THE DISSOLUTION OF GOETHITE IN AQUEOUS
SOLUTIONS OF SULPHUR DIOXIDE

BY

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The leaching of goethite in perchloric acid ("direct leaching") and in acidified sulphur dioxide solutions ("reductive leaching or dissolution") has been investigated. The effects of temperature, hydrogen ion concentration, sulphur dioxide partial pressure, stirring speed and sample weight on the reductive leach rate have been studied. The enhancement of the reductive leach rate as a consequence of adding cupric ions was also investigated.

A leaching mechanism was proposed for the direct and uncatalyzed reductive dissolution. Protonation of the oxide surface sites, described by a Langmuir Adsorption Isotherm, resulted in the formation of ferric-hydroxy species. These either desorbed (the single solution step in direct leaching) or underwent the adsorption of a sulphur dioxide molecule possibly followed by another hydrogen ion. The overall reductive leach rate was a function of the desorption of the intermediate and the final surface species.

Cupric ions did not appear to directly catalyze a step in the postulated reductive dissolution mechanism. Rather, the essential feature of their catalytic role was thought to be an electron exchange reaction between Cu$^{I}$ and Fe$^{III}$ on the oxide surface to form cupric and ferrous ions in solution. An anionic cuprous species capable of adsorbing on the oxide surface was formed by cupric ion reduction with aqueous sulphur dioxide and subsequent complexing with bisulphite and/or sulphite ions.

A comparison of the reductive leach rates of magnetite and hematite with goethite was made both with and without the presence of cupric ions.
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1. INTRODUCTION

1.1 General

The leaching of iron oxides from silicate minerals is a widely practised industrial process (1). The presence of iron oxides in silica and alumino-silicates lowers their commercial value in such processes as high quality glass-making (silica sands) and paper filling and coating (kaolinite).

Potential applications for the leaching of iron oxides also exist in the metallurgical industry for treating residues from various processes, and possibly for upgrading low grade iron ores. Solution mining of hydrated iron oxide ores with aqueous sulphur dioxide solutions has also been proposed (2).

The increase in demand for iron powders may be met by a leach and gaseous reduction reaction, with iron oxide ores as the raw material (3).

Goethite, α-FeOOH, is the most common iron mineral contaminating industrially important silicate minerals. Although many studies on the direct and reductive leaching of other iron oxides have been reported (4-14), there has been less work done on the kinetics and mechanism of goethite dissolution (1,10,11,15-18).

Industrially, goethite has been leached from acidified clays by the
addition of sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, at room temperature (1). Dithionite was either added to the clay suspension, or produced in it by a variety of ways. This method of iron removal suffered from the poor stability of dithionites in acidic aqueous solutions, the relative chemical inertness of dehydrated iron oxides to dithionites, and the relative expensiveness of dithionites.

This investigation was undertaken to determine the kinetics and mechanisms involved in the reductive dissolution of goethite using acidified sulphur dioxide solutions, with and without catalysts.

1.2 Iron Oxides

The preparation and properties of iron oxides have been reviewed (15,17).

Goethite is equivalent to ferric oxide monohydrate, $\alpha$-$\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. Dehydration to $\alpha$-$\text{Fe}_2\text{O}_3$ is reported as occurring between 120-150°C (19-22). The transition is believed to be pH dependent, goethite being converted to hematite after a few weeks in 0.1 N HCl at 100°C (23).

As a consequence of the reported transition temperature, the majority of experiments were carried out at 110°C or less.

1.3 Review of Related Work

1.3.1 Reductive Dissolution of Iron Oxides by Aqueous Sulphur Dioxide

Monhemius (15) has reviewed the reactions between ferric ions ($\text{Fe}^{\text{III}}$) and aqueous sulphur dioxide in homogeneous systems and in a heterogeneous system using freshly precipitated ferric hydroxide (4).
Monhemius (15,16) studied the reductive dissolution of goethite in acidified sulphur dioxide solutions. Perchloric acid was used to acidify solutions since the perchlorate anion has very weak complexing powers, and the strong acid merely behaves as a source of hydrogen ions. His experiments suffered from poor reproducibility and corrosion of his (steel) equipment. He found that the leaching rate at first increased with time, becoming linear after one hour. The leaching rate increased with aqueous sulphur dioxide concentration in a non-linear fashion. At low (< 0.2 Molar) aqueous sulphur dioxide concentrations ([SO₂•Aq]), the rate of leaching was approximately independent of sample weight, perchloric acid concentration (over the range 0.07 to 0.28 M) and aqueous sulphur dioxide concentration. At higher aqueous sulphur dioxide concentrations the reaction became heterogeneously controlled, with the leach rate becoming inversely proportional to the hydrogen ion concentration. The reaction rate increased with increase in aqueous sulphur dioxide concentration.

Attempting to develop a leaching mechanism common to both goethite and hematite, for both direct and reductive dissolution, Monhemius postulated the following mechanism: (slightly revised as a consequence of later information).

1. Hydration of the hematite surface to become similar to goethite:

\[
\frac{1}{\text{Fe}_2\text{O}_3} + \text{H}_2\text{O} \quad \xrightleftharpoons{K_1} \quad \frac{2}{\text{FeOOH}}
\]

/ denotes the oxide surface.
With synthetic hematite this reaction was reported as having been very slow (21), whereas it was rapid with natural hematite (24). Infrared absorption studies had identified hydroxyl (OH) groups on the α-ferric oxide surface (25). Two hydroxyl groups were formed as a consequence of the reaction between a chemisorbed water molecule and a surface oxide ion. The chemisorbed water prevented the complete surface coverage of α-ferric oxide by a monolayer of physisorbed water (26). It may be removed by high temperature activation.

Goethite exhibited complete surface coverage by water and per unit surface area was more reactive towards water than hematite. Hydroxyl groups in goethite had been detected by infrared spectros copy (27). Hydrated hematite surfaces had been found to have the properties of goethite (24).

2. Protonation of the hydrated surface:

\[
\text{FeOOH} + \text{H}^+ \underset{\text{fast}}{\text{K}_2} \text{Fe(OH)}_2^{\oplus}
\]

\(\oplus\) denotes a positive surface charge.

The zero points of charge (z.p.c.) of natural hematite and natural goethite were reported to be at approximately pH 6.7 (27,28). The actual value of the z.p.c. depended on such factors as purity and hydration state. Synthetic hematite had a z.p.c. at pH 8.5. At hydrogen ion concentrations greater than that corresponding to a pH of 6.7 the surfaces developed positive charges.

Proton adsorption and positive charge development on hydrated iron
oxide surfaces had been investigated by several authors (28-31). The existence of a goethite-like layer on hematite immersed in water was inferred from the results of one investigation (30).

3. Double protonation of the surface:

\[ \text{Fe(OH)}_2^+ + H^+ \xrightleftharpoons{K_3} \text{FeOH}^+ + H_2O. \]

This had been postulated as occurring at pH values less than about 2 on hematite (32).

4. Anion adsorption:

\[ \text{FeOH}^+ + X^- \xrightleftharpoons{K_4} \text{Fe(OH)}X^+ \]

The ability of anions to adsorb on goethite and hydrated ferric oxide had been extensively reported (5,6,33-35). It had been shown that when some anions were adsorbed on goethite they might be coordinated with Fe$^{3+}$ (35). The rate of dissolution of hematite had been shown to decrease in the order HF > HCl > H$_2$SO$_4$ > HClO$_4$, in accord with the decrease in complexing power of the anion for Fe$^{3+}$ (5). A subsequent investigation had shown that other factors were also important in determining the dissolution rate (6). The anions adsorbed as a consequence of the net positive charge on the hematite/goethite surface in low pH solution. Adsorption of anions was pH dependent. In a system with more than one anion present, the one which was most able to increase the negative charge of the surface was preferentially adsorbed (35).
5. Desorption of a hydroxy-ferric complex:

\[
\frac{1}{\text{Fe(OH)}X^{\ominus}} \xrightarrow{k_5} \text{Fe(OH)}X^{\ominus,(aq)}.
\]

Rate equation:

\[
\frac{d[\text{Fe}_{aq}^{\ominus}]}{dt} = k_5K_4K_3[H^+][X^-][1/\text{Fe(OH)}_2^{\ominus}]
\]

By postulating that \([1/\text{Fe(OH)}_2^{\ominus}]\) was a constant, since the establishment of equilibria 1 and 2 (\(K_1\) and \(K_2\)) were assumed to be fast, this expression accounted for the results of the experiments on the direct dissolution of goethite and hematite.

Monhemius considered that aqueous sulphur dioxide molecules were the leaching species in the reductive dissolution experiments, and proposed a dual dissolution mechanism based on the direct dissolution model (16):

Mechanism (a). After steps 1 and 2:

6. Adsorption of aqueous sulphur dioxide molecules:

\[
/\text{Fe(OH)}_2^{\ominus} + 2\text{SO}_2_{aq} \xrightarrow{K_6} /\text{Fe(SO}_3)_2^{\ominus} + 2H^+
\]

\(\ominus\) denotes a negative surface charge.

7. Desorption of a ferric sulphite complex:

\[
/\text{Fe(SO}_3)_2^{\ominus} \xrightarrow{k_7} \text{Fe(SO}_3)_2^{-,(aq)}
\]

Ferric ions were known to complex with bisulphite and sulphite anions (36).
Rate equation:
\[
\frac{d[Fe_{aq}]}{dt} = \frac{k_7 K_6 [SO_{2\,aq}]^2 [Fe(OH)_2]}{[H^+]^2}
\]

Mechanism (b). After steps 1 and 2:

8. Adsorption of aqueous sulphur dioxide molecules:

\[
\frac{K_8}{[Fe(OH)_2]^2 + 2SO_{2\,aq}} \rightleftharpoons \frac{K_9}{Fe(HSO_3)_2}
\]

9. Desorption of a ferric bisulphite complex:

\[
Fe(HSO_3)_2^{\oplus} \rightarrow k_9 Fe(HSO_3)_2^{+}
\]

Rate equation:
\[
\frac{d[Fe_{aq}]}{dt} = k_9 K_8 [SO_{2\,aq}]^2 [Fe(OH)_2]
\]

The rate of dissolution was the sum of these two rate equations (mechanisms (a) and (b)). Mechanism (a) was considered to be more important at low [SO_{2\,aq}], low [H^+], since the anionic ferric sulphite complex formed could readsoorb onto the positively charged surface. Homogeneous control then resulted, the rate determining step being the reduction of ferric to ferrous in solution (4).

Surana (17,18) continued the study of the direct and reductive dissolution of goethite. Using acidified aqueous solutions of sulphur dioxide, he observed a continually increasing rate of dissolution for
experiments of 2 1/2 hours duration. He found that the rate was linear with sulphur dioxide partial pressure over the range 2.3 to 23.3 p.s.i. The rate was always greater for sulphur dioxide solutions acidified with 0.5 M HClO₄ than for those with 0.15 M HClO₄. The rate controlling step was heterogeneous under all conditions studied. The continually increasing rate of dissolution was not due to autocatalysis by the iron leached into solution.

Surana postulated that the increasing rate of leaching was due to surface morphology changes on the dissolving oxide. His dissolution mechanism involved the following steps:

1. Protonation of the surface:

   \[
   \text{FeOOH} + H^+ \xrightleftharpoons{K_1} \text{FeO}^2 + H_2O.
   \]

2. Anion adsorption:

   \[
   \text{FeO}^2 + X^- \xrightleftharpoons{K_2} \text{FeOX}
   \]

3. Desorption of a complex ferric ion: (at low acid concentrations)

   \[
   \text{FeOX} \xrightarrow{k_3} \text{FeOX}(aq)
   \]

Rate equation:

\[
\frac{d[\text{Fe}^{\text{aq}}]}{dt} = k_3 K_1 K_2 [\text{FeOOH}]_{a\text{H}^+a\text{X}^-}
\]

\(a\) denotes activity. \([\text{FeOOH}]\) was assumed to be constant.
The complexing power of the anion for ferric ion determined the value of $K_2$ and thus the overall leaching rate. Strong complexing anions resulted in fast leach rates.

