two hydrogen ions, or one hydrogen and one chloride ion are involved in the reaction. Unfortunately, the tests in mixed HCl-KCl solutions were not extended into this concentration range, so definite conclusions regarding the roles of H⁺ and Cl⁻ ions in this region cannot be drawn.

It is now well established that oxide surfaces are hydrated to a greater or lesser extent in aqueous solutions. Several investigations have been made of the adsorption of ions at the ferric oxide-solution interface, and models proposed for the nature of the oxide surface at this interface. Parks and de Bruyn view the process as occurring in two steps; a surface hydration, followed by dissociation of the surface hydroxide. The hydration step may be visualized as an attempt
by the exposed surface atoms to complete their coordination shell of nearest neighbours. Exposed cations accomplish this by pulling an OH\textsuperscript{-} ion or water molecule and the oxygen ions by pulling a proton from the aqueous solution, the net result being that the surface is covered by a hydroxyl layer with the cations buried below the surface. The process by which the surface charge is established may be viewed as either an adsorption of H\textsuperscript{+} or OH\textsuperscript{-} ions, or as a dissociation of surface sites which may assume a positive or negative charge.

To explain the results of a study of the kinetics of proton adsorption at the ferric oxide-solution interface, Onoda and de Bruyn postulated the existence of a goethite-like interphase separating the bulk anhydrous oxide from the solution phase. The composition of this transition region would be expected to vary with the pH of the solution, and it is not certain that the surface would have the form suggested by Onoda and de Bruyn under the highly acid conditions of the present study, since their experiments were performed in solutions of relatively high pH. However, for present purposes, it is sufficient to assume simple hydration of the surface as suggested by Parks and de Bruyn, and shown schematically below:
The evidence available does not allow a reaction mechanism to be deduced with certainty. However, a tentative mechanism which is consistent with the observed results is suggested for the dissolution of ferric oxide in HCl solutions. For convenience, a site on the oxide surface can be represented by:

\[ \text{s-Fe-OH} \]

In strongly acid solutions, this is likely to be partly protonated, and an equilibrium can be written as follows:

\[ \text{s-Fe-OH} + \text{H}^+ \xrightleftharpoons{K_1} \text{s-Fe}^+ + \text{H}_2\text{O} \]  \[1\]

The surface site constitutes an ion-exchange position, which may adsorb a chloride ion:

\[ \text{s-Fe}^+ + \text{Cl}^- \xrightarrow{K_2} \text{s-Fe-Cl} \]  \[2\]

The complexed ferric ion may now desorb from the surface. To account for the fact that the activation energy for the dissolution is similar in different acids, this is postulated to be the rate-determining step in the sequence:

\[ \text{s-Fe-Cl} \xrightarrow{K_1} \text{s-Fe}^+ + \text{Cl}^- \xrightarrow{K_2} \text{FeCl}_\text{aq} \]  \[3\]

The overall reaction can be represented by:

\[ \text{s-Fe-OH} + \text{H}^+ + \text{Cl}^- \rightarrow \text{FeCl}_\text{aq} + \text{H}_2\text{O} \]  \[4\]

and the rate equation is:

\[ \frac{d(\text{Fe})}{dt} = -k_1k_2k_1\left[ \text{s-Fe-OH} \right] a_{\text{H}^+} a_{\text{Cl}^-} \]  \[5\]

where \( \left[ \text{s-Fe-OH} \right] \) represents the number of active sites on the surface, and \( a_{\text{H}^+} \) and \( a_{\text{Cl}^-} \) - the activities of \( \text{H}^+ \) and \( \text{Cl}^- \) ions in the solution.

If the number of sites on the surface is assumed constant, then the rate is seen to depend on the \( \text{H}^+ \) and \( \text{Cl}^- \) ionic activities. The above
would therefore appear to be a reasonable qualitative explanation of the mechanism of dissolution in the range 0-2N. Different absolute rates in various acids can be attributed to differences in the value of $K_2$, i.e. effectively, differences in the complexing affinity of the anion for ferric iron. Azuma and Kametani have shown a positive correlation between the rates in various acids and the association constants of their anions for $Fe^{+++}$. It is not suggested that the species $FeOCl_{aq}$ necessarily exists as such, but it is likely that an intermediate of this type will precede the formation of the final product.

