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Recovery of manganese from oxidized ores as iron-and phosphorus-free soluble salts

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RECOVERY OF MANGANESE FROM OXIDIZED ORES AS IRON-AND

PHOSPHORUS-FREE SOLUBLE SALTS

By

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THESIS

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INTRODUCTION

There is a great demand at present for this country to develop its manganese resources. The hazards encountered because of the present international crisis make it almost impossible to import high-grade ores. Manganese is one of the most important strategic metals because it is vital to the production of steel. After the stock piles are depleted and the imports decreased, the deficit must be supplied by the domestic deposits.

A great deal of research has been done to concentrate the domestic low-grade ores but new problems have always been encountered. The differences in the properties of the low-grade ores from various sections of the country require the application of a large number of different treatments.

Because phosphorus is such an undesirable element in the production of iron and steel it is, therefore, necessary to eliminate it from the manganese concentrate used in this industry. Some of the larger domestic manganese deposits have a high phosphorus content. The concentrates produced from these deposits by the current methods often contained enough phosphorus to make them unsuitable for use in iron and steel production. It was believed the phosphorus could be eliminated if the ore were sulfated with sulfur dioxide in the gaseous state at elevated temperatures and the soluble manganous sulfate extracted with

water.

The presence of iron in the manganese concentrate is undesirable only because it presents a problem of corrosion[1] in the evaporation of the leaching solution to recover the manganese. By sulfating the ore at temperatures above that at which ferrous and ferric sulfates decompose to give the water-insoluble oxides, no iron should be extracted in the leaching of the sulfated ore with water.

These factors led to the selection of this subject as a research problem.

(1) Dean, R. S., Leaver, E. S., and Joseph, T. L. Manganese. U. S. Bureau of Mines. Information Circular 6770. 1934. p. 183.

REVIEW OF PREVIOUS WORK

As a result of the importance of manganese in the production of iron and steel the metallurgy of manganese was developed simultaneously with that of iron. There were enough high-grade ores available to this country so the process was essentially a reduction with carbon in a blast furnace to produce a manganese-iron alloy (ferromanganese). The more siliceous ores were treated in the blast furnace to produce spiegeleisen, an alloy of iron-silicon-manganese.

Practically all of the high-grade ores used in this country were imported from Africa, Brazil, Chile, Cuba, India, the Philippine Islands and the U. S. S. R. [2]. The low-grade ores in this country were seriously considered as a source of manganese for the first time in 1914. A number of large deposits[3] of low-grade ores were discovered in various sections of this country which warranted investigation. A few processes were developed but were discontinued soon after the war because high-grade ores were again available. In recent years this work has received even greater attention than before.

One type of process for producing a high-grade manganese concentrate that received a great deal of attention

(2) U. S. Bureau of Mines. Minerals Yearbook, 1940.
     Manganese and manganiferous ores. p. 583.

(3) Dean, R.S., Leaver, E.S., and Joseph, T.L. Manganese.
     U. S. Bureau of Mines. Information Circular 6770.
     1934. pp. 168-9.

was the hydrometallurgical treatment. The treatment of low-grade manganese ores by this type of process presented a difficult problem in comparison with the usual leaching processes used in recovering the precious metals or copper. In the extraction of manganese by such methods, the solvent must be cheap or must lend itself to regeneration for repeated use in the process at a low cost. Another problem was the recovery of the manganese from the leaching solution. The feasibility of the treatment employed was governed by the cost of such treatment and the selling price of the product.

"From a hydrometallurgical standpoint manganese ores may be divided into several types: (1) Ores in which the manganese mineral is readily soluble in at least one solvent; (2) ores in which the manganese requires preliminary treatment to make it soluble; (3) ores containing manganese in insoluble form; (4) ores which destroy excessive amounts of solvents due to soluble impurities; (5) ores which present physical properties that increase the cost of treatment."[4]

Group (1) will include the higher oxides, such as pyrolusite and braunite. Rhodochrosite will be classified in group (2) because it requires a preliminary roast to expel the carbon dioxide. The ores that make up group (3) are rhodonite and the partially oxidized black silicate.

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(4) Ibid. p. 167.

Group (4) is represented by ores having a high lime content, causing excessive acid consumption. Ores containing clay and talc make up group (5).

One of the first important processes developed for treating domestic low-grade manganese ores was the Leaver drum-leaching process[5] for which E. S. Leaver received a patent[6] in 1918. The higher oxides of manganese readily dissolved in a hot sulfurous acid solution. This was accomplished by passing hot smelter gases containing from 2 to 6 per cent sulfur dioxide countercurrent to a pulp of the 20-mesh ore in water. The manganese was recovered from the solution by evaporation followed by sintering. This regenerated the sulfur dioxide to be used again in the process.

Another important process was the Bradley process[7]. The ore was crushed to minus 65-mesh and roasted at 400° C in a reducing atmosphere of producer or blast furnace gas. This treatment converted the manganese dioxide to manganous oxide and the ferric oxide to the magnetic oxide and a small amount of ferrous oxide according to the following equations:

$$MnO_2 + CO \longrightarrow MnO + CO_2$$

(5) Ibid. pp. 180-3.

(6) Leaver, E. S. Leaver drum-leaching process. U. S. Pat. 243,015, Nov. 18, 1918.

(7) Zapffe, Carl. Leaching manganese from the siliceous iron ores of Minnesota. Eng. Mining J. Vol. 127, pp. 1039-40 and Vol. 128, pp. 14-9 (1929).

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

The manganese was extracted from the reduced ore by leaching with an ammonium sulfate solution. This dissolved the manganous and ferrous oxides and liberated ammonia. The pulp was filtered and the ammonia passed into the filtrate to precipitate manganous hydroxide and regenerate ammonium sulfate. Air was passed through the solution to convert the manganous hydroxide to the partially dehydrated manganic hydroxide according to the following equation[8]:

$$2Mn(OH)_2 + O \longrightarrow 2MnO \cdot OH + H_2O$$

The precipitate was filtered off dried and converted to the high-temperature oxides by a sintering operation, thus producing a product satisfactory for ferromanganese production.

Professor A. T. Sweet and his associates at the Michigan School of Mines developed two processes[9] for sulfating manganese ores. One was called the "Sweet ammonia process" and the other was called the "Sweet acid process".

In the ammonia process the ore was crushed to minus 65-mesh, mixed with ammonium sulfate and moistened. This pulp was roasted to drive off the carbon dioxide and ammonia. These gases were passed into water forming an ammonium carbonate solution which was used later as the pre-

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(8) Dean, R.S., Leaver, E.S., and Joseph, T.L. Manganese U. S. Bureau of Mines. Information Circular 6770. 1934. p. 177.

(9) Ibid. pp. 177-80.

cipitant. The roasted pulp was leached with water in a countercurrent system. The manganese was removed from the clarified leach solution by precipitating it with the ammonium carbonate solution and thus regenerating the ammonium sulfate. The manganous carbonate was filtered off and converted to a manganese sinter. This process is especially applicable to ores high in carbonates.

