Direct Biohydrometallurgical Extraction of Iron from Ore Final Technical Report

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Authors: T. C. Eisele – Principal Investigator

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Department of Chemical Engineering Michigan Technological University 1400 Townsend Drive Houghton, MI 49931 - 1295

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Abstract

A completely novel approach to iron extraction was investigated, based on reductive leaching of iron by anaerobic bacteria. Microorganisms were collected from an anaerobic bog where natural seepage of dissolved iron was observed. This mixed culture was used to reduce insoluble iron in a magnetite ore to the soluble ferrous (Fe⁺²) state. While dissolution rates were slow, concentrations of dissolved iron as high as 3487 mg/l could be reached if sufficient time was allowed. A factorial study of the effects of trace nutrients and different forms of organic matter indicated that the best dissolution rates and highest dissolved iron concentrations were achieved using soluble carbohydrate (sucrose) as the bacterial food source, and that nutrients other than nitrogen, phosphorus, potassium, sodium, and acetate were not necessary. A key factor in reaching high levels of dissolved iron was maintaining a high level of carbon dioxide in solution, since the solubility of iron carbonates increases markedly as the quantity of dissolved carbon dioxide increases.

Once the iron is dissolved, it has been demonstrated that the ferrous iron can then be electroplated from solution, provided that the concentration of iron is sufficiently high and the hydrogen ion concentration is sufficiently low. However, if the leaching solution is electrolyzed directly, organic matter precipitates at the cathode along with the metallic iron. To prevent this problem, the ferrous iron should be separated from the bulk solution in a more concentrated, purified form. One route to accomplishing this is to take advantage of the change in solubility of ferrous iron as a function of carbon dioxide concentration. By cycling the concentration of carbon dioxide in solution, it is possible to produce an iron-rich concentrate that should be suitiable for electrolysis. This represents the first viable hydrometallurgical method for leaching iron directly from ore and producing metallic iron.

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Introduction

The current method of primary iron production from ore is highly energy-intensive, requiring the ore to be ground to a powder, concentrated, agglomerated into pellets, hardened by heating to 1200°C to produce iron oxide pellets, only to be cooled to ambient temperature for shipping, and then re-heated to approximately 1500°C once they arrive at the blast furnace. The energy needed to grind the ore, heat and harden the pellets, and smelt the pellets to iron is completely wasted. In order to save this energy, a completely different approach is needed where the iron is extracted from ore, purified, and converted to metal at near ambient temperatures. Additionally, the U. S. iron ore industry is currently completely dependent on the blast furnaces to buy the iron oxide pellets that they produce. By producing metallic iron directly at the mine site, the iron ore producers will be able to greatly expand their potential markets and improve their competitive position. If this is not done, the iron ore industry will slowly vanish along with the last US blast furnaces.

The approach investigated in this project was to take advantage of recently-discovered bacteria that convert iron from the highly-insoluble Fe⁺³ form, to the much more soluble Fe⁺² form. This will make it practical to leach iron from ore by hydrometallurgical methods, similar to those which have become major production methods of other metals, particularly copper and precious metals. The benefits of replacing a pyrometallurgical process with a hydrometallurgical technique is that it allows the processing to be done at ambient temperatures, which improves energy efficiency by eliminating the need to heat and melt the ore. In the past, hydrometallurgical extraction of iron from ore has been considered uneconomical, because traditional methods have required the purchase of large quantities of acids that were consumed by the ore during iron dissolution. However, by using bacterial iron reduction, these reagents can be eliminated and replaced with low-cost biomass.

It has been discovered that certain bacteria (for example, *Geobacter metallireducens* and *Shewanella putrefaciens*) will, as a part of their metabolism, reduce Fe^{+3} to Fe^{+2} under anaerobic conditions (Lovley, 2000). These bacteria, and others like them, use the Fe^{+3} as the terminal electron acceptor in their metabolism of organic compounds, a function that is normally filled by oxygen for aerobic organisms. Without such a terminal electron acceptor, they would be unable to metabolize the organic material. In the course of metabolizing organic matter, bacteria also produce organic acids such as acetic acid ($HC_2H_3O_2$), and the carbon dioxide that they also produce acidifies the solution if it is retained in solution. These acids react with the reduced iron oxides to produce soluble salts.

The organic matter used in this process would be any material subject to decomposition by bacteria, including sawmill chips and dust, papermaking sludges, miscellaneous biomass, waste carbohydrates, or even sewage sludges. Each of these would be decomposed by the bacteria to form organic acids, carbon dioxide, and water.

The objective of this study was to determine how to best promote the dissolution of iron using iron-reducing bacteria, determine the concentrations of iron that could be reached in the leaching solution, and investigate the feasibility of directly electroplating metallic iron from the leaching solution.