At high acid concentrations:

4. Double protonation of the surface after anion adsorption:

$$\frac{\text{FeOX}}{\text{Fe(OH)X}^\ominus} + H^+ \xrightleftharpoons[\text{K}_4]{\text{/Fe(OH)X}^\ominus}$$

5. Desorption of a ferric complex:

$$\frac{\text{Fe(OH)X}^\ominus}{\text{Fe(OH)}^+ \text{(aq)}} \xrightarrow[\text{k}_5]{\text{Fe(OH)}^+ \text{(aq)}}$$

Rate equation:

$$\frac{d[\text{Fe}_{\text{aq}}]}{dt} = k_5k_4\frac{[\text{FeOX}]}{[\text{Fe}(\text{OH})^-]}a_{H^+}$$

$$= k_5k_4k_1k_2\frac{\text{a}_{\text{H}^+}}{\text{a}_{\text{X}^-}}$$

Surana postulated that for reductive dissolution with acidified aqueous sulphur dioxide solutions, the active anion was bisulphite, i.e. $X^- \equiv \text{HSO}_3^-$, The rate of leaching was therefore a function of $a_{H^+}$ and $a_{\text{HSO}_3^-}$, and, since these were related to the concentration of aqueous sulphur dioxide, the sulphur dioxide partial pressure.
1.3.2 Reductive Dissolution of Manganese Dioxide by Aqueous Sulphur Dioxide

The ability of aqueous solutions of sulphur dioxide to leach manganese dioxide has been known for some time. The kinetics and mechanism have been investigated (4,37-39). The dissolution was found to proceed by two reaction paths (37): 1. A slow reaction involving bisulphite ions; 2. A very fast reaction involving neutral aqueous sulphur dioxide molecules. Under the experimental conditions utilized, a slow chemical reaction was rate-limiting in 1; diffusion of sulphur dioxide molecules through the oxide boundary layer was rate-limiting in 2.

The rate equation at 25°C, with a stirring speed of 500 r.p.m. was:

\[ \frac{d[Mn_{aq}]}{dt} = \frac{590[SO_2_{aq}] + 60[HSO_3^-]}{1 + 15[HSO_3^-] + 8[H^+]}. \]

The leach rate at 25°C, pH 1.24, \([SO_2_{aq}] = 0.199 \text{ M}, [HSO_3^-] = 0.058 \text{ M},\) was \(8.3 \times 10^{-5}\) moles Mn cm\(^{-2}\) min\(^{-1}\). This is comparable with the leach rates of metals.

The adsorption of \(H^+\) and \(HSO_3^-\) ions had an inhibiting effect on the rate under the low stirring speeds utilized. Under conditions of low pH the calculated activation energy was \(4.5 \pm 0.2\) kcal mole\(^{-1}\). This was in good agreement with the theoretical value of the activation energy for diffusion of sulphur dioxide molecules in water at infinite dilution, \(4.3\) kcal mole\(^{-1}\).

Experiments (38) at much higher stirring speeds (2,300 r.p.m.) showed that for dissolution by mechanism 2, the rate became dependent
on the chemical reaction between undissociated aqueous sulphur dioxide molecules and manganese dioxide. The activation energy was estimated to be 7.3 kcal mole\(^{-1}\).

The rate equation at 25°C, with stirring speeds in excess of 2,300 r.p.m. was:

\[
\frac{d[Mn_{aq}]}{dt} = \frac{1200[SO_2_{aq}] + 60[HSO_3^-]}{1 + 0.65[SO_2_{aq}] + 0.8[HSO_3^-]}
\]

1.3.3 Catalysis of the Dissolution of Oxides

1.3.3.a Iron Oxides

Monhemius (15,16) added copper ions to his goethite/acidified sulphur dioxide solution system in the form of cupric perchlorate. Cupric ions were known to catalyze the homogeneous reduction of ferric ions to ferrous ions (40). He found that copper additions could catalyze the dissolution under certain conditions, and found an activation energy of 23.1 kcal mole\(^{-1}\). The rate control at low [SO\(_2\)\(_{aq}\)] changed from homogeneous to heterogeneous control on the addition of cupric ions.

Monhemius postulated that the cupric ions catalyzed the reduction of aqueous complex ferric ions. The catalyzed rate-determining step was then the desorption of species from the surface, and not as before, the reduction of ferric complex ions in solution to prevent their readsorption. In addition, the increase in leach rate observed with large additions of copper was thought to be due to some surface reaction involving cuprous ions.
1.3.3.b  Manganese Dioxide

The direct dissolution of manganese dioxide in sulphuric and perchloric acids has been investigated in the presence of ferrous ions (41). The overall chemical reaction has been shown to be:

\[ \text{MnO}_2 + 2\text{Fe}^{2+} + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \]

Experiments were performed under conditions where the reaction rate was independent of the concentration of ferrous, ferric, manganous and hydrogen ions and bulk diffusion in solution.

The reaction rate in a perchlorate medium was much less than that in a sulphate medium under the same conditions. When the ferrous ion concentration was less than 0.01 M the rate was first order in respect of this component. The adsorption of added cupric ions on the manganese dioxide surface was found to retard the reaction. The reaction was heterogeneously controlled.

The experimental evidence suggested the following mechanism: the rate-determining step occurred on the surface, and depended on the surface concentration of ferrous ions at active sites, or the ease of ferrous ion migration to them. The observed anion effect was explained by postulating that an electron exchange reaction between Mn$^{IV}$ and Fe$^{2+}$ resulted in the formation of Mn$^{III}$ and Fe$^{3+}$. In perchloric acid media the Mn$_2$O$_3$ formed inhibited further reaction at the active sites and dissolution occurred uniformly over the surface as observed. Sulphate anions, adsorbed in sulphuric acid media, complexed the Mn$^{III}$ and permitted a further electron exchange reaction. The dissolution reaction then
proceeded unhindered at such active sites as crystal boundaries, causing the surface pitting observed.

1.3.3. c  Zinc-Ferrite, ZnFe$_2$O$_4$

The dissolution of zinc-ferrite in sulphuric acid has been investigated with and without the presence of ferrous ions in the leach solution (42). Ferrous ions were shown to increase the rate of dissolution, as did cathodic polarization of the sample. Ferrous ions were oxidized to ferric during the experiments; the presence of ferric ions lowered the rate of dissolution. The rate of dissolution was proportional to the square root of the concentration of ferrous ions under the conditions studied.

The researchers explained their results in the following way. Cathodic polarization of the zinc-ferrite surface, or the adsorption of a reducing agent on the surface, resulted in the formation of an anion vacancy:

$$\text{Fe}^{II} (\text{H}_2\text{O})_6^{2+} \overset{\text{ads}}{\rightleftharpoons} \text{Fe}^{III} \text{OH}(\text{H}_2\text{O})_5^{2+} + \text{H}_2\text{O}$$

$$\frac{\text{H}_2\text{O}}{\text{solid}} \rightleftharpoons \frac{\text{H}_2\text{O}}{\text{solid}}^{2-} + \text{H}$$

$$\text{Fe}^{III} \overset{\text{solid}}{\rightleftharpoons} \text{Fe}^{II} \overset{\text{solid}}{\rightleftharpoons} \text{Fe}^{2+} \overset{\text{aq}}{\rightleftharpoons}$$

k was low and rate-determining.

The presence of ferric ion was said to decrease the adsorption of hydrogen free radicals (H) or ferrous ions. The mechanism of dissolution
rate enhancement by anion vacancy increase had been postulated to explain the results of their earlier leaching experiments on specially heat-treated ferrites without the addition of ferrous ions or cathodic polarization. No experiments were undertaken with a different anion present.

1.3.3.d Uranium Dioxide

The oxidative acid dissolution of uranium oxides is an important industrial process which has undergone much investigation. In particular, the use of oxidants other than oxygen has been investigated in an effort to improve on the leaching kinetics. Laxen (43) has made an extensive study of the effect of adding ferric ions to the leach solution, and has also reviewed earlier work in this field.

Laxen measured the increase in acid dissolution rate of uranium dioxide upon addition of ferric ions with the following anions present: perchlorate - no effect, very low dissolution rate; nitrate - no effect; chloride - slight rate increase; sulphate - large rate increase. The activation energy with sulphate anions present was 15.8 kcal mole$^{-1}$. No effect was observed when the stirring speed was varied from 200 to 600 r.p.m. The dissolution rate reached a maximum at pH 2 for leach solutions with constant perchlorate ion concentration. A similar maximum was found using leach solutions with a fixed initial sulphate ion concentration. In these solutions the pH was varied by the addition of perchloric acid.

When the ferric ion concentration was raised the dissolution rate increased in a manner described by a Freundlich adsorption isotherm.
The addition of ferrous ions reduced the dissolution rate by a greater amount than did the addition of equivalent concentrations of Ni\(^{2+}\), Co\(^{2+}\), Cu\(^{2+}\), and Mn\(^{2+}\).

These results indicated that the rate-determining step was a chemical reaction occurring on the uranium dioxide surface. The form of the dependence of the dissolution rate on the ferric ion concentration showed that the adsorption of a ferric-containing species was important.

Laxen drew attention to the strong similarities between his system and homogeneous electron exchange reactions such as the \(\text{Fe}^{2+}/\text{Fe}^{3+}\) redox couple. In this system the rate constant for electron exchange is markedly affected by the presence of certain anions in solution. The rate constant for electron exchange between the aquo-complexed ions is very small. On addition of anions it increases in the order: \(\text{H}_2\text{O}^+<\text{Cl}^<-\text{S}_4\text{O}_6^{2-}\). Sulphate anions are particularly favorable for conducting electrons between \(\text{Fe}^{3+}\) and \(\text{Fe}^{2+}\) or for reducing steric hindrances to electron exchange.

Since these various effects paralleled the results of the experiments on the heterogeneous dissolution of uranium dioxide, it was considered that the barriers hindering the electron exchange in the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) system were at least similar to those affecting the ferric ion promoted dissolution of uranium dioxide. Uranium dioxide was leached by oxidizing the \(\text{U}^{IV}\) to the more soluble \(\text{U}^{VI}\). The pH of the solution and the anion concentration determined what ferric complexes were formed and their concentration. The peak dissolution rates coincided with the maximum concentration of the ferric complex considered to be most capable of adsorbing and undergoing an electron exchange reaction with the \(\text{U}^{IV}\) and \(\text{U}^{V}\) species.
on the oxide surface.

Adsorption of cations other than ferric reduced the surface area available for reaction and consequently lowered the dissolution rate. Ferrous ions were presumed to be more efficient at adsorbing on active surface sites.

Since no attempt was made to regenerate the ferric ions, this method of promoting the dissolution rate could not be considered to be a truly catalytic reaction.

1.4 The Sulphur-Dioxide-Water System

Sulphur dioxide is moderately soluble in water and the following major species have been detected:

1. \( \text{SO}_2 \cdot x\text{H}_2\text{O} \), a clathrate of the gas hydrate type (44-46) with \( x \approx 7 \). Undissociated, aqueous sulphur dioxide will be referred to as \( \text{SO}_2 \text{aq}^- \).

2. \( \text{H}^+; \text{HSO}_3^- \). Ionization leads to the formation of the bisulphite anion, \( \text{HSO}_3^- \):

\[
\text{SO}_2 \text{aq}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^- \quad (K_1)
\]

3. \( \text{SO}_3^{2-} \). Further ionization gives the sulphite anion, \( \text{SO}_3^{2-} \):

\[
\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-} \quad (K_2)
\]

4. \( \text{HS}_2\text{O}_5^-; \text{S}_2\text{O}_5^{2-} \). With a high concentration of \( \text{SO}_2 \text{aq}^- \) both the pyrobisulphite anion, \( \text{HS}_2\text{O}_5^- \), and the pyrosulphite anion, \( \text{S}_2\text{O}_5^{2-} \), are formed:
Evidence for the existence of unchanged aqueous sulphur dioxide molecules was obtained from ultraviolet absorption spectra (47-50) and Raman spectroscopy (51-53). Simon and Waldmann (54-56) undertook a Raman spectroscopic study of aqueous sulphur dioxide solutions and identified the bisulphite, pyrobisulphite and pyrosulphite anions, though in very low concentrations. At 20°C, $K = \frac{[S_{2}O_{5}^{2-}]}{[HSO_{3}^{-}]^{2}} = 7(10^{-2})$ (57).

Studies of aqueous solutions of sulphur dioxide and of solid mixtures of sulphur dioxide and water by infrared spectroscopy (58,59) had, like all previous studies, failed to detect "sulphurous acid", $H_{2}SO_{3}$. It was therefore considered that $H_{2}SO_{3}$ either did not exist or was present in very small amounts.

The equilibrium between $SO_{2}^{aq}$ and $H^{+}, HSO_{3}^{-}$ has been reported as being established instantaneously - within $10^{-6}$ second (60).

Aqueous solutions of sulphur dioxide possess reducing properties (44):

$$SO_{4}^{2-} + 4H^{+} + 2e^{-} = SO_{2}^{aq} + 2H_{2}O \quad E^{o} = 0.17 \text{ v}$$

$$S_{2}O_{6}^{2-} + 4H^{+} + 2e^{-} = 2SO_{2}^{aq} + 2H_{2}O \quad E^{o} = 0.57 \text{ v}.$$ 

Ostwald (61) and Barth (62) showed that aqueous sulphur dioxide solutions behave as monobasic acids even at high dilutions. The first dissociation constant for aqueous sulphur dioxide is given by:
\[
K_1 = \frac{[H^+][HSO_3^-]}{[SO_2 \text{ aq}]} - 18 -
\]

or, more correctly, in activities:

\[
K_1 = \frac{a_{H^+} \cdot a_{HSO_3^-}}{a_{SO_2 \text{ aq}} \cdot a_{H_2O}}
\]

\(K_1\) is equivalent to the "apparent" dissociation constant, \(K_a\), of Campbell and Maass (63):

\[
K_a = \frac{[H^+][HSO_3^-]}{[SO_2 \text{ aq}]+[H_2SO_3]}
\]

since \([H_2SO_3] \to 0\).