The acid process is applicable to ores low in lime and magnesia. The ore was crushed to minus 65-mesh, mixed with sulfuric acid and roasted in a Herreshoff roasting furnace with a maximum temperature of 790° C. The roasted ore was leached with water and the solution filtered. The filtrate was evaporated to precipitate manganous sulfate which was converted to the high temperature oxides of manganese by sintering.

The U. S. Bureau of Mines has done a great deal of research recently in producing ferromanganese from domestic low-grade ores. The investigations included laboratory studies concerned with ore dressing, hydrometallurgy, electrometallurgy and pyrometallurgy. Pilot plants have been, or are being, constructed for the purpose of intensive study of the various phases of the manganese metallurgy.

A large number of ores have been studied from an ore dressing standpoint and approximately four out of five may be concentrated to ferro-grade with an average recovery of 75 per cent of the manganese in the ore. Each ore has been

found to present a distinct ore dressing problem. The
methods of ore dressing employed by the Bureau of Mines
are[10]: Log washing and rejecting of clays and slimes;
attrition grinding; jigging; "sink-and-float", employing
an aqueous suspension of finely divided galena; tabling
in closed circuit with grinding; tabling classified and un-
classified feeds; flotation of manganese minerals; flotation
of calcite, fluorite and gypsum; flotation of siliceous
material by the use of cationic reagents; table agglomer-
ation; slime treatment; and magnetic separation. In most
cases a combination of several of these methods was em-
ployed in concentrating the ore. The recoveries of mangan-
ese ranged from 20 to 95 per cent of that present in the
ore.

Ores not amenable to concentration by ore dressing or
hydrometallurgical processes may be smelted with iron or
copper sulfides to a manganese matte and refined to a 60
per cent manganese product that meets ferro-grade specifi-
cations[11]. The types of manganese ores best suited to
matte-smelting are those which contain twice as much silica
as lime plus magnesia.

Low-grade domestic manganese ores not amenable to con-

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(10)   Dean, R.S. Progress Reports-Metallurgical Division.
       U. S. Bureau of Mines. Report of Investigations,
       3600. 1941. pp. 10-3.

(11)   Ibid. pp. 15-9.

centration were studied from the hydrometallurgical stand-point[12]. Of the large number of proposed hydrometallur-gical processes only those that were promising and well known and a few that appeared applicable were studied in-tensively.

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(12) Ibid. pp. 20-3.

EQUIPMENT

A few experiments in the early part of this study were performed in a single-tube high-temperature combustion furnace.

The remainder of the experiments were done in a two-tube Burrell high-temperature furnace. This furnace was equipped with a thermocouple attached to a calibrated temperature indicator.

REAGENTS

Potassium Permanganate Solution

This solution was prepared in carboy lots by dissolving enough potassium permanganate in distilled water to make a solution of approximately 0.1 N strength. This solution was allowed to age to insure a more constant strength. Weighed samples of 0.25 g of standard sodium oxalate dissolved in 250 ml of 1:20 sulfuric acid at 65° C were titrated with the permanganate solution in the standardization.

Ferrous Sulfate Solution

This solution was prepared to be approximately 0.3 N by dissolving about 85 grams of reagent grade ferrous sulfate ($FeSO_4 \cdot 7H_2O$) per liter of solution that contained 10 ml of sulfuric acid (sp. g. 1.84). Whenever this solution was used it was standardized against standard potassium permanganate solution.

Ammonium Sulfate Solution

This was a water solution containing 60 grams of ammonium sulfate per liter.

Wood's Reagent

This was a water solution containing 100 grams of ammonium molybdate $\left[(NH_4)_6Mo_7O_{24} \cdot 4H_2O\right]$ and 250 ml of nitric acid (Sp. g. 1.41) per liter.

Potassium Thiocyanate

This was a water solution containing 100 grams of potassium thiocyanate per liter.

Sulfur Dioxide

In the early part of the work this gas was produced by treating sodium bisulfite with 50 per cent sulfuric acid. Later a cylinder of liquid sulfur dioxide was used.

SAMPLES

The samples used in this research came from the various sections of the United States having deposits of low-grade manganese ores. Some of these samples were concentrates produced by various ore dressing methods.

In most of the experiments performed in this work the five Arkansas wad ores whose analyses are given in Table I were used. In the early part of the work the samples were used as obtained but later all were ground to minus 100-mesh.

Table I. Analyses of the Arkansas Wad Ores.

Ore	Mn	Fe	CaO	SiO_2	P	Insol.
Ark A	23.95	21.16	7.62	7.34	2.42	10.56
Ark B	31.18	24.90	----	3.40	0.22	5.92
Ark C	30.34	21.25	0.56	6.64	0.61	11.62
Ark D	32.04	13.56	5.79	9.32	1.68	13.68
Ark E	27.15	23.78	4.11	7.04	1.45	9.56

PROCEDURES

Determination of Manganese

The manganese in each leaching was determined by the Volhard[13] method. Two ml of sulfuric acid (sp. g. 1.84) and 10 grams of zinc sulfate were added to the leach solution. After the zinc sulfate was dissolved an emulsion of zinc oxide in water was added in excess to neutralize the acid and precipitate any iron and aluminum that may have been extracted. The solution was diluted to 500 ml. Aliquot portions of this solution were heated to boiling and titrated hot with a standard potassium permanganate solution.

Detection of Phosphorus

Qualitative tests were made for phosphorus by acidifying a portion of the leach solution with nitric acid. The solution was heated to about 70° C and about 10 ml of Wood's reagent were added. The solution was vigorously shaken for a few minutes and set aside for about one hour. A yellow precipitate of ammonium phosphomolybdate indicated the presence of phosphorus in the solution.

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(13) Lord, N.W. and Demorest, D.J. Metallurgical Analysis. 5th ed. N.Y., McGraw-Hill, 1924. pp.81-4.

Detection of Iron

The qualitative tests were made for iron by acidifying a portion of the leach solution with nitric acid and oxidizing to the ferric state with hydrogen peroxide. Potassium thiocyanate was then added which produced a red color of potassium ferri-thiocyanate when iron was present.

PRELIMINARY EXPERIMENTS

Weighed samples of the manganese ores were placed in the single tube combustion furnace at approximately 600° C and sulfur dioxide, produced by the action of sulfuric acid on sodium bisulfite, was passed through the furnace for different time intervals. In a few of the experiments air was mixed with the sulfur dioxide. The samples were leached with water and the amount of manganese in each leaching was determined. Qualitative tests were made for iron and phosphorus in each leach solution.

The experiments in which air was mixed with sulfur dioxide gave a slightly greater yield of soluble manganese salts than did those in which only sulfur dioxide was used. However, the solutions showed the presence of iron and phosphorus. The presence of iron and phosphorus in the filtrate may be explained by the oxidation of sulfur dioxide to sulfur trioxide in the tube. This condensed with the water vapor present to form sulfuric acid in the colder portion of the tube. The sulfuric acid was washed out of the tube with the ore and extracted both iron and phosphorus. Contact with the sulfuric acid in this case could be avoided if the samples were placed in combustion boats. This procedure was adopted in all of the succeeding experiments.

The results of these experiments are shown in Table II.

