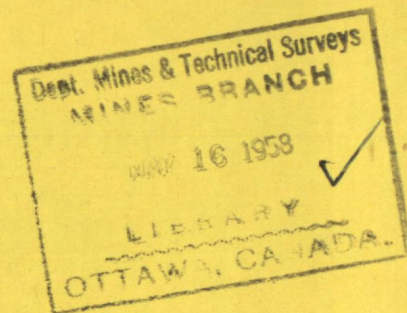




CANADA



THE LEACHING OF MANGANESE
FROM PYROLUSITE ORE BY PYRITE

by

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The Leaching of Manganese from Pyrolusite Ore by Pyrite¹

G. THOMAS² and B. J. P. WHALLEY³

A new method of leaching low-grade manganese ore (< 5% Mn) utilizing pyrite as a reagent was developed. By heating an aerated slurry of ore and pyrite and by recycling the leach liquor at controlled acidity to attack fresh ore, a manganous sulphate solution free of iron was obtained which when heated to about 175°C., yielded manganous sulphate monohydrate. During the leaching process, iron in the liquor was alternately oxidized by the pyrolusite and reduced by the pyrite. In an alternative leaching procedure, the heating of an aqueous slurry of pyrite in an autoclave first under oxygen pressure and then in the absence of oxygen produced an acidic ferrous sulphate solution suitable for the subsequent leaching of pyrolusite ore at ambient temperatures.

IN conjunction with a major iron mining operation in Ontario, a large annual tonnage of manganiferous low-grade iron ore is brought to the surface as waste material. The average composition of this material is 50% silica, 40% iron oxides, 6% clay and accessory minerals and 4% manganese oxides, principally pyrolusite, MnO_2 . If the manganese could be recovered from this waste material, the amount available would almost satisfy Canada's annual manganese requirement of 30,000 tons. During a Mines Branch investigation of this material, a new process for leaching manganese was developed. This paper describes the development and chemistry of the leaching process.

There is an abundant literature on processes for the recovery of manganese from relatively high-grade pyrolusite ore. Of the many processes, the most interesting approach for the recovery of manganese from this low-grade material appeared to be that based on the use of pickle liquor from the steel industry. Hoak and Coull⁽¹⁾

have shown that pickle liquor, which contains free sulphuric acid and ferrous sulphate, would give a 98% extraction from ores containing 15 to 25% manganese. There are many literature references⁽²⁻⁵⁾ stating that sulphuric acid and ferrous sulphate are formed, in the presence of water, by the air oxidation of the relatively cheap and abundant mineral pyrite, FeS_2 . It seemed reasonable therefore to determine if manganese could be leached from an aerated slurry of pyrolusite ore using pyrite as the leaching agent.

Experimental leaching of manganese dioxide

The initial experimental work to test the feasibility of leaching pyrolusite ore by pyrite was done using pure manganese dioxide. When a slurry of pyrite (80% minus 200 mesh) and manganese dioxide in water was treated at 175°C. and under 100 psig oxygen pressure for two hours in an autoclave, very little manganese was dissolved. Although

manganese dioxide is insoluble in dilute sulphuric acid, the addition of this acid was found to accelerate the dissolution of manganese dioxide by pyrite. For example, when 1% v/v H_2SO_4 was substituted for water in the above experiment, the manganese was dissolved completely in two hours.

Additional experiments were done to determine the effect of lower temperatures on the dissolution of manganese dioxide. The experimental conditions and results for these experiments, given in Figure 1, curve 1, show that the dissolution of manganese by pyrite in 1% v/v H_2SO_4 was complete after two hours at 110°C. Analysis of the leach liquors from these experiments showed that high manganese:iron ratios of from 8:1 to 42:1 were obtained.

A pachuca was used for many of the subsequent experiments. It consisted of a glass cylinder fitted with a sintered glass disc in its conical base for air dispersion. In an experiment using the pachuca, air at atmospheric pressure was bubbled through a slurry of 2 gm manganese dioxide and 2 gm pyrite in 500 ml 2% v/v H_2SO_4 at 90°C. Under these leaching conditions with the open vessel, the MnO_2 was completely dissolved in six hours.

Experimental leaching of pyrolusite ore

To determine if pyrite could be used to leach manganese from the low-grade pyrolusite ore, samples of ore containing 3.7% Mn were treated at various temperatures in an autoclave for two hours with 1% v/v H_2SO_4 and 100 psig oxygen pressure. The results of these experiments are shown in Figure 1, curve 2. A con-

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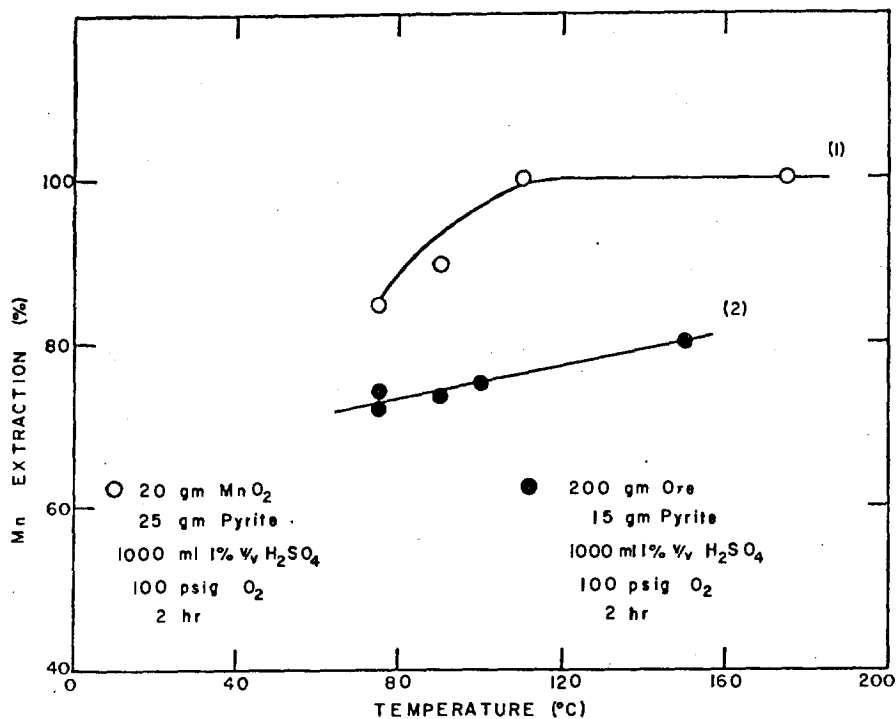