Campbell and Maass (63) calculated values of \(K_1\) from conductivity measurements made over a range of aqueous sulphur dioxide concentrations and at temperatures up to 90°C. \(K_1\) decreased with temperature but was virtually independent of \([SO_2 \text{ aq}]\) up to 8%.

Johnstone and Leppla (64) recalculated \(K_1\) from the conductivity data of Campbell and Maass (63) and Morgan and Maass (65) using activities rather than concentrations.

Tartar and Garretson (66) calculated \(K_1\) and \(K_2\) at 25°C from E.M.F. measurements on suitable cells. They found \(K_1 = 1.72 \times 10^{-2}\), \(K_2 = 6.24 \times 10^{-8}\). Their value of \(K_2\) was in reasonably good agreement with the results of other workers which they enumerated. Subsequently Cuta et al. (67) obtained a value of 7.10 \(10^{-8}\) at 25°C from potentiometric and spectrophotometric measurements.
Ellis and Anderson (68) calculated values of $K_1$ at 25°C at pressures up to 2000 atm. by conductance measurements. They found $K_1 = 1.39 \times 10^{-2}$ at 1 atm and no appreciable change at pressures up to at least 5 atm.

Rabe and Harris (69) developed an expression for calculating $K_1$ at any temperature, $T^{\circ}A$, from earlier conductivity measurements (64,68). Their equation:

$$K_1 = \exp \left( \frac{1972.5}{T} - 10.967 \right).$$

Arkhipova et al. (70) gave values for $K_1$ at 10, 25 and 35°C of 1.8 ($10^{-2}$), 1.3 ($10^{-2}$) and 1.0 ($10^{-2}$) respectively.

Table I gives values of $K_1$ at different temperatures according to the various authors. Values of $K_1$ are plotted against temperature in Figure 1. From this graph were taken the values of $K_1$ used to calculate bisulphite and hydrogen ion concentrations at 80, 90, 100, 110 and 120°C; namely $3.95 \times 10^{-3}$, $3.20 \times 10^{-3}$, $2.70 \times 10^{-3}$, $2.35 \times 10^{-3}$ and $2.05 \times 10^{-3}$ respectively.

Although various authors gave sulphur dioxide solubility data, only several (63,69,71,72) had conducted studies over a large temperature range. Of these, only Campbell and Maass (63) had also gathered data at high concentrations of dissolved sulphur dioxide. The available data was used to construct the isobars in Figure 2, relating solubility, $C_{SO_2}$, to temperature. The density of sulphur dioxide at N.T.P. was taken to be 2.9269 g.l$^{-1}$ (73). From all this data it was possible to calculate the equilibrium molar concentrations of $SO_2\text{aq}$, $H^+$ and $HSO_3^-$ at the temperatures, pH values and the partial pressures of sulphur dioxide of interest.
<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Campbell and Maass</th>
<th>Johnstone and Leppla</th>
<th>Tartar and Carretson</th>
<th>Ellis and Anderson</th>
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<th>Arklipova et al.</th>
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* Calculated.

**TABLE I.** Variation of the first dissociation constant \((x \times 10^3)\) of aqueous sulphur dioxide with temperature.
FIGURE I. Variation of the first dissociation constant of aqueous sulphur dioxide with temperature.
FIGURE 2. Variation of the water solubility of sulphur dioxide with temperature at various partial pressures.
In these calculations it was assumed that at all temperatures and pH values the concentrations of all other sulphur-containing ions except $\text{HSO}_3^-$ were zero, i.e. $C_{\text{SO}_2} = [\text{SO}_2^{\text{aq}}] + [\text{HSO}_3^-]$. It was also assumed that the concentration of all aqueous sulphur dioxide species, $C_{\text{SO}_2}$, was constant for a given partial pressure of sulphur dioxide at a fixed temperature and was not influenced by pH changes nor by the addition of sulphite salts. In all calculations concentrations were used rather than activities since activity coefficients were only known at $25^\circ\text{C}$ (74). Mean activity coefficients of aqueous sulphur dioxide have been estimated at temperatures up to $130^\circ\text{C}$, over a wide concentration range (69).

1.5 Scope of the Investigation

The main aim of the investigation was to gain an understanding of the mechanism and kinetics of the reductive dissolution of goethite in aqueous sulphur dioxide solutions. To accomplish this it was first necessary to extend our understanding of the mechanism and kinetics of the direct dissolution of goethite in perchloric acid, which was subsequently used to vary the pH of the leaching solutions in the main study.

Since the reductive dissolution was kinetically slow, various cationic additions were made in order to catalyze the dissolution. Of these, only the addition of copper was found to be of value. A further investigation was undertaken to try to understand the mechanism by which the copper could catalyze the reductive dissolution.
A comparison of the uncatalyzed and copper-catalyzed rates were also made for two other important naturally occurring iron oxides, magnetite and hematite.
2. EXPERIMENTAL

2.1 Materials

Natural oxide ores were used in all experiments.

Goethite. The goethite originated from Biwabik, Minnesota, and was supplied by Ward's Natural Science Establishment, Inc., New York (10).

Magnetite. The magnetite originated from the Queen Charlotte Islands, British Columbia, and was obtained from the Mineral Engineering Department of the University of British Columbia, Vancouver (14).

Hematite. The hematite originated from Ishpeming, Michigan, and was also supplied by Ward's (14).

2.1.1 Preparation

The as-received ores were first mechanically- or hammer-crushed and then hand-mulled to the required particle size range. For gravimetric and spectrographic analysis, and for all leaching experiments, the ores were wet-screened to -70+140 mesh number, U.S. standard seives.

The magnetite particulate feed was mechanically purified by discarding material not adhering to a permanent magnet, and then treated with 20% nitric acid for about 16 hours at room temperature to remove the exposed sulphides. After subsequent re-screening only a trace of sulphides remained.
2.1.2 Identification

Goethite. X-ray diffraction analysis using Co Kα₁ radiation in conjunction with an Fe filter confirmed that the ore contained iron in the form of goethite together with a sizeable amount of α-quartz. Table II.

Magnetite and Hematite. These ores had been the subject of a direct acid leaching investigation by Devuyst (14). His X-ray diffraction analysis had shown them to be very pure.

2.1.3 Analysis

Sized samples of the ores were analyzed gravimetrically for their iron, silica and moisture contents and spectrographically for other impurities by Can Test Ltd., Vancouver. Gravimetric results are shown in Table III, with the iron values being converted to the pure relevant oxide. The spectrographic results in Table IV give weight percentage concentrations for those elements detected except iron and silicon. All other elements were either not detected (N.D.), were present only in trace amounts, or were non-detectable.

The gravimetric results showed that for the goethite ore, the iron was not all present in the form of goethite. Analysis showed only 7.09 g contained water in 100 g sample, corresponding to 69.93 g goethite and 43.95 g iron, if it was all contained as goethite. If the remaining 8.26 g iron were all in the form of hematite, then it would weigh 11.81 g. The contribution of goethite, silica, hematite and uncontained water to the ore's composition then would be 99.37%.
Experimental Data | ASTM powder diffraction file
---|---
-270 mesh ore | 3.0249; α-FeOOH | 5.0490; α-SiO₂

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TABLE II. X-Ray diffraction data for goethite ore.
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<th>Hematite</th>
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* Spectrographic

TABLE III. Gravimetric analysis for principal ore components.
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</table>

**TABLE IV.** Spectrographic analysis of sized ores.
Since 30% of the goethite ore was contaminants it was necessary to prepare a very large, well-mixed quantity of sized ore to reduce the likelihood of sample and leach rate irreproducibility. Depending on the leaching characteristics of the hematite ore, it might be necessary to apply some correction to the leach rates of the goethite ore to take into account the 12% hematite present.

The magnetite and hematite analyses were incomplete. The weight percentage of silicon dioxide given for the magnetite ore was not very accurate since it was obtained spectrographically.

The total goethite surface area in a 1 g goethite ore sample was calculated assuming the goethite particles were pure and perfectly spherical, and had a density of 4.3 g cm\(^{-3}\) (73). If all the goethite spheres had a diameter equivalent to a mesh number of 70, then the total surface area would have been 46.5 cm\(^2\). Had the diameter been equivalent to a mesh number of 140, then the total surface area would have been 92.9 cm\(^2\).

In practice the goethite was not all present as spheres, and there was a spectrum of particle sizes between mesh numbers 70 and 140. If the total goethite surface area was taken as 75 cm\(^2\), then to convert the leach rates expressed in the text as mg Fe hr\(^{-1}\) (g goethite ore\(^{-1}\)) to absolute rates moles Fe cm\(^{-2}\)min\(^{-1}\), the multiplication factor would be 3.98 \(10^{-9}\).

2.2 Equipment

All experiments were performed in either one of two essentially identical totally corrosion-resistant autoclaves. The autoclave bodies were of 2 l. capacity and were fabricated by the Pfaudler Company, New York.
They consisted of round-bottomed cylindrical mild steel pressure vessels internally lined with Glasteel 3315. An autoclave head was made of 316 stainless steel, machined to allow a Teflon plate to be firmly secured by four tantalum bolts and Teflon washers to the internal surface, Figures 3 and 4. The bolts were equally spaced around the circumference of a circle of radius 1 1/16", measured from the centre of the autoclave head.

All the tantalum used in the construction of the autoclave was supplied by Teledyne Wah Chang Albany, Oregon.

Low pressure stainless steel fittings were used to connect two 1/16" stainless steel gas lines to the outward facing ends of two of the tantalum bolts. A 1/8" diameter zirconium sampling tube and a thermistor probe were attached with similar fittings to the other bolts.

The model 410 thermistor probe was supplied by the Yellow Springs Instrument Co., Inc., Ohio.

The gas inlet and gas outlet tantalum bolts were diametrically opposite each other and had small holes drilled through their centres to permit the flow of gas. The other tantalum bolts had holes drilled through their centres wide enough for the sampling tube or thermistor probe to pass through. In addition, they were internally threaded to allow a Teflon sleeve to fit over the tube and a Teflon well to fit over the probe, each forming a gas-tight seal. The Teflon sleeve, well and the thermistor probe were all long enough for their ends to be well below the leach solution level. In order to prevent the passage of fine ore into the sampling tube, a fritted glass filter was affixed to the lower end of the Teflon sleeve.
FIGURE 3. Cross-sectional view of the autoclave head; north-south orientation.

ZIRCONIUM SAMPLING TUBE

STIRRING SHAFT

THERMISTOR PROBE

SLEEVES

FRITTED GLASS FILTER

STIRRING SHAFT PLUS IMPELLER AND PROPELLER

WELL

316 S.S.

TEFLON.

TANTALUM.

DRAWN TO SCALE.
FIGURE 4. Cross-sectional view of the autoclave head; east-west orientation.
A simple tantalum sampling valve screwed onto the other end of the zirconium tube enabled samples to be taken using the internal pressure to expel the solution. A cylindrical copper jacket was affixed to the zirconium tube between the autoclave head and the sampling valve. Cold water was passed through this jacket to cool the leach solution sampled.

A Yellow Springs Instrument Co., Inc. model 71 A Thermistemp temperature controller, together with a Parr Instrument Co., Illinois, stirrer type pressure reaction apparatus - model 4501 - was used to maintain the leach solution within ± 1.5°C of the desired temperature. The model 4501 consisted of a 1500 watt output electric heater, Variac type W 10 M autotransformer (General Radio Co., Massachusetts), and a Bodine Electric Company, Chicago, a.c. motor to provide stirring.

Driving pulleys of different diameters were used to vary the stirring speed. Solution stirring for gas, solid and liquid dispersion was provided by a Teflon-covered tantalum shaft fitted with a Teflon impeller and Teflon propeller. The tantalum shaft passed through a Teflon cord-packed gland at the centre of the outer side of the autoclave head. The zip joint Teflon cord was supplied by the Crane Packing Company, Illinois. A pressure seal was kept by tightening this gland by means of a bolt whenever necessary. The stirring shaft was kept rotating about the central axis of the autoclave by two bearings at either end of a housing above the packing gland. Cooling water was circulated in a copper pipe wrapped around the outer surface of the packing gland.

The head was clamped to the autoclave body by means of a hardened steel split ring with six compression bolts. An excellent pressure seal
was obtained by coating the area of the steel pressure vessel in contact with both the Teflon plate of the head and the glass lining with Silicone Sealant, manufactured by Dow Corning Silicones, Vancouver. This procedure had the added advantage of ensuring no corrosion at the glass/metal boundary.

Teflon tape was used on all threaded connections.