Table II. Preliminary Experiments

Exp. No.	Sample	Temp. °C. (Appr- ox.)	Dur- ation of SO_2 (min.)	Dur- ation of air (min.)	Per Cent of total Mn re- covered	Fe	P
1	Ark D	600	50	none	22.70	-	-
2	Ark C	"	50	none	46.17	-	-
3	"	"	60	60	48.32	-	-
4	"	"	90	90	58.75	+	+
5	"	"	180	180	63.40	+	+
6	"	"	180	none	52.36	-	-
7	"	25	180	none	31.16	-	-

DETERMINATION OF OPTIMUM TEMPERATURE

A series of experiments was performed to determine the optimum temperature for sulfating oxidized manganese ores with sulfur dioxide gas. All conditions of the experiments were maintained constant except the temperature which was varied from 300° to 1000° C at 100° intervals. A weighed sample of Arkansas C ore was placed in an alundum combustion boat and treated in the Burrell furnace with sulfur dioxide, generated by the action of sulfuric acid on sodium bisulfite, for one hour at each temperature. The cooled sample was leached with water and the soluble manganese determined. The insoluble residues from the water leach were further treated with excess 1:20 sulfuric acid to recover the manganese soluble in acid in addition to that soluble in water. Qualitative tests were also made on each leaching for iron and phosphorus.

Table III presents the results of this series of experiments. The optimum temperature for sulfating manganese ores with sulfur dioxide was found, by these experiments, to be about 650° C as can be seen from Figure 1.

Table III.   Effect of Temperature on Extraction.
(Time - 1 hour;   Ore - Arkansas C)

Exp. No.	Temp. in °C.	Water leaching			Leached from insoluble residues with 1:20 H_2SO_4		
		Per cent of total Mn	Fe	P	Per cent of total Mn	Fe	P
1	300	12.71	-	-	2.06	+	+
2	400	19.94	-	-	1.98	+	+
3	500	35.09	-	-	2.88	+	+
4	600	45.40	-	-	3.50	+	+
5	700	45.36	-	-	5.38	+	+
6	800	37.14	-	-	8.63	+	+
7	900	38.74	-	-	6.35	+	+
8	1000	9.36	-	-	6.86	+	+

Figure 1. EFFECT OF TEMPERATURE ON RECOVERY

Recovery of Manganese (Per cent of Total)

Temperature in Degrees Centigrade

—o— Extracted with Water.
—◎— Extracted with Sulfuric Acid.
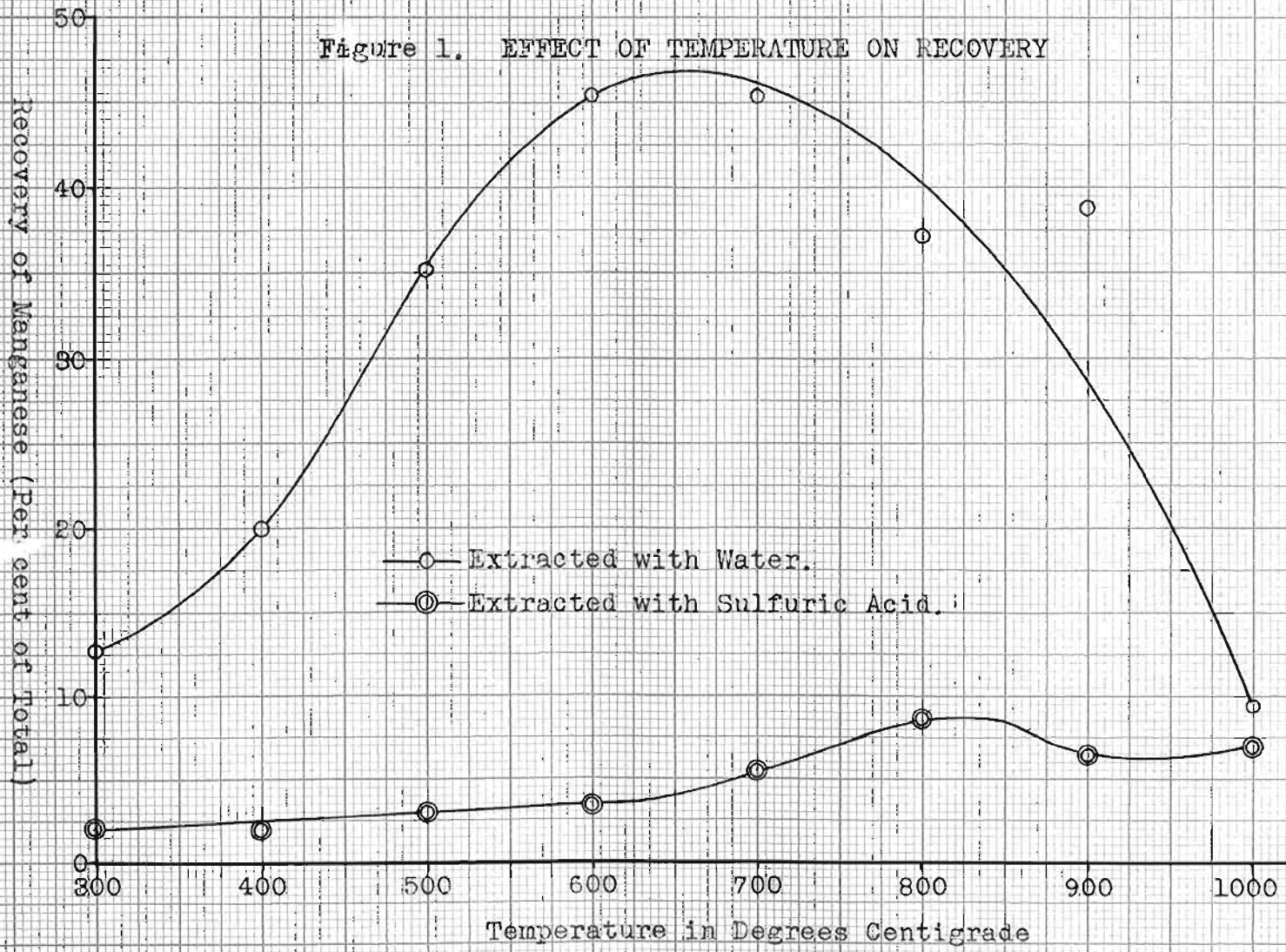
This optimum temperature is above the decomposition temperature [14] of ferrous sulfate (480° C) and, therefore, no iron should be extracted with water. Above 700° C the amount of extraction of manganese drops off rapidly because manganous sulfate begins to decompose at 699° C [14].

The additional manganese extracted with acid probably existed as manganous sulfite and oxide. The reactions involved are probably the following:

$$MnSO_3 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + SO_2$$
$$MnO + H_2SO_4 \longrightarrow MnSO_4 + H_2O$$

The increase in acid soluble manganese above 700° C (Fig.1) was probably due to decomposition of manganous sulfate into an oxide of manganese and sulfur trioxide. The drop in acid soluble manganese above 800° C was probably caused by conversion of the manganese oxide to the insoluble high temperature oxide.

