

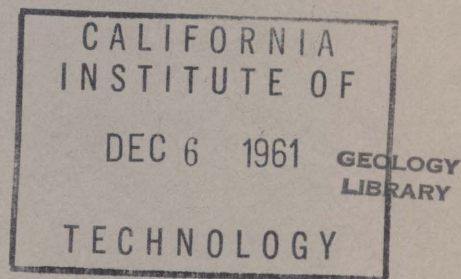
149

RI bureau of mines  
report of investigations 5887

Geol.

## EVALUATING CUYUNA MANGANESE RESOURCES BY SULFATIZING

By Charles Prasky, R. L. Marovelli, and F. E. Joyce, Jr.



metadc38692

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

1961





# EVALUATING CUYUNA MANGANESE RESOURCES BY SULFATIZING

By Charles Prasky, R. L. Marovelli, and F. E. Joyce, Jr.

\* \* \* \* \* report of investigations 5887



UNITED STATES DEPARTMENT OF THE INTERIOR  
Stewart L. Udall, Secretary

BUREAU OF MINES  
Marling J. Ankeny, Director

This publication has been cataloged as follows:

**Prasky, Charles**

Evaluating Cuyuna manganese resources by sulfatizing, by Charles Prasky, R. L. Marovelli, and F. E. Joyce, Jr. [Washington] U. S. Dept. of the Interior, Bureau of Mines [1961]

ii, 27 p. illus., maps. 27 cm. (U. S. Bureau of Mines. Report of investigations, 5887)

1. Manganese. I. Title. II. Cuyuna manganese resources. (Series)

TN23.U7 no. 5887 622.06173

U. S. Dept. of the Interior Library

## CONTENTS

	<u>Page</u>
Introduction and summary.....	1
Acknowledgments.....	3
Estimate of potential ore resources.....	3
Preparation and chemical analysis of samples.....	9
Bench-scale sulfatizing procedure.....	16
Results and discussion.....	20
Conclusions.....	27

## ILLUSTRATIONS

### Fig.

1. Plan map showing general location of the main iron formation, North range, Cuyuna district, Crow Wing County, Minn.....	4
2. Plan map showing general geology and location of sample group (A).....	5
3. Plan map showing general geology and location of sample groups (B), (C), (D), (E), (F), (G), and (H).....	6
4. Plan map showing general geology and location of sample group (I).....	7
5. Schematic view of bench-scale sulfatizing apparatus.....	17
6. Cross section of preheater and converter assembly..	18
7. Detail of rotary-drum furnace.....	19

## TABLES

	<u>Page</u>
1. Potential ore estimates.....	8
2. Summary of resources and calculated grades.....	8
3. Pertinent data on Bureau of Mines bulk samples.....	9
4. Chemical analyses of unoxidized manganiferous carbonate slate samples.....	10
5. Chemical analyses of oxidized manganiferous samples.	11
6. Minerals or mineral groups present in unoxidized carbonate slate samples.....	12
7. Minerals or mineral groups present in oxidized samples.....	13
8. Chemical analyses and weight composition of the coarse ore and pellet mixture, representing the second representative part of the unoxidized carbonate slate samples.....	14
9. Chemical analyses and weight composition of the coarse ore and pellet mixture, representing the second representative part of the oxidized samples	15
10. Effect of gas composition on sulfatization of standard carbonate slate pellets at 700° C., 7-hour roast.....	19
11. Effect of temperature on sulfatization of standard carbonate slate pellets, 7-hour roast.....	20
12. Effect of time on sulfatization of standard car- bonate slate pellets at 700° C., 35.7 percent SO <sub>2</sub> gas.....	20
13. Sulfatization results for pellets prepared from the first representative part of the unoxidized carbonate slate samples.....	21
14. Sulfatization results for pellets prepared from the first representative part of the oxidized samples	22
15. Estimate of manganese recoverable by sulfatization from potential resources.....	22
16. Sulfatization results for the coarse ore and pellet mixtures prepared from the second representative part of the unoxidized carbonate slate samples...	24
17. Sulfatization results for the coarse ore and pellet mixtures prepared from the second representative part of the oxidized samples.....	26

# EVALUATING CUYUNA MANGANESE RESOURCES BY SULFATIZING<sup>1</sup>

by

Charles Prasky,<sup>2</sup> R. L. Marovelli,<sup>3</sup> and F. E. Joyce, Jr.<sup>4</sup>

---

## INTRODUCTION AND SUMMARY

The objective of this investigation by the Bureau of Mines was to determine the response to sulfatization of diverse low-grade manganiferous materials in the iron formation of the Cuyuna district. In line with this objective a bench-scale sulfatizing procedure was developed that was less expensive and more rapid than pilot-plant methods. Samples from the central and southwestern parts of the North range were tested. Results of evaluating a total of 46 pelletized samples, originating in areas with an estimated potential resource of 94 million long tons with a manganese content of 7 percent, indicates that approximately 87 percent of the manganese may be recovered as a synthetic manganese ore. This is equivalent to more than 12 million long tons of a metallurgical-grade ore, containing 46 percent manganese. It is anticipated that a premium product, containing over 50 percent manganese, may be obtained by sulfatizing procedures.

This report is part of a continuing investigation<sup>5 6</sup> of Cuyuna iron range manganese deposits in Crow Wing County, Minn. Lewis and coworkers describe the manganiferous iron formation in the bedrock of the Cuyuna district and include a description of a high-temperature differential sulfatizing process for recovering a ferrograde manganese product. The low-grade manganiferous

---

<sup>1</sup>Work on manuscript completed August 1960.

<sup>2</sup>Supervising extractive metallurgist, Minneapolis Metallurgy Research Center, Bureau of Mines, Minneapolis, Minn.

<sup>3</sup>Mining methods research engineer, Minneapolis Mining Research Center, Bureau of Mines, Minneapolis, Minn.

<sup>4</sup>Extractive metallurgist, Minneapolis Metallurgy Research Center, Bureau of Mines, Minneapolis, Minn.

<sup>5</sup>Lewis, W. E., Heising, L. F., Pennington, J. W., and Prasky, Charles, Investigation of the Cuyuna Iron-Range Manganese Deposits, Crow Wing County, Minn. Progress Report 1: Bureau of Mines Rept. of Investigations 5400, 1958, 49 pp.

<sup>6</sup>Heising, L. F., Marovelli, R. L., Wasson, P. A., Cooke, S. R. B., and Pennington, J. W. Core-Drill Sampling of Cuyuna-Range Manganiferous Iron Formations, Crow Wing County, Minn. Bureau of Mines Rept. of Investigations 5450, 1959, 34 pp.

materials are not merchantable and vary widely in chemical and physical character. Relatively few of these samples have been evaluated by the sulfatizing process on a pilot-plant scale.

The sulfatizing process consists essentially of three steps: (1) Roasting crushed rock in an atmosphere of sulfur dioxide gas and air by a continuous-countercurrent method, (2) water-leaching of manganese sulfate from the sulfatized product, and (3) recovery of a ferrograde  $Mn_3O_4$  product from the leach solution by evaporation of water and thermal decomposition of the resulting manganese sulfate crystals. Details and advantages of the process have been published.<sup>7</sup> This report is concerned with only the first step.