Executive Summary

The existing technology for production of metallic iron from ore is all based on extremely high-temperature pyrometallurgical processing, at temperatures as high as 1500°C. These temperatures are achieved by combustion of fossil fuels, primarily coal, and these fuels also act as reducing agents to convert iron oxide to metallic iron. As a result of the high temperatures and significant fuel use, the production of metallic iron from ore is environmentally objectionable and consumes a tremendous amount of energy.

There is potential for improving energy efficiency and reducing emissions if metallic iron can be produced from ore using hydrometallugical extraction techniques, where the iron is selectively dissolved (leached) from the ore and recovered as metal by electrolysis (electrowinning). While hydrometallurgical extraction based on leaching/electrowinning is used with great success for other metals, particularly copper and gold, to date there has been no practical technique for hydrometallurgical extraction of iron. The problems in iron extraction by this means have been:

- 1. The standard leaching method is dissolution of fully-oxidized ore by acid. However, iron oxidized to the Fe⁺³ (ferric) state requires a very acidic solution to dissolve, and this results in very high acid consumption.
- 2. Electrolysis of Fe⁺³ solution to produce metallic iron is inefficient, because the Fe⁺³ must first be converted to Fe⁺². The Fe⁺² can then recirculate back to the anode of the electrolysis cell and oxidize back to Fe⁺³. This recirculation wastes energy. Also, in order to keep Fe⁺³ dissolved, the solution must be kept very acidic, resulting in a high H⁺ concentration. This results in significant hydrogen generation instead of plating metallic iron, which reduces efficiency still further.

The solution to both of these problems is to use a reductive leaching process, dissolving iron in the Fe⁺² (ferrous) state. This has the advantages that, first, ferrous iron salts are considerably more soluble than ferric iron salts, and so will dissolve under only mildly acidic conditions. Second, the ferrous iron is much easier to recover by electrolysis than is ferric iron, because (a) only two electrons must be provided instead of three, and (b) it can be electrolyzed from solutions with a relatively low H⁺ concentration, which minimizes hydrogen generation.

The process developed in this project consists of three stages: (1) bacterial iron dissolution; (2) ferrous iron purification; and (3) iron electrolysis.

The bacterial iron dissolution stage takes advantage of anaerobic iron-reducing bacteria, which convert Fe⁺³ to Fe⁺² in the absence of gaseous oxygen while converting organic matter to carbon dioxide. The Fe⁺² then dissolves in the leaching solution and is transported out of the leaching vessel. This stage was successfully accomplished in this project, using bacteria collected from an anerobic bog environment which was observed to be releasing dissolved iron. The anaerobic bacteria have slow growth rates, but once established they dissolved iron from a magnetite-bearing or at a satisfactory rate.

Experimentation has shown that the most satisfactory route for ferrous iron purification will be to take advantage of solubility variations caused by changing carbon dioxide levels. Ferrous iron readily precipitates as iron carbonate (FeCO₃) at moderate carbon dioxide concentrations, but when carbon dioxide levels in solution are elevated, the iron carbonate is soluble. Since bacteria

are generating carbon dioxide at the same time as they are reducing ferric iron, retaining this carbon dioxide in solution keeps the iron soluble. Once solution is removed from the leaching area, the carbon dioxide can be allowed to dissipate, causing the iron carbonate to precipitate in a purified form. This is expected to be much easier to implement on a large scale than the alternative, which would be to use solvent extraction to selectively concentrate the ferrous iron.

Once the solution of ferrous iron is purified, electrolysis to form metallic iron is relatively straightforward, using a diaphragm electrolysis cell to prevent the dissolved iron from contacting the anode and becoming oxidized. Metallic iron was successfully plated from ferrous ion solutions where the anion was acetate, which is an organic anion that would serve as food for the anaerobic bacteria and would therefore not present any toxicity problems when solutions are recycled.

The overall process as it is planned to be implemented on a larger scale is as shown in Figure 1.

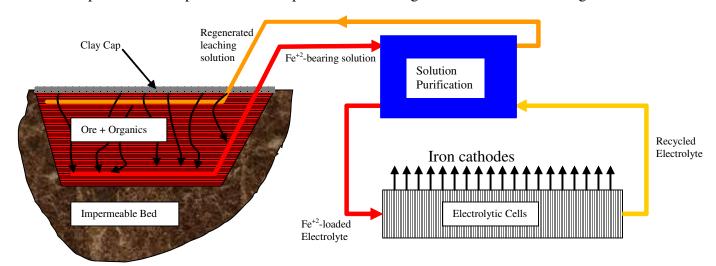


Figure 1: Full scale implementation of the bacterial leaching process.