Sulfur trioxide fumes began to appear at 600° C and as the temperature was increased greater quantities of the dense white fumes were formed. This was probably caused by the oxidation of the sulfur dioxide according to the following equation:

$$MnO_2 + SO_2 \longrightarrow MnO + SO_3$$

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(14) Hodgman, C.D., and Holmes, H.N. Handbook of Chemistry and Physics. 25th ed. Cleveland, Chemical Rubber Publishing Co., 1941. p. 1449.

EFFECT OF TIME ON REACTION

In this series of experiments all conditions were maintained constant except time which was varied from 5 to 210 minutes at 5 and 30 minute intervals. Two gram samples of Arkansas C ore in combustion boats were placed in the furnace at 650° C and sulfur dioxide was passed through the furnace for the different time intervals. After cooling the samples they were leached with water and the soluble manganese determined. The insoluble residues were leached with an ammonium sulfate solution (60 g. $(NH_4)_2SO_4$ per liter). The additional manganese extracted was considered to have been in the form of manganous oxide.

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

Qualitative tests for iron and phosphorus were negative in each experiment. The results of these experiments will be found in Table IV and Figure 2.

Table IV.   Effect of Time on Extraction.
(Temperature - 650° C;   Ore - Arkansas C)

Exp. No.	Time in min.	Water leaching			Leached from insoluble residues with $(NH_4)_2SO_4$		
		Per cent of total Mn	Fe	P	Per cent of total Mn	Fe	P
1	5	34.10	-	-			
2	10	40.04	-	-			
3	15	40.95	-	-			
4	30	50.41	-	-	0.71	-	-
5	60	42.02	-	-	1.18	-	-
6	90	42.67	-	-	1.07	-	-
7	120	53.15	-	-	0.66	-	-
8	150	47.44	-	-	0.77	-	-
9	180	51.60	-	-	0.54	-	-
10	210	51.83	-	-	0.55	-	-

Figure 2. EFFECT OF TIME OF TREATMENT ON RECOVERY

Recovery of Manganese (Per cent of Total)

Time of Treatment in Minutes

○ Extracted with Water.
◎ Extracted with Ammonium Sulfate.
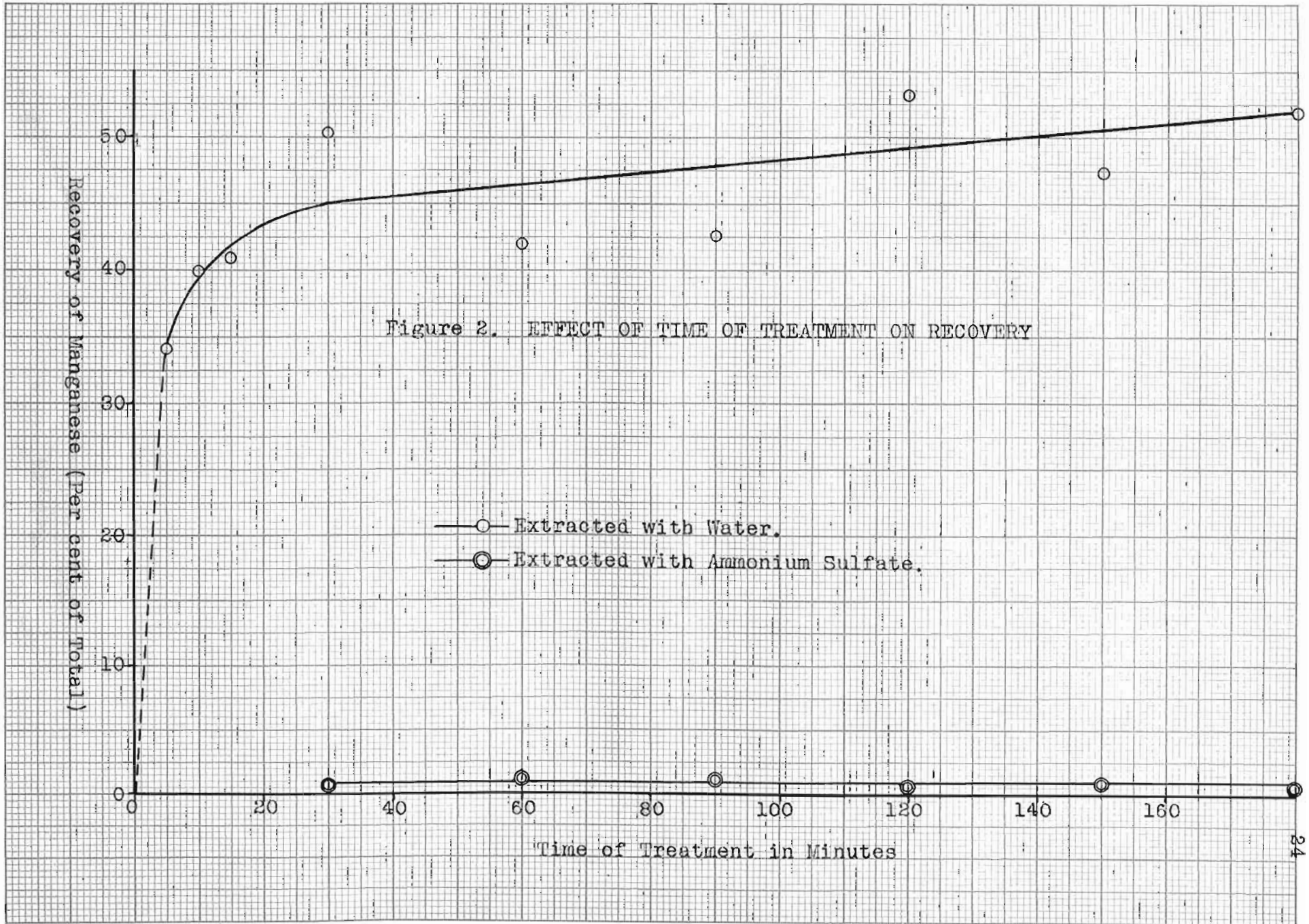
From Figure 2 it appears that the reaction was nearly
complete in 15 minutes after which the increase in amount
of water-soluble manganese was small. The small increase
after 15 minutes was probably caused by the slow diffusion
of the gas into the ore particles. A time of 45 minutes was
selected for all the remaining experiments. This would
insure a fairly complete reaction because it would tend
to offset variations in the treatment that could not be con-
trolled.

A comparison of the extractions of additional manganese
with sulfuric acid and ammonium sulfate (Tables III & IV)
indicated that only a small amount of manganous oxide was
present and extracted with ammonium sulfate. A greater
amount was present as the sulfite as indicated by the ex-
traction with acid.

The reduction of a portion of the manganese dioxide by
sulfur dioxide according to the equation:

$$MnO_2 + SO_2 \longrightarrow MnO + SO_3$$

is a possible explanation of the presence of manganous oxide.
The sulfite was probably produced by a direct combination of
the monoxide and sulfur dioxide, represented by the equation:

$$MnO + SO_2 \longrightarrow MnSO_3$$

COMPARISON OF TREATMENTS USING SULFUR DIOXIDE
WITH SULFUR DIOXIDE-AIR MIXTURE

Earlier in this study an increase in amount of extraction was noticed when air was mixed with sulfur dioxide. In this group of experiments samples of each of the five Arkansas wad ores were treated with sulfur dioxide and a sulfur dioxide-air mixture at 650° C for 45 minutes in the Burrell furnace. The cooled samples were leached with water and the soluble manganese determined. Qualitative tests for iron and phosphorus were negative.

