AMMONIUM SULPHATE LEACHING
OF LOW-GRADE MANGANESE ORES OF TENNESSEE

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PREFACE

Within the Tennessee Valley district there exists a large number of deposits of low-grade manganese ores in which the manganese is largely locked up in the form of the higher oxides of manganese. Most of these low-grade ores contain an appreciable amount of iron which complicates the matter of their concentration and of obtaining a product of high purity. The object of this work is to determine a satisfactory method for concentrating the manganese content of these low-grade ores to a product of a high degree of purity.

GENERAL SURVEY OF FIELD

Manganese is used in the production of steel for three purposes. It removes the excess oxygen in the steel and prevents the formation of blow holes. Also it converts the sulfur content to MnS which is necessary if the steel is to be worked or rolled, otherwise the sulfur goes to FeS which forms hard crystals that cut the metal when it is rolled. Third, the addition of manganese to steels gives it well known and highly desirable physical properties. The use of manganese alloy steels is one of the important developments of modern metallurgy.

Low-grade ores cannot be used in the production of metallurgical manganese. There is a lower limit to the manganese content of useful ores and an upper limit to the silica content. Consequently before the low-grade manganese ores can be of any real value a process for the concentration and purification of these ores must be developed.

The common methods of manganese concentration may be divided into five classes which will be discussed separately below.

HAND PICKING is at present used on Tennessee manganese ores, however the rejected material still carries 25 - 30% manganese.

WET CONCENTRATION by such methods as flotation will work to some extent but the composition of the product is not sufficiently high in manganese in present state of the art.

MAGNETIC SEPARATION can be used to remove magnetite from the ores but the composition of the product is apt to be variable and the method has been successful to a very limited extent.

PYROMETALLURGICAL methods have been developed but they are too costly to use in any case but emergency.

CHEMICAL EXTRACTION methods seem to have advantage over all other processes. They may be adapted to almost any ore. They should recover almost all of the manganese, and should give an uniform product.

The product of chemical methods would probably be one of the oxides. This oxide could be briquetted and sintered to give a structurally strong material suitable for use in blast furnaces. Another method would be to reduce this very high grade product with carbon in an electric furnace. The resulting ferro-manganese would have a high manganese content and would be low in silica, sulfur and phosphorus.

There are a number of difficulties involved in the hydrometallurgy of low-grade manganese ores. A large amount of chemical in the solvent solution is necessary to react with the manganese content to effect dissolution necessary for separation and removal of the ore residue. The solvent must therefore either be very cheap or through regeneration become available for reuse at a low cost. Another problem is the recovery of the manganese from the solvent solution.

The feasibility of treating low-grade manganese ores by hydrometallurgical processes is dependent upon the cost of treatment and the selling price of the manganese product. The difficulty and consequent cost of getting the manganese into solution coupled with the ease of getting a product of high purity from solution favor the preparation of high-grade products such as those used in the textile industry and in the manufacture of electric batteries, glass, pottery, tile, brick, paint, ink and fertilizers.

The Bradley process of manganese recovery by ammonium sulphate leaching seems to be the most practical method as it has received wide attention throughout the country.

STATEMENT OF PURPOSE

The purpose of this series of experiments is to determine whether the Bradley process is applicable to the low-grade manganese ores of the Tennessee Valley.

GENERAL THEORY

Three essential chemical processes are involved in this process, namely, reduction, leaching and precipitation.

The manganese ore must be first subjected to selective roasting in a reducing atmosphere of some gas containing principally CO and H_2. City gas was found suitable for this purpose in this experiment. The reduction converts the higher oxides of manganese to MnO and reduces most of the iron to the magnetic oxide Fe_3O_4.[1] About 10% of the iron goes to FeO if the temperature of roasting does not exceed 400° Centigrade.

$$MnO_2 + H_2 \rightarrow MnO + H_2O$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$$

All of the manganese oxides excepting braunite are subject to reduction. The carbonate also is reduced at this temperature but the silicates require a very high temperature for reduction to MnO.[1]

[1] Carl Zappfe. Eng. Mining J. 128, 14-19 (1929)

The roasting can be made selective by keeping the temperature at 400° C or less. That is, the manganese oxides are reduced before the iron oxides, and by the time the manganese oxides are reduced to MnO, only about 10% of the ferric oxide is reduced to FeO.