The Cuyuna iron-ore district extends northeast about 68 miles through parts of Morrison, Crow Wing, and Aitkin Counties, Minn. Most of the mining activity has been on the North range in Crow Wing County in an area about 10 miles long and 3 miles wide. The manganiferous bulk samples obtained for this investigation were taken from lean-ore stockpiles or open-pit exposures that were accessible in the central and southwestern parts of the North range.

With few exceptions, all production of iron or manganiferous iron ores has come from one stratigraphic unit described as the main iron formation.<sup>8</sup> A thin- and a thick-bedded facies are general rock types that may be differentiated within this unit.

Potential ore resources summarized previously, with a cutoff at 1 percent manganese, indicated that these manganiferous deposits in central Minnesota collectively totaled over 433 million long tons; the manganese content ranged from a trace to 16 percent but averaged 6 percent.<sup>9</sup> This estimate included a large tonnage of outlying lean manganiferous material other than the main iron formation.

The Federal Bureau of Mines revised estimate for the North range in 1959 included only the main iron formation. This estimate indicated approximately 243 million long tons of potential manganiferous ore, containing over 2 percent manganese and averaging 8 percent manganese and 32 percent iron. In the central and southwestern parts of the North range, there are approximately 140 million long tons (averaging 8 percent manganese and 33 percent iron). This tonnage is subdivided into 94 million long tons (averaging 7 percent manganese and 34 percent iron), for which representative samples were obtained, and 46 million long tons, for which no representative samples were available. Old mill tailings relating to the latter tonnage were available for the sulfatizing investigation.

---

<sup>7</sup>Work cited in footnote 5, pp. 37-49.

<sup>8</sup>Schmidt, R. G., and Dutton, C. E. Geology of the South-Central Part of the North Range, Cuyuna District, Minnesota: U.S. Geol. Survey, Mineral Investigations Field Studies, Map MF 99, Sheet 3, 1957.

<sup>9</sup>Work cited in footnote 5, pp. 25-28.



## ACKNOWLEDGMENTS

The Minnesota Department of Taxation permitted an examination of their exploration and mining records and the following iron mining companies permitted sampling of their nonmerchantable materials: Robert M. Adams Co., The M. A. Hanna Co., Pickands-Mather & Co., and Pittsburgh Pacific Co.

## ESTIMATE OF POTENTIAL ORE RESOURCES

Estimates were based on exploration and development data reported periodically by the various mining companies to the Minnesota Department of Taxation. The iron content of the Cuyuna materials was usually given, but the manganese content was sometimes omitted in the reports.

Only lean noncommercial manganiferous iron formation that contained 2 percent or more manganese was included in the recent estimate. Material with a marketable iron or combined manganese-iron content is normally included in the Cuyuna iron reserves and therefore was excluded from the estimate of potential manganese resources. The selection of 2 percent manganese as a lower limit was arbitrary but it did follow a classification<sup>10</sup> whereby iron ores containing this quantity of manganese are termed manganiferous.

Potential ores were classified as either measured-indicated or inferred, and the probable mining method was indicated as either open-pit or underground. They were also classified geologically as primary thin- or thick-bedded iron formation. This classification was based on the Cuyuna bedrock geology as interpreted and mapped by Schmidt and Dutton.<sup>11</sup> The main iron formation of the North range is shown in figure 1.

From analyses of the Cuyuna unoxidized iron formation, Schmidt<sup>12</sup> indicates an original iron content that ranged from 18 to 35 percent and a manganese content that ranged from less than 1 to 11 percent. By a process of oxidation and enrichment commercial iron ores or manganiferous iron ores have formed.

In the following discussion of material types, ore may refer to iron content or to combined iron-manganese content. Manganese content may be insignificant in any of the material types.

1. Unoxidized thin-bedded iron formation that, because of widespread carbonate occurrence, is commonly called carbonate slate. Minerals include quartz, iron silicates (minnesotaite and stilpnomelane), iron and manganese carbonates (isomorphous series of calcites rich in iron, manganese, and magnesium), magnetite, and small amounts of pyrite.

---

<sup>10</sup>American Iron Ore Association (Cleveland, Ohio) Iron Ore: 1958, p. 91.

<sup>11</sup>Work cited in footnote 8, p. 34.

<sup>12</sup>Schmidt, R. G., Bedrock Geology of the Southwestern Part of the North Range, Cuyuna District, Minnesota: Geol. Survey, Mineral Investigations Field Studies, Map MF 181, Sheet 6, 1958.