Table V shows that in each case the highest percentage extraction was obtained when a mixture of air and sulfur dioxide was used. These results indicated the possibility of using dilute gases. This was investigated later in this study.

Table **V**. Comparison of Treatments.

(Temperature 650°C.; Time — 45 minutes)

Exp. No.	Ore	Extraction from SO_2 treatment			Extraction from Air-SO_2 treatment		
		Per cent of total Mn	Fe	P	Per cent of total Mn	Fe	P
1 & 2	Ark A	43.77	—	—	59.75	—	—
3 & 4	Ark B	63.83	—	—	77.87	—	—
5 & 6	Ark C	49.25	—	—	55.14	—	—
7 & 8	Ark D	27.06	—	—	40.60	—	—
9 & 10	Ark E	31.98	—	—	42.63	—	—

CALIBRATION OF FLOW-RATE APPARATUS

A cylinder of liquid sulfur dioxide was obtained to make it possible to control the rate at which the gas was used. The compressed air produced at the power plant was used. Mixing of the gases was attained by passing them into a Woulff bottle, then through a tube loosely packed with glass wool and then to the furnace.

A capillary tube was placed in each line as an orifice. The back pressure was measured in each line by the use of a water manometer. Each capillary tube was calibrated by passing air through at different rates and measuring the time taken to displace a measured volume of water. The rate, in liters of gas at room temperature per minute, was plotted against the pressure, in inches of water, to obtain the curves in Figure 3. The rate of flow was very small and, therefore, neither circuit caused a back pressure in the other.

Figure 3. MANOMETER CALIBRATION CURVES
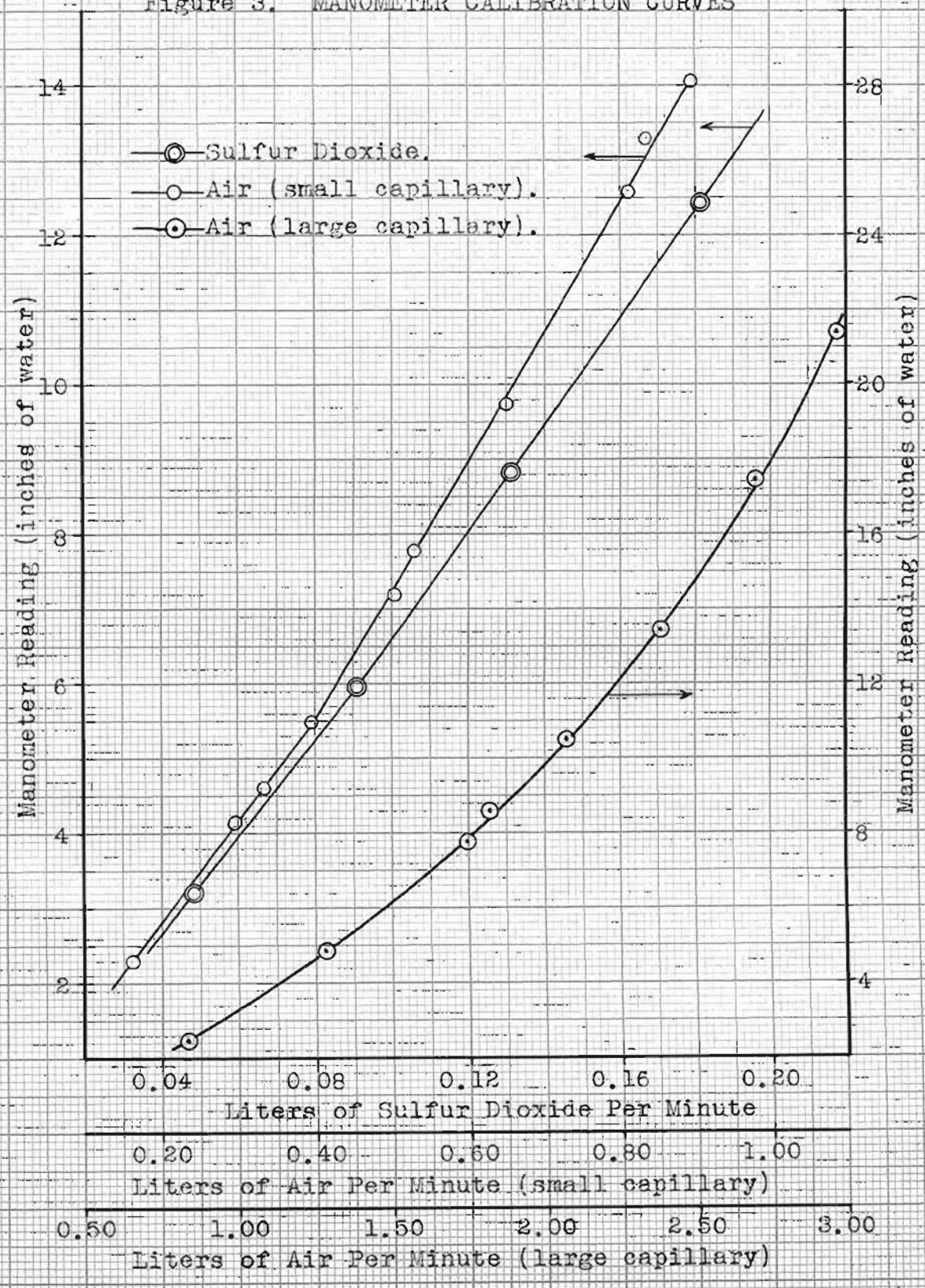
THE EFFECT OF SULFUR DIOXIDE CONCENTRATION

All conditions of these experiments were maintained constant except the concentration of sulfur dioxide. This was varied by changing the rate of flow of air but keeping the rate of sulfur dioxide constant at 0.154 liters per minute. This was done to give a more logical basis for comparison of the results of the different experiments. Samples of each of the five Arkansas wad ores were used.

The samples were placed in the furnace at 650° C. and treated with the different gas mixtures for 45 minutes each. The cooled samples were extracted with water and the amount of soluble manganese determined. No iron or phosphorus was present in the leachings. Tables VI to X and Figure 4 present the results of these experiments.