Figure 1—Effect of temperature on the extraction of manganese from ore and from MnO_2 in the presence of pyrite.

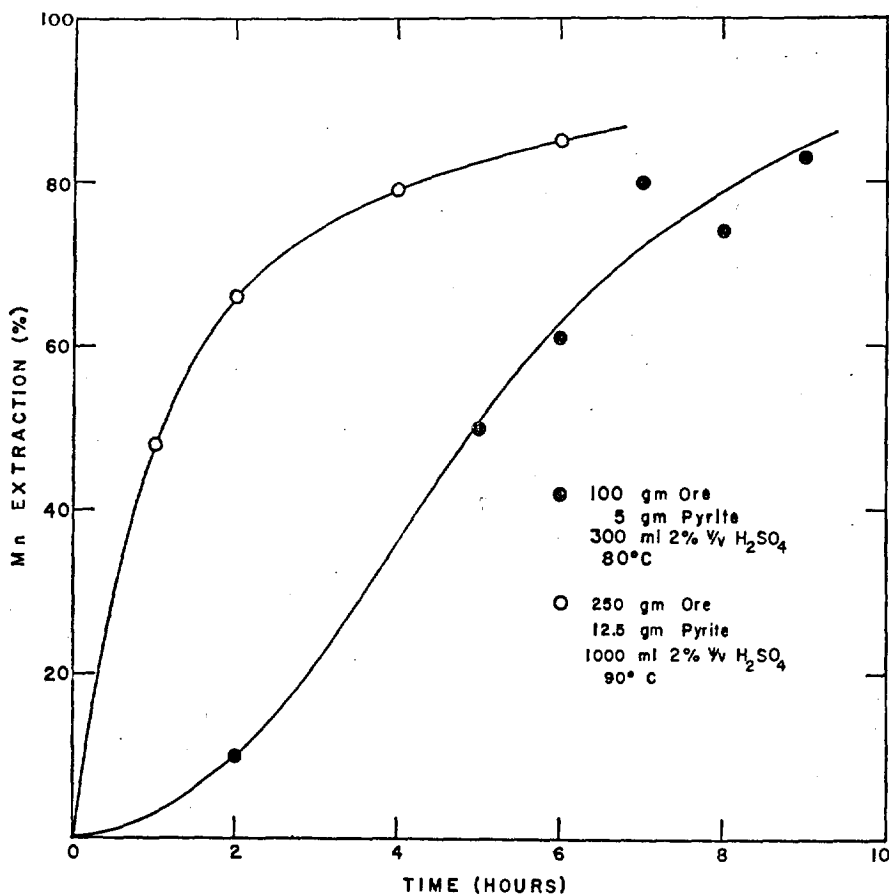


Figure 2—Rate of extraction of manganese from ore in the presence of pyrite.

parison of these results with those for the leaching of manganese from pure MnO_2 , curve 1, shows that the leaching of manganese from the ore was somewhat slower but nevertheless promising.

Additional experiments on the leaching of pyrolusite ore were then done in an open vessel. The leaching experiments were done with pyrite and 2% v/v H_2SO_4 in a pachuca at temperatures of 80°C. and 90°C. and

with acid to ore ratios of 3:1 and 4:1 with results as shown in Figure 2*. By the combined use of the higher temperature and the higher acid to ore ratio, a more rapid extraction of manganese was obtained. After several hours, the percentage extraction of manganese was approximately the same in both experiments. The two experiments show that with an adequate amount of acid and with suitable reaction conditions of time and temperature, open vessels can be used for leaching operations.

Having produced manganous sulphate liquors by single-stage leaching, it was necessary to determine if recycling would build up the concentration of manganese in the liquor. An aerated slurry of 200 gm 4.3% Mn ore and 10 gm pyrite in 800 ml 2% v/v H_2SO_4 (pH 0.4) was heated in a pachuca at 90°C. for four hours. After separating the leach liquor from the ore, some water was added to the liquor to compensate for that which adhered to the ore. The pH of the liquor was restored from approximately 1.0 to its original value of 0.4 with about 25 gm conc. H_2SO_4 and the liquor was recycled with fresh ore and pyrite to the pachuca. The process was repeated for 11 cycles with the acidity of the leach liquor adjusted only for the first six cycles.

Figure 3 shows that during the first six cycles, when H_2SO_4 additions were made, there was a build up in the manganous sulphate concentration of the leach liquor to about 100 gm $MnSO_4$ /l. Although the average manganese extraction was 65%, in certain cycles the extraction was as high as 90%. Subsequent to the sixth cycle, the manganese concentration of the liquor increased slightly and then decreased. The decrease was probably due to a combination of the lower manganese extraction during the last few cycles and the dilution involved at each cycle in restoring the volume of the liquor to its initial value. During the cyclic leaching experiments, about two moles of sulphuric acid were required for every mole of manganese that was leached.