The reduced oxides, that is MnO and FeO, will dissolve in ammonium sulfate solution with the liberation of NH_3 gas.

$$MnO + (NH_4)_2SO_4 \rightleftharpoons MnSO_4 + 2NH_3 + H_2O$$

$$FeO + (NH_4)_2SO_4 \rightleftharpoons FeSO_4 + 2NH_3 + H_2O.$$

The equilibrium constants of the above reactions are such that by increasing the concentration of $(NH_4)_2SO_4$ the reactions may be driven to the right. Or, by increasing the concentration of the NH_3, the reactions are driven to the left. The success of the process hinges upon this fact. By employment of countercurrent leaching and countercurrent precipitation, the concentrations may be varied so manganese goes into solution in the leaching and is thrown out of solution in the precipitation stage. The reagent used, $(NH_4)_2SO_4$, is recycled without appreciable loss because it is consumed in the leaching operation and regenerated in the precipitation step.

The leaching process is carried out in such a way that the leach liquor flows countercurrent to the reduced ore. Hence iron, which is the last to be taken up by the fresh leaching liquor from the spent ore, is

the first to be thrown down as the spent leaching liquor bearing considerable ferrous sulfate comes in contact with the fresh ore. This feature effects another very important separation of the manganese and iron, the latter ending up in the solids discharged from the leacher, or tailings.

A third important feature of this procedure is inherent in the precipitation process. Theoretically, ammonia liberated from the leaching reaction, is passed countercurrent with the spent leaching liquor, to regenerate the ammonium sulfate for further leaching. At this point a final removal of iron from the manganese can be effected if necessary since it will be the first to precipitate and can be removed and discarded.

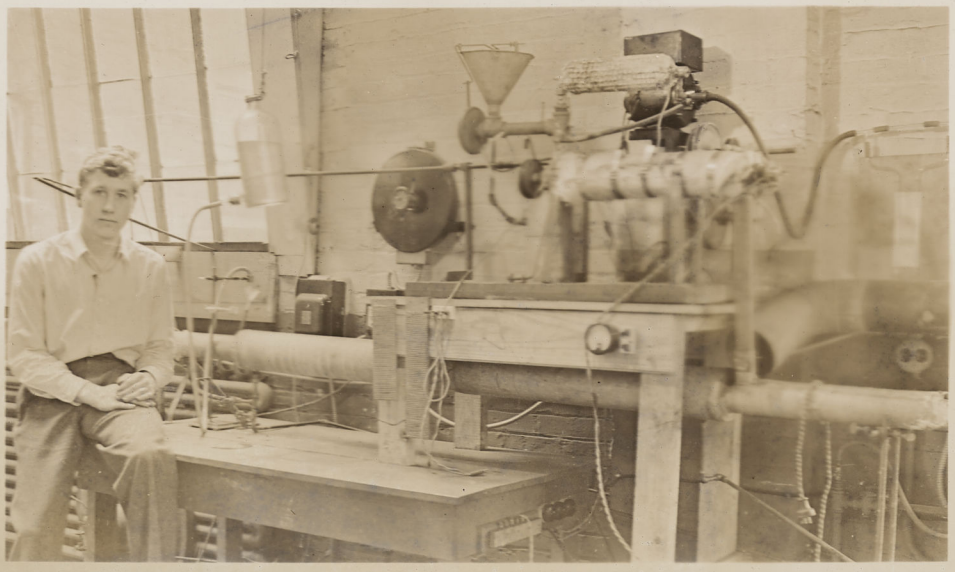
The manganese on the addition of ammonium hydroxide forms manganous hydroxide.