The linear dependence of rate on hydrogen ion activity observed at higher HCl concentrations may result from the shifting of the equilibrium of equation [2] well to the right. Dissolution may then proceed via another protonation of the surface site:

$$Fe-O-Cl + H^+ \xrightleftharpoons{K_3} FeCl^{++} + OH^- \quad [6]$$

(or possibly $Fe-O-Cl + H^+ \xrightleftharpoons{K_3} Fe-OH-Cl^+$)

which would be followed by the rate-determining desorption of the Fe complex:

$$Fe^{++} \xrightarrow{k_2} FeCl^{++}_{aq} \quad [7]$$

The rate equation is then:

$$\frac{d(Fe)}{dt} = k_2K_3 [Fe-O-Cl]_{aq} a_{H^+}$$
CONCLUSIONS

(1) The dissolution of $\alpha$-Fe$_2$O$_3$ in HCl solutions is highly anisotropic, the basal surface dissolving at a rate an order of magnitude greater than that of any of the other surfaces examined. The effect is also evident in dissolution in H$_2$SO$_4$, HNO$_3$, and HClO$_4$. This anisotropy is attributed to a difference in the relative numbers of active dissolution sites available on the various crystal surfaces. This is due ultimately to the highly anisotropic nature of the hematite crystal structure, and possibly also to a greater density of dislocations on the basal plane.

(2) The use of pressed polycrystalline specimens for dissolution rate studies on anisotropic materials can give rise to confusing results due to preferential leaching of favourably oriented grains leading to an increase in available surface area.

(3) The dissolution rate is controlled by a surface reaction.

(4) The strong dependence of the rate on HCl concentration is due to the large increase in hydrogen ion activity with acid concentration. The rate of dissolution depends on the anion as well as the hydrogen ion concentration in solution. Whether this implies direct participation of the anions in the reaction, or whether it is a secondary effect due to changes in hydrogen ion activity brought about by the addition of chloride ions, has not been conclusively determined.

(5) A tentative mechanism for the dissolution reaction involves protonation of the hydrated oxide surface, adsorption of a chloride ion, and the rate-determining desorption of the ferric-chloride complex.
Suggestions for future work

(1) The role of the anion in the dissolution reaction at low acid concentrations is not yet clear. To some extent this is due to the choice of KCl as a source of excess Cl\(^-\) ions in the solutions. A better choice would have been LiCl, since the Li\(^+\) ion is closer in size to the H\(^+\) ion than is the K\(^+\) ion, and the activity coefficient of HCl in mixed HCl-LiCl solutions is little affected by the addition of LiCl at a constant LiCl + HCl molality. An investigation of dissolution in solutions of this type might throw more light on the reaction mechanism. Extension of this work to other acids would determine whether or not the anion effect is restricted to HCl solutions.

(2) The dissolution of goethite (\(\alpha\)-FeOOH) in SO\(_2\) solutions has recently been investigated. Since it appears that the initial step in the dissolution of hematite is the hydration of the surface to give a structure analogous to that of goethite, it would be informative to compare the dissolution of hematite in SO\(_2\) solutions.

(3) High purity synthetically grown single crystals of\(\alpha\)-Al\(_2\)O\(_3\) and \(\alpha\)-Cr\(_2\)O\(_3\) (isomorphous with \(\alpha\)-Fe\(_2\)O\(_3\)) are commercially available. Dissolution tests on material of this kind would eliminate the uncertainties of the present study on natural crystals, and by testing specimens in which various amounts of deformation had been introduced, it might be possible to decide whether dislocations contribute significantly to the enhanced dissolution of the basal plane, or whether this is due entirely to the anisotropy of the rhombohedral crystal structure.
REFERENCES

22. H. Siebert, W. V. Youdelis, J. Leja and E. O. Lilge in "Unit Processes
in hydrometallurgy", Gordon and Breach Science Publishers, Inc.,

1729 (1948).
60 (1938).
34. H. C. Gatos, Science, 137, 311 (1962).
183 (1958).
Note: In most of the tests on powder specimens, 0.1 gm of $\alpha$-Fe$_2$O$_3$ powder was used. However, in some tests, where the expected rate was low, 0.2 gm samples were used. All rates given in the following tables have been normalized to apply to the dissolution of 0.1 gm samples.
APPENDIX A