A pressure gauge was situated on the dry, inlet gas line side of an autoclave to minimize possible corrosion. The Duraguage (Ashcroft, U.S.A.) was graduated in 1 p.s.i. divisions from 0 to 100 p.s.i.g. During an experiment a low, continuous flow of sulphur dioxide gas was allowed to pass through the autoclave to prevent any possible gas line corrosion products from entering the autoclave. Dry, cold sulphur dioxide was non-corrosive, so any corrosion would only have occurred in the exit gas line where the sulphur dioxide was wet and hot. These corrosion products would be swept away into the bubblers by the gas stream. Needle valves situated at convenient points allowed flushing of the autoclave with nitrogen or sulphur dioxide and were used for fine pressure control, Figure 5.

"Blank runs", with all reagents present except ore, were often carried out on both autoclaves to ensure that no iron was entering the leach solution as a consequence of corrosion of the apparatus. These runs showed that there was no detectable corrosion. An experiment performed in one autoclave was normally repeated in the other. No systematic difference in leach rates could be detected for those experiments performed in both autoclaves.
FIGURE 5  Schematic arrangement of the gas lines.
2.3 Reagents

Distilled water was used for all solutions. All chemicals used were reagent grade. The nitrogen gas was supplied by Canadian Liquid Air. Matheson of Canada supplied the anhydrous grade sulphur dioxide. Gases were used direct from their cylinders.

2.4 Experimental Procedure

A weighed (1, 2, 3, or 5 g) sample of ore was placed in a thoroughly cleaned autoclave body together with reagents and sufficient distilled water to make a solution volume of 1195 ml. The autoclave head and body were sealed together and placed in the furnace. During rapid heating to the desired temperature the autoclave was purged with nitrogen at least six times.

A purging cycle consisted of filling the autoclave with nitrogen to 50 p.s.i.g., with solution stirring to remove dissolved oxygen; then venting to a small positive pressure. When the desired solution temperature was reached the Variac was used as a fine temperature controller in conjunction with the Thermistemp. The stirring was stopped and the autoclave was twice flushed out with sulphur dioxide to the maximum attainable pressure (about 35 p.s.i.g.). Stirring was then restarted and sulphur dioxide was reintroduced to the desired partial pressure, with a very low bleed of gas leaving the autoclave. A waiting period of at least thirty minutes was allowed in order to ensure equilibrium between the gaseous and liquid phases and between the furnace and the autoclave and its contents.
A 10 ml sample of the leach solution was then removed from the autoclave and discarded. This procedure flushed out the sampling tube and the 10 ml graduated cylinder used to measure sample volumes. A further 5 ml sample was taken and saved. When analyzed for iron, this sample was taken as a blank (zero time, zero dissolved iron) for subsequent leaching rate calculations.

Further samples were taken in an identical manner at thirty minute intervals. A leaching run was at least four hours in duration, with no change in conditions except the reduction in leach solution volume as a consequence of sampling. Water vapour loss as a consequence of the slow bleed of gas through the autoclave was negligible. Corrections were applied when calculating the leach rates to take into account the iron in solution lost by sampling.

Apart from the stirring speed variation experiments, the stirrer was always rotated at 1100 r.p.m. At this speed all the ore was in suspension and sulphur dioxide was rapidly absorbed by the solution.

A disadvantage of this experimental arrangement was the limited range of sulphur dioxide partial pressure available. The maximum pressure available was the vapour pressure of the liquid sulphur dioxide in the cylinder. At the ambient laboratory temperature, this was about 36 p.s.i.g. maximum. Higher partial pressures could have been obtained by heating a suitable reservoir vessel containing liquid sulphur dioxide transferred from the cylinder, but this was not attempted. Alternatively, the aqueous sulphur dioxide concentration could have been increased by adding certain chemicals, soluble in the leach solution, which could
increase the solubility. Chemicals which are capable of doing this and which can remain inert to the effects of sulphur dioxide at high temperatures include dimethyl formamide and dimethyl sulfoxide. This approach was also not attempted.

Perchloric acid and sodium sulphite were used to adjust the pH of the aqueous sulphur dioxide solutions.

The maximum sampling error was estimated to be $\pm 3\%$, whilst the maximum error in calculating the leach rate was estimated to be $\pm 5\%$.

2.5 Analytical Techniques

2.5.1 Iron

The concentration of iron in the sample solutions was measured colorimetrically by means of the orange-red ferrous complex of 1,10-orthophenanthroline. Hydroxylamine hydrochloride was used to reduce all iron in solution to the ferrous state. A sodium acetate-acetic acid buffer solution was used to keep the hydrogen ion concentration in the range 4-5 pH units.

A composite reagent solution was made up containing 163.2 g $1^{-1}$ anhydrous sodium acetate, 162 ml $1^{-1}$ glacial acetic acid, 2 g $1^{-1}$ hydroxylamine hydrochloride, and 0.3 g $1^{-1}$ 1,10-orthophenanthroline. A few drops of concentrated hydrochloric acid was added to the distilled water used to dissolve the 1,10-orthophenanthroline. 90 ml of the composite reagent was then added to a suitable amount of the 5 ml sample of the leach solution. This was made up to 100 ml and after thorough mixing was left for at least thirty minutes to allow the colour to completely develop. The optical density of each solution
was measured on a Beckman Model B Spectrophotometer using light of wavelength 512 μm. The concentration of iron was read directly from a calibration curve prepared by using standard iron solutions.

Since the presence of certain anions and cations interferes with the determination of iron by this method, it was necessary to find the maximum permissible concentrations of perchloric acid, cupric perchlorate and sodium sulphite that could be present in a sample without ill effect. This was accomplished by doping standard iron solutions with the above chemicals. The maximum permissible concentrations of these compounds were well above those used in subsequent experiments.

2.5.2 Copper

The concentration of copper in the sample solutions was measured with a Unicam Model SP90 Atomic Absorption Spectrophotometer. A copper lamp was used to provide light of wavelength 324.8 μm. An air/acetylene flame was used to dissociate the copper in the sample into the atomic and excited states. The absorption of light by the ground state atoms was measured and knowing the absorption resulting from standard copper solutions it was possible to measure the sample copper concentration.
3. RESULTS

Graphs of the amount of iron leached into solution against time were linear for most runs with all ores. Under conditions of high aqueous sulphur dioxide concentration and high acidity, some runs experienced an initial increase in leach rate which lasted up to one hour unless the perchloric acid concentration was greater than 0.75 Molar. Under those conditions the rate of leaching only became constant after three hours.

The rates of leaching under the various conditions investigated have been tabulated and graphs have been drawn to illustrate important trends.

3.1 Goethite

3.1.1 Direct Dissolution in Perchloric Acid

Experiments were undertaken on 1 g samples at 110°C, under a nitrogen atmosphere. The measured rates at different concentrations of perchloric acid up to 6 Molar are given in Table V.

3.1.2 Reductive Dissolution in Aqueous Sulphur Dioxide Solutions

3.1.2.a Variation in Stirring Speed

One gram samples were leached at 110°C, 25 p.s.i.a. SO₂, 0.21 M HClO₄.
### TABLE V. Leach rates of 1 g goethite samples at 110°C; mg Fe hr$^{-1}$.

<table>
<thead>
<tr>
<th>$P_{SO_2}$ p.s.i.a.</th>
<th>$C_{SO_2}$ Molar</th>
<th>HClO$_4$ Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.105</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.067</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.134</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>0.200</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>0.266</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>0.330</td>
<td>8.75</td>
</tr>
<tr>
<td></td>
<td>0.395</td>
<td>10.40</td>
</tr>
</tbody>
</table>

Note: The table presents the leach rates of 1 g goethite samples at 110°C, with the concentration of $C_{SO_2}$ (Molar) and $P_{SO_2}$ (p.s.i.a.) as variables. Each cell represents the mg Fe hr$^{-1}$ for the corresponding conditions.
under three different stirring conditions, 620, 1100, and 2000 r.p.m., Table VI.

3.1.2.b Variation in Sulphur Dioxide Partial Pressure

Four series of experiments were undertaken at 110°C on 1 g samples where the sulphur dioxide partial pressure was increased by 5 p.s.i.a. intervals up to a maximum of 30 p.s.i.a. Each series had a different perchloric acid concentration: series 1 - no added acid; 2 - 0.105 M HClO₄; 3 - 0.21 M HClO₄; 4 - 0.75 M HClO₄. The corresponding concentrations of molecular and ionic species present under these conditions are given in Table VII. Leaching rates are in Table V.

3.1.2.c Variation in Hydrogen Ion Concentration

In addition to the four different acid concentration series (3.1.2.b), higher perchloric acid concentration experiments were undertaken on 1 g samples at 110°C, 25 p.s.i.a. SO₂, Table V. In these experiments it was found that the leach rate increased with time, only becoming constant after about 3 hours. The leach rates quoted in Table V were the final observed rates, as illustrated by the graph, Figure 6.

3.1.2.d Variation in Sample Weight

In order to determine whether a homogeneous or heterogeneous reaction was rate-controlling, two series of experiments were conducted with different sample weights at 110°C, 10 p.s.i.a. SO₂. In one series 1 g and 2 g samples were leached in 0.105 M HClO₄. In the other series 1,
<table>
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<th>R.P.M.</th>
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<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>620</td>
<td>1,100</td>
<td>2,000</td>
</tr>
<tr>
<td>Leach Rate, ( \text{mg Fe hr}^{-1} )</td>
<td>14.6</td>
<td>15.2</td>
<td>13.4</td>
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<tr>
<td></td>
<td>14.7</td>
<td>15.8</td>
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</tr>
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</table>

**TABLE VI.** Variation of leach rate with stirrer speed.

1 g goethite samples; 110°C; 25 p.s.i.a. \( \text{SO}_2 \); 0.21 M \( \text{HClO}_4 \).
<table>
<thead>
<tr>
<th>$C_{SO_2}$ Molar</th>
<th>$[H^+]$, $[SO_2\text{aq}]$ Molar</th>
<th>HClO$_4$ Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.067</td>
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<td>0.0556</td>
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<td>0.1174</td>
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<td>0.2421</td>
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<td></td>
<td>0.3033</td>
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<tr>
<td>0.395</td>
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<tr>
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<td>0.3657</td>
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<th>0.1050</th>
<th>0.2100</th>
<th>0.7500</th>
<th>1.5000</th>
<th>3.0000</th>
<th>4.5000</th>
<th>6.0000</th>
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<td>0.067</td>
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<td>0.2107</td>
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<td></td>
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<td>0.0663</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.134</td>
<td>0.1079</td>
<td>0.2115</td>
<td>0.7504</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1311</td>
<td>0.1325</td>
<td>0.1336</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.200</td>
<td>0.1092</td>
<td>0.2122</td>
<td>0.7506</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1958</td>
<td>0.1978</td>
<td>0.1994</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.266</td>
<td>0.1105</td>
<td>0.2129</td>
<td>0.7508</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2605</td>
<td>0.2631</td>
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</tr>
<tr>
<td>0.330</td>
<td>0.1118</td>
<td>0.2136</td>
<td>0.7510</td>
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<td></td>
<td>0.3232</td>
<td>0.3264</td>
<td>0.3291</td>
<td>0.3295</td>
<td>0.3297</td>
<td>0.3298</td>
<td></td>
</tr>
<tr>
<td>0.395</td>
<td>0.1130</td>
<td>0.2143</td>
<td>0.7512</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>0.3870</td>
<td>0.3907</td>
<td>0.3938</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**TABLE VII.** Concentrations of aqueous species at 110°C.
FIGURE 6. Amounts of iron leached from 1 g. goethite samples with time at 110°C, 25 P.S.I.A. SO₂ different acidities.
2 and 3 g samples were leached in 0.21 M HClO$_4$, Table VIII.

3.1.2.e Variation in Temperature

Experiments were carried out to enable an apparent activation energy to be calculated. One gram samples were leached in 0.21 M HClO$_4$ containing a constant C$_{SO_2}$ (= 0.266 M). Leach rates were measured at 80, 90, 100, 110 and 120°C, Table IX.

3.1.2.f Effect of Ferrous Ions in Solution

In order to determine whether the dissolution reaction was autocatalyzed by the ferrous ions formed by the reductive leaching of goethite, experiments were conducted at low and high acidities with a large initial addition of ferrous ions. One gram samples were used at 110°C, 25 p.s.i.a. SO$_2$, in both experiments. With no perchloric acid present 335 mg of iron (5(10$^{-3}$) M) was added as ferrous sulphate. With 3.0 M perchloric acid 134 mg of iron (2(10$^{-3}$) M) was added as ferrous perchlorate. In the high acidity experiment the rate of leaching increased during the first three hours, becoming constant after this time. The leach rate quoted in Table XVIII was the final observed rate. This behaviour was also noticed for the identical experiment with no initial added ferrous ions.

3.1.3 Catalysis of the Reductive Dissolution by the Addition of Cupric Ions

Cupric ions were added as cupric perchlorate, Cu(ClO$_4$)$_2$.6H$_2$O. The samples of leach solution were analyzed for both iron and copper
TABLE VIII. Variation of leach rate with sample weight. Goethite samples; 110°C; 10 p.s.i.a. SO₂.