$$MnSO_4 + NH_4OH \rightleftarrows Mn(OH)_2 + (NH_4)SO_4$$

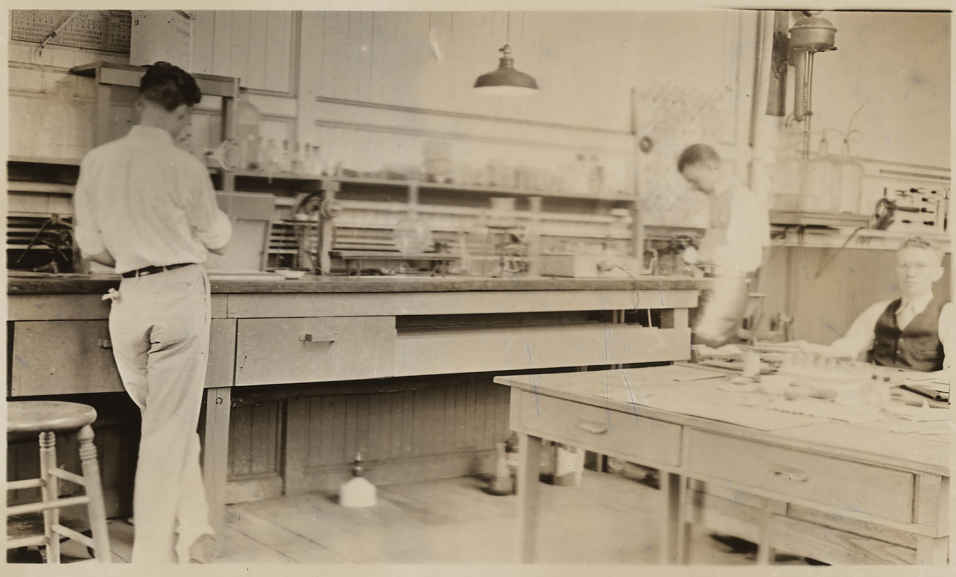
When air is bubbled through the solution the flocculent precipitate of manganous hydroxide forms a hydrated oxide.

$$4Mn(OH)_2 + O_2 \rightarrow 4MnO(OH) + 2H_2O$$

The oxidation of the manganous hydroxide causes the precipitation to be more complete. The resulting form also settles more readily.