Table VI. Effect of SO_2 Concentration on Arkansas C Ore.
(S0$_2$ rate - 0.154 liter per minute)
(Temperature - 650° C; Time - 45 minutes)

Exp. No.	SO$_2$ conc. (per cent by vol.)	Per cent of total Mn re-covered	Fe	P
1	4.8	42.44	-	-
2	7.6	44.84	-	-
3	10.5	44.91	-	-
4	13.7	47.53	-	-
5	16.6	48.51	-	-
6	20.3	49.54	-	-
7	27.6	51.01	-	-
8	39.9	51.74	-	-
9	64.4	51.36	-	-
10	100.0	49.82	-	-

Table VII. Effect of SO_2 Concentration on Arkansas A Ore.
(SO$_2$ rate – 0.154 liter per minute)
(Temperature – 650° C; Time – 45 minutes)

Exp. No.	SO$_2$ conc. (per cent by vol.)	per cent of total Mn re-covered	Fe	P
11	5	38.47	–	–
12	10	42.71	–	–
13	15	46.39	–	–
14	20	48.91	–	–
15	30	52.12	–	–
16	60	54.32	–	–
17	100	46.80	–	–

Table VIII. Effect of SO2 Concentration on Arkansas B Ore.
(SO$_2$ rate - 0.154 liter per minute)
(Temperature - 650° C; Time - 45 minutes)

Exp. No.	SO$_2$ conc. (Per cent by vol.)	Per cent of total Mn re- covered	Fe	P
18	5	50.16	-	-
19	10	51.23	-	-
20	15	55.53	-	-
21	20	59.34	-	-
22	30	61.16	-	-
23	40	63.48	-	-
24	50	64.98	-	-

Table IX.   Effect of SO_2 Concentration on Arkansas D Ore
(SO$_2$ rate - 0.154 liter per minute)
(Temperature-650°C; Time-45 minutes)

Exp. No.	SO$_2$ conc) (per cent by vol.)	Per cent of total Mn re-covered	Fe	P
25	5	23.90	-	-
26	10	26.80	-	-
27	15	29.32	-	-
28	20	29.53	-	-
29	30	32.09	-	-
30	40	33.20	-	-
31	50	33.24	-	-

Table X. Effect of SO_2 Concentration on Arkansas E Ore.
(SO_2 rate - 0.154 liter per minute)
(Temperature - 650° C; Time - 45 minutes)

Exp. No.	SO_2 conc. (per cent by vol.)	Per cent of total Mn recovered	Fe	P
32	5	26.25	-	-
33	10	28.30	-	-
34	15	32.67	-	-
35	20	33.10	-	-
36	30	33.99	-	-
37	40	35.68	-	-
38	50	35.60	-	-

Figure 4. EFFECT OF SULFUR DIOXIDE CONCENTRATION ON RECOVERY

Recovery of Manganese (Per cent of Total)

Sulfur Dioxide Concentration (Per cent by Volume)

--○-- Arkansas A Ore.
--◍-- Arkansas B Ore.
--◎-- Arkansas C Ore.
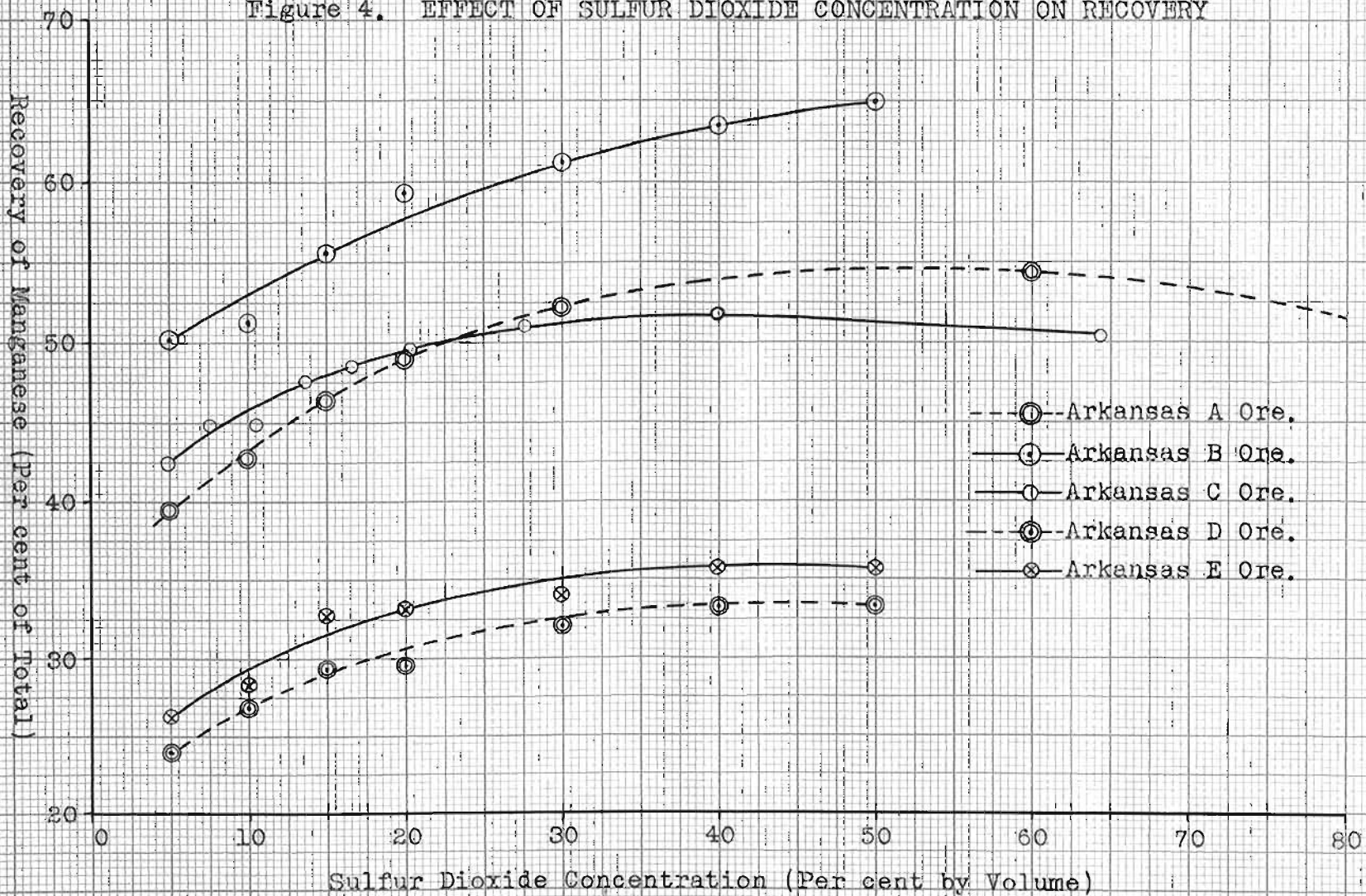--◉-- Arkansas D Ore.
--⊗-- Arkansas E Ore.

Figure 4 indicates that there was very little increase in the amount of soluble manganese salts when sulfur dioxide concentrations above 30 per cent were used. After the concentration exceeded 50 per cent there seemed to be a slight decrease in the amount of manganese extracted. These results show that concentrations as low as 5 per cent of sulfur dioxide gave fair extractions. This is significant because if such a method for sulfating manganese ores were employed it would be possible to utilize many of the waste smelter gases containing sulfur dioxide in such low concentrations.

It was noted that the maximum recovery in these experiments was lower than in previous ones in which the sulfur dioxide was produced by the action of sulfuric acid on sodium bisulfite. On examination of the equation:

$$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$$

it was noted that water was produced and the heat of reaction was probably sufficient to vaporize a portion of it. The action of the vaporized water probably caused this increase in percentage extraction.

EFFECT OF MOISTURE ON EXTRACTION

In this series of experiments the effect of different amounts of moisture on the percentage extraction was determined. The amount of moisture was controlled by adding water from a burette through a capillary tube to a heated portion of the furnace tube. This caused the water to vaporize and mix with the entering air and sulfur dioxide.