Energy Savings. The primary energy savings would be the elimination of the energy that is currently used to heat pellets and to heat the blast furnace. Sintering of conventional pellets requires 400 - 700 MJ per metric ton depending on the type of ore used to make the pellets, and an additional 250 MJ per metric ton is required when fluxed pellets are produced, and so fluxed hematite pellets require up to 950 MJ per metric ton to sinter (AISE, 1999). In addition, blast furnace operation requires 23,360 MJ/metric ton of hot metal. Total energy consumption by iron production using conventional methods is therefore 24,310 MJ/metric ton of iron. In the biohydrometallurgical process, the expected energy consumption is expected to be 22,229 MJ/metric ton of iron, which reduces energy consumption by 2,080 MJ/metric ton of iron compared to the blast furnace.

Environmental Benefits. The biohydrometallurgical process would eliminate the need for coke entirely, thereby eliminating the environmental issues associated with the toxic and carcinogenic emissions from coke production and from coke combustion in the blast furnace. The CO₂ directly emitted by the process will be entirely from biomass, and therefore is part of the natural carbon cycle. This will replace the 2.023 tons of fossil CO₂ that is currently emitted per ton of hot metal.

Theoretical Background

The primary interest in iron-reducing bacteria to date has been their geochemical role, as they are responsible for the bulk of the soluble iron in the environment (Childers et al., 2002). Under normal circumstances, iron oxidizes to the ferric form, which forms extremely insoluble oxides and hydroxides. Since iron is a necessary nutrient for most organisms, it can only be made biologically available if it is chemically reduced, and so the iron-reducing bacteria serve a critical role in the cycling of iron in the ecosystem. However, it has not previously been considered that dissolution of iron by these bacteria could have an economically important role in industry, particularly in the production of iron from ore.

Hydrometallurgical metal extractions have been developed for metals other than iron, most notably for copper. The hydrometallurgical approach has significant advantages for the environment, as selectively dissolving and reprecipitating metal has much lower emissions to the atmosphere than traditional smelting and other high-temperature pyrometallurgical processes. While non-ferrous metals can be recovered by hydrometallurgical means, it has long been assumed that iron could not be recovered in this way. This was due to the belief that the best approach would be similar to what is used for recovery of copper oxides: dissolve the iron oxides in strong acid such as sulfuric or hydrochloric acid. For iron dissolution, this would result in prohibitive reagent consumption, and the resulting dissolved iron would be so acidic that electrolysis of the metal from solution would be impractical

To make hydrometallurgy of iron practical, a completely different approach is needed. The iron-reducing bacteria provide the key to this approach, as they can, in the course of their metabolism, convert iron oxides into a soluble state that can be dissolved readily at moderate pH. This would require only a source of organics, and the presence of the right anaerobic iron-reducing bacteria, to efficiently dissolve iron.

In order to metabolize organic material, all organisms need a "terminal electron acceptor" to complete the oxidation/reduction reaction. As the organic matter is oxidized during metabolism, some other material must be reduced. For aerobic organisms, the terminal electron acceptor is oxygen being converted to either water or carbon dioxide. However, in anaerobic environments, elemental oxygen is not available and so some other electron acceptor is needed. The most common possibilities, in order of the amount of energy that organisms using them can recover, are as follows:

$$NO_3^- => N_2$$

 $Fe^{+3} => Fe^{+2}$
 $SO_4^{-2} => HS^-$
 $CO_2 => CH_4$

Of these, only the nitrate reduction reaction is more energetically favorable than the iron reduction reaction, and so iron reduction provides an energy advantage for the microorganisms compared to sulfate reduction or methane production. In a situation such as iron ore leaching, ferric iron (Fe⁺³) will be the most plentiful electron acceptor, and so iron-reducing bacteria will have a definite selective advantage.

Iron-reducing bacteria have been shown to be able to be able to use a variety of compounds as their source of organic matter, including acetate (Lovley, 2000), fulvic acids, dissolved organics, and humic acids (Petruzzelli et al., 2005). A number of different iron-bearing minerals are potentially available as the source of ferric iron, but the one that requires the least reduction to convert fully to the ferrous (Fe^{+2}) is magnetite, Fe_3O_4 (which can also be written as $FeO \cdot Fe_2O_3$). For bacteria metabolizing acetate while dissolving magnetite, the basic reaction is:

$$20H^{+} + 4Fe_{3}O_{4} + CH_{3}COOH ==> 2FeCO_{3} + 10Fe^{+2} + 12H_{2}O$$
 (eq. 1)

From this, it can be seen that a single acetate molecule provides enough reducing power to produce twelve soluble ferrous ions from magnetite. However, acid is also necessary as hydrogen ions are consumed by the reaction, with 21 hydrogen ions needed for every 12 ferrous ions solubilized, or 1.75 H⁺ per Fe⁺². There are three sources for these hydrogen ions: first, they can be regenerated when iron is electroplated from solution:

$$2H_2O + 2Fe^{+2} = > + 2Fe^0 + 4H^+$$
 (eq. 2)

which provides two H⁺ per Fe⁺². However, until electroplating and solution recycle is established, this is not available.