Roasting and leaching apparatus



Analytical table

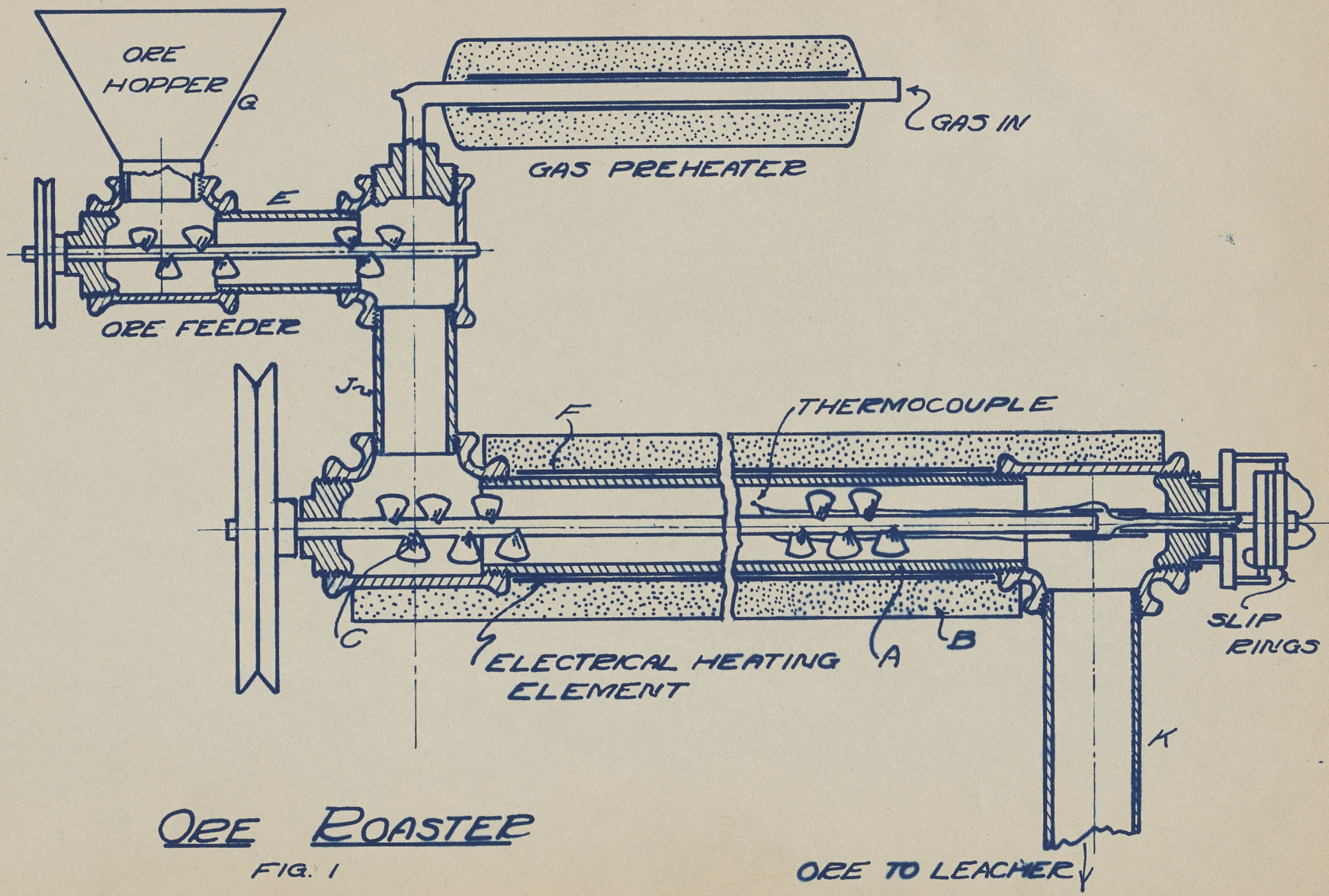
DESCRIPTION OF APPARATUS

The roaster, fig. 1, consists of an inch and one quarter pipe (A), sixteen inches in length. The pipe is insulated on the outside by three layers of asbestos paper and wound with chromel resistance wire (F). Additional wrappings of asbestos paper over the wire serves to protect it from the air. The pipe and heating element are lagged with 85% magnesia pipe covering. Pipe tees are screwed on either end of the pipe as shown in the diagram. The ore is fed out of a funnel (G) by a screw contained in the pipe E. The ore drops through pipe J into the furnace where it is caught by the screw (C) and carried through the furnace. The screw consists of a rod with ears welded on angularly at intervals. Strips of sheet iron are brazed to the sides of the ears so that the ore is picked up and dropped as the screw turns.

The hot ore freshly roasted drops through the pipe (K) into the leacher. The gas preheater is located as shown. City gas flows concurrent with the ore to prevent clogging of the ore in pipe K.

The ore feeder runs at a speed of approximately 2.4 RPM and delivers 4.2 gms. per minute of ore to the furnace. The furnace screw turns at the rate of 10 RPM and requires thirty minutes to carry the ore through the furnace.

The leacher, fig. 2, is a long hollow centered spiral screw contained in a close fitting sheet iron