Samples of the Arkansas C ore and one of the Texas concentrates were treated with this mixture of moist gases at 650° C for 45 minutes with constant rates of sulfur dioxide and air. The cooled samples were leached with water and the soluble manganese determined. Qualitative tests were made for phosphorus and iron. The percentage composition of the gases was calculated, assuming that all the water added was vaporized and passed through the furnace.

The results of Table XI indicate that maximum extraction was obtained with gases containing from 25 to 30 per cent (by volume) moisture. Traces of iron were found in some of the leachings but no phosphorus was found in any. A considerably greater extraction was obtained with moist than with dry gases.

Table XI. Effect of Moisture on Manganese Recovery.
(SO$_2$ rate – 0.077 liter per minute)
(Temperature – 650° C; Time – 45 minutes)

Exp. No.	Ore	Gas composition (per cent by vol)			Per cent of total Mn re-covered	Fe	P
		Air	SO$_2$	H$_2$O			
1	Ark C	70	30	0	51.58	–	–
2	"	71.5	25.2	3.3	59.57	+	–
3	"	63.0	22.2	14.8	61.06	+	–
4	"	58.3	20.5	21.2	62.79	+	–
5	"	55.0	19.3	25.7	64.39	+	–
6	"	50.8	17.9	31.3	64.46	+	–
7	"	50.4	17.8	31.8	64.53	+	–
8	"	45.7	16.1	38.2	64.23	+	–
9	Texas A	70	30	0	14.12	–	–
10	"	71.5	25.2	3.3	20.67	–	–
11	"	59.1	20.8	20.1	29.07	–	–
12	"	52.8	18.6	28.6	30.21	–	–
13	"	44.5	15.7	39.8	31.00	–	–

RELATION BETWEEN AMOUNT OF MANGANESE AS THE
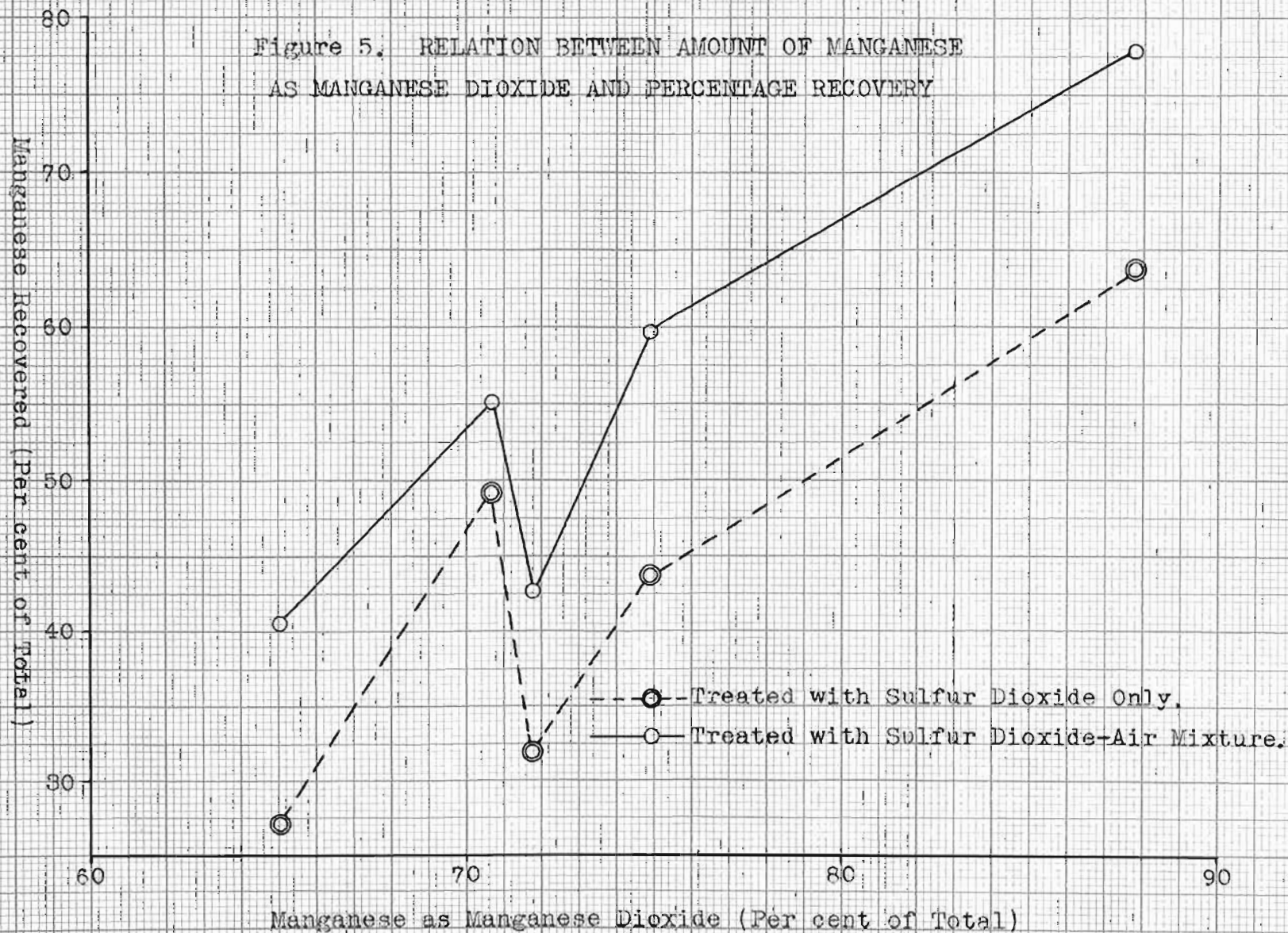## DIOXIDE AND PERCENTAGE EXTRACTION

It was thought that the amount of extraction was directly effected by the percentage of the manganese in the ore as manganese dioxide. The available oxygen was determined and considered to be a measure of the manganese dioxide present.

One-half gram samples of the ores were placed in 250 ml Erlenmeyer flasks and 25 ml of approximately 0.3 N ferrous sulfate solution and 10 ml of 50 per cent sulfuric acid were added. The samples were digested at slow boiling for one hour. To prevent excessive evaporation the flasks were covered with watch glasses. The samples were cooled, the residue filtered off, washed and the excess ferrous sulfate in the filtrate titrated with a standard potassium permanganate solution. Blanks were treated the same as the samples to determine the permanganate equivalent of the ferrous sulfate. The amount of manganese dioxide in each sample, calculated from the amount of available oxygen, is given in Table XII.

Table XII. Manganese Dioxide by Available Oxygen.