The second source for hydrogen ions is organic acids produced by breakdown of carbohydrates and other organics. Acetic acid is readily produced by many organisms as they metabolize sucrose, cellulose, or similar compounds, and this generates acidity that can be used to dissolve ferrous iron. However, in order for this to be a significant source of acidity, a large supply of organics must be available.

A third source of hydrogen ions is dissolved carbon dioxide. When it enters solution, carbon dioxide undergoes the following reaction:

$$CO_2 + H_2O ==> 2H^+ + CO_3^{-2}$$
 (eq. 3)

Combining equation 3 with equation 1 indicates that adding carbon dioxide to the system at the rate of 10 moles per 12 moles of iron solubilized would be sufficient to keep the iron in solution. Since carbon dioxide is naturally formed as the endproduct of the metabolism of organic material, it is readily available for the process. Simply retaining the carbon dioxide in the system will therefore allow it to build up to useful levels for iron solubilization.

Experimental

Materials

The iron ore used in this project was obtained from an iron ore processor in the Lake Superior iron ore district. Two types of ore were used: 1) A magnetite concentrate, which was approximately 95% magnetite (Fe₃O₄) and had been ground to a particle size approximately 90% finer than 25 micrometers; and 2) Raw ore from the plant feed, which was approximately 50% magnetite and had been crushed to pass approximately 4 mm using a cone crusher. In both cases, the primary gangue mineral was silica (SiO₂).

Source of Bacteria

The key to the entire process is the use of iron-reducing bacteria. Initially, bacteria from the American Type Culture Collection were considered, specifically *Geobacter metallireducens* and *Shewanella putrefaciens*. However, attempts to use these organisms by the investigator were not successful due to difficulties in culturing and establishing the organisms on the magnetite-bearing ore used in the project. A key reason for this is that these bacteria apparently require the presence of other bactera in order to efficiently reduce iron that is in the solid state (Straub and Schink, 2004). An alternative source of a mixed culture of bacteria, preferably already adapted to iron dissolution, was therefore needed.

It is well-known that iron-reducing bacteria are common in anaerobic bogs, and their presence is often indicated by seepages of water that precipitates iron hydroxide on contact with air. Such a bog was located west of Michigan Tech. University, as shown by the photograph in Figure 2, below. A sample of approximately 1 kg of soil was collected from this site at a depth of 0.3 meters, and immediately sealed to prevent access of air.



Figure 2: Iron-bearing seepage from an anaerobic bog in Adams Township, Houghton County, Michigan (long. 88.61089W, lat. 47.11854N). This seepage indicated the presence of bacteria capable of both reducing and solubilizind iron.

Bacterial Culture Procedures

Growth Media. The basic growth media used was derived from ATCC Medium 1768(ATCC, 2005), used for culturing of *Geobacter metallireducens*. The original medium contained ferric citrate as the iron source for the bacteria to reduce, which for purposes of this research was eliminated since the iron would be provided by the ore substrate being leached. Vitamin and mineral supplements that were present in the ATCC media were only added to some experiments, to determine whether they had a significant effect on iron leaching. Also, sucrose was added as a source of organic matter to allow fermentative bacteria to produce organic acids

and carbon dioxide that would aid in iron solubilization. The resulting growth media formulation was as shown in Table 1. The solution was then autoclaved to sterilize it, and cooled before use.

Table 1: Basic growth media used in this project. The natural pH of this solution was

approximately 6.4.

NH ₄ Cl	0.25 g
NaH ₂ PO ₄	0.6 g
KCl	0.1 g
NaC ₂ H ₃ O ₂	10 g
Sucrose	5 g
Distilled Water	To 1 liter

Some experiments included Wolfe's vitamin solution and Wolfe's mineral solution, which had been recommended for supporting the growth of *Geobacter metallireducens* (ATCC, 2005). These were used to determine whether they were necessary for the bacteria isolated from the anaerobic bog for use in this project. The formulations for these supplements, as provided in premixed, sterile solutions by ATCC, are given in Table 2.

Table 2: Formulations of ATCC vitamin and mineral supplements

Vitamin Supplement,		Mineral Supplement,	
ATCC Cat. No. MD-VS		ATCC Cat. No. MD-TMS	
Biotin	2 mg	Nitrilotriacetic Acid	1.5 g
Folic Acid	2 mg	MgSO ₄ ·7H ₂ O	3.0 g
Pyridoxine Hydrochloride	10 mg	MnSO ₄ ·H ₂ O	0.5 g
Thiamine HCl	5 mg	NaCl	1.0 g
Riboflavin	5 mg	FeSO ₄ ·7H ₂ O	0.1 g
Nicotinic Acid	5 mg	CoCl ₂ ·6H ₂ O	0.1 g
Calcium D-(+) -pantothenate	5 mg	CaCl ₂	0.1 g
Vitamin B12	0.1 mg	ZnSO ₄ ·7H ₂ O	0.1 g
p-Aminobenzoic Acid	5 mg	CuSO ₄ ·5H ₂ O	0.01 g
Thioctic Acid	5 mg	$AlK(SO_4)_2 \cdot 12 H_2O$	0.01 g
Distilled Water	1.0 L	H_3BO_4	0.01 g
		Na ₂ MoO ₄ ·2H ₂ O	0.01 g
		Distilled Water	1.0 L