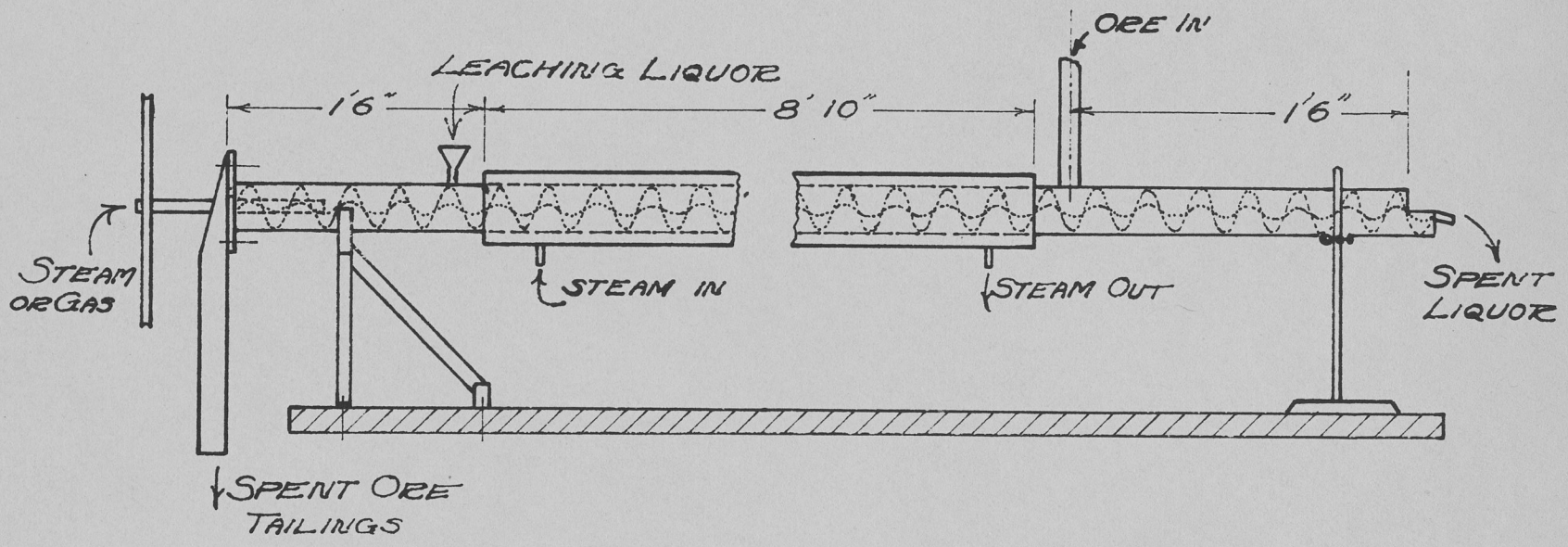


ORE ROASTER

FIG. 1

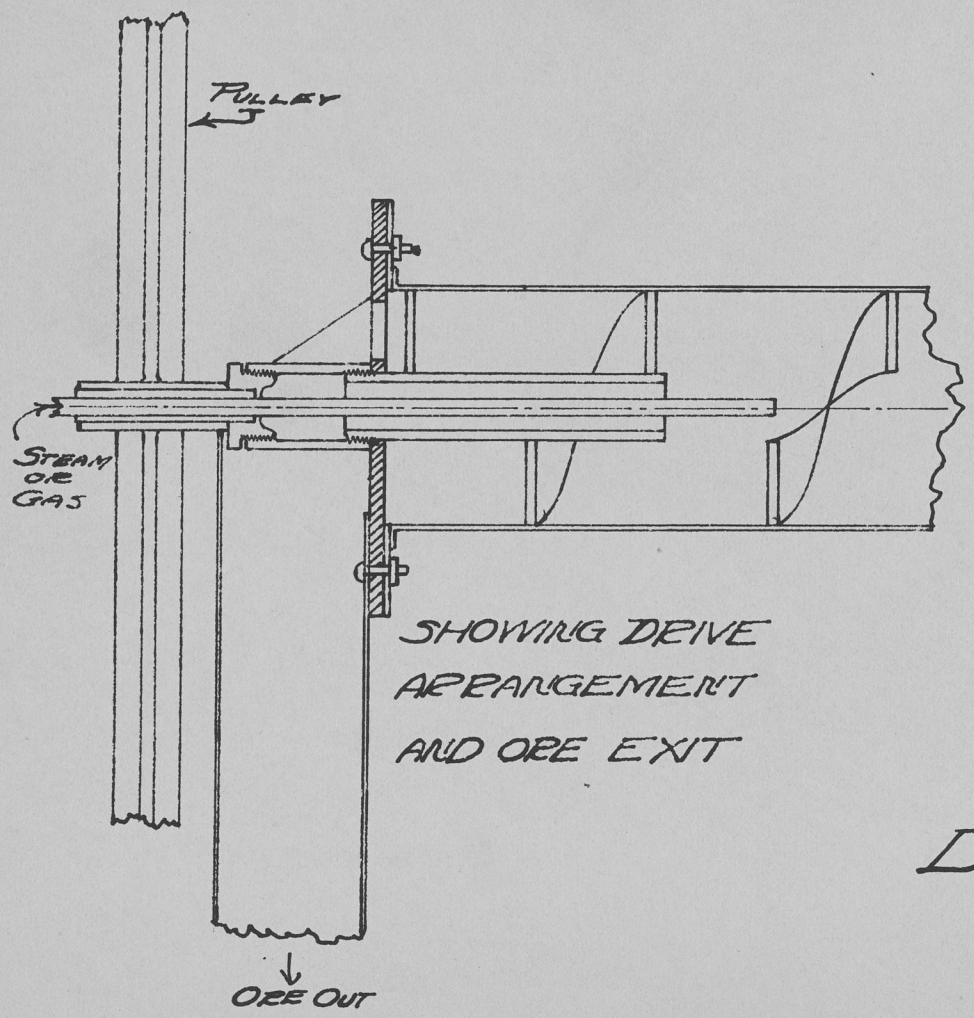
tube (A). The screw is 8' 10" in length, has an outside diameter of three inches and an inside diameter of 1.3 inches. The pitch of the screw is 3.25" and it turns at a rate of 1.5 RPM. The leacher is inclined 1.188 inches vertically over the length ,which corresponds to an angle of 0° 40'. The solids outlet is the highest point of the leacher, and the screw drags the ore upwards towards the drive wheel. Ore stays in the leacher for about one hour before it is ejected at the upper end. The middle portion of the leacher is surrounded by a steam jacket as shown in the diagram.