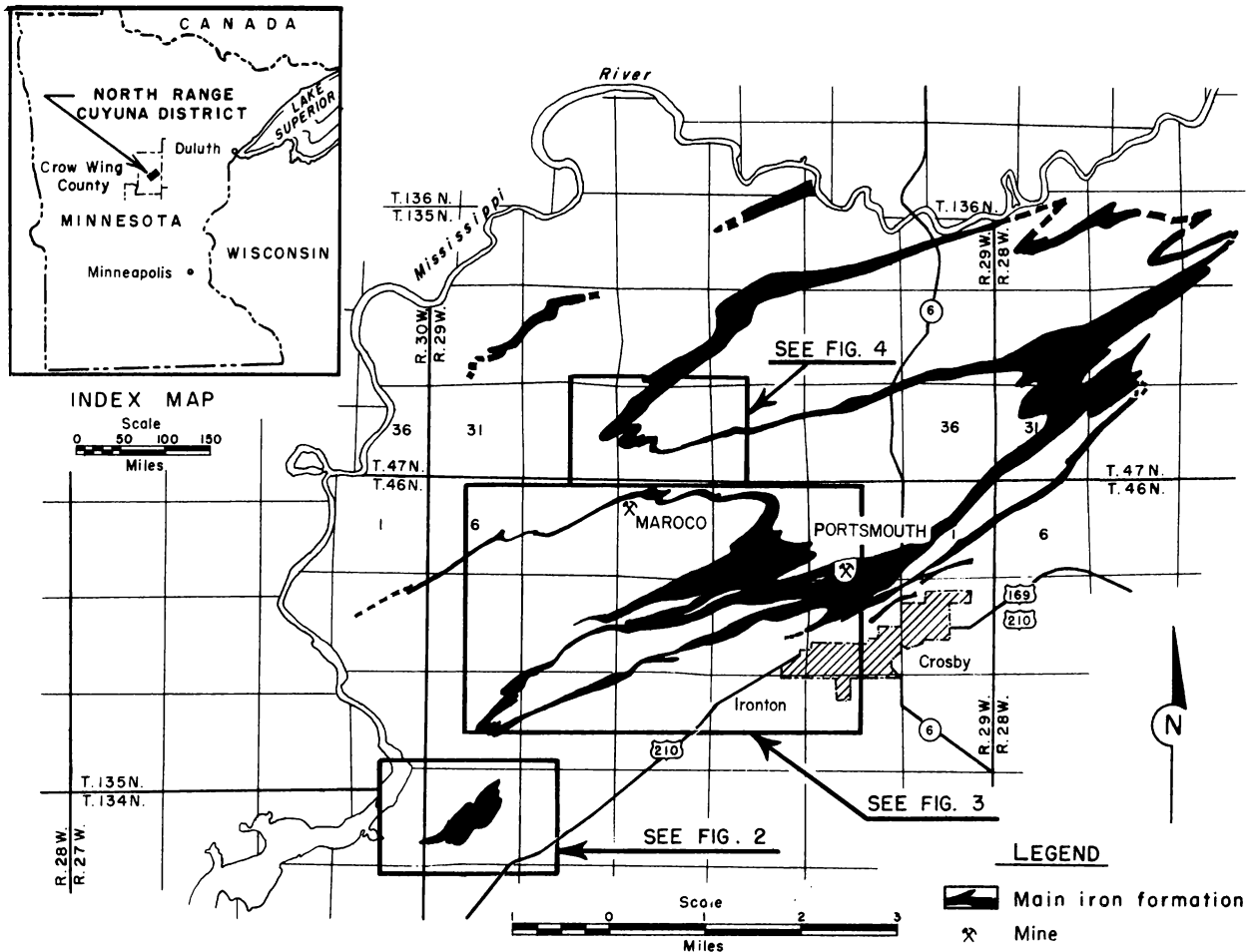


FIGURE 1. - Plan Map Showing General Location of the Main Iron Formation, North Range, Cuyuna District, Crow Wing County, Minn. Geology after U. S. Geological Survey.

2. Oxidized derivatives of the foregoing material. When enriched to ore grade, this material is commonly called brown ore. The principal identifiable manganese oxides are manganese limonite, manganite, and psilomelane.

3. Oxidized thick-bedded iron formation, which is composed largely of thick-bedded cherts. Material enriched to ore grade is called black ore. Minerals include quartz and the iron and manganese oxides; magnetite and minnesotaite occur in small amounts.

There are no known occurrences of unoxidized thick-bedded iron formation. Schmidt stated that the general absence of silicates and carbonates in this facies suggests that the original minerals were oxides or that the cherty rocks were more readily fractured and therefore more susceptible to oxidation.<sup>13</sup> In a study of thin-bedded samples, Blake showed that manganese-bearing iron

<sup>13</sup>Work cited in footnote 8.

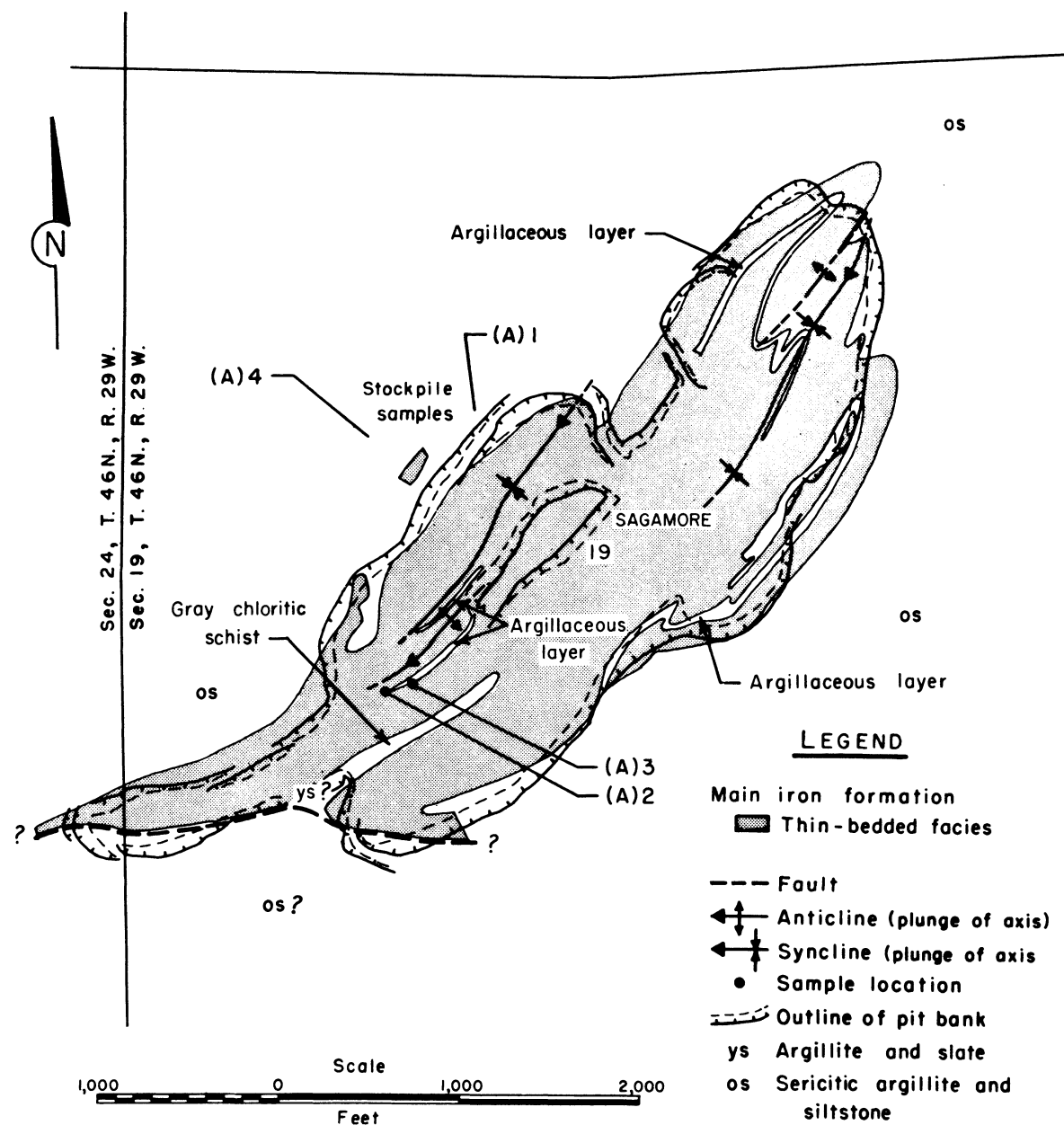


FIGURE 2. - Plan Map Showing General Geology and Location of Sample Group (A).  
Geology after U. S. Geological Survey.

carbonates may be the primary source of manganese in ores derived from the thin-bedded facies.<sup>14</sup>

A total of approximately 140 million long tons of material, averaging 8 percent manganese and 33 percent iron, was estimated for the central and

<sup>14</sup>Blake, R. L. A Study of the Iron Silicate Minerals With Special Emphasis on the Iron-Formation in the Cuyuna District, Minnesota: Pres. at Inst. of Lake Superior Geology, Apr. 21-22, 1958.