After six cycles, the leach liquor contained 3 gm Fe^{+++} /l and 7 gm Fe^{++} /l. An important fact noted during later cycles was that when the pH increased to above approximately 1.5, the iron was precipitated by hydrolysis; after cycle 8, no iron was detected in the leach liquor. Hence, the cyclic leaching of manganese from the low-grade pyrolusite ore produced a strong manganous sulphate solution that was free of iron.

*In all graphs where pressures are not indicated, the experiments were done at atmospheric pressure in a pachuca.

Evaporation of the recycled leach liquor gave a hydrated manganous sulphate. The main impurities were Al, Ca, Mg, and Si, and these comprised less than 4% by weight of the manganous sulphate. Manganous sulphate monohydrate, the solubility of which decreases at high temperatures, was recovered by heating the recycled leach liquor to about 175°C. in a closed tube, using a thermal precipitation method developed at the Mines Branch.*

Study of the leaching reactions

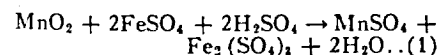
To elucidate the chemistry of the leaching process, a number of experiments were done with ore or pure MnO₂ using a glass pachuca and a reaction temperature of 90°C.

The effect of pyrite in the leaching process

To demonstrate that the leaching of manganese involved more than a simple acid leach, the following experiment was done. An aerated slurry of ore in 2% v/v H₂SO₄ was heated for two hours in the absence of pyrite. The extraction of manganese was about 7%. (Possibly this represents the percentage of the manganese that is present in the divalent state in the ore). As soon as pyrite was added, the percentage extraction of manganese from the pyrolusite ore was greatly increased as shown in Figure 4.**

Reactions of ferrous sulphate in the leaching process

Since ferrous sulphate is probably the main leaching reagent in the process, a study was made of its relevant reactions and their comparative rates. The reaction by which manganese dioxide is dissolved by an acidic ferrous sulphate solution is usually written as (6)



The rate of this reaction was very rapid at 90°C. as shown by Figure 5, with the dissolution of the manganese dioxide being complete in about one minute. In agreement with Equation 1, the curves of Figure 5 show a change in pH and in ferrous ion concentration during the dissolution of the manganese.

Although the reaction of ferrous sulphate with manganese dioxide is fast, the formation of ferrous sulphate

*In preparation for publication.

**When pyrrhotite, Fe₇S₈, was substituted for pyrite, no significant change was observed in the leaching reaction rate. See also recent paper by Bjorling(11) on the autoclave leaching of manganese ore by pyrrhotite.

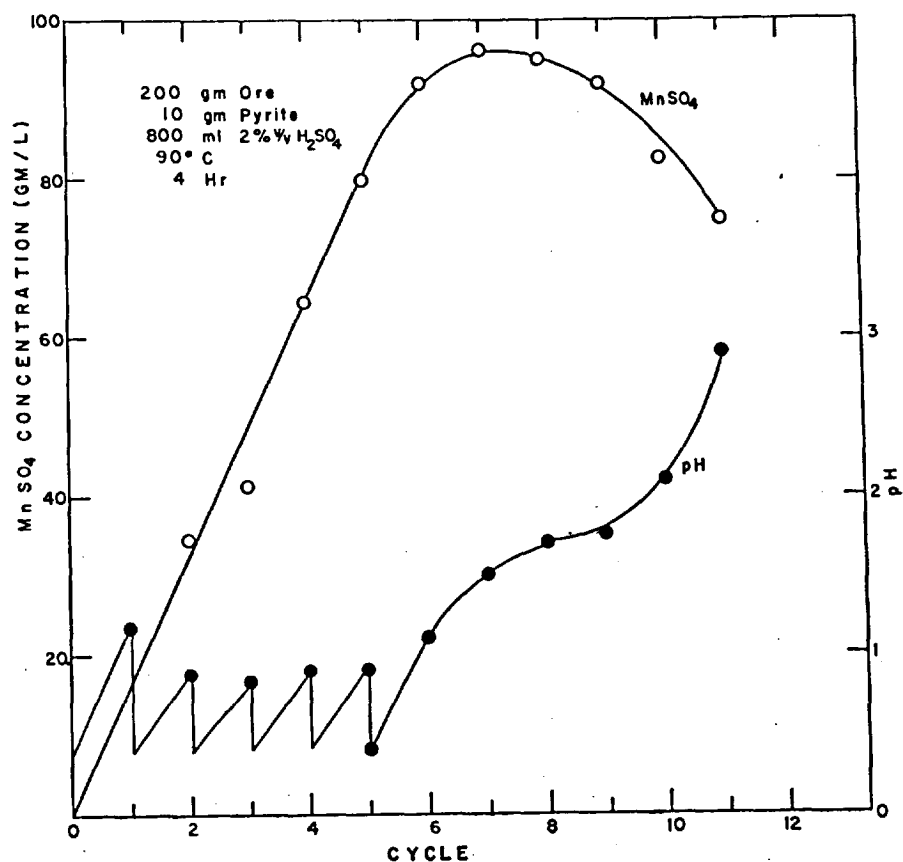


Figure 3—Cyclic extraction of manganese from ore in the presence of pyrite.