Static Flask Apparatus. Initial experiments to examine growth rates and the effects of nutrient media modifications were carried out in static flasks, as shown in Figure 3. These were Ehrlenmeyer flasks closed with a fermentation lock, which was a water trap designed so that gases evolved by the bacteria could escape but air could not enter. Powdered magnetite concentrate was added to each flask to act as an iron source. This magnetite had been obtained from a nearby iron ore producer. The flask was then filled with media, inoculated with the desired bacterial culture, and closed for extended periods of time to allow the slow-growing anaerobic bacteria to establish themselves and dissolve iron.

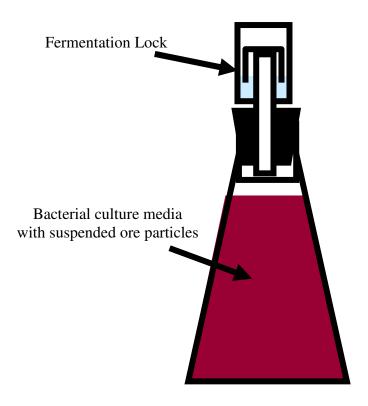


Figure 3. Static flask configuration for initial bacterial leaching tests

Continuous column apparatus. Once the appropriate media formulation, growth conditions, and bacterial stock for inoculation were established in the static flasks, a continuous leaching column was established for long-term experimentation. This column was transparent PVC, 3 inches (6.45 cm) in diameter, filled with crushed ore (top size of 4 mm) to a depth of 23.6 inches (60 cm). The column held 6 kg of crushed ore, and the basic configuration was as shown in Figure 4. To begin the experiment, the column was charged with crushed ore, and initially flooded with distilled water to displace gaseous oxygen from the system. It was then inoculated by introducing 1 liter of growth media with active bacterial culture through the fresh media reservoir. After inoculation, small quantities of fresh media were added on a daily basis, which entered at the base of the column. Media displaced from the top of the column was then collected for analysis. A fermentation lock at the top of the column allowed excess carbon dioxide to escape, but prevented air from entering the column. One problem encountered was that it was possible to withdraw solution faster than fresh media was added, which could cause small quantities of air to be pulled into the column through the fermentation lock. This air was prevented from reaching the active solution by a plug of cotton batting in the top of the column that prevented air diffusion back into the body of the column.

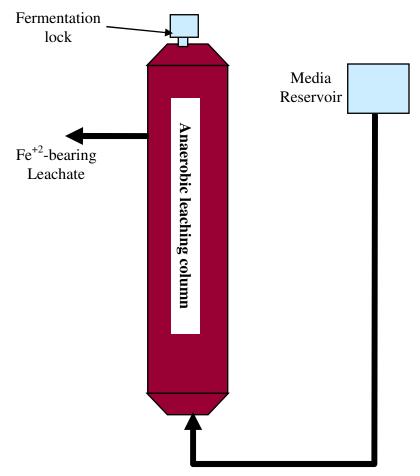


Figure 4: Basic configuration of the long-term continuous leach column. Fresh media was added to the media reservoir to gravity-feed into the base of the column, and the solution displaced by the fresh media was collected as the sample for analysis.

Iron Analysis Procedure

The procedure used for iron analysis was a spectrophotometric method based on the strongly-colored complex that 1,10 phenanthroline forms with Fe⁺² in aqueous solution (Day and Underwood, 1986). The procedure was as follows:

- 1. Prepare three solutions:
 - a. 0.1 g of 1,10 phenanthroline in 100 ml distilled water (complexing agent)
 - b. 10 g of hydroxylamine hydrochloride in 100 ml distilled water (reducing agent)
 - c. 10 g of sodium acetate in 100 ml of distilled water (pH buffer)
- 2. Prepare standards of known iron concentration from a 1000 ppm commercial Fe standard, to be used in determining the instrument calibration curve.
- 3. Add a precisely-measured quantity of sample or standard to a 100 ml volumetric flask
- 4. Add 1 ml of hydroxylamine hydrochloride solution (solution b), 8 ml of sodium acetate solution (solution c) and 10 ml of phenanthroline solution (solution a).