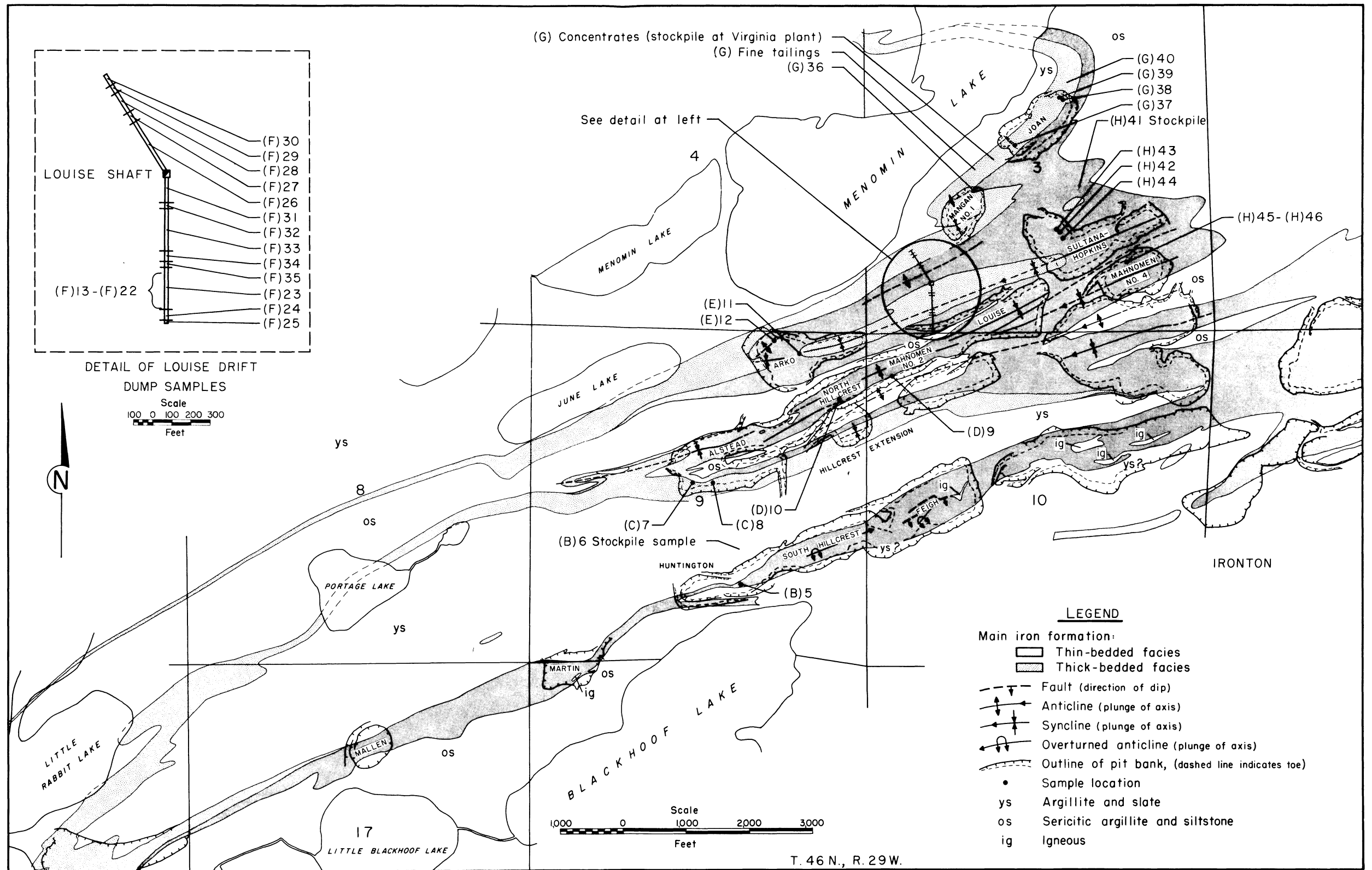


FIGURE 3. - Plan Map Showing General Geology and Location of Sample Groups (B), (C), (D), (E), (F), (G), and (H). Geology after U. S. Geological Survey.

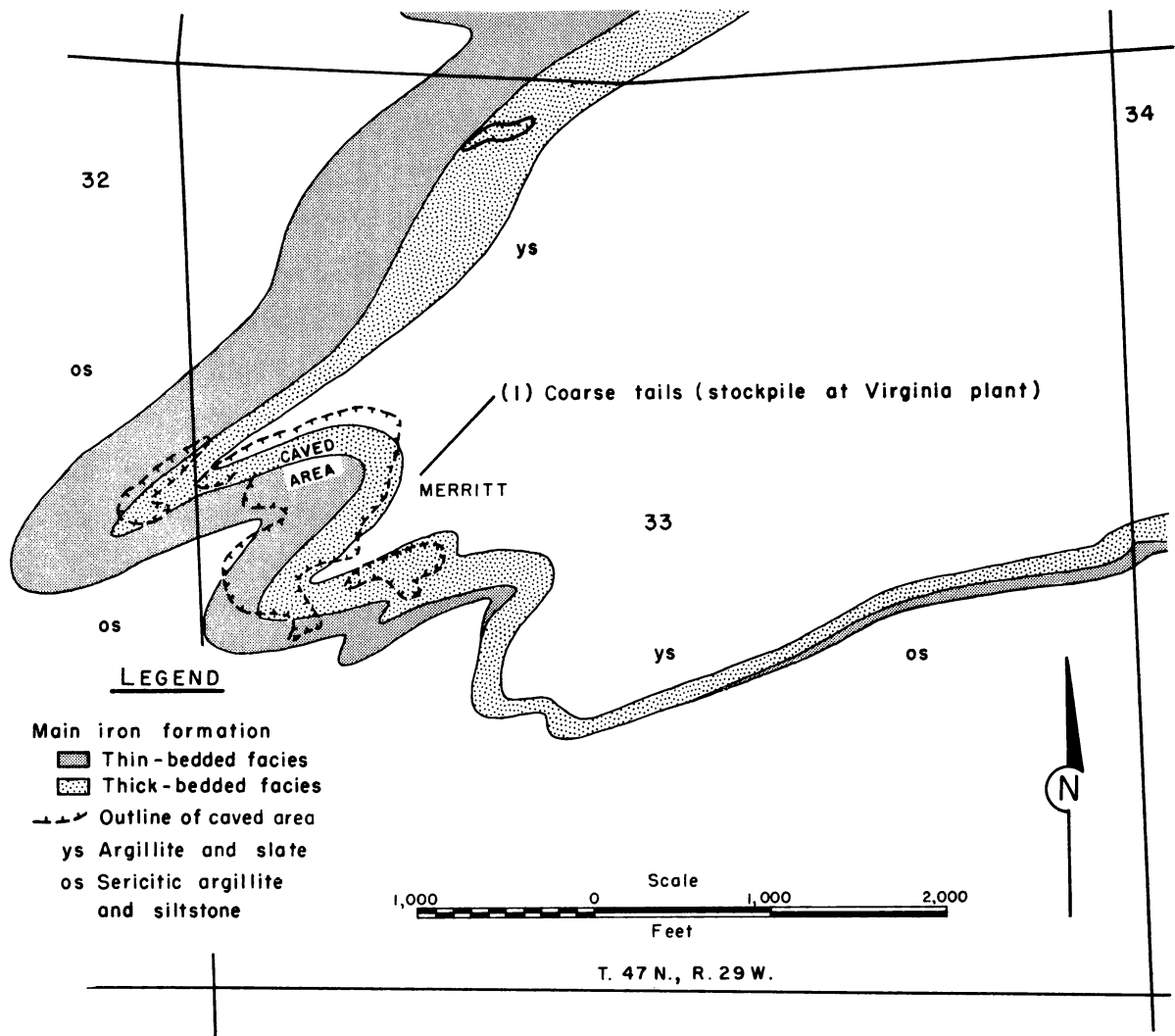


FIGURE 4. - Plan Map Showing General Geology and Location of Sample Group (I).  
Geology after U. S. Geological Survey.

southwestern parts of the North range. These tonnages are present in nine individual potential ore bodies, ranging in size from 3 to 46 million long tons and containing from 6 to 10 percent manganese. The potential ore bodies were outlined on the basis of their location along some structural feature that suggested consideration as a mining unit. Their approximate locations, designated as A through I, are shown in figures 2, 3, and 4.