<table>
<thead>
<tr>
<th>HClO₄ Molar</th>
<th>0.105</th>
<th>0.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Weight</td>
<td>1 g</td>
<td>2 g</td>
</tr>
<tr>
<td>Leach Rate, mg Fe hr⁻¹</td>
<td>7.2</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>7.3</td>
</tr>
</tbody>
</table>

TABLE IX. Variation of leach rate with temperature. 1 g goethite samples; C_{SO₂} = 0.266 M; 0.21 M HClO₄.
concentrations. In all experiments some copper was lost. Unless otherwise stated, the loss never exceeded 10%, and this loss was not considered when calculating the leach rate. Unlike the uncatalyzed experiments, the copper catalyzed experiments resulted in the precipitation of a very fine black powder on the Teflon and glass surfaces below the leach solution level.

The maximum concentration of copper added was kept as low as possible for two reasons. Firstly, too high a concentration of copper interfered with the colorimetric method used for the estimation of iron. Secondly, it was necessary to show that copper did in fact behave as a catalyst and not as a reagent being consumed by the dissolution reaction.

3.1.3.a Variation in Concentration of Cupric Ions

Experiments were undertaken where the concentration of copper was varied, keeping all other conditions constant.

At 110°C, 25 p.s.i.a. \( \text{SO}_2 \), 0.21 M \( \text{HClO}_4 \), the cupric ion concentration was varied over an order of magnitude, from \( 10^{-3} \) M to \( 10^{-2} \) M. At the same temperature and sulphur dioxide partial pressure, but with no added acid, a smaller cupric ion concentration range was investigated. Table X.

At 90°C, no added acid, cupric ion concentrations of \( 10^{-3} \), \( 2(10^{-3}) \), and \( 3(10^{-3}) \) M were investigated at three sulphur dioxide partial pressures: 14.7, 24.7, and 34.7 p.s.i.a. Table XI.
### TABLE X. Variation of leach rate with cupric ion concentration at 110°C. 1 g goethite samples; 25 p.s.i.a. SO₂.

<table>
<thead>
<tr>
<th>[Cu²⁺] Molar</th>
<th>Leach Rate</th>
<th>mg Fe hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.2</td>
<td>8.75</td>
</tr>
<tr>
<td></td>
<td>15.8</td>
<td>9.35</td>
</tr>
<tr>
<td></td>
<td>16.3</td>
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</tr>
<tr>
<td>10⁻³</td>
<td></td>
<td>129.0</td>
</tr>
<tr>
<td>2(10⁻³)</td>
<td>43.9</td>
<td>235.0</td>
</tr>
<tr>
<td>4(10⁻³)</td>
<td>71.9</td>
<td></td>
</tr>
<tr>
<td>6(10⁻³)</td>
<td>96.1</td>
<td></td>
</tr>
<tr>
<td>8(10⁻³)</td>
<td>121.0</td>
<td></td>
</tr>
<tr>
<td>10⁻²</td>
<td>147.0</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE XI. Variation of leach rate with cupric ion concentration at and sulphur dioxide partial pressure at 90°C. 1 g goethite samples; mg Fe hr⁻¹.

<table>
<thead>
<tr>
<th>P.SO₂ p.s.i.a.</th>
<th>[Cu²⁺] Molar</th>
<th>0</th>
<th>10⁻³</th>
<th>2(10⁻³)</th>
<th>3(10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td></td>
<td>2.6</td>
<td>48.5</td>
<td>73.2</td>
<td>96.0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>52.0</td>
<td>76.5</td>
<td>108.0</td>
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<tr>
<td></td>
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<td>54.7</td>
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<td>24.7</td>
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<td>39.0</td>
<td>80.0</td>
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<td>52.3</td>
<td>84.6</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>49.0</td>
<td>91.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1.3.b Variation in Partial Pressure of Sulphur Dioxide

The effect of increasing the sulphur dioxide partial pressure was investigated at 90°C, no added acid, for cupric ion concentrations of \(10^{-3}\) and \(2(10^{-3})\) M. Experiments were performed at 14.7, 24.7, and 34.7 p.s.i.a. \(\text{SO}_2\). Table XI. The concentrations of species in solution at 90°C are given in Table XII.

3.1.3.c Variation in Hydrogen Ion Concentration

At 110°C, 25 p.s.i.a. \(\text{SO}_2\), the added cupric ion concentration was \(2(10^{-3})\) M, and leaching rates were measured at no added acid, 0.105 M \(\text{HClO}_4\) and 0.21 M \(\text{HClO}_4\). Table XIII.

At 90°C, 14.7 p.s.i.a. \(\text{SO}_2\), the added cupric ion concentration was \(10^{-3}\) M and a much wider pH range was studied. At high pH (> 2) sample analysis showed that copper was continually lost from solution during a run. Metallic copper was precipitated from solution and covered the Teflon and glass surfaces under the solution level with a lustrous bronze-coloured film. Graphs of amount of iron leached into solution against time showed a dissolution rate which decreased with time. The rates quoted in Table XIV for these high pH experiments (marked with an asterisk) were initial leach rates, taken when the loss in copper from solution was still less than 10%. They were only considered to be minimum possible rates.

3.1.3.d Variation in Sample Weight

Experiments with 1, 2, and 3 g samples were conducted at 110°C, 25 p.s.i.a. \(\text{SO}_2\), 0.21 M \(\text{HClO}_4\), Table XV. At this pH and temperature, the
TABLE XII. Concentrations of aqueous species at 90°C.

<table>
<thead>
<tr>
<th>$P_{SO_2}$ p.s.i.a.</th>
<th>$C_{SO_2}$ Molar</th>
<th>$[H^+]$, $[SO_2_{aq}]$ Molar</th>
<th>$Na_2SO_3$ Molar</th>
<th>$HClO_4$ Molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td>0.266</td>
<td>$[H^+]$ 0.0010 0.0049 0.0276 0.1124 0.2139</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[SO_2_{aq}]$ 0.0650 0.1611 0.2384 0.2586 0.2621</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24.7</td>
<td>0.441</td>
<td>$[H^+]$ - - 0.0360 - -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[SO_2_{aq}]$ - - 0.4050 - -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>34.7</td>
<td>0.609</td>
<td>$[H^+]$ - - 0.0426 - -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[SO_2_{aq}]$ - - 0.5664 - -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HC\textsubscript{10}O\textsubscript{4} Molar</td>
<td>Leach Rate mg Fe hr\textsuperscript{-1}</td>
<td>0.21</td>
<td>0.105</td>
<td>0</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

**TABLE XIII.** Variation of leach rate with pH at 110°C with a cupric ion concentration of 2(10\textsuperscript{-3}) M. 1 g goethite samples; 25 p.s.i.a. S\textsubscript{0}\textsuperscript{2}.

<table>
<thead>
<tr>
<th>HC\textsubscript{10}O\textsubscript{4} Molar</th>
<th>Na\textsubscript{2}S\textsubscript{0}\textsubscript{3} Molar</th>
<th>pH (-\log_{10}[\text{H}^+])</th>
<th>Leach Rate mg Fe hr\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0</td>
<td>0.670</td>
<td>7.2 7.7</td>
</tr>
<tr>
<td>0.105</td>
<td>0</td>
<td>0.949</td>
<td>12.1 13.1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1.559</td>
<td>48.5 52.0 54.7</td>
</tr>
<tr>
<td>0</td>
<td>0.05</td>
<td>2.310</td>
<td>74.1* 87.0*</td>
</tr>
<tr>
<td>0</td>
<td>0.10</td>
<td>3.000</td>
<td>76.1* 86.7*</td>
</tr>
</tbody>
</table>

* Initial rates; Cu\textsuperscript{2+} precipitated during run.

**TABLE XIV.** Variation of leach rate with pH at 90°C with a cupric ion concentration of 10\textsuperscript{-3} M. 1 g goethite samples; 14.7 p.s.i.a. S\textsubscript{0}\textsuperscript{2}.
TABLE XV. Variation of leach rate with sample weight at 110°C with a cupric ion concentration of $2 \times 10^{-3}$ M. Goethite samples; 25 p.s.i.g. SO$_2$; 0.21 M HClO$_4$.  

<table>
<thead>
<tr>
<th>[Cu$^{2+}$] Molar</th>
<th>Sample Weight</th>
<th>1 g</th>
<th>2 g</th>
<th>3 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{-3}$</td>
<td>Leach Rate, mg Fe hr$^{-1}$</td>
<td>43.9</td>
<td>60.8</td>
<td>78.5</td>
</tr>
<tr>
<td>0</td>
<td>*1</td>
<td>15.8</td>
<td>31.6</td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>*2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td></td>
<td>28.1</td>
<td>29.2</td>
<td>31.1</td>
</tr>
</tbody>
</table>

*1 Average of three rates.

*2 Rates calculated from known heterogeneous control of uncatalyzed reaction.
uncatalyzed rate was appreciable. Also included in Table XV were the calculated uncatalyzed rates for 1, 2, and 3 g samples based on the averaged measured 1 g rates, assuming heterogeneous control, as indicated by the results in Table VIII. The differences between the measured catalyzed rates and the calculated uncatalyzed rates were also tabulated.

At 90°C, 14.7 p.s.i.a. S\textsubscript{2}O\textsubscript{4}, experiments were undertaken with 1, 2, and 5 g samples with solutions at three different pH values. One series had an added cupric ion concentration of 10\textsuperscript{-3} M, the other 2(10\textsuperscript{-3}) M. Table XVI.

### 3.1.3.e Variation in Temperature

Experiments were conducted at 80, 90, 100 and 110°C at constant $C_{\text{SO}_2}$ (= 0.266 M) and almost constant hydrogen ion concentration. Table XVII.

### 3.1.4. Effect on the Reductive Dissolution of the Addition of Other Cations

The cations that were individually added to a typical leach solution fulfilled one or both of these conditions: 1. They had, like copper, two oxidation states whose redox potential was close to that of the $\text{SO}_2^2-/\text{SO}_4^{2-}$ or $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. 2. They had, like copper cations, the ability to form complex anions with bisulphite or sulphite ions, in one or more oxidation states.

Whenever possible, the cation was added as the perchlorate. Experiments were conducted at 110°C, 25 p.s.i.a. S\textsubscript{2}O\textsubscript{4}, no added acid.
<table>
<thead>
<tr>
<th>HClO₄ Molar</th>
<th>0.21</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₃</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>[Cu²⁺]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Weight</td>
<td>1 g</td>
<td>2 g</td>
<td>1 g</td>
</tr>
<tr>
<td>10⁻³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leach Rate</td>
<td>7.2</td>
<td>7.7</td>
<td>11.1</td>
</tr>
<tr>
<td>2(10⁻³) mg Fe hr⁻¹</td>
<td>-</td>
<td>-</td>
<td>73.2</td>
</tr>
</tbody>
</table>

*Initial rates - Cu²⁺ precipitated during run.

TABLE XVI. Variation of leach rate with sample weight at 90°C with cupric ion concentrations of 10⁻³ and 2(10⁻³) M. Goethite samples, 14.7 p.s.i.a. SO₂.
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{SO_2} ) p.s.i.a.</td>
<td>12.2</td>
<td>14.7</td>
<td>17.7</td>
<td>20.0</td>
</tr>
<tr>
<td>( HCIO_4 ) Molar</td>
<td>0</td>
<td>0</td>
<td>0.0046</td>
<td>0.0078</td>
</tr>
<tr>
<td>( Na_2SO_3 ) Molar</td>
<td>0.0034</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>([H^+]) Molar</td>
<td>0.0271</td>
<td>0.0276</td>
<td>0.0280</td>
<td>0.0282</td>
</tr>
<tr>
<td>([SO_2 \text{ aq}]) Molar</td>
<td>0.2321</td>
<td>0.2384</td>
<td>0.2426</td>
<td>0.2456</td>
</tr>
<tr>
<td>Leach Rate, mg Fe hr(^{-1})</td>
<td>28.1</td>
<td>48.5</td>
<td>79.9</td>
<td>142.0</td>
</tr>
</tbody>
</table>

**TABLE XVII.** Variation of leach rate with temperature with a cupric ion concentration of \(10^{-3}\) M. 1 g goethite samples; \(C_{SO_2} = 0.266\) M.
(unless stated). Table XVIII.

3.1.5 **Effect on the Reductive Dissolution of the Addition of Oxalate Anions**

Oxalate anions were added either as uranyl oxalate, UO$_2$C$_2$O$_4$·3H$_2$O, or as oxalic acid, H$_2$C$_2$O$_4$·2H$_2$O. Experiments at 110°C, 25 p.s.i.a. SO$_2$, were continued for 5 1/2 hours. Table XIX.

3.2 **Magnetite**

3.2.1 **Reductive Dissolution in Aqueous Sulphur Dioxide Solutions**

A 1 g sample of magnetite was leached at 110°C, 25 p.s.i.a. SO$_2$, 0.21 M HCIO$_4$. Table XX.