- 5. Dilute to 100 ml mark with distilled water, mix, and let stand for at least 10 minutes to allow the color to standardize.
- 6. Transfer a portion of the solution from the volumetric flask to a cuvette, and measure the absorbance value relative to distilled water at a light wavelength of 508 nanometers.
- 7. Determine the calibration equation using the standards of known concentration, and calculate iron concentrations in the cuvette using Beer's Law
- 8. Based on the dilution of analysis sample in the 100 ml flask, calculate the original concentration of iron in the analysis sample.

Electrolysis

A small electrolysis cell was used for iron electroplating experiments. The cell was a 100 ml pyrex vessel with a graphite anode and a titanium cathode, powered by a variable-voltage DC power supply. The anode and cathode were separated by at least one, and more commonly two, porous polyethylene barriers, as shown in Figure 5. This configuration was used to prevent dissolved iron from coming in contact with the anode and oxidizing, while also preventing excessive amounts of organic matter from reaching the cathode where it would form a black carbonaceous deposit.

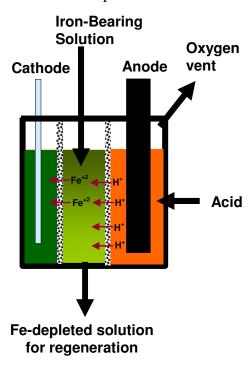


Figure 5: schematic of electrolysis cell used in this project.

Solution Purification

Once the long-term column had been established, sufficient amounts of iron-bearing leachate was available to attempt precipitation of ferrous iron for solution purification. This was done

using a 500 ml separatory funnel, vented at the top to allow carbon dioxide to escape while iron-bearing precipitate concentrated at the base.

Results and Discussion

Static Flask Results

The first experiments with the static flask were simply to establish that the bacteria could grow and solubilize iron. These experiments used 250 ml static flasks containing 10 grams of magnetite concentrate, and the growth medium was the standard medium given in Table 1, with each liter of media supplemented with 10 ml of each of the vitamin and mineral supplements given in Table 2. The flasks were inoculated with 5 ml of water from the bacteria-bearing bog soil sample, and allowed to run for extremely extended periods. The microorganisms initially began visible fermentation after a lag period of approximately one week, and began to generate significant quantities of carbon dioxide that bubbled visibly through the fermentation locks. After approximately three weeks, carbon dioxide generation largely ceased and the iron content had reached approximately 100 mg/l. However, the iron concentration continued to rise slowly over an extended period, ultimately reaching a level of 3487 mg/l after a period of 1 year. This indicated that a significant level of iron dissolution could be achieved provided that sufficient time was allowed.

The next series of experiments were conducted to determine the best organic matter source for the bacteria to use in dissolving iron. All of the test flasks contained 10 g of magnetite concentrate as the iron source, and acetate ions as an organic matter source. Two other forms of organic matter were also examined as supplements to the acetate:

- 1. Sucrose
- 2. Cellulose (cotton)

The effect of adding vitamin and mineral supplements was also considered in the experiment. A set of eight static flasks were prepared using a factorial design to evaluate the effectiveness of each type of organic matter. The experimental design, and the resulting iron concentrations in solution after 40 days of microbial activity, are given in Table 3.

It is immediately obvious that the addition of vitamin/mineral supplement had no systematic effect on the iron dissolution. It was therefore of minimal benefit. The negligible effect of the vitamin/mineral supplements was probably due to the availability of trace minerals in the ore being dissolved, and to the mixed culture of different species of microorganism being able to provide a variety of trace vitamins.

The presence of cellulose, in the form of cotton, does have a small positive effect, and its presence appears to increase dissolved iron levels by an average of 31 mg/l. However, the main effect of adding sucrose is very large, producing an average increase in the iron concentration of 270 mg/l for a 40-day leach. This indicates that, at least in the relatively short term, the microbial iron dissolution functions best when a highly soluble carbohydrate is available.

It should be noted that, in an industrial situation, it will be impractical to maintain a pure culture of a single organism, and in fact it would probably be undesirable to do so. It is likely that the best results will be obtained by a combination of at least two classes of microorganisms: one type to degrade complex organics, such as cellulose and other biomass, into soluble organics; and a

second type to use the soluble organics to reduce ferric iron to soluble ferrous iron. In such a mixed culture of organisms, cellulose and related materials would be expected to be much more effective in aiding the solubilization of iron than is apparent in these experiments.

Table 3: Effects of two different organic matter sources and vitamin/mineral supplement on the quantity of iron dissolved. A + value indicates that the substance was present in the flask, and a – indicates that it was absent.