Tonnages were estimated by the end-area method. A tonnage factor of 15 cubic feet per long ton was used, except for the Sagamore deposit when a factor of 12 was used.

Potential ore resources are shown in table 1. A summary of the resources and grade of ore was prepared from exploration and development data reported to the Minnesota Department of Taxation (table 2). The estimates were classed as measured-indicated and inferred, according to Bureau of Mines and Geological Survey usage.

TABLE 1. - Potential ore estimates

Area	Lithologic type	Tonnage (million long tons)			
		Probable open-pit		Probable underground	
		Measured-indicated	Inferred	Measured-indicated	Inferred
A.....	Thin-bedded.....	5.7	7.0	-	-
B.....	.....do.....	1.5	4.7	4.5	2.6
	Thick bedded.....	-	-	1.1	1.0
C.....	Undifferentiated <sup>1</sup> .....	1.4	-	.9	2.2
D.....	Thin-bedded.....	3.4	2.4	-	.9
E.....	.....do.....	1.7	2.9	-	-
	Thick-bedded.....	.3	.3	-	-
	Undifferentiated.....	-	-	.5	5.5
F.....	Thin-bedded.....	4.3	9.4	.5	.4
	Thick-bedded.....	3.0	5.7	.7	.7
G.....	.....do.....	1.1	2.5	-	-
H.....	Thin-bedded.....	7.1	7.6	-	-
I.....	.....do.....	-	11.9	-	8.4
	Thick-bedded.....	-	4.0	.9	11.2
	Undifferentiated.....	7.3	-	2.3	-
	Total.....	36.8	58.4	11.4	32.9
	Grand total (open pit and underground)...	-	-	-	139.5

<sup>1</sup>Combined thin- and thick-bedded facies or transitional.

TABLE 2. - Summary of resources and calculated grades

Resource	Tonnage (million long tons)	Calculated grade, percent <sup>1</sup>	
		Mn	Fe
A.....	12.7	6.7	36.3
B.....	15.4	6.0	35.3
C.....	4.5	8.4	34.1
D.....	6.7	6.5	32.0
E.....	11.2	7.2	32.9
F.....	24.7	7.9	31.6
G.....	3.6	7.5	32.0
H.....	14.7	6.8	34.6
I.....	46.0	10.9	32.3
Total.....	139.5	<sup>2</sup> 8.3	<sup>2</sup> 33.2

<sup>1</sup>Computed from data obtained from the Minnesota Department of Taxation.

<sup>2</sup>Average.

Measured tonnages are resources, for which size, shape, and mineral content are well established.

Indicated tonnages are computed partly from specific measurements and partly from projection for a reasonable distance on geologic evidence.



Inferred tonnages are estimates based largely on a broad knowledge of the geologic character of the deposit, for which there are few if any samples or measurements.

#### PREPARATION AND CHEMICAL ANALYSIS OF SAMPLES

Bulk samples of crude material that was obtained for metallurgical testing were numbered and assigned a letter prefix, A to I, to indicate the corresponding resource area; pertinent data on these samples are shown in table 3. Also shown are three process samples: One fine tailing, one coarse tailing, and one heavy-media concentrate. Two additional bulk samples, one each from the Maroco and Portsmouth mines, originated outside the resource area.

TABLE 3. - Pertinent data on Bureau of Mines bulk samples

Sample No.	Source	Weight	Remarks
(A)1.....	Sagamore stockpile, N. wall.	70 tons	Unoxidized carbonate.
(A)2.....	Sagamore, SW at pit bottom..	89 tons	Do.
(A)3.....	.....do.....	300 lb.	Do.
(A)4.....	Sagamore stockpile.....	35 tons	Mixture of oxidized and unoxidized carbonate bearing material.
(B)5.....	Huntington.....	324 lb.	Oxidized.
(B)6.....	Huntington stockpile.....	<sup>1</sup> 35 tons	Do.
(C)7,(C)8....	South Alstead, S. wall.....	<sup>2</sup> 330 lb.	Do.
(D)9.....	Mahnomen No. 2, S. wall.....	315 lb.	Unoxidized carbonate.
(D)10.....	North Hillcrest, S. wall....	209 lb.	Do.
(E)11.....	Arko, E. side.....	318 lb.	Do.
(E)12.....	Arko, NW. wall.....	280 lb.	Do.
(F)13-(F)22...	Louise stockpiles <sup>3</sup> .....	<sup>2</sup> 54 lb.	Do.
(F)23.....	.....do.....	300 lb.	Do.
(F)24,(F)25...	.....do.....	<sup>2</sup> 300 lb.	More oxidized.
(F)26-(F)35...	.....do.....	<sup>2</sup> 302 lb.	Oxidized.
(G)36.....	Mangan No. 1, NE. wall.....	287 lb.	Unoxidized carbonate.
(G)37.....	Joan, SW. wall.....	334 lb.	Oxidized.
(G)38,(G)39...	Joan, NE. wall.....	<sup>2</sup> 301 lb.	Do.
(G)40.....	Joan.....	<sup>1</sup> 35 tons	Do.
(G) <sup>4</sup> .....	Mangan-Joan.....	324 lb.	Oxidized tailings.
(G) <sup>5</sup> .....	Joan, Stai, and Mangan stockpile.....	377 lb.	Oxidized heavy-media concentrate. <sup>6</sup>
(H)41.....	Hopkins stockpile.....	312 lb.	Unoxidized carbonate.
(H)42-(H)44...	Hopkins pit.....	<sup>2</sup> 311 lb.	Do.
(H)45,(H)46...	Mahnomen No. 4, N. wall.....	<sup>2</sup> 320 lb.	Do.
(I) <sup>7</sup> .....	Merritt stockpile.....	364 lb.	Oxidized coarse tailings.
SP 5.....	Maroco mine.....	48 tons	Unoxidized carbonate.
SP 6.....	Portsmouth mine.....	<sup>1</sup> 50 tons	Oxidized.

<sup>1</sup>Estimated. <sup>2</sup>Average. <sup>3</sup>(F)13-(F)22 represented material removed and stockpiled from 175 ft. of underground drift. (F)23 was identical with the preceding 10 samples, but represented an additional 40 ft. of drift. (F)24 and (F)25 were similar material, somewhat more oxidized. Combined, the samples represented 278 ft. of underground drift. 10 additional samples (F)26-(F)35, were considered oxidized and represented 1,095 ft. of underground drift. The total footage samples was 1,373 ft. <sup>4</sup>Fine tails. <sup>5</sup>Concentrate. <sup>6</sup>Marketable material. <sup>7</sup>Coarse tails.