TABLE A1

Effect of temperature on the rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder in HCl solutions (Figures 5, 6 and 7).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Rate mgms/min.</th>
<th>Temp. °C</th>
<th>Rate mgms/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.050</td>
<td>75</td>
<td>0.056x10^{-2}</td>
</tr>
<tr>
<td>75</td>
<td>0.130</td>
<td>80</td>
<td>0.085x10^{-2}</td>
</tr>
<tr>
<td>85</td>
<td>0.312</td>
<td>85</td>
<td>0.108x10^{-2}</td>
</tr>
<tr>
<td>95</td>
<td>0.688</td>
<td>90</td>
<td>0.257x10^{-2}</td>
</tr>
</tbody>
</table>
### TABLE A2

Effect of HCl concentration on the rate of dissolution of α-Fe₂O₃ powder at 85°C. (Figures 8, 9 and 10).

<table>
<thead>
<tr>
<th>Normality</th>
<th>Hydrogen ion activity ( a_{H^+} )</th>
<th>Rate mgms/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.15</td>
<td>0.011x10⁻² **</td>
</tr>
<tr>
<td>0.5</td>
<td>0.35</td>
<td>0.11x10⁻² **</td>
</tr>
<tr>
<td>1.0</td>
<td>0.72</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.005</td>
</tr>
<tr>
<td>2.0</td>
<td>1.78</td>
<td>0.033</td>
</tr>
<tr>
<td>3.0</td>
<td>3.39</td>
<td>0.096</td>
</tr>
<tr>
<td>4.0</td>
<td>5.89</td>
<td>0.191</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.179</td>
</tr>
<tr>
<td>5.0</td>
<td>10.0</td>
<td>0.312</td>
</tr>
<tr>
<td>6.0</td>
<td>16.9</td>
<td>0.536</td>
</tr>
<tr>
<td>7.0</td>
<td>27.0</td>
<td>0.783</td>
</tr>
</tbody>
</table>

* See Appendix C for estimation of activities.

** ** 0.2 gm. samples.
APPENDIX A

TABLE A3

Effect of varying hydrogen ion concentration at constant chloride ion concentration on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C. (Figure 11(a), (b) and (c)).

<table>
<thead>
<tr>
<th>[Cl$^-$] = 5.0N</th>
<th>[Cl$^-$] = 3.0N</th>
<th>[Cl$^-$] = 2.0N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H$^+$] Rate mgms/min.</td>
<td>[H$^+$] Rate mgms/min.</td>
<td>[H$^+$] Rate mgms/min.</td>
</tr>
<tr>
<td>3.9 0.253</td>
<td>2.0 0.053</td>
<td>1.0 0.012*</td>
</tr>
<tr>
<td>4.0 0.257</td>
<td></td>
<td>1.5 0.022</td>
</tr>
<tr>
<td>4.25 0.264</td>
<td>2.25 0.056</td>
<td>1.75 0.025</td>
</tr>
<tr>
<td></td>
<td>0.272</td>
<td>0.062</td>
</tr>
<tr>
<td>4.5 0.285</td>
<td>2.5 0.075</td>
<td></td>
</tr>
<tr>
<td>4.75 0.298</td>
<td>2.75 0.081</td>
<td></td>
</tr>
<tr>
<td>5.0 0.312</td>
<td>3.0 0.096</td>
<td>* 0.2 gm sample</td>
</tr>
</tbody>
</table>
APPENDIX A

TABLE A4.

Effect of chloride ion concentration at constant hydrogen ion concentration on rate of dissolution of $\alpha$-Fe$_2$O$_3$ powder at 85°C. (Figures 10(a), (b) and (c)).

<table>
<thead>
<tr>
<th>$[H^+]$ = 1.0N</th>
<th>$[H^+] = 2.0N$</th>
<th>$[H^+] = 4.0N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Cl^-]$</td>
<td>Rate mgms/min.</td>
<td>$[Cl^-]$</td>
</tr>
<tr>
<td>1.0</td>
<td>0.006*</td>
<td>2.0</td>
</tr>
<tr>
<td>1.5</td>
<td>0.008*</td>
<td>2.5</td>
</tr>
<tr>
<td>2.0</td>
<td>0.012</td>
<td>3.0</td>
</tr>
<tr>
<td>2.5</td>
<td>0.016</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 0.2 gm samples

5.25  0.270
APPENDIX A

TABLE A5

Effect of crystal orientation on the rate of dissolution of natural hematite in 5.0 N HCl at 85°C. (Figure 16).