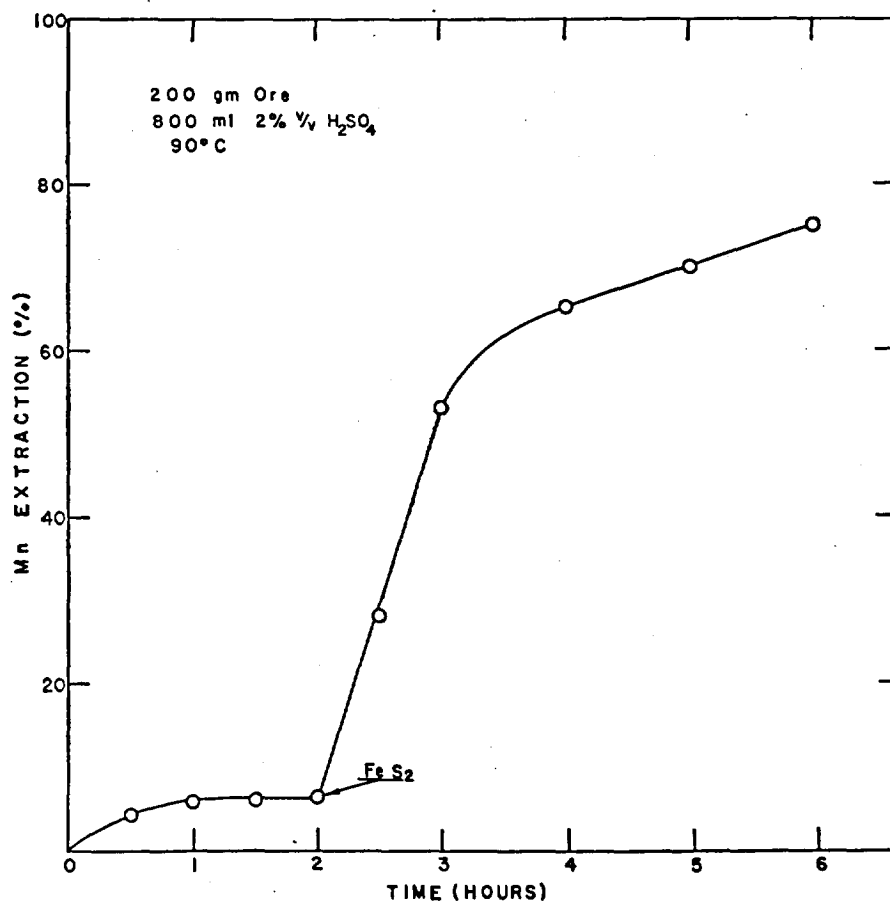


Figure 4—Effect of addition of pyrite on extraction of manganese from ore.

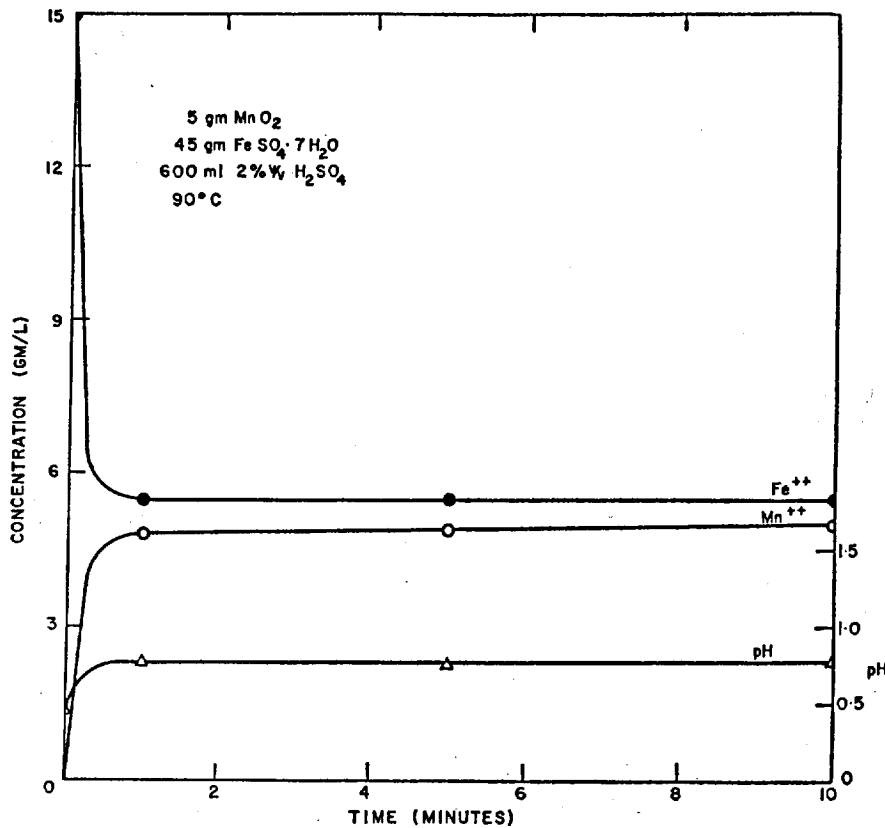


Figure 5—Rate of reduction of MnO_2 by ferrous sulphate.