Samples were grouped arbitrarily on the basis of their carbon dioxide content, using 4 percent as the dividing line: (1) The unoxidized carbonate slates (the unoxidized thin-bedded iron formation), and (2) the oxidized materials (the partly oxidized thin- and thick-bedded iron formation). Chemical analyses of each group are shown in tables 4 and 5.

TABLE 4. - Chemical analyses of unoxidized manganiferous carbonate slate samples

Sample No.	Percent									
	Mn	Fe	CO <sub>2</sub>	C <sup>1</sup>	SiO <sub>2</sub>	CaO	MgO	P	Al <sub>2</sub> O <sub>3</sub>	S
(A)1.....	7.01	24.94	18.56	0.11	30.12	1.14	3.72	0.158	1.35	0.03
(A)2.....	5.96	20.22	11.69	.26	38.40	.40	3.99	.165	5.90	.08
(A)3.....	6.51	24.48	19.35	.22	29.68	1.28	4.39	.096	2.67	.03
(A)4.....	4.48	36.79	7.63	.15	23.94	.76	1.73	.207	1.29	.03
(D)9.....	5.61	26.76	16.00	.07	31.60	.88	4.37	.159	1.47	.08
(D)10.....	8.62	24.32	22.02	.07	23.82	1.16	4.79	.164	2.17	.01
(E)11.....	7.50	21.47	16.69	.15	31.62	4.98	4.00	.144	2.67	.02
(E)12.....	9.34	28.66	17.38	.11	19.26	3.64	2.60	.291	1.89	.04
(F)13.....	6.27	28.13	14.02	.04	31.64	1.70	3.56	.095	1.35	.03
(F)14.....	8.55	25.47	21.11	.04	24.52	2.20	3.09	.207	2.26	.07
(F)15.....	5.97	23.41	7.11	.04	41.78	.58	2.17	.117	.98	.02
(F)16.....	7.90	26.60	18.94	.01	25.62	1.86	3.10	.159	2.32	.01
(F)17.....	6.42	28.35	20.81	.07	24.92	1.50	3.21	.225	2.39	.02
(F)18.....	5.79	28.05	18.31	.07	27.32	1.48	3.24	.177	2.20	.04
(F)19.....	6.45	26.60	16.72	.11	28.12	1.58	3.37	.198	2.98	.03
(F)20.....	5.36	26.91	15.54	.07	32.82	1.34	3.06	.147	2.13	.04
(F)21.....	6.21	27.67	18.18	.07	29.02	1.26	2.93	.189	2.11	.03
(F)22.....	6.09	26.60	16.20	.07	32.04	1.24	2.91	.153	1.83	.03
(F)23.....	6.98	26.64	8.51	.30	32.58	1.62	2.46	.156	3.31	.05
(F)24.....	10.28	31.37	5.22	.07	29.54	1.30	1.45	.064	1.38	.08
(G)36.....	8.62	25.77	12.05	.07	30.88	1.28	1.69	.179	1.96	.12
(H)41.....	5.58	29.12	13.60	.22	32.54	.86	2.55	.179	1.75	1.03
(H)42.....	4.88	30.40	11.39	.04	31.42	1.24	2.50	.222	2.24	.05
(H)43.....	6.99	31.93	6.05	.07	31.42	2.48	2.01	.099	1.33	.01
(H)44.....	5.73	28.73	14.70	.07	29.98	2.28	2.22	.285	2.52	.02
(H)45.....	4.81	29.65	11.95	.11	31.70	2.08	3.27	.200	2.32	.03
(H)46.....	5.88	26.15	13.52	.04	31.06	1.46	3.59	.201	3.24	.01
SP 5 <sup>2</sup> .....	6.51	27.59	10.38	.15	30.42	5.62	2.30	.210	2.73	.04

<sup>1</sup>Other than CO<sub>2</sub>

<sup>2</sup>Maroco ramp.

Coarse pieces were selected from each sample for petrographic examination. Identification of minerals or mineral groups in order of decreasing abundance is shown for the two groups in tables 6 and 7. Minerals present in trace amounts are not listed.

Two representative parts of each sample, except for one sample of fine tailing, were prepared to determine the relative response of pellets and coarse ore to sulfatization. One part of each and the fine tailing sample

as well were ground to minus 65-mesh and agglomerated into minus 3/8 plus 1/4-inch pellets for testing. The second part of each sample was crushed to minus 3/8-inch, the same size used previously in the pilot plant. Minus 6-mesh material was removed by screening, crushed to minus 65-mesh, rolled into minus 3/8 plus 1/4-inch pellets, and recombined with the minus 3/8-inch plus 6-mesh coarse ore. Tables 8 and 9 show chemical analyses and relative proportions of coarse ore and pellets prepared from the second part.

TABLE 5. - Chemical analyses of oxidized manganiferous samples

Sample No.	Percent									
	Mn	Fe	CO <sub>2</sub>	C <sup>1</sup>	SiO <sub>2</sub>	CaO	MgO	P	Al <sub>2</sub> O <sub>3</sub>	S
(B)5.....	6.81	22.88	1.29	0.01	47.62	2.48	1.99	0.083	1.90	0.02
(B)6.....	5.81	37.05	1.82	.02	24.00	1.02	.94	.159	2.84	.01
(C)7.....	3.50	28.89	1.18	.01	44.20	1.06	.77	.140	3.13	.02
(C)8.....	5.63	32.61	2.74	.01	28.32	2.16	.67	.354	4.18	.01
(F)25.....	8.39	36.10	1.79	.07	27.42	.64	.91	.068	2.09	.02
(F)26.....	5.57	30.77	.54	.01	39.64	.58	.33	.125	3.79	.01
(F)27.....	2.70	28.97	.26	.01	45.68	1.06	.65	.109	4.40	.03
(F)28.....	8.26	29.12	.40	.01	35.86	1.34	.86	.131	3.08	.01
(F)29.....	5.08	32.42	.39	.01	36.68	.82	.49	.135	2.65	.03
(F)30.....	2.30	31.00	1.76	.01	44.46	.72	.73	.155	1.73	.03
(F)31.....	7.59	28.30	.95	.01	40.34	1.42	.45	.079	3.28	.03
(F)32.....	5.39	30.25	.26	.01	40.58	1.50	.60	.052	4.26	.02
(F)33.....	4.71	28.97	.54	.01	40.98	1.80	.73	.103	4.48	.02
(F)34.....	6.73	31.60	.40	.01	32.36	.98	.45	.138	4.58	.01
(F)35.....	7.50	29.57	3.15	.01	33.58	.96	1.26	.105	3.17	.03
(G)37.....	12.54	22.35	.51	.01	44.58	1.14	.40	.061	1.30	.01
(G)38.....	9.73	22.04	.64	.01	47.54	1.68	.50	.065	1.47	.01
(G)39.....	5.61	28.66	.18	.01	47.32	1.34	.36	.058	1.40	.02
(G)40.....	10.78	26.06	.03	.01	39.20	.72	1.10	.156	3.06	.03
(G) <sup>2</sup> .....	1.95	20.45	.44	.01	62.90	.90	.50	.076	1.47	.02
(G) <sup>3</sup> .....	13.74	34.67	.76	.01	21.90	1.92	.63	.108	1.95	.01
(I) <sup>4</sup> .....	6.05	27.52	1.69	.01	42.24	3.86	1.31	.081	1.55	.03
SP 6 <sup>5</sup> .....	4.13	39.78	.01	.01	32.58	.88	.80	.052	1.89	.02

<sup>1</sup>Other than CO<sub>2</sub>.