<table>
<thead>
<tr>
<th>Crystal orientation</th>
<th>Rate mgm.cm.$^{-2}$ min.$^{-1}$ x 10$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>2.61</td>
</tr>
<tr>
<td>(1120)</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
</tr>
<tr>
<td>(10$ar{1}$1)</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>(10$ar{1}$0)</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>(22$ar{4}$3)</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>0.32</td>
</tr>
</tbody>
</table>
Effect of temperature on the rate of dissolution of (0001), (1010) and (2243) surfaces of natural hematite in 5.0N HCl (Figure 18).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Rate (mgm.cm.$^{-2}$ min.$^{-1}$ x $10^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0001)</td>
</tr>
<tr>
<td>75</td>
<td>1.04</td>
</tr>
<tr>
<td>85</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>2.61</td>
</tr>
<tr>
<td>95</td>
<td>6.15</td>
</tr>
</tbody>
</table>
**APPENDIX A**

**TABLE A7**

Effect of HCl concentration on the rate of dissolution of the basal (0001) surface of natural hematite at 85°C. (Figure 19).

<table>
<thead>
<tr>
<th>HCl concentration (normality)</th>
<th>Rate $\text{mgm. cm.}^{-2} \text{min.}^{-1} \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.56</td>
</tr>
<tr>
<td>4.0</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>1.39</td>
</tr>
<tr>
<td>5.0</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>2.61</td>
</tr>
<tr>
<td>6.0</td>
<td>4.76</td>
</tr>
</tbody>
</table>
# APPENDIX B

## TABLE B1

X-ray diffraction results for various $\alpha$-Fe$_2$O$_3$ specimens used in this study.
Radiation FeK$\alpha$, Mn Filter.

<table>
<thead>
<tr>
<th>ASTM Powder Diffraction File</th>
<th>Baker and Adams Reagent Grade $\alpha$-Fe$_2$O$_3$</th>
<th>Synthetic Powder Specimen (Sintered 60 hrs. at 1200°C)</th>
<th>Brazilian Hematite Crystals (Sintered 12 hrs. at 1100°C)</th>
<th>Polycrystalline Sintered Specimen (Sintered 12 hrs. at 1100°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>$I/I_1$</td>
<td>$\theta$</td>
<td>$I/I_1$</td>
<td>$\theta$</td>
</tr>
<tr>
<td>3.66</td>
<td>25</td>
<td>3.67</td>
<td>35</td>
<td>3.67</td>
</tr>
<tr>
<td>2.69</td>
<td>100</td>
<td>2.69</td>
<td>100</td>
<td>2.69</td>
</tr>
<tr>
<td>2.51</td>
<td>50</td>
<td>2.51</td>
<td>70</td>
<td>2.51</td>
</tr>
<tr>
<td>2.201</td>
<td>30</td>
<td>2.20</td>
<td>30</td>
<td>2.20</td>
</tr>
<tr>
<td>1.838</td>
<td>40</td>
<td>1.84</td>
<td>40</td>
<td>1.84</td>
</tr>
<tr>
<td>1.690</td>
<td>60</td>
<td>1.69</td>
<td>45</td>
<td>1.69</td>
</tr>
<tr>
<td>1.596</td>
<td>16</td>
<td>1.60</td>
<td>15</td>
<td>1.60</td>
</tr>
<tr>
<td>1.484</td>
<td>35</td>
<td>1.48</td>
<td>30</td>
<td>1.48</td>
</tr>
<tr>
<td>1.452</td>
<td>35</td>
<td>1.45</td>
<td>25</td>
<td>1.45</td>
</tr>
</tbody>
</table>

**Note:** Since the diffraction peaks were relatively narrow and sharp, their heights were taken to be an approximate measure of their intensity, relative to the height of the strongest peak.
APPENDIX C

Estimation of Hydrogen Ion Activity in HCl Solutions

The activity of an electrolyte which ionizes as

\[ X = n^+ X^+ + n^- X^- \]

is defined by

\[ a = a_+ \cdot a_- \]

where \( a_+ \) and \( a_- \) are the ionic activities.