3.2.2 **Catalysis of the Reductive Dissolution by the Addition of Cupric Ions**

A 1 g sample of magnetite was leached at 90°C, 14.7 p.s.i.a. SO$_2$, with an initial cupric ion concentration of 10$^{-3}$ M. Table XX.

3.3 **Hematite**

3.3.1 **Reductive Dissolution in Aqueous Sulphur Dioxide Solutions**

A 1 g sample of hematite was leached at 110°C, 25 p.s.i.a. SO$_2$. Table XXI.

3.3.2 **Catalysis of the Reductive Dissolution by the Addition of Cupric Ions**

A 1 g sample of hematite was leached at 110°C, 25 p.s.i.a. SO$_2$, with an initial cupric ion concentration of 10$^{-3}$ M. Table XXI.
<table>
<thead>
<tr>
<th>Cation</th>
<th>Compound</th>
<th>Type</th>
<th>Concentration</th>
<th>Rate  mg hr^{-1}</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No Additions</td>
</tr>
<tr>
<td>Mn^{II}</td>
<td>Perchlorate</td>
<td>1.</td>
<td>10^{-3}</td>
<td>9.35</td>
<td>pH rose to 3.5 units</td>
</tr>
<tr>
<td>Sn^{II}</td>
<td>Chloride</td>
<td>1.</td>
<td>5(10^{-3})</td>
<td>11.7</td>
<td>+0.21 M HClO_4 to acidify</td>
</tr>
<tr>
<td>(V^V)</td>
<td>Sodium Vanadate</td>
<td>1.</td>
<td>5(10^{-3})</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Co^{II}</td>
<td>Perchlorate</td>
<td>1,2.</td>
<td>10^{-3}</td>
<td>7.05</td>
<td>Co^{III} unstable</td>
</tr>
<tr>
<td>Cr^{III}</td>
<td>Perchlorate</td>
<td>1,2.</td>
<td>5(10^{-3})</td>
<td>4.4</td>
<td>Cr^{II} unstable</td>
</tr>
<tr>
<td>Hg^{II}</td>
<td>Perchlorate Solution</td>
<td>1,2.</td>
<td>3(10^{-2})</td>
<td>15.0</td>
<td>Hg° formed</td>
</tr>
<tr>
<td>Ag^I</td>
<td>Sulphate</td>
<td>2.</td>
<td>10^{-3}</td>
<td>7.1</td>
<td>Ag^II unstable</td>
</tr>
<tr>
<td>Cd^{II}</td>
<td>Sulphate</td>
<td>2.</td>
<td>5(10^{-3})</td>
<td>7.55</td>
<td>Cd^I unstable</td>
</tr>
<tr>
<td>Tl^I</td>
<td>Nitrate</td>
<td>2.</td>
<td>10^{-3}</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>(VI)</td>
<td>Uranyl Nitrate</td>
<td>1,2.</td>
<td>5(10^{-3})</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Fe^{II}</td>
<td>Ferrous Sulphate</td>
<td>-</td>
<td>5(10^{-3})</td>
<td>10.4</td>
<td>Autocatalysis Experiment</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27.6 27.3</td>
<td>3.0 M HClO_4;</td>
</tr>
<tr>
<td>Fe^{II}</td>
<td>Ferrous Perchlorate</td>
<td>-</td>
<td>2(10^{-3})</td>
<td>29.6</td>
<td>Autocatalysis Experiment</td>
</tr>
</tbody>
</table>

TABLE XVIII. Effect on leach rate of the addition of various cations.
1 g goethite samples; 110°C; 25 p.s.i.a. SO_2.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Concen. Molar</th>
<th>Rate ( \text{mg hr}^{-1} )</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>8.75 9.35</td>
<td>No Additions</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}_2\text{O}_4\cdot\text{2H}_2\text{O} )</td>
<td>( 10^{-3} )</td>
<td>28.8</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{C}_2\text{O}_4\cdot\text{2H}_2\text{O} )</td>
<td>( 5(10^{-3}) )</td>
<td>68.0</td>
<td></td>
</tr>
<tr>
<td>( \text{UO}_2\text{C}_2\text{O}_4\cdot\text{3H}_2\text{O} )</td>
<td>( 5(10^{-3}) )</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>( \text{UO}_2\text{C}_2\text{O}_4\cdot\text{3H}_2\text{O} )</td>
<td>( 5(10^{-3}) )</td>
<td>41.1</td>
<td>0.14 N ( \text{H}_2\text{SO}_4 )</td>
</tr>
</tbody>
</table>

**TABLE XIX.** Effect on leach rate of the addition of oxalate anions. 1 g goethite samples; 110°C; 25 p.s.i.a. \( \text{SO}_2 \).
<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$P_{SO_2}$ p.s.i.a.</th>
<th>HClO$_4$ Molar</th>
<th>[Cu$^{2+}$] Molar</th>
<th>Leach Rate mg Fe hr$^{-1}$ Magnetite</th>
<th>Leach Rate mg Fe hr$^{-1}$ Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>25.0</td>
<td>0.21</td>
<td>0</td>
<td>19.3</td>
<td>15.2, 15.8, 16.3</td>
</tr>
<tr>
<td>90</td>
<td>14.7</td>
<td>0</td>
<td>0.001</td>
<td>111.7</td>
<td>48.5, 52.0, 54.7</td>
</tr>
</tbody>
</table>

**TABLE XX.** Comparison of the leach rates of magnetite and goethite under identical conditions. 1 g samples.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$P_{SO_2}$ p.s.i.a.</th>
<th>HClO$_4$ Molar</th>
<th>[Cu$^{2+}$] Molar</th>
<th>Leach Rate mg Fe hr$^{-1}$ Hematite</th>
<th>Leach Rate mg Fe hr$^{-1}$ Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0.90</td>
<td>8.75, 9.35</td>
</tr>
<tr>
<td>110</td>
<td>25</td>
<td>0</td>
<td>0.001</td>
<td>32.7</td>
<td>129.0</td>
</tr>
</tbody>
</table>

**TABLE XXI.** Comparison of the leach rates of hematite and goethite under identical conditions. 1 g samples.
4. DISCUSSION

The constant leach rates observed in all low acid \((<0.75 \text{ M } [\text{H}^+])\) experiments showed that anisotropic leaching was not observable. The constant leach rates also showed that autocatalysis by ferrous ions did not occur to any appreciable extent.

Since the dissolution rate of the hematite was so low, no correction was applied to the leach rates of goethite samples to take into account the hematite present in that ore.

Because of the absence of high temperature data on the activity coefficients of perchloric acid solutions, and aqueous sulphur dioxide solutions, concentrations were used throughout the discussion.

4.1 Goethite

4.1.1 Direct Dissolution in Perchloric Acid

The leach rates have been plotted against hydrogen ion concentration, assuming 100% ionization, in Figure 7. The form of a curve that best fits the experimental results is an adsorption isotherm in hydrogen ion concentration:

\[
\text{rate} = \frac{\text{constant}_1 [\text{H}^+]}{1 + \text{constant}_2 [\text{H}^+]} \quad \text{(Langmuir)}
\]
FIGURE 7. Variation of the direct perchloric acid leach rate with hydrogen ion concentration. Ig. goethite samples; 110°C.
Postulated mechanism:

1. Protonation of a surface site:

\[
\text{FeOOH} + \text{H}^+ \xrightleftharpoons{K_1} \text{Fe(OH)}^+ \text{Θ}_1 \to \text{Fe(OH)}^- \text{Θ}_2
\]

1a. Desorption of an hydroxy-ferric species:

\[
\text{Fe(OH)}^+ \text{Θ}_2 \xrightarrow{k_1} \text{Fe(OH)}^+ \text{Θ}_2 \text{aq} \quad (28)
\]

/ denotes the surface of the oxide.

K and k are equilibrium and rate constants respectively. Θ denotes a surface charge.

\(\theta_1\) and \(\theta_2\) are the fractions of the total active surface area occupied by FeOOH and Fe(OH) \(\Theta\) species respectively.

i.e.,

\[
\theta_1 + \theta_2 = 1
\]

\[
\theta_2 = K_1[H^+]\theta_1
\]

\[
\theta_1 = \frac{1}{1 + K_1[H^+]} \]

Rate of Dissolution = \(\frac{d[\text{Fe}_{\text{aq}}]}{dt}\) = \(k_1\theta_2\)

\[
\frac{d[\text{Fe}_{\text{aq}}]}{dt} = \frac{k_1K_1[H^+]}{1 + K_1[H^+]}
\]

The constants \(k_1\) and \(K_1\) were evaluated by substituting the averaged leach rates measured at two different hydrogen ion concentrations into the above equation and solving simultaneously. Using the averaged rates...
at 0.75 M and 6.0 M \([H^+]\), the constants had the following values:

\[ k_1 = 4.584; \ K_1 = 0.688 \]

The theoretical rate is:

\[ \frac{3.153[H^+]}{1 + 0.688[H^+]} \]

This curve was also plotted on Figure 7, and fitted the experimental data at other hydrogen ion concentrations. The good correlation between the observed and theoretical rates justified the assumption in the postulated mechanism that perchlorate anions did not affect the leach rate, even if they adsorbed on the surface. This was also justified by their known low complexing power for ferric ions (37).

4.1.2 Reductive Dissolution in Aqueous Sulphur Dioxide Solutions

The variable stirring speed experiments (Table VI) indicated that, under those conditions, the rate of the dissolution reaction was not controlled by the diffusion of species to or away from the surface of the oxide. If the reaction were diffusion controlled, then a large variation in leaching rate with stirring speed should have been observed.

The variable sample weight experiments (Table VIII) showed that the dissolution reaction was heterogeneously controlled, i.e. occurred at the oxide surface.

If the reaction were homogeneously controlled, i.e. the slow step was one which occurred in solution, then the rate with 2 or 3 g samples should have been equal to the rate with a 1 g sample. Since
The rates with 2 and 3 g samples were twice and thrice the rate with a 1 g sample respectively, the slow step was one which occurred exclusively at the oxide surface.

The apparent activation energy was calculated from the experimental data at 80, 90, 100, 110 and 120°C (Table IX) using the Arrhenius equation:

\[
\text{Rate} = K \exp\left(-\frac{E_A}{RT}\right)
\]

where \(K\) = a pre-exponential factor.

\(R\) = the gas constant, 1.987 cal.°A\(^{-1}\)

\(T\) = temperature, °A

\(E_A\) = apparent activation energy.

Rearranging, \(\log_{10}(\text{rate}) \propto -\frac{E_A}{2.3026R} \cdot \left(\frac{1}{T}\right)\). A graph of \(\log_{10}(\text{rate})\) against \(\frac{1}{T}\) was a good straight line (obtained by linear regression analysis), the gradient being equal to \(-\frac{E_A}{2.3026R}\) (Figure 8).

Hence \(E_A = 16.38 \pm 0.75\) kcal mole\(^{-1}\).

This value was well above the normal maximum-observed apparent activation energy for a diffusion-controlled reaction, 6.5 kcal mole\(^{-1}\).

The experiments performed with additions of ferrous ion had similar leach rates to identical experiments with no initial ferrous ions (Table XVIII). This was additional proof that no autocatalysis occurred.

A graph of leach rate against aqueous sulphur dioxide concentration, Figure 9, showed that the rate was first order in \([\text{SO}_2\text{aq}]\) under the
FIGURE 8. Arrhenius plot of log$_{10}$ (reductive leach rate) against the reciprocal of the absolute temperature.

SLOPE = $-3.580$

$E_A = 16.38 \text{k cal. mole}^{-1}$
FIGURE 9. Reductive leach rates plotted against aqueous sulphur dioxide concentration.

Ig. goethite samples; 110°C.
conditions studied. In addition, the leach rate increased for a given
\([\text{SO}_2\text{aq}]\) as the perchloric acid concentration was increased. The
incremental increases in leach rate as \([\text{H}^+]\) increased at constant
\([\text{SO}_2\text{aq}]\) were greater at higher \([\text{SO}_2\text{aq}]\).

The increase in leach rate with \([\text{H}^+]\), at constant sulphur dioxide
partial pressure, was typified by the graph of the results at \(c_{\text{SO}_2} = 0.33\) M. Figure 10. The increase in leach rate with increasing \([\text{H}^+]\)
fell until the rate became first order in \([\text{H}^+]\) at \(> 0.75\) M \([\text{H}^+]\). However,
at hydrogen ion concentrations greater than this value the leaching
behaviour was anomalous (Figure 6).

These curved plots were not a consequence of autocatalysis since
the experiment at 110°C, 25 p.s.i.a. \(\text{SO}_2\), with 3.0 M HClO\(_4\) and \(2(10^{-3})\) M
added ferrous ion was similarly curved, and had a final leach rate
comparable with that of an identical experiment with no initial
ferrous ion addition. Table XVIII.