Cellulose	Sucrose	Vitamin/Mineral	Dissolved iron after
(5 grams)	(5 grams)	(10 ml per liter)	40 days, mg/l
+	+	+	299
-	+	+	314
+	-	+	54
-	-	+	4
+	+	-	326
-	+	-	270
+	-	-	52
-	-	-	19

Continuous Column Results

Since the static flask experiments had established that the basic nutrient solution containing sucrose (shown in Table 1) produced good iron dissolution in a reasonably short time, this nutrient solution was used to establish the long-term leaching column with 6 kg of coarse crushed ore. The objective was to establish a continuous system where fresh media would enter the base of the column, be gradually metabolized to generate carbon dioxide and reduce/dissolve iron as it rose through the column, and exit as an enriched iron-bearing solution. After establishing and inoculating the column, the iron concentration in the product was monitored on a daily basis by collecting 50 ml of solution for analysis. The results are shown in Figure 6.

Initially, the activity in the column passed through a "lag phase" of approximately 5 days before the iron content began to increase. The iron levels then began increasing on an exponential curve as the bacteria rapidly grew and established themselves. The concentration then began to level off at approximately 200 mg/l (ppm) after roughly 30 days.

It was noted very early on that, while the samples collected from the column were initially clear, if they were allowed to stand for more than a few hours they began to precipitate a pale yellow material in the bottom of the sample container. This was determined to be iron-rich material, which did not appear to form due to oxidation, since it formed even when the sample was closed and kept away from oxygen. Its formation could be prevented by adding a small quantity (1 ml) of hydrochloric acid as a preservative. When the acid was added, it was noted that gas was evolved, which was apparently carbon dioxide. Further examination of the products formed and the potential iron-bearing compounds indicated that the precipitate was ferrous iron carbonate, and that it was precipitating due to decreasing carbon dioxide levels in the solution.

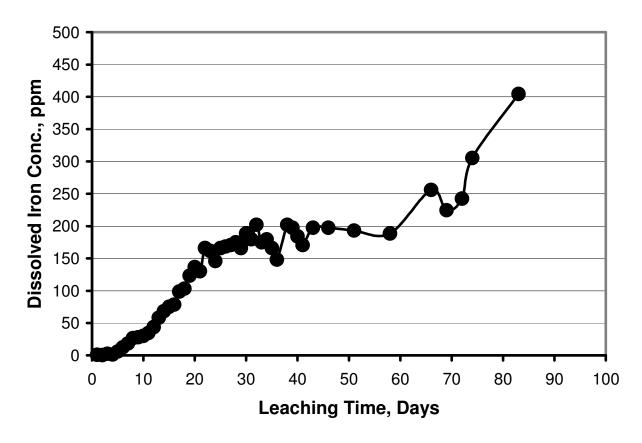


Figure 6: Iron concentration as a function of time. The sucrose content of the fresh media being added to the column was doubled at day 58, which subsequently lead to a marked increase in the dissolved iron content of the leachate.

Since carbon dioxide was forming continuously in the column, it contained essentially 100% carbon dioxide at 1 atmosphere pressure. As a result, at 25°C the solution as it exited the column would contain an estimated 0.03 moles CO₂ per liter of water. This would result in a ferrous carbonate solubility of approximately 720 mg/l (Linke and Seidell, 1958), compared to a reported value of only 67 mg/l in the absence of gaseous CO₂ (Weast, 1985).

The iron content of the column leachate shown in Figure 6 initially reached a plateau at 200 mg/l, which is much below the theoretical level of 720 mg/l that was expected if the solution was saturated with carbon dioxide at 1 atmosphere pressure. This plateau was noted to occur after the column had largely ceased to generate carbon dioxide by fermentation of the sucrose. When the sucrose content was subsequently increased, carbon dioxide production resumed and the dissolved iron content in the leachate was rapidly elevated. This indicates that, in an industrial application, it would be important to retain and recycle carbon dioxide in the system to maintain high iron solubility.

Iron Precipitation

While it was observed that an iron-rich precipitate was formed from the leachate as the carbon dioxide left the solution, the small quantities of sample initially collected did not allow enough of the precipitate to be collected for analysis. In order to analyze the precipitate, a large sample of

600 ml was collected in a separatory funnel, vented to the atmosphere so that carbon dioxide could escape from solution. After 24 hours, the precipitate had concentrated into 10 ml of liquid, which was removed, filtered, and dried. A total of 0.0133 g of precipitate was recovered from the filter. Analysis by X-ray diffraction indicated that the precipitate was amorphous, and so no crystalline phases could be identified. The precipitate was then dissolved in hydrochloric acid, diluted to 100 ml, and analyzed for iron content using the phenanthroline method. Based on this analysis, the precipitate was estimated to be 21% Fe by weight.