The furnace and leacher are both connected by belts to a slow turning shaft. The shaft is driven by a one-quarter horse-power electric motor through a system of pulleys.

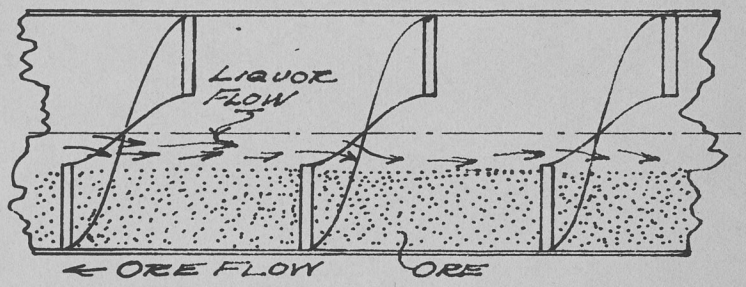


COUNTERCURRENT LEACHER

FIG. 2



SHOWING DRIVE ARRANGEMENT AND ORE EXIT



SHOWING FLOW OF ORE AND LEACHING LIQUOR

DETAIL OF LEACHER

FIG. 3

EXPERIMENTAL PROCEDURE

In making a run with the set up of reducing furnace and leacher combined, the current was turned on the furnace and the gas preheater. When they came up to the required temperature, e.g. 700-750° C, the ore feed to the reducing furnace together with the flow of city gas was started. After a steady state of flow had been attained in the furnace, the proper adjustment of the external rheostat maintained the temperature evenly. After a matter of thirty minutes the reduced ore fell through the discharge pipe into the leacher. At this time the flow of $(NH_4)_2SO_4$ solution through the apparatus was started. The temperature of the liquor was maintained at the boiling point by the steam jacket. Also at this time either city gas or steam was forced down the center of the leacher to sweep out the NH_3 formed by the leaching.

The furnace temperature and the flow of liquor received careful attention. The leacher was kept running after the furnace was shut off until the last sample of spent ore tailings had been taken. It was found unnecessary to filter the liquor which the leacher discharged as there was absolutely no ore carried over by the liquor. The settling portion of the leacher worked perfectly at any rate.

Samples of the tailings of the ore discharged from the leacher were taken at the beginning and end of the runs as well as at regular intervals between.

The clear liquor discharged from the leacher was put in an open can and brought to nearly boiling. Ammonium hydroxide in excess was added and also air was bubbled through the solution. The temperature was maintained above 80° C for 20 minutes, and air bubbling was continued. The precipitate formed was washed with hot water by decantation, eight to ten times as the precipitate has the quality of retaining dissolved salts. The washed precipitate was filtered off and dried at approximately 90° C.

OBSERVATIONS

The leaching of the ore required that the NH_3 formed be swept out of the leacher. City gas or steam was used for this purpose to prevent the re-precipitation of dissolved manganese in the leacher. It was observed that a dark scum of precipitated substances was formed on the surface of the liquor in the lower end of the leacher. This was evidently due to the oxidizing action of the air.

It was observed that the leach liquor contained less and less iron as the leacher filled with ore, the counter-flow extraction effectively eliminating

the iron.

The reduced ore oxidizes rapidly and it was found necessary to put the ore discharged from the furnace immediately into the leacher. This was done by mounting the furnace above the leacher and letting the reduced ore drop through a pipe into the leacher. The gas which was run through the furnace also went down this same pipe so that there was no danger of re-oxidation.