The curved plots might be the results of dissolution anisotropy
at these high hydrogen ion concentration experiments. It was considered
unlikely that the curved plots could be a consequence of a slow rate
of attainment of the equilibrium concentration of \(\text{SO}_2\text{aq}\) in solution
at the high \([\text{H}^+]\) which prevailed. An experiment was performed on a
1 g goethite sample at 110°C, 25 p.s.i.a. \(\text{SO}_2, 3.0\) M HClO\(_4\) to investigate
this possibility. After four hours leaching, the leach rate had
become constant at 26.4 mg hr\(^{-1}\). The autoclave and contents were
cooled to room temperature and the sulphur dioxide was expelled from
the autoclave under continuous stirring and flushing with nitrogen.
When it was considered that sufficient time had elapsed for the
FIGURE 10. Reductive leach rates at 25 PS.I.A. SO₂ plotted against hydrogen ion concentration. Ig. goethite samples; 110°C.
expulsion of almost (if not) all the sulphur dioxide, the autoclave and contents were again heated to 110°C. After readmission of sulphur dioxide to a partial pressure of 25 p.s.i.a., the leaching experiment was continued. No curving was observed, and for the three hours of the continued experiment the leach rate was constant at 28.0 mg hr⁻¹. The solubility of sulphur dioxide in the high hydrogen ion concentration experiments was assumed to be unaffected by the hydrogen ions due to a lack of data to the contrary.

Because of all these uncertainties, the high perchloric acid concentration experimental data was not taken into consideration in the development of a leaching mechanism.

All the straight lines in Figures 9 and 10 were obtained by linear regression analysis of the relevant experimental results.

In postulating the following mechanism, all the above facts, the theory reviewed earlier, and the observed hydrogen ion adsorption isotherm for direct perchloric acid leaching, have been taken into consideration.

Postulated Mechanism:

1. Protonation of a surface site:

\[
\begin{align*}
\text{FeOOH} + H^+ & \overset{K_1}{\rightarrow} \text{Fe(OH)}_2^+ \\
\theta_1 & \rightarrow \theta_2
\end{align*}
\]

2. Adsorption of an aqueous sulphur dioxide molecule on a protonated surface site:

\[
\begin{align*}
\text{Fe(OH)}_2^+ + SO_2 \text{aq} & \overset{K_2}{\rightarrow} \text{Fe(OH)}_2SO_2^+ \\
\theta_2 & \rightarrow \theta_3
\end{align*}
\]
3. Second protonation of a protonated site already containing an adsorbed sulphur dioxide molecule:

\[
\frac{\text{Fe(OH)}_2\text{SO}_2^{\oplus} + H^+}{\text{Fe(OH)}_2\text{SO}_2^{\oplus}} \xrightleftharpoons{K_3} \frac{\text{Fe(OH)}_2\text{HSO}_2^{\oplus}}{\theta_4}
\]

The following leaching reactions are possible if solution of iron from all surface sites is considered:

1a. \(\frac{\text{Fe(OH)}_2^{\oplus}}{\text{Fe(OH)}_2(aq)} \xrightarrow{k_1} \theta_2\)

2a. \(\frac{\text{Fe(OH)}_2\text{SO}_2^{\oplus}}{\text{FeSO}_3^{\oplus} + H_2O} \xrightarrow{k_2} \theta_3\)

3a. \(\frac{\text{Fe(OH)}_2\text{HSO}_2^{\oplus}}{\text{FeHSO}_3^{2+} + H_2O} \xrightarrow{k_3} \theta_4\)

4. Reduction of ferric ions in solution:

Ferrous ions were formed in solution by the reductive action of aqueous sulphur dioxide or anions derived from its dissociation (4). No ferric ions were detected in leach solutions analyzed for both ferric and ferrous ions independently. Consequently the reduction in solution was very fast.

\[
\theta_1 + \theta_2 + \theta_3 + \theta_4 = 1
\]

\[
\theta_2 = K_1[H^+]\theta_1
\]
\[ \theta_3 = K_1 K_2 [H^+] [SO_2 \text{aq}] \theta_1 \]

\[ \theta_4 = K_1 K_2 K_3 [H^+]^2 [SO_2 \text{aq}] \theta_1 \]

/Fe(OH)$_2$HSO$_2$\textsuperscript{2+} sites were expected to be highly transitory and thus \( \theta_4 \to 0 \).

Hence

\[ \theta_1 = \frac{1}{1 + K_1 [H^+] + K_1 K_2 [H^+] [SO_2 \text{aq}]} \]

The rate of dissolution is:

\[ \frac{d[Fe_{\text{aq}}]}{dt} = k_1 \theta_2 + k_2 \theta_3 + k_3 \theta_4 \]

\[ \frac{d[Fe_{\text{aq}}]}{dt} = \frac{K_1 [H^+](k_1 k_2 K_2 [SO_2 \text{aq}] + k_3 K_2 K_3 [H^+] [SO_2 \text{aq}])}{1 + K_1 [H^+] + K_1 K_2 [H^+] [SO_2 \text{aq}]} \]

The groups of constants were evaluated by substituting the leaching rates (as predicted by the linear regression analysis) at the low [H$^+$] experiments with constant [SO$_2$ \text{aq}] = 0.30 M into the above equation and solving simultaneously.

When the values of \( K_1 \) and \( k_1 \) were taken to be those of the direct perchloric acid leaching mechanism, the theoretical rate became:

\[ \text{Rate}_{\text{th.}} = \frac{[H^+](3.153 + 2705.67[SO_2 \text{aq}] + 984.53[H^+][SO_2 \text{aq}])}{1 + 0.688[H^+] + 183.99[H^+][SO_2 \text{aq}]} \]

Although this theoretical expression accurately predicted the experimentally observed leach rates at [SO$_2$ \text{aq}] = 0.30 M, it failed
when applied to other hydrogen ion and aqueous sulphur dioxide concentrations.

The equilibrium constant in the direct perchloric acid leaching, $K_1$, should have been expressed in activities:

$$K_1 = \frac{a/Fe(OH)_2^\oplus}{a_{H^+} \cdot a/FeOOH} = \frac{\gamma/Fe(OH)_2^\oplus/[Fe(OH)_2^\oplus]}{\gamma_{H^+}[H^+] \cdot \gamma/FeOOH/[FeOOH]}$$

The presence of aqueous sulphur dioxide, bisulphite anions and other sulphur-containing species in solution might result in their adsorption without significant reaction on unprotonated /FeOOH surface sites. This would reduce the activity of such surface sites in comparison with the direct perchloric acid leaching. The activity of the protonated /Fe(OH)$_2^\oplus$ sites might change for a similar reason. Consequently the value of $K_1$ in the reductive dissolution experiments might be expected to have an apparently different value from that in the direct leaching investigation. Since $K_1$ was related to a fixed concentration of the protonated sites (1 g sample of ore) it also would be expected to have a different apparent value.

The theoretical expression was re-solved for all groups of constants, using results from the linear regression analysis at [SO$_2$$_{aq}$] = 0.30 M, low [H$^+$], and [SO$_2$$_{aq}$] = 0.1994 M, [H$^+$] = 0.7506 M. Analysis showed that the denominator term $K_1 K_2 [H^+] [SO_2_{aq}]$ → zero, i.e. $\theta_3 \to$ zero. This was expected since no adsorption isotherm in [SO$_2$$_{aq}$] was observed.
\[
\text{Rate}_{\text{th.}} = \frac{[H^+](195.19 + 2063.27[SO_2 \text{aq}] + 984.50[H^+][SO_2 \text{aq}])}{1 + 55.185[H^+]}
\]

with \( K_1 = 55.185 \)

\( k_1 = 3.537 \)

\( k_2K_2 = 37.388 \)

\( k_3K_2K_3 = 17.840 \)

This expression was plotted against \([SO_2 \text{aq}]\) on the graph, Figure 11. It described the linear regression analyses of the experimental results at the four different low perchloric acid concentrations fairly accurately. With constant \( C_{SO_2} = 0.33 \text{ M} \), the theoretical rate expression was plotted against \([H^+]\) on the graph, Figure 12. At high perchloric acid concentrations (> 0.75 M), the theoretical expression predicted greater leach rates than those experimentally measured under somewhat obscure conditions.

Although many other different reaction mechanisms were tried, none was even remotely successful in accounting for the experimental results. Included in the mechanisms tried was one based on the adsorption of an aqueous sulphur dioxide molecule followed by protonation.

Physically, the postulated mechanism seemed difficult to comprehend since it required that a neutral, though solvated and possibly polarized, sulphur dioxide molecule should adsorb on or adjacent to a positively charged site. However, neutral aqueous sulphur dioxide molecules have been found to leach manganese dioxide \((37,38)\), although a mechanism was not proposed.
FIGURE II. Comparison of the experimental and theoretical leach rates—variation with aqueous sulphur dioxide concentration.
FIGURE 12. Comparison of the experimental and theoretical leach rates—variation with hydrogen ion concentration at 25 P.S.I.A. $\text{SO}_2$. 
The bisulphite anion was ruled out as a leaching species on account of the high rates of dissolution measured when its concentration was extremely small. However, in the postulated theoretical rate expression $[\text{SO}_2\text{aq}]$ could be replaced without effect by $\frac{[\text{H}^+][\text{HSO}_3^-]}{K}$, where $K$ = first dissociation constant of aqueous sulphur dioxide. Such an expression required that an extra protonation step occurred in the reaction mechanism, followed or preceded by the adsorption of a bisulphite anion instead of a sulphur dioxide molecule. This was considered highly unlikely in view of the apparent lack of such an occurrence even at high $[\text{H}^+]$ in the direct perchloric acid leaching.

4.1.3 Catalysis of the Reductive Dissolution by the Addition of Cupric Ions

Cupric ions are reduced in aqueous sulphur dioxide:

$$2\text{Cu}^{2+} + \text{SO}_2\text{aq} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Cu}^{+} + \text{SO}_4^{2-} + 4\text{H}^+$$

The formation of cuprous ions is favoured by a high concentration of $\text{SO}_2\text{aq}$, and low concentrations of $\text{SO}_4^{2-}$ and $\text{H}^+$ (high $\text{pH}$).

Cuprous ions are unstable in aqueous solution unless complexed:

$$2\text{Cu}^{+} \rightleftharpoons \text{Cu}^{2+} + \text{Cu}^{0+}$$

At high pH, high $[\text{SO}_2\text{aq}]$, cuprous ions may be reduced to copper metal:
Copper metal dissolves slowly in aqueous sulphur dioxide with the formation of insoluble, black cupric sulphide (75):

\[ 2\text{Cu}^0 + 2\text{S}0_2 \text{aq} \rightarrow \text{CuS} + \text{Cu}^{2+} + \text{S}0_4^{2-} \]

It was concluded that the fine black powder found adhering to the Teflon and glass surfaces below solution level in copper catalyzed experiments was cupric sulphide, formed in this manner.

Cuprous ions are strongly complexed by HSO\(_3^-\) and S0\(_3^{2-}\) anions (36), forming species of the form: \(\text{Cu}^{(\text{HSO}_3)}^{(n-1)-}\) and \(\text{Cu}^{(\text{SO}_3)}^{(2m-1)-}\). It was thought that the formation of these complexes stabilized the cuprous ions, preventing excessive disproportionation and reduction in low pH leach solutions. At high pH and possibly at high \([\text{S}0_2 \text{aq}]\) (15), the cuprous complexes were unable to prevent reduction to metal.

Since the system was so complex, it was difficult to obtain a meaningful activation energy for the reduction of cupric ions to cuprous ions by aqueous sulphur dioxide. However, a method of recovering copper as cuprous chloride from leach solutions containing cupric ions is of relevance. The "Hunt and Douglas" process (circa 1881) involved reducing a solution of cupric chloride with aqueous sulphur dioxide and collecting the cuprous chloride precipitated from solution:

\[ 2\text{CuCl}_2 + \text{S}0_2 \text{aq} + 2\text{H}_2\text{O} \rightarrow 2\text{CuCl}^+ + 2\text{HCl} + \text{H}_2\text{SO}_4 \]
It was noted that the reaction was slow at room temperature but very rapid between 80 and 90°C (76). This implied that the activation energy for the reduction of cupric ions to cuprous ions by aqueous sulphur dioxide was large.

At 110°C the leach rate was found to have a first order dependence on the initial concentration of cupric ions. Table X; Figure 13. At 90°C, 14.7 p.s.i.a. SO₂, a similar first order dependence was observed for \([\text{Cu}^{2+}] \approx 10^{-3} \) M. Table XI; Figure 14. The straight lines were obtained by linear regression analysis of the experimental results.

The pH of the leach solution was found to have a great effect on the rate of dissolution. Tables XIII, XIV. At 110°C the leach rate became so great at high pH that it was found necessary to investigate the cupric catalyzed system at 90°C. Also, the runs at 90°C did not suffer from having a high rate of uncatalyzed dissolution.

The observation that at 110°C, \(C_{\text{SO}_2} = 0.33 \) M, \([\text{Cu}^{2+}] = 2(10^{-3})\) M, \([\text{H}^+] = 0.0267\) M, all the iron was in solution within three hours proved the existence of a fast catalytic mechanism.