Ore	Avail-able O_2 (g./g.)	MnO_2 (g./g.)	Mn as MnO_2 (g./g.)	Mn in ore (g./g.)	Per cent of total Mn as MnO_2
Ark A	0.05223	0.2838	0.1793	0.2395	74.87
Ark B	0.07975	0.0433	0.2738	0.3118	87.81
Ark C	0.06248	0.3395	0.2144	0.3034	70.68
Ark D	0.06068	0.3296	0.2083	0.3204	65.02
Ark E	0.05676	0.3084	0.1949	0.2715	71.79
Texas A	0.07302	0.3967	0.2508	0.4053	61.88
Texas B	0.06248	0.3394	0.2146	0.2727	78.68
Okla. B	0.09818	0.5333	0.3372	0.4760	70.84
" A	0.09925	0.5392	0.3409	0.3950	86.30
Ga A	0.1125	0.6114	0.3866	0.4171	92.67
Ga B	0.08304	0.4512	0.2852	0.3173	89.58
Ga C	0.04338	0.2357	0.1490	o.1605	92.83
Minn A	0.02258	0.1227	0.07757	0.1563	49.63
Va A	0.07419	0.4031	0.2548	0.2976	85.63

Figure 5. RELATION BETWEEN AMOUNT OF MANGANESE
AS MANGANESE DIOXIDE AND PERCENTAGE RECOVERY

Manganese Recovered (Per cent of Total)

Manganese as Manganese Dioxide (Per cent of Total)

- -O- Treated with Sulfur Dioxide Only.
- O- Treated with Sulfur Dioxide-Air Mixture.

The relation between the amount of manganese dioxide and percentage extraction (Figure 5) was obtained by plotting the percentage extraction data of Table V (p. 27) against the percentage of manganese in the ore as manganese dioxide. Only the data from the Arkansas wad ores was used because these ores were similar in composition and type.

These curves indicate a fairly direct relation between the manganese dioxide and the amount of extraction. The irregularity caused by Arkansas D ore was probably due to greater density compared to the other samples, causing less surface area exposed per unit of weight. If there was a relation between the amount of extraction and percentage of manganese as manganese dioxide, the reaction involved could probably be represented by the equation:

$$MnO_2 + SO_2 \longrightarrow MnSO_4$$

SULFATING DIFFERENT TYPES OF ORES WITH

DILUTE SULFUR DIOXIDE GAS

A number of ores and concentrates from the various sections of the United States were treated for 45 minutes in the furnace at 650° C with a mixture of air and sulfur dioxide (30 percent by volume of sulfur dioxide). The rate of sulfur dioxide was maintained at 0.154 liters per minute in all the experiments. The cooled samples were leached with water and the solutions analyzed for manganese. Qualitative tests were made for iron and phosphorus.

The percentage extraction of the total manganese from the various samples varied from about 7 to 70 per cent. Taken as a group the concentrates gave a lower extraction than the low-grade ores. This was probably caused by greater density. It was noted that the samples giving the lowest extractions of manganese usually exhibited the greater density.

Those samples having high iron content showed traces of iron in the leachings but none showed the presence of phosphorus. The results of these experiments are presented in Tables XIII and XIV.

Table XIII.   Treatment of Different Types of Ores.
(SO_2 rate - 0.154 liter per minute; SO_2 concentration -
30 per cent by volume; Temperature-650°C;   Time - 45 minutes)

Exp. No.	Ore	Per cent in the ore	Per cent of total Mn recovered	Fe	P
1	N.C.	43.6	38.76	-	-
2	Colo.	15.4	7.14	-	-
3	Ga.	2.4	71.16	+	-
4	Wis.	7.9	27.17	+	-
5	N.D.	3.7	61.05	-	-
6	Minn.	14.3	40.05	-	-
7	W.Va.	3.4	50.92	+	-
8	N.M.	15.9	31.35	-	-
9	Tex.	31.4	10.16	-	-
10	Ark.	19.9	54.52	-	-
11	Va.	22.8	72.24	+	-
12	Mo.	19.6	24.23	-	-

Table XIV. Treatment of Several Manganese Concentrates.
(SO_2 rate - 0.154 liter per minute; SO_2 concentration - 30 per cent by volume; Temperature-650° C; Time - 45 minutes)

Exp. No.	Concentrate	Per cent Mn in sample	Per cent of total Mn recovered	Fe	P
13	Texas A	40.53	14.12	-	-
14	Texas B	27.27	15.55	-	-
15	Okla. B	47.6	21.70	-	-
16	Okla. A	39.5	33.17	-	-
17	Ga A	41.71	43.67	-	-
18	Ga B	31.73	30.39	-	-
19	Ga C	16.05	46.40	+	-
20	Minn A	15.63	45.74	+	-
21	Va A	29.76	24.85	-	-

EFFICIENCY TESTS

A series of experiments was performed to determine the efficiency of extraction in producing solutions having high manganese content. The samples were treated with a sulfur dioxide-air mixture at 650° C for 45 minutes. Each sample was leached with a small measured volume of water and the residue washed several times with a few ml of water in each washing. The amount of manganese in this concentrated solution was determined. The residue was then leached with a large volume of water to remove the remainder of the soluble manganese and its amount determined. From these results the efficiency of extraction was calculated by using the following equation:

$$\text{Efficiency} = \frac{\text{Mn in first leach}}{\text{Total water-soluble Mn}} \times 100$$

These results indicated that it was feasible to produce solutions containing 5 per cent manganese without losing very much of the soluble manganese in the residues. Concentrations of manganese as were obtained in these experiments are high enough to make these solutions satisfactory for the production of electrolytic manganese. The manganese could also be precipitated by one of several different methods.

The results of these experiments are presented in Table XV.

Table XV. Efficiency of Extraction.

Exp. No.	Ore	cc. H_2O in first leach	Per cent to-tal Mn in first leach	Amount of H_2O-sol-uble Mn (Per cent of total	Mn conc. in first leach(Per cent bas-ed on wt. water)	Effi-ciency
1	Ark C	100	48.18	48.99	1.17	98.4
2	"	40	54.19	55.09	3.29	98.5
3	"	25	49.55	55.06	4.82	91.7
4	"	30	62.33	63.64	5.20	98.0

SUMMARY

1.   The optimum temperature for sulfating oxidized manganese ores was found to be 650° C.

2.   The reaction between the sulfur dioxide and the minus 100-mesh ores was nearly complete in 15 minutes. The slight increase after 15 minutes was probably due to the slow diffusion of the gases into the ore particles.

3.   The concentration of sulfur dioxide giving maximum recovery was found to be approximately 30 per cent by volume. Slightly smaller amounts of soluble salts were produced with the lower concentrations of sulfur dioxide.

4.   Moist gases produced greater quantities of soluble salts than did dry gases. For the samples examined it was found that gases containing from 25 to 30 percent moisture by volume gave maximum yields.

5.   The treatment of the various types of ores gave recoveries of from 7 to 80 per cent of the manganese present in the ore.

6.   Phosphorus was eliminated in each experiment except in those in which acid was used in the leaching.

7.   A few solutions gave positive tests for iron but the solutions containing the larger quantities of iron were analyzed and found to contain less than 0.6 per cent based on the weight of the original ore sample.

8.   A solution containing as much as 5.2 per cent of manganese free of iron and phosphorus was obtained.

9. The manganous sulfate solution may be used for the recovery of manganese by many available methods.

10. The manganous sulfate solution contained a higher concentration of manganous ion than is required in the electrolytic reduction of manganous sulfate.

11. This method seems particularly adaptable to Arkansas wad ores containing from 23 to 32 per cent manganese.

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