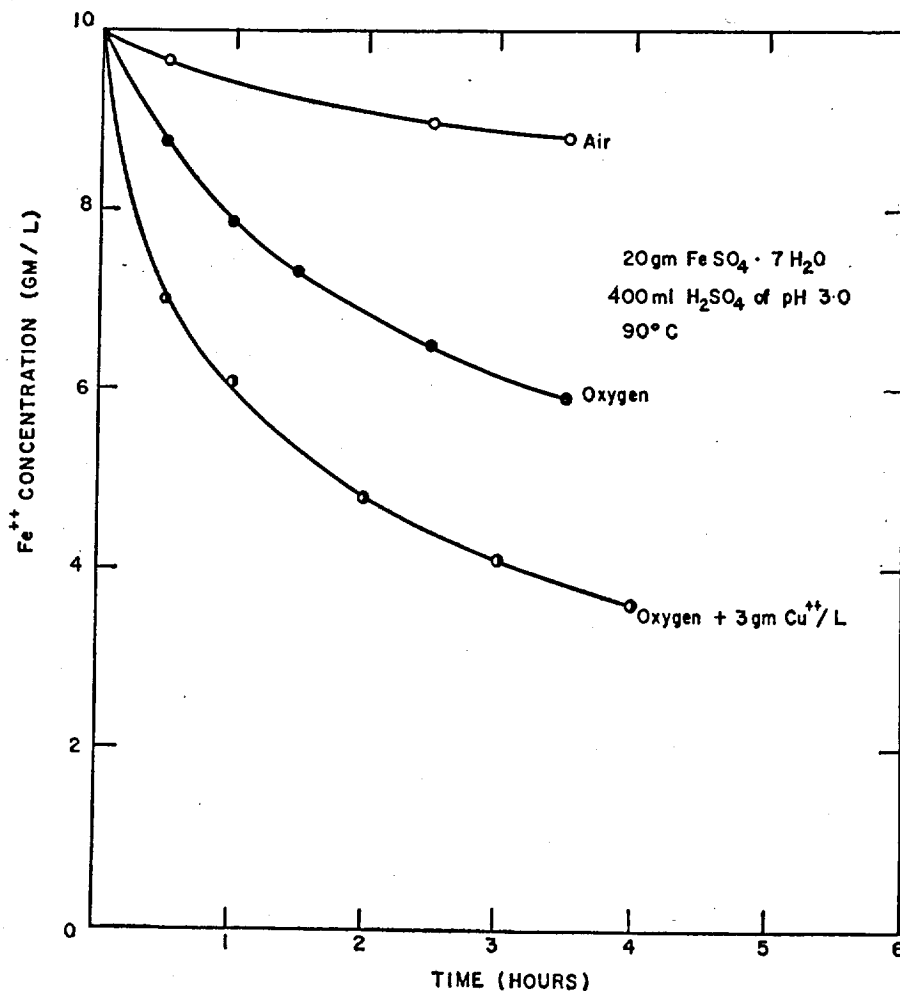
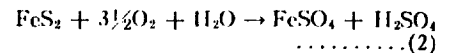


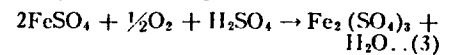
Figure 6—Rate of oxidation of ferrous sulphate by air and by oxygen.

from pyrite (5) is known to be slow.



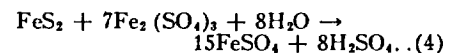
For example, only 5% of the pyrite was oxidized in four hours when a slurry of minus 200 mesh pyrite in dilute H_2SO_4 of pH 1.0 at $90^\circ C$. was aerated with oxygen. No significant change in the reaction rate was observed when an H_2SO_4 solution of pH 0.4 was used.

The ferrous sulphate formed by reaction 2 may be oxidized (4,5) by oxygen according to



The removal of ferrous ion by this reaction might be expected to interfere with the leaching of pyrolusite by reaction 1. However, Figure 6 shows that even when copper sulphate is present as a catalyst, the oxidation of ferrous sulphate by air or oxygen is relatively slow. Hence the air oxidation of ferrous ion in acidic solution is not likely to impede the leaching operations.

Although equations 2 and 3 indicate that ferric sulphate could be formed when pyrite is oxidized, no ferric ion was detected when acidic slurries of pyrite at $90^\circ C$. were aerated at atmospheric pressure. Any ferric ion that was formed must have been reduced again by the residual pyrite, possibly by a reaction such as (2)



The rate of reduction of a ferric sulphate solution by minus 200 mesh pyrite is shown graphically by Figure 7. Although this is a slow reaction, it might be, for liquors containing ferric sulphate, the main source of ferrous ion for leaching pyrolusite ore.

The effect of acid concentration and of ferric sulphate addition on the leaching process

In the first experiment, a slurry of MnO_2 and pyrite in an H_2SO_4 solution of pH 0.4 at $90^\circ C$. was aerated with oxygen. Figure 8 shows that the manganese was dissolved at a uniform rate; after four hours approximately 80% of the manganese had reacted with the pyrite to form manganese and ferric ions. The initial rise in the pH of the solution was probably due to the impurity siderite, $FeCO_3$, that was present in the pyrite and the subsequent progressive rise in the pH was likely due to the dissolution of the manganese dioxide.

When dilute H_2SO_4 of pH 1.0 was substituted for acid of pH 0.4 in the above experiment, the results shown

in Figure 9 were obtained. With the dilute acid of this experiment, most of the acid was soon used up and the remaining was insufficient to keep ferric ion in solution. The curves show that for pH values above approximately 1.7, the rate of dissolution of manganese was very slow.

The effect of adding ferric sulphate to an acidic aerated slurry of MnO_2 and pyrite, as shown by a comparison of Figure 8 with Figure 10, was to increase the rate of dissolution of the MnO_2 . Evidently the ferric sulphate was reduced by the pyrite to form ferrous sulphate which reacted rapidly with the MnO_2 . The ferric ion continued to be reduced by the pyrite after all the MnO_2 had dissolved.

Autoclave-produced acidic ferrous sulphate solutions

Since the leaching of pyrolusite ore by pyrite consumes acid, an alternative procedure was investigated. The objective was to adapt the oxidation of an aqueous slurry of pyrite in an autoclave (7-10) for the production of an acidic ferrous sulphate solution. Hoak and Coull (1) have shown previously that pyrolusite ore can be leached rapidly at ambient temperatures with acidic solutions of ferrous sulphate.