ROASTING AND LEACHING DATA

Run #1 May 6,1935

Ore feed	4.15 gms./min.	
Furnace temperature	700° C	
Gas flow	4.64 l/min.	Countercurrent
Liquor feed	125 cc/min.	
Approximate time of run	2 hours	
Manganese content of ore	31.9%	

Analysis of Tailings

	I (1 hour)	II (1.5 hours)	III (2 hours)
Percent Mn	9.47	8.90	11.70
Percent SiO_2	29.92	26.55	22.22
Gms.Mn/gm.SiO_2	.3170	.3358	.5260
Gms.Mn/gm.SiO_2 in orig. ore	2.202	2.202	2.202
Gms.Mn Extr./ gm.SiO_2	1.885	1.866	1.676
Gms.Mn Extr./ gm.raw ore	.273	.2705	.243
Roasting and Leaching Efficiency	85.6%	84.7%	76.1%

Due to operating difficulties in this run, no data were taken on the precipitation of Mn from the leach liquor.

ROASTING AND LEACHING DATA

Run #2 May 9,1935

Ore feed	4.15 gms./min.
Furnace temperature	700° C
Gas flow	4.64 l/min. Concurrent
Liquor feed	125 cc/min.
Approximate time of run	3 hours
Manganese content of ore	31.9%

Analysis of Tailings

	I (1.5 hours)	II (2 hours)	III (2.5hours)	IV (3 hours)
Percent Mn	9.80	11.02	11.87	11.73
Percent SiO_2	28.33	25.34	21.61	21.54
Gms.Mn/gm.SiO_2	.3460	.4360	.5480	.5460
Gms.Mn/gm.SiO_2 in orig.ore	2.202	2.202	2.202	2.202
Gms.Mn/Extr./ gm. SiO_2	1.856	1.766	1.654	1.656
Gms.Mn Extr./ gm.orig.ore	.2685	.2560	.2400	.2400
Roasting and Leaching Efficiency	84.2	80.2	75.2	75.2

Concentrate	Mn	41.4%
	Fe	9.27%
	SiO_2	None
	Al_2O_3	Trace

The duration of this test was only three hours and hardly allowed the leacher to fill with ore. Hence the liquor contained much iron and less manganese.

ROASTING AND LEACHING DATA

Run #3 May 14,1935

Ore feed	4.15 gms/min.
Furnace temperature	750° C
Gas flow	4.64 l/min. Concurrent
Liquor feed	150 cc/min.
Approximate time of run	6 hours
Manganese content of ore	31.9%

Analysis of Tailings

	I (3 hours)	II (4 hours)	III (5 hours)	IV (6 hours)
Percent Mn	17.6	16.6	15.4	14.05
Percent SiO_2	22.94	24.48	27.14	29.02
Gms. Mn/gm. SiO_2	.868	.678	.567	.484
Gms. Mn/gm. SiO_2 in orig. ore	2.202	2.202	2.202	2.202
Gms. Mn Extr./ gm. SiO_2	1.334	1.524	1.632	1.718
Gms. Mn Extr./ gm. orig. ore	.193	.221	.2362	.249
Roasting and Leaching Efficiency	60.5%	69.2%	74.1%	78.0%

Concentrate		
	Mn	65.6%
	Fe	0.8%
	SiO_2	None
	Al_2O_3	Trace

The concentrate here was precipitated from liquor which came out after the leacher was full of ore and was consequently low in iron and high in manganese.

RESULTS

Taking the best results of our experiments it seems that the Bradley process extracts at least 85% of the manganese in the ore, This is far better recovery than that obtained in any other method of concentration other than chemical. The percentage of manganese in the best concentrate exceeds that in pure MnO_2. The iron content is almost negligible so that the product is pure enough for many uses besides metallurgical.

Assuming that no other elements are present in the concentrate than Mn and O_2, the manganese is calculated to be in the form of Mn_2O_3.

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APPENDIX

The manganese ore used in these experiments came from Cedar Hill, Tennessee. It was the residue left from the handpicking operation at that mine. The ore taken from the waste heap was made up of pebbles from one-quarter to three-eight's of an inch in diameter. This ore was pulverized in a roller mill. After pulverizing most of the ore would pass a two hundred mesh screen. The object of the fine pulverizing was to increase the rate of reaction in both roasting and leaching. An analysis of the ore is given below.

Mn	31.39%
Fe	14.92%
CaO	trace
P	0.43%
Insoluble	16.34%
Loss on ignition	11.52%

The ammonium sulphate used for leaching in these experiments was crude commercial ammonium sulphate. This sulphate was made up into a 10% solution and kept in a large tank while the experiments were being made.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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