Electrolysis

Due to the small quantities of leach solution avaliable early in this project, initial electrolysis experiments were conducted with synthetic solutions of iron acetate. It was established that iron could be satisfactorily plated from an iron acetate solution, produced by dissolving steel wool in a 1% acetic acid solution. This resulted in a solution pH of 3.78. Iron could be plated from this solution at a potential of 5.0 volts, at dissolved iron concentrations as low as 165 mg/l

Based on the conditions for the synthetic solution electrolysis, a sample of leachate was electrolyzed directly in the cell. The leachate pH was 4.48, and 50 ml of the solution was added to the cathode compartment of the electrolysis cell. This experiment produced small nodules of hard, strongly magnetic material combined with a black, gelatinous, nonmagnetic precipitate. A total of 0.15 g of magnetic material was recovered, and was confirmed to consist of metallic iron by X-ray diffraction. This conclusively demonstrated that the basic principle of bacterial iron dissolution followed by electrowinning of metallic iron was technically feasible.

The nonmagnetic precipitate appeared to be formed from residual organic matter in the solution. It is therefore important that the solution be purified to minimize the amount of organic matter prior to electrowinning.

Industrial processing scheme

Based on the experimental results, the most practical route for industrial-scale iron production would be as follows:

- 1. Carry out the bacterial reduction and dissolution of iron in a leaching configuration that allows carbon dioxide to be retained in the system. Organic matter to provide reducing power and food for bacterial growth may be provided by soluble carbohydrates such as sucrose, or potentially by combining the ore with cellulose-bearing biomass. In a full-scale operation, the leaching would ideally be carried out in a pit with an impermeable clay cap that could be buried at sufficient depth for the carbon dioxide partial pressure to be elevated above atmospheric pressure.
- 2. Recover the iron from solution by reducing the dissolved carbon dioxide concentration in the solution, either by purging with deoxygenated air or by applying a partial vacuum to draw the carbon dioxide out of solution. This would cause the amorphous iron-bearing precipitate to concentrate into a small volume an to separate it from the organic matter remaining in solution. After iron removal, additional bacterial nutrients would be added to the solution if necessary, and the solution would be returned to the leaching zone.
- 3. The iron-rich precipitate would be transferred to an electrowinning cell, where it would be redissolved in a suitable electrolyte such as acetate or sulfate solution. This would allow the metallic iron to be plated from solution with minimal interference from the

presence of organic matter. In the process of electroplating metallic iron at the cathode, H+ ions would be produced at the anode in sufficient quantities to continue dissolving the iron-rich precipitate. Use of an acetate solution would allow a small portion of the electrowinning solution to be diverted back to the leaching operation, where the acetate would be metabolized. This would tend to prevent accumulations of excessive quantities of trace impurities in the electrowinning operation.

The first application of this technology would be as an adjunct to existing iron ore mining operations. An ideal situation would be an abandoned mining pit, which could be fitted with solution injection pipework, then gradually filled with a combination of iron-bearing ore tailings and metabolizable organic matter. The tailings would be available as a byproduct of the existing operation, and their diversion to the leaching pit rather than to a tailings impoundment would be very economical. Once the pit was filled, it would be capped, covered, and filled with water. It would then be inoculated with an appropriate bacterial culture. Once this was done, the installation would begin producing dissolved iron at a rate that would take many years to completely dissolve the ore, allowing the plant to continue producing iron for extended periods without the need to move additional large quantities of ore. It would therefore provide a source of continuing revenue for the mine well after the primary high-grade deposit was exhausted.

This project was carried out on a laboratory scale, and generated the results necessary for carrying out pilot-scale studies to determine the behavior of the process upon scaleup. Pilot-scale studies will need to use approximately 1 metric ton of ore in order to produce sufficient quantities of leach solutions to fully develop the solution purification and iron electrowinning stages.

Conclusions

This project has confirmed the technical feasibility of a biohydrometallurgical route for selectively leaching iron from ores, followed by electrowinning of metallic iron. Anaerobic bacteria that are common in swamp and bog environments have been demonstrated to be capable reducing iron to the Fe⁺² state, solubilizing it from magnetite-bearing ore. Carbon dioxide produced by the bacterial metabolism should be retained in the system, as a high concentration of carbon dioxide in solution greatly enhances the solubility of the reduced iron.

Solution purification is a key feature needed for electrowinning the dissolved iron as metal, as the presence of organics can produce an interfering precipitate during electrolysis. While it would be technically feasible to use a solvent extraction process, similar to that used in copper hydrometallurgy, to recover and purify the dissolved iron, a much more cost-effective route is suggested by the variations in iron solubility caused by dissolved carbon dioxide. If the iron is dissolved at a high carbon dioxide concentration, it can then be reprecipitated by removing the carbon dioxide from solution. This results in the formation of an amorphous, iron-rich precipitate that can be separated from the leaching solution, leaving the organics behind. This concentrated precipitate can then be redissolved and electrolyzed to recover the iron as metal.

This is the first time that a completely hydrometallurgical process for metallic iron production has been shown to be technically feasible. Initially it will be a useful adjunct to existing iron production methods, but over time it is expected that, as is already happening in the copper industry, the hydrometallurgical route will completely replace the existing high-temperature, energy-intensive pyrometallurgical methods for producing metallic iron.

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