In one experiment, a slurry of pyrite in 2% v/v H_2SO_4 was heated in an autoclave at a temperature of $110^\circ C$. and under an oxygen pressure of 300 psig. The acid was added to decrease the precipitation of ferric ion by hydrolysis in the initial stages of the reaction. About 60% of the pyrite was oxidized in five hours with nearly 70% of the pyritic sulphur being changed to sulphate sulphur and 30% being recovered as elemental sulphur. This autoclave treatment produced an acidic liquor containing predominantly ferric sulphate. To obtain a ferrous sulphate liquor, the same experiment was repeated but the oxygen was released after three hours and replaced by nitrogen.

Figure 11 shows that the treatment of pyrite in an autoclave produced quickly a liquor containing both ferrous and ferric sulphate. When a high oxygen pressure was present, the iron was changed mainly to the ferric state. When the oxygen was replaced by nitrogen, the reduction of the ferric ion by pyrite produced an acidic liquor containing approximately 200 gm $FeSO_4$ / 60 gm $Fe_2(SO_4)_3$ / 1 and 70 gm H_2SO_4 / 1. This autoclave liquor is similar in composition to pickle liquor which has been reported (1) to be suitable for leaching pyrolusite ore at room temperature. The autoclave process appears to be a con-

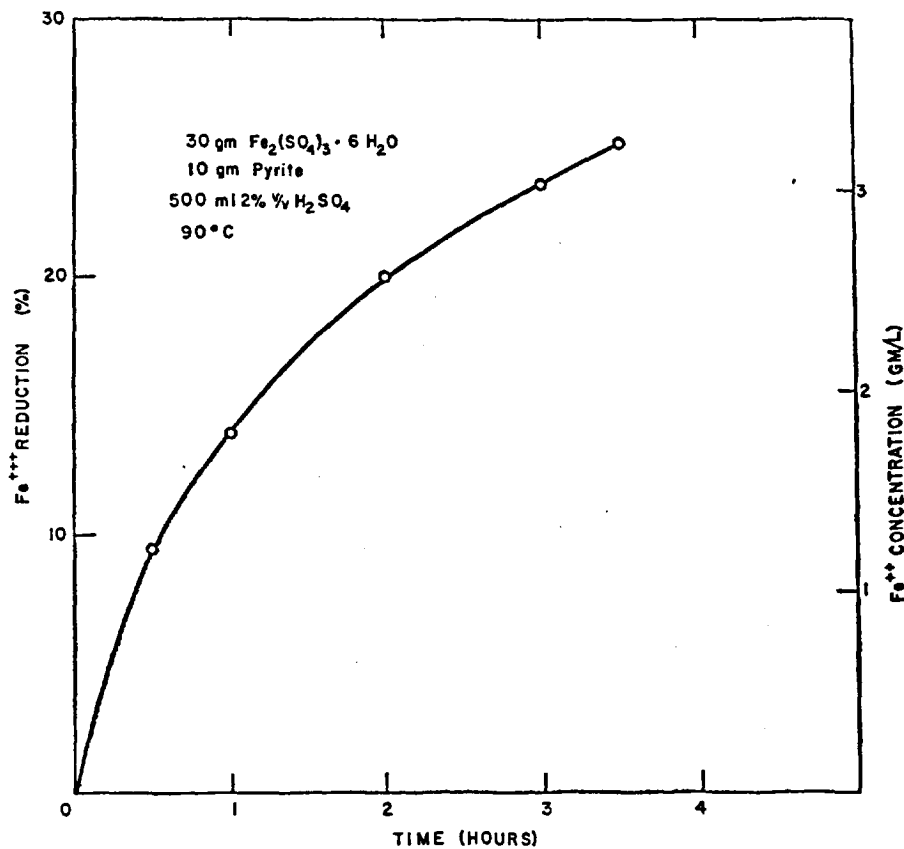


Figure 7—Rate of reduction of ferric sulphate by pyrite.

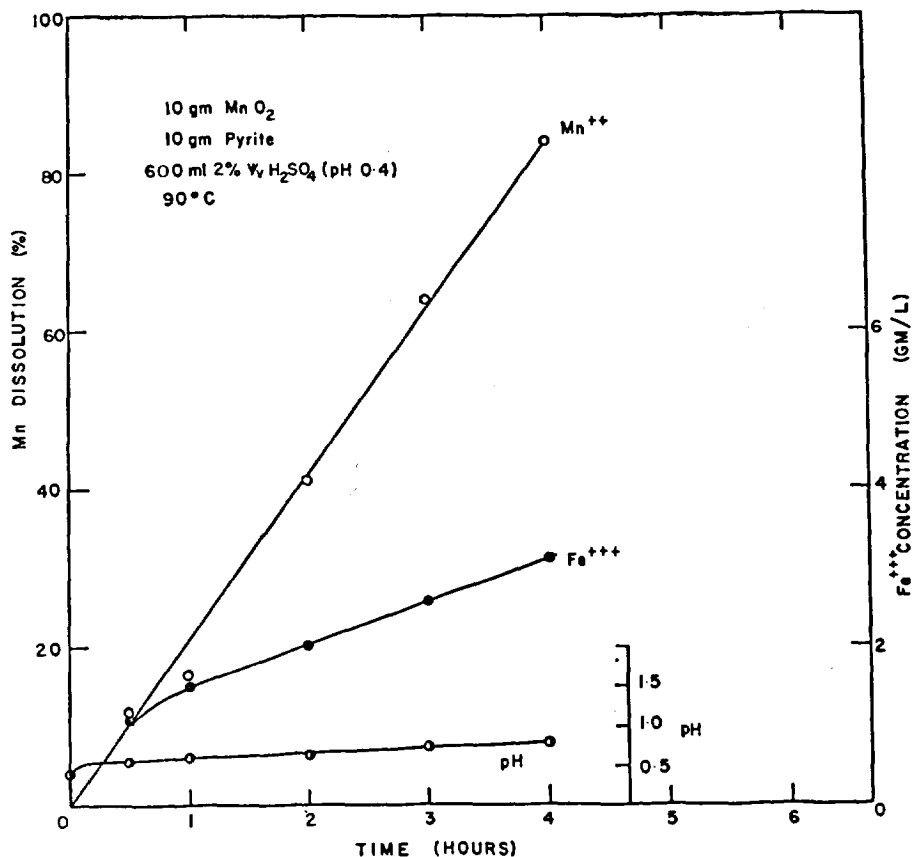


Figure 8—Rate of dissolution of MnO_2 in 2% v/v H_2SO_4 in the presence of pyrite.