A graph of pH against leach rate for the experiments at 90°C, \([\text{Cu}^{2+}] = 10^{-3} \) M, \(C_{\text{SO}_2} = 0.266\) M showed how the leach rate rose dramatically as the pH increased from 1 to 2 units. Figure 15. The constant leach rate observed between pH 2 and 3 was probably genuine, but the rates measured might have been low due to the precipitation of copper metal from solution. The large decrease in \([\text{SO}_2^{\text{aq}}]\) probably had some effect.

The results obtained from the experiments varying the partial pressure of sulphur dioxide were complicated by the fact that at there
FIGURE 13. Variation of leach rate with cupric ion concentration at 110°C, 25 P.S.I.A. SO₂. Ig. goethite samples.
Figure 14. Variation of leach rate with cupric ion concentration at 90°C, 14.7 PS.I.A. SO₂, 1g. goethite samples.
FIGURE 15. Variation of leach rate with pH at 90°C. 1g. goethite samples; 14.7 P.S.I.A. SO₂; 10⁻³ M [Cu²⁺].
was a slight pH variation (from 1.371 at 34.7 p.s.i.a. to 1.559 at 14.7 p.s.i.a.). This was in the range where there was a maximum change in leach rate with hydrogen ion concentration. From Figure 15, estimates were made of the rate of leaching with $[\text{Cu}^{2+}] = 10^{-3}$ M, 14.7 p.s.i.a. SO$_2$, but with $[\text{H}^+] = 0.0360$ M (40.5 mg hr$^{-1}$) and $[\text{H}^+] = 0.0426$ M (34.0 mg hr$^{-1}$), corresponding to the pH of the solutions with sulphur dioxide partial pressures of 24.7 and 34.7 p.s.i.a. respectively. Since these values were lower than the averaged experimentally obtained rates at the same pH but with higher sulphur dioxide partial pressure, it was concluded that the higher the sulphur di oxide partial pressure the greater the leach rate. The increase in the rate of dissolution may have been due to the higher [SO$_2$]$_{aq}$ and/or the higher [HSO$_3$] and [SO$_3^{2-}$].

The variable sample weight experiments at 110 °C, Table XV, indicated that the catalyzed and uncatalyzed dissolution reactions were able to occur simultaneously. At the high $[\text{H}^+]$ and $[\text{SO}_2]_{aq}$ of these experiments the catalyzed reaction was homogeneously controlled.

At 90°C, Table XVI, the catalyzed rate was also homogeneously controlled at high $[\text{H}^+]$. As the pH was increased the control became mixed, and the rate-controlling step tended to become more heterogeneous for low sample weights. However, the experiments on 1, 2, and 5 g samples at $[\text{H}^+] = 0.0276$ M, $[\text{Cu}^{2+}] = 10^{-3}$ M showed that the control tended to become homogeneous for sample weights greater than or equal to 5 g. Figure 16.

The apparent activation energy was calculated from the results in Table XVII using the Arrhenius equation. A value of $13.94 \pm 1.00$ kcal mole$^{-1}$ was obtained from the slope of a line obtained by linear regression
FIGURE 16. Variation of leach rate with goethite sample weight at 90°C; 14.7 PS I.A. SO₂; 10⁻³ M [Cu²⁺].
analysis of the experimental data. Figure 17. This value of the apparent activation energy indicated that the diffusion of species in solution was not the rate-controlling step.

Because of the lack of data on the many equilibria present in the copper catalyzed system and the apparent complexity of the experimental results, a quantitative analysis was impossible. However, the following qualitative mechanism was postulated, bearing in mind the experimental trends and their similarity to the oxidative, ferric ion promoted leaching of uranium dioxide (43).

The role of aqueous sulphur dioxide was four-fold:

1. It leached the goethite by the same mechanism as in the uncatalyzed system.

2. It reduced cupric ions to cuprous ions, which were considered to be the "catalyzed" leaching species.

3. By dissociating, it provided bisulphite and/or sulphite anions which formed stable anionic complexes with the cuprous ions. In the form of such an anionic complex, a cuprous ion adsorbed on the surface of the oxide and underwent an electron-exchange reaction with a surface Fe^{III} species. The Fe^{II} and Cu^{II} species produced desorbed, forming ferrous and cupric ions in solution. The cupric ion was again reduced by the aqueous sulphur dioxide and this behaviour justified the use of the term "catalysis".

4. It redissolved part of the copper metal precipitated from solution:

\[ 2\text{Cu}^0 + 2\text{SO}_2^{\text{aq}} \rightarrow \text{CuS}^+ + \text{Cu}^{2+} + \text{SO}_4^{2-} \]
FIGURE 17. Arrhenius plot of $\log_{10}$ (catalysed leach rate) against the reciprocal of the absolute temperature.

SLOPE $=-3.057$

$E_A=13.94$ kcal. mole$^{-1}$
The leach rate was therefore directly proportional to the concentration of cuprous ion, which in turn was proportional to the initial concentration of cupric ion. A first order dependence of the leach rate on the initial cupric ion concentration was observed.

At a fixed initial cupric ion concentration, the leach rate depended directly upon the concentration or rate of formation of cuprous ions. Factors which theoretically increased the concentration of cuprous ions were high temperatures and, according to the Law of Mass Action applied to the equilibrium:

$$2Cu^{2+} + SO_2_{aq} + 2H_2O \rightleftharpoons 2Cu^+ + SO_4^{2-} + 4H^+,$$

high $[SO_2_{aq}]$, low $[H^+]$ and low $[SO_4^{2-}]$. Leach rates were increased by raising the temperature and the aqueous sulphur dioxide concentration, and by reducing the hydrogen ion concentration.

The leach rate also depended upon the formation of an anionic cuprous complex which:

1. was strong enough to stabilize the Cu$^+$ state against further reduction or disproportionation;

2. had a favourable charge and stoichiometry for adsorption on the oxide surface and subsequent electron exchange between Cu$^+$ and Fe$^{III}$ (possibly via a suitable bridging ligand). High pH and $[SO_2_{aq}]$ favoured the formation of complex anionic cuprous species because of the greater concentrations of bisulphite and/or sulphite ions. However, at the higher pH and $[SO_2_{aq}]$ the reduction of cuprous ions to copper
metal was favoured. The effects that these considerations had on the leach rate were not apparent because the leach rate was increased by the greater concentration of cuprous ions formed under identical circumstances.

The reduction of cupric ions to cuprous ions was shown to be taking place exclusively in solution by the variable sample weight experiments. At low pH the rate of formation of cuprous ions was slow and this was the homogeneous catalyzed-rate-determining step. As the pH was raised the rate of formation of cuprous ions became fast enough at 90°C for a surface reaction to become the slow, purely heterogeneous, rate-controlling step.

4.1.4 Effect on the Reductive Dissolution of the Addition of Other Cations

Of the other cations added to a typical leach solution only mercury was found to promote the dissolution of goethite. Table XVIII. However, the conditions of the experiment were too reducing and/or the mercurous-bisulphite or -sulphite complexes were not strong enough to prevent the precipitation of mercury metal.

Cations (type 2) capable of forming bisulphite or sulphite species which could adsorb on the goethite surface were added with no resultant increase in leach rate. This was considered as additional evidence for the assumption that increasing the surface concentration of bisulphite or sulphite ions does not increase the rate of dissolution.

The reasons for the failure of the cations to promote or catalyze the leach rate were not investigated.
However it was possible to speculate that they may have failed because of one or more of these reasons:

1. No stable higher or lower oxidation state in the leach solution.
2. Thermodynamics and/or kinetics were not favourable for the reduction of the cation in the higher oxidation state by aqueous sulphur dioxide.
3. Thermodynamics and/or kinetics were not favourable for the oxidation of the cation in the lower oxidation state by $\text{Fe}^{\text{III}}$ on the goethite surface.
4. Inability of the cation in the lower oxidation state to form an anionic complex capable of adsorbing on the goethite surface.
5. Reduction of the cation to metal.

It may be possible that any of these cations might catalyze the dissolution of goethite if certain specific anions were present in the solution capable of complexing the cation in such a manner as to overcome the thermodynamic, kinetic, or stability barriers. The direct leaching of hematite by oxalic acid in the absence of oxygen was catalyzed by the addition of a small amount of ferrous oxalate, but was unaffected by the addition of ortho-phenanthroline, a stronger ferrous ion complexer (13,14).

4.1.5 Effect on the Reductive Dissolution of the Addition of Oxalate Anions

The catalytic effect of oxalate anions was observed when uranyl oxalate was used to investigate the possibility that $\text{U}^{\text{VI}}$ might catalyze the reductive dissolution of goethite. Table XIX. Although the effect
was not investigated thoroughly, the observed pH and oxalate concentration
dependency of the leach rate was reminiscent of Devuyst's ferrous
oxalate catalyzed, direct oxalic acid leaching of hematite (13,14).
In the oxalate catalyzed, reductive dissolution of goethite, the
necessary ferrous ions were provided by the normal uncatalyzed leaching
mechanism. Apparently, as found by Devuyst, the presence of ferrous
ions over and above a certain low concentration had no extra catalytic
effect. In his work the limit was the maximum solubility of ferrous
oxalate. In this work the limit might have been the ferrous ion
concentration at equilibrium with the much lower oxalate ion concentration.

4.2 Magnetite

A detailed investigation of the reductive dissolution of magnetite
by aqueous sulphur dioxide solutions was not carried out.

The two experiments undertaken with and without the addition of
cupric ions (Table XX) showed that in both systems the magnetite
had comparable leach rates to goethite after normalisation of the
different ores' iron contents.

4.3 Hematite

Although a full investigation of the reductive dissolution of
hematite by aqueous sulphur dioxide solutions was not carried out,
the two experiments performed showed anomalous behaviour compared with
goethite (Table XXI).
The normalized uncatalyzed leach rate was an order of magnitude lower than the comparable rates for goethite, even though the surfaces were reported to be similar in aqueous solution, Section 1.3.1. The slow rate of dissolution of hematite could have been due to a slow rate of hydration of hematite to produce a surface similar to goethite. However, although this could have been true for synthetic hematite (21), it is supposedly not true for natural hematite (24).

The copper catalyzed leach rate of hematite was more comparable with that of goethite. Since a quantitative analysis was not made of the catalyzed dissolution of goethite, no attempt was made to take into account the catalyzed dissolution of the hematite present in the goethite ore.
5. CONCLUSIONS

5.1 Summary

1. A mechanism has been proposed to explain how goethite was leached by perchloric acid. The rate of dissolution at 110°C was found to be described by the equation:

\[
\frac{d[Fe_{aq}]}{dt} = \frac{3.153[H^+]}{1 + 0.688[H^+]}
\]

2. A mechanism was also proposed to account for the reductive dissolution of goethite in acidified aqueous sulphur dioxide solutions. The rate of dissolution at 110°C was found to be described by the equation:

\[
\frac{d[Fe_{aq}]}{dt} = \frac{[H^+](195.19 + 2063.27[S0_{2\,aq}] + 984.50[H^+][S0_{2\,aq}])}{1 + 55.185[H^+]}
\]

The rate controlling step was heterogeneous.

3. A qualitative mechanism was proposed to describe the role of cupric ions in increasing the reductive leach rate of goethite. Cuprous ions, formed by the reduction of cupric ions by sulphur dioxide molecules in solution, were thought to have been adsorbed on the
goethite surface as a suitable anionic complex. Electron exchange between Fe$^{III}$ and Cu$^{I}$ was followed by the desorption of ferrous and cupric ions into solution. Cupric ions were therefore catalytic agents. The reduction of cupric ions to cuprous ions was the rate controlling step at low pH. At higher pH the control was mixed for low sample weights of ore.

4. Both magnetite and hematite leached at comparable rates with goethite in the cupric ion catalyzed system. Although the reductive leach rate of magnetite was comparable with goethite's in the uncatalyzed system, that of hematite was an order of magnitude lower.

5.2 Suggestions for Future Work

1. The uncatalyzed reductive leaching of goethite could be examined at high acidity and at much higher aqueous sulphur dioxide concentrations.

2. A detailed investigation of the reductive leaching of both magnetite and hematite in aqueous sulphur dioxide solutions could be made. This might explain the anomalous dissolution behaviour of hematite in the uncatalyzed system.

3. The cupric ion catalyzed reductive dissolution of goethite could be investigated in the presence of an anion having a strong complexing power for cuprous ions. This might have the effect of stabilizing the cuprous ion so that further reduction or disproportionation was impossible, even at high pH. The anionic cuprous complex would have to be able to adsorb on the oxide surface and permit electron exchange between Cu$^{I}$ and Fe$^{III}$.
4. The cupric ion catalyzed, reductive dissolution of goethite in aqueous sulphur dioxide solutions was apparently rate-limited by the formation of cuprous ions. It might be possible that the presence of another soluble reducing gas in the autoclave (in addition to sulphur dioxide) might speed up the reduction of cupric ions with no adverse side-effects.

5. The apparent catalytic effects of mercuric cations and oxalate anions would be worth investigating.
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