<sup>2</sup>Fine tails.

<sup>3</sup>Concentrate.

<sup>4</sup>Coarse tails.

<sup>5</sup>Portsmouth.

TABLE 6. - Minerals or mineral groups present in unoxidized carbonate slate samples

Sample No.	Minerals or mineral groups (in order of decreasing abundance)
(A)1.....	Carbonate, stilpnomelane, quartz, goethite.
(A)2.....	Carbonate, stilpnomelane, chlorite, quartz, iron-oxide.
(A)3.....	Carbonate, stilpnomelane, quartz.
(A)4.....	Goethite, carbonate, quartz, stilpnomelane.
(D)9.....	Carbonate, stilpnomelane, minnesotaite, quartz.
(D)10.....	Carbonate, stilpnomelane, quartz.
(E)11.....	Carbonate, stilpnomelane, magnetite, quartz, hematite.
(E)12.....	Carbonate, stilpnomelane, quartz, goethite, minnesotaite, magnetite, hematite.
(F)13.....	Carbonate, quartz, goethite, stilpnomelane, minnesotaite, magnetite.
(F)14.....	Carbonate, minnesotaite, stilpnomelane, quartz, magnetite.
(F)15.....	Quartz, carbonate, goethite, hematite, manganese oxides, magnetite.
(F)16.....	Carbonate, stilpnomelane, magnetite, quartz.
(F)17.....	Carbonate, quartz, chlorite, magnetite, hematite.
(F)18.....	Carbonate, quartz, stilpnomelane, magnetite.
(F)19.....	Carbonate, stilpnomelane, hematite, quartz, magnetite.
(F)20.....	Carbonate, stilpnomelane, minnesotaite, quartz, magnetite.
(F)21.....	Carbonate, stilpnomelane, quartz, hematite, goethite, magnetite.
(F)22.....	Carbonate, minnesotaite, stilpnomelane, magnetite.
(F)23.....	Carbonate, magnetite, stilpnomelane, quartz, chlorite, goethite, hematite.
(F)24.....	Quartz, carbonate, stilpnomelane, hematite, magnetite, goethite, chlorite, manganese oxide(s).
(G)36.....	Goethite, quartz, carbonate, minnesotaite.
(H)41.....	Carbonate, stilpnomelane, minnesotaite, magnetite, hematite, quartz.
(H)42.....	Do.
(H)43.....	Carbonate, hematite, minnesotaite, quartz.
(H)44.....	Carbonate, stilpnomelane, minnesotaite, goethite, magnetite, hematite, chlorite.
(H)45 .....	Carbonate, stilpnomelane, minnesotaite, quartz, ferric oxide.
(H)46.....	Carbonate, stilpnomelane, ferric oxide, green silicate, quartz, minnesotaite.
SP 5 <sup>1</sup> .....	Quartz, hematite, carbonate, goethite, stilpnomelane, manganese oxide(s), minnesotaite.

<sup>1</sup>Maroco ramp.

TABLE 7. - Minerals or mineral groups present  
in oxidized samples

Sample No.	Minerals or mineral groups (in order of decreasing abundance)
(B)5.....	Quartz, goethite, hematite, manganese oxide(s).
(B)6.....	Goethite, quartz, manganese oxide(s), carbonate, hematite, iron-silicates.
(C)7.....	Quartz, hematite, goethite, clay, carbonate.
(C)8.....	Quartz, goethite, carbonate, hematite, manganese oxide(s).
(F)25.....	Quartz, hematite, carbonate, magnetite, goethite, manganese oxide(s).
(F)26.....	Quartz, hematite, magnetite, manganese oxide(s), goethite.
(F)27.....	Do.
(F)28.....	Quartz, hematite, goethite, magnetite, carbonate.
(F)29.....	Quartz, goethite, hematite, manganese oxide(s), magnetite.
(F)30.....	Quartz, carbonate, goethite, hematite, stilpnomelane, manganese oxide(s).
(F)31.....	Quartz, hematite, manganese oxide(s), magnetite.
(F)32.....	Quartz, hematite, goethite, manganese oxide(s).
(F)33.....	Quartz, goethite, hematite, carbonate, manganese oxide(s), magnetite.
(F)34.....	Quartz, manganese oxide(s), hematite, goethite.
(F)35.....	Quartz, goethite, hematite, carbonate, manganese oxide(s).
(G)37.....	Quartz, hematite, goethite, magnetite, manganese oxide(s).
(G)38.....	Quartz, hematite, goethite, manganese oxide(s).
(G)39.....	Quartz, hematite, magnetite, manganese oxide(s).
(G)40.....	Quartz, hematite, manganese oxide(s), goethite, magnetite.
(G) <sup>1</sup> .....	Quartz, goethite, hematite, magnetite, manganese oxide(s).
(G) <sup>2</sup> .....	Quartz, hematite, goethite, manganese oxide(s), magnetite.
(I) <sup>3</sup> .....	Quartz, hematite, goethite, magnetite, manganese oxide(s).
SP 6 <sup>4</sup> .....	Quartz, hematite, magnetite, goethite, manganese oxide(s).

<sup>1</sup> Fine tails.

<sup>2</sup> Concentrate.

<sup>3</sup> Coarse tails.

<sup>4</sup> Portsmouth.

TABLE 8. - Chemical analyses and weight composition of the coarse ore and pellet mixture, representing the second representative part of the unoxidized carbonate slate samples

No.	Sample	Weight-percent	Percent		
			Mn	Fe	CO <sub>2</sub>
(A)1.....	A <sup>1</sup> .....	51.7	7.03	24.94	17.92
	B <sup>2</sup> .....	48.3	7.01	25.01	15.25
(A)2.....	A.....	55.4	6.51	20.53	13.97
	B.....	44.6	5.23	18.55	11.33
(A)3.....	A.....	49.7	6.51	24.48	19.52
	B.....	50.3	6.51	24.48	19.52
(A)4.....	A.....	60.3	4.10	38.17	8.88
	B.....	39.7	5.15	34.18	9.90
(D)9.....	A.....	44.1	5.48	27.97	16.27
	B.....	55.9	5.48	28.73	16.43
(D)10.....	A.....	67.4	8.77	24.32	22.29
	B.....	32.6	8.77	24.32	22.12
(E)11.....	A.....	65.5	7.50	21.38	17.59
	B.....	34.5	7.73	21.47	17.24
(E)12.....	A.....	49.4	9.31	28.66	17.79
	B.....	50.6	9.22	28.66	17.79
(F)13.....	A.....	64.1	6.39	27.75	14.33
	B.....	35.9	6.27	27.98	14.16
(F)14.....	A.....	51.1	8.68	25.24	21.74
	B.....	48.9	8.68	25.24	21.90
(F)15.....	A.....	49.7	5.54	23.56	5.93
	B.....	50.3	6.75	23.18	8.56
(F)16.....	A.....	46.8	7.90	26.60	18.45
	B.....	53.2	7.90	26.60	18.94
(F)17.....	A.....	57.1	6.39	28.35	21.08
	B.....	42.9	6.42	28.35	20.75
(F)18.....	A.....	63.0	5.82	27.90	18.81
	B.....	37.0	5.79	27.97	18.51
(F)19.....	A.....	52.0	6.45	26.76	16.47
	B.....	48.0	6.33	26.91	17.13
(F)20.....	A.....	62.3	5.48	27.06	15.48
	B.....	37.7	5.51	26.99	15.81
(F)21.....	A.....	47.4	6.33	27.52	18.76
	B.....	52.6	6.21	27.59	18.45
(F)22.....	A.....	53.3	6.15	26.76	16.80
	B.....	46.7	6.12	26.76	16.14
(F)23.....	A.....	53.9	7.87	26.57	14.28
	B.....	46.1	7.62	26.57	13.73
(F)24.....	A.....	57.9	8.57	35.20	3.02
	B.....	42.1	9.85	32.57	4.12
(G)36.....	A.....	49.2	9.28	24.63	13.18
	B.....	50.8	8.35	26.30	11.73
(H)41.....	A.....	53.3	5.54	29.12	15.30
	B.....	46.7	5.70	29.12	14.60