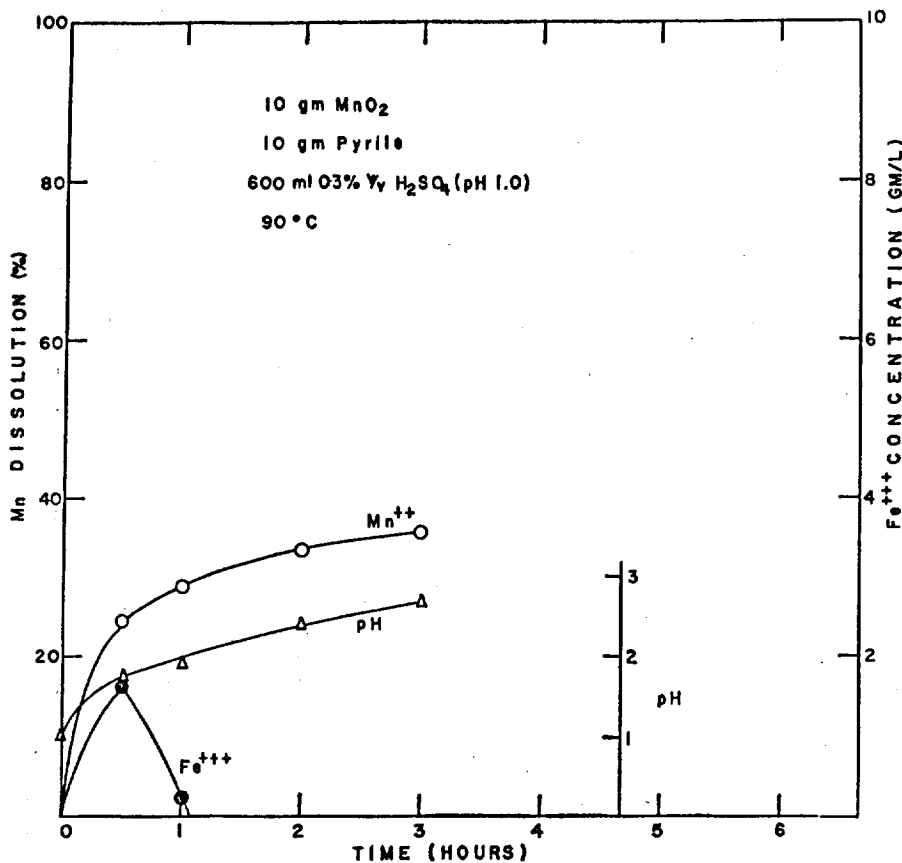


Figure 9—Rate of dissolution of MnO_2 in 0.3% v/v H_2SO_4 in the presence of pyrite.

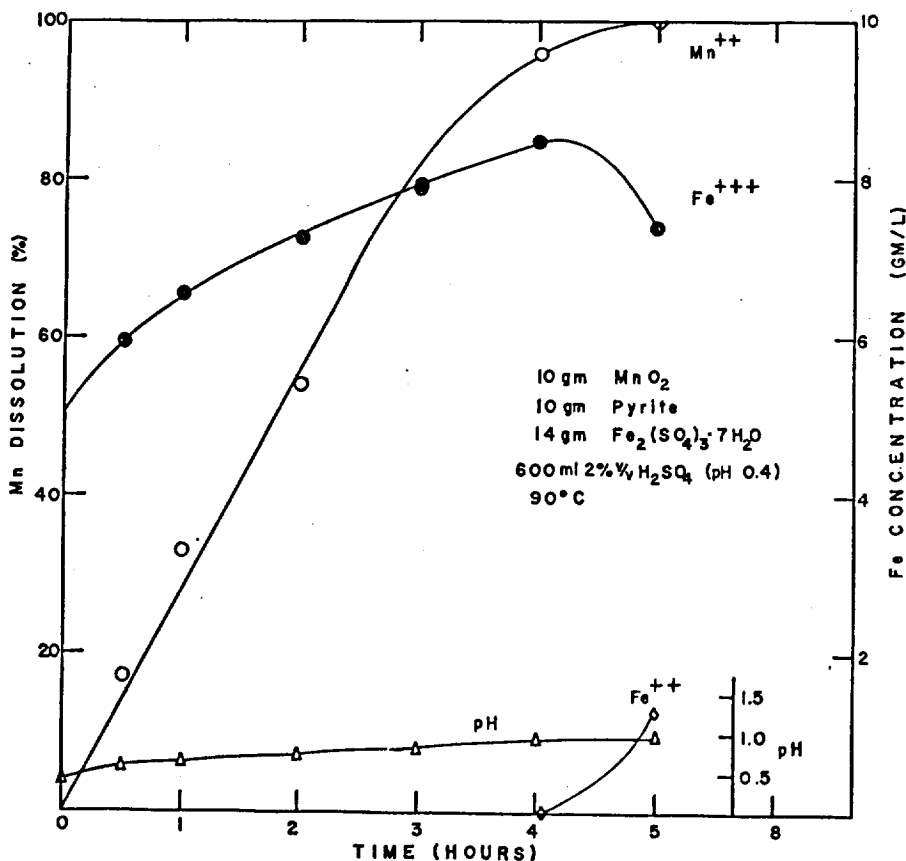


Figure 10—Rate of dissolution of MnO_2 in 2% v/v H_2SO_4 in the presence of pyrite and ferric sulphate.