The mean ionic activity is defined by

\[ a^+ = a_n^+ \]

where \( n = n^+ + n^- \).

For HCl, which ionizes as

\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]

\[ a = a_+ \cdot a_- \]

and

\[ a_+ = (a_+ \cdot a_-)^{1/2} \]

The mean molality, \( m^+ \), is defined by

\[ m^+ = m(n^+ n^-) \]

\[ = m \text{ in the case of a } 1-1 \text{ electrolyte} \]

The mean activity coefficient \( \gamma^+ = a_+^+ \), so that

\[ m \gamma^+ = (a_+ \cdot a_-)^{1/2} \]

If we assume

\[ a_+ = a \]

then

\[ a_+ = m \gamma^+ \]

Several groups of investigators have calculated values of \( \gamma^+ \) from measurements of the EMF of the cell

\[ \text{Me}/\text{HCl}(m)/\text{AgCl} - \text{Ag} \]

Harned and Ehlers determined activity coefficients in solutions ranging from 0.004 m to 4 m between 0 and 60°C. Åkerlöf and Teare extended these measurements to the range 3 m to 16 m, between 0 and 50°C. Faita and Massini have recently redetermined \( \gamma^+ \) in the range 0.00555 m to 9.251 m and 0 to 50°C. In order to obtain values of
the activity coefficient for use in this study, it was necessary to extrapolate the above data to the experimental temperature (85°C).

For particular values of \( m \), \( \gamma^\pm \) in the relevant concentration range was plotted as a function of temperature (on log-log coordinates), and the lines extrapolated to 85°C. Values of \( \gamma^\pm \) determined in this way are plotted as a function of molality in Figure C1.

![Figure C1: Mean activity coefficient of hydrochloric acid in aqueous solution at 85°C, determined by extrapolation of literature data in the range 0 - 60°C.](image)

Density data in the International Critical Tables were used to convert molarity values to molalities. Early conductivity measurements and more recent vapour pressure determinations suggest that dissociation is incomplete in HCl solutions as dilute as 0.1 molar. However, agreement between values for the degree of dissociation determined by these two methods is very poor. Application of proton magnetic resonance methods to the study of concentrated...
acid solutions has yielded evidence that HCl is fully dissociated even in 12 molar solutions. In view of the conflicting evidence, it was decided to assume for the purposes of this study that dissociation is complete in all solutions.

Hydrogen ion activities were calculated from

\[ a_{H^+} = m \gamma^\pm \]

where \( a_{H^+} \) = hydrogen ion activity

\( m \) = molality

\( \gamma^\pm \) = ionic activity coefficient.

Table C 1 shows values of \( m \), \( \gamma^\pm \) and the calculated values of \( a_{H^+} \) for the concentration range of this study.

**TABLE C 1**

Hydrogen Ion Activities in HCl Solutions at 85°C

<table>
<thead>
<tr>
<th>HCl normality</th>
<th>HCL molality m</th>
<th>( \gamma^\pm )</th>
<th>( a_{H^+} = m \gamma^\pm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.20</td>
<td>0.73</td>
<td>0.15</td>
</tr>
<tr>
<td>0.5</td>
<td>0.51</td>
<td>0.69</td>
<td>0.35</td>
</tr>
<tr>
<td>1.0</td>
<td>1.02</td>
<td>0.71</td>
<td>0.72</td>
</tr>
<tr>
<td>2.0</td>
<td>2.09</td>
<td>0.85</td>
<td>1.78</td>
</tr>
<tr>
<td>3.0</td>
<td>3.20</td>
<td>1.06</td>
<td>3.39</td>
</tr>
<tr>
<td>4.0</td>
<td>4.36</td>
<td>1.35</td>
<td>5.89</td>
</tr>
<tr>
<td>5.0</td>
<td>5.57</td>
<td>1.80</td>
<td>10.0</td>
</tr>
<tr>
<td>6.0</td>
<td>6.84</td>
<td>2.48</td>
<td>16.9</td>
</tr>
<tr>
<td>7.0</td>
<td>8.18</td>
<td>3.30</td>
<td>27.0</td>
</tr>
</tbody>
</table>