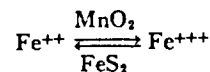
venient method of producing an acidic ferrous sulphate liquor for leaching purposes.

Summary and Conclusions

Manganese was extracted from a pyrolusite ore (4% Mn) by heating an aerated aqueous slurry of ore and pyrite. A rapid extraction of manganese was obtained by leaching the ore in an autoclave at high oxygen pressures and high temperatures. It was found that satisfactory extraction could be obtained, at a slower rate, by using open vessels and relatively low temperatures. A temperature of $90^\circ C$. was used for most of the experimental work since adequate extractions could be obtained in a relatively short time, e.g. manganese extractions of up to 90% were obtained within four hours. For commercial operations, prolonged leaching periods at lower temperatures might be more economical.

Recycling the leach liquor at controlled acidity to leach additional ore gave a concentrated solution containing about 100 gm $MnSO_4/1$. Approximately two moles of sulphuric acid were required to dissolve one mole of pyrolusite from the ore. Evaporation of the recycled solution gave an iron-free hydrated manganous sulphate of which the main impurities, Al, Ca, Mg and Si, comprised less than 4% by weight of the product. Manganous sulphate was recovered using substantially less heat when evaporation was replaced by heating the recycled solution to about $175^\circ C$. to precipitate manganous sulphate monohydrate.

Although many chemical reactions are undoubtedly involved, the leaching of pyrolusite ore by this process is essentially the reduction of MnO_2 by ferrous ion to acid-solution divalent manganese. The ferrous ion is obtained from the reaction of pyrite with air or with ferric ion. During the dissolution of manganese, the iron is alternately oxidized by the pyrolusite and reduced by the pyrite, as shown by



i.e. the ferrous ion is continuously regenerated during the leaching process.

By heating an aqueous slurry of pyrite at $110^\circ C$. in an autoclave, first under oxygen pressure and then in the absence of oxygen, a concentrated acidic solution of ferrous sulphate (200 gm $FeSO_4/1$) was obtained. Hoak and Coull⁽¹⁾ found that solutions of similar composition were

suitable for leaching pyrolusite ore at room temperature. Hence, for large-scale leaching operations with the low-grade ore used in this investigation, two leaching procedures might be feasible. In the one process, the leaching would be done by heating aerated slurries of ore, pyrite, acid and water in pachuca. In the alternative process, pyrite and water, in amounts small in comparison with that of the ore, would be treated in autoclaves to produce acidic solutions of ferrous sulphate for the subsequent leaching of ore at ambient temperatures.

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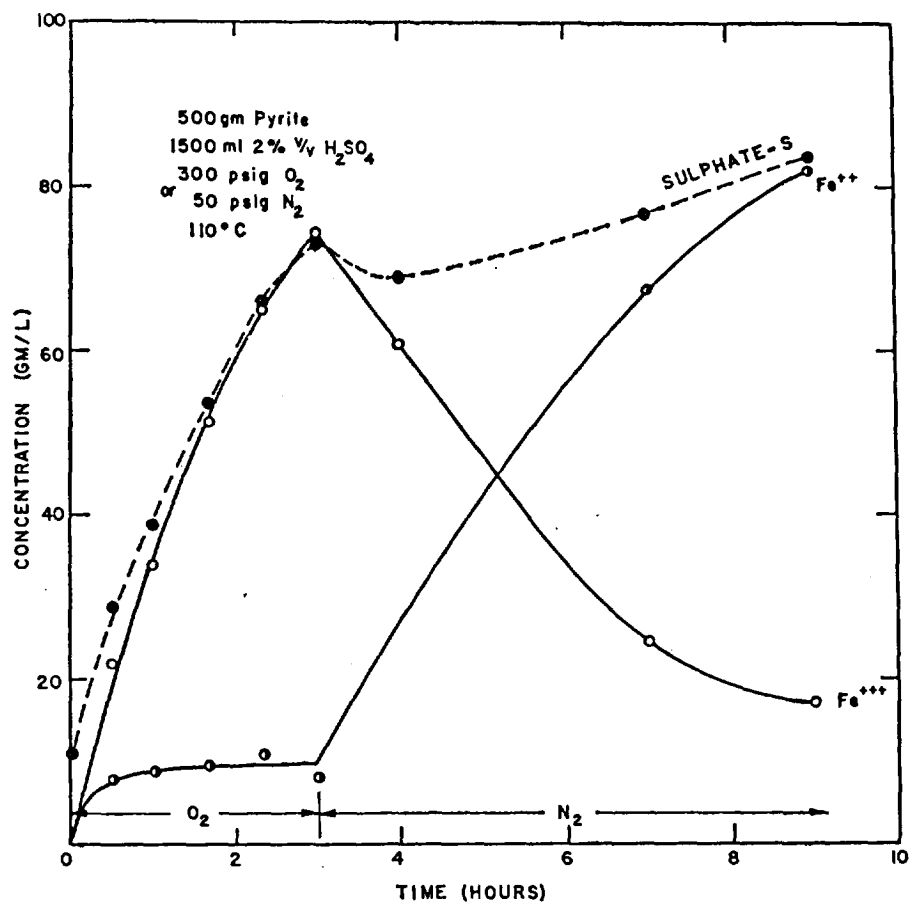


Figure 11—Production of an acidic ferrous sulphate solution by heating pyrite in an autoclave.