See footnotes at end of table.



TABLE 8. - Chemical analyses and weight composition of the coarse ore and pellet mixture, representing the second representative part of the unoxidized carbonate slate samples (Con.)

No.	Sample	Weight-percent	Percent		
			Mn	Fe	CO <sub>2</sub>
(H)42.....	A.....	53.1	5.00	31.17	11.53
	B.....	46.9	5.00	31.40	11.73
(H)43.....	A.....	53.3	6.63	32.30	5.14
	B.....	46.7	6.09	32.15	4.94
(H)44.....	A.....	55.6	5.79	28.50	14.64
	B.....	44.4	5.76	28.58	14.97
(H)45.....	A.....	48.4	4.91	29.12	12.69
	B.....	51.6	4.81	29.27	12.36
(H)46.....	A.....	51.2	5.88	26.23	13.99
	B.....	48.8	5.88	26.15	13.99
SP 5 <sup>3</sup> .....	A.....	58.6	6.31	26.98	10.46
	B.....	41.4	6.34	27.05	10.61

<sup>1</sup>Coarse ore component (minus 3/8-inch- plus 6-mesh).

<sup>2</sup>Pellet component (minus 6-mesh material ground to minus 65-mesh and rolled into minus 3/8- plus 1/4-inch pellets).

<sup>3</sup>Maroco ramp.

TABLE 9. - Chemical analyses and weight composition of the coarse ore and pellet mixture, representing the second representative part of the oxidized samples

No.	Sample	Weight-percent	Percent		
			Mn	Fe	CO <sub>2</sub>
(B)5 .....	A <sup>1</sup> .....	49.6	6.51	21.29	1.98
	B <sup>2</sup> .....	50.4	6.69	21.59	1.38
(B)6.....	A.....	50.0	5.57	38.10	1.64
	B.....	50.0	4.71	36.38	2.46
(C)7.....	A.....	49.5	10.73	35.43	1.52
	B.....	50.5	8.86	38.16	1.25
(C)8.....	A.....	64.3	6.33	35.02	3.29
	B.....	35.7	5.94	32.69	2.81
(F)25.....	A.....	44.4	10.59	34.75	2.19
	B.....	55.6	11.11	31.82	2.19
(F)26.....	A.....	50.0	7.96	29.05	.14
	B.....	50.0	4.99	30.32	.14
(F)27.....	A.....	56.5	4.65	31.52	.55
	B.....	43.5	3.40	30.02	.27
(F)28.....	A.....	42.9	9.64	29.87	.41
	B.....	57.1	9.21	29.57	.41
(F)29.....	A.....	44.2	4.80	28.22	<.01
	B.....	55.8	5.57	32.34	.69
(F)30.....	A.....	45.5	2.50	34.00	2.61
	B.....	54.5	2.20	29.27	.96

See footnotes at end of table.

TABLE 9. - Chemical analyses and weight composition of the coarse ore and pellet mixture, representing the second representative part of the oxidized samples (Con.)

No.	Sample	Weight-percent	Percent		
			Mn	Fe	CO <sub>2</sub>
(F)31.....	A.....	46.0	11.08	25.67	.41
	B.....	54.0	7.50	28.22	.82
(F)32.....	A.....	50.0	3.80	30.25	.27
	B.....	50.0	3.98	31.37	.41
(F)33.....	A.....	57.1	12.36	24.39	.55
	B.....	42.9	9.18	27.02	1.10
(F)34.....	A.....	50.0	11.05	34.07	.27
	B.....	50.0	7.07	32.05	.27
(F)35.....	A.....	40.0	8.42	30.92	2.47
	B.....	60.0	7.28	29.20	2.75
(G)37.....	A.....	50.4	12.11	22.20	.26
	B.....	49.6	11.33	22.35	.26
(G)38.....	A.....	46.9	9.82	20.53	.72
	B.....	53.1	8.74	24.10	.53
(G)39.....	A.....	55.0	5.94	29.65	.13
	B.....	45.0	5.91	29.50	.13
(G)40.....	A.....	56.2	10.38	30.20	.01
	B.....	43.8	10.26	29.28	.02
(G) <sup>3 4</sup> .....	.....	100.0	1.95	20.45	.46
(G) <sup>5</sup> .....	A.....	50.8	13.17	35.73	.79
	B.....	49.2	12.88	37.63	.59
(I) <sup>6</sup> .....	A.....	47.9	6.21	30.11	1.84
	B.....	52.1	6.21	26.76	2.04
SP 6 <sup>7</sup> .....	A.....	61.9	4.68	36.48	.01
	B.....	38.1	5.23	37.17	.01

<sup>1</sup>Coarse ore component (minus 3/8-inch plus 6-mesh).

<sup>2</sup>Pellet component (minus 6-mesh material ground to minus 65-mesh and rolled into minus 3/8- plus 1/4-inch pellets).

<sup>3</sup>Fines from tailings pond (ground to minus 65-mesh and rolled with water into minus 3/8- plus 1/4-inch pellets).

<sup>4</sup>Fine tails.

<sup>5</sup>Concentrate.

<sup>6</sup>Coarse tails.

<sup>7</sup>Portsmouth.

#### BENCH-SCALE SULFATIZING PROCEDURE

Considerable difficulty was experienced in developing a bench-scale procedure to obtain sulfatizing results that were not only consistent but also comparable to continuous-countercurrent treatment in a 20-inch-diameter shaft furnace.<sup>15</sup> Several continuous methods were tried and found to be unsuccessful because of the mechanical difficulties generally associated with scaled-down equipment. Satisfactory results were obtained by sulfatizing the ore batchwise in a rotary drum furnace with an excess of strong sulfatizing gas, which was prepared by passing sulfur dioxide and air through a heated bed of V<sub>2</sub>O<sub>5</sub> catalyst. A schematic view of the bench-scale apparatus is shown in figure 5.

<sup>15</sup> Work cited in footnote 5, (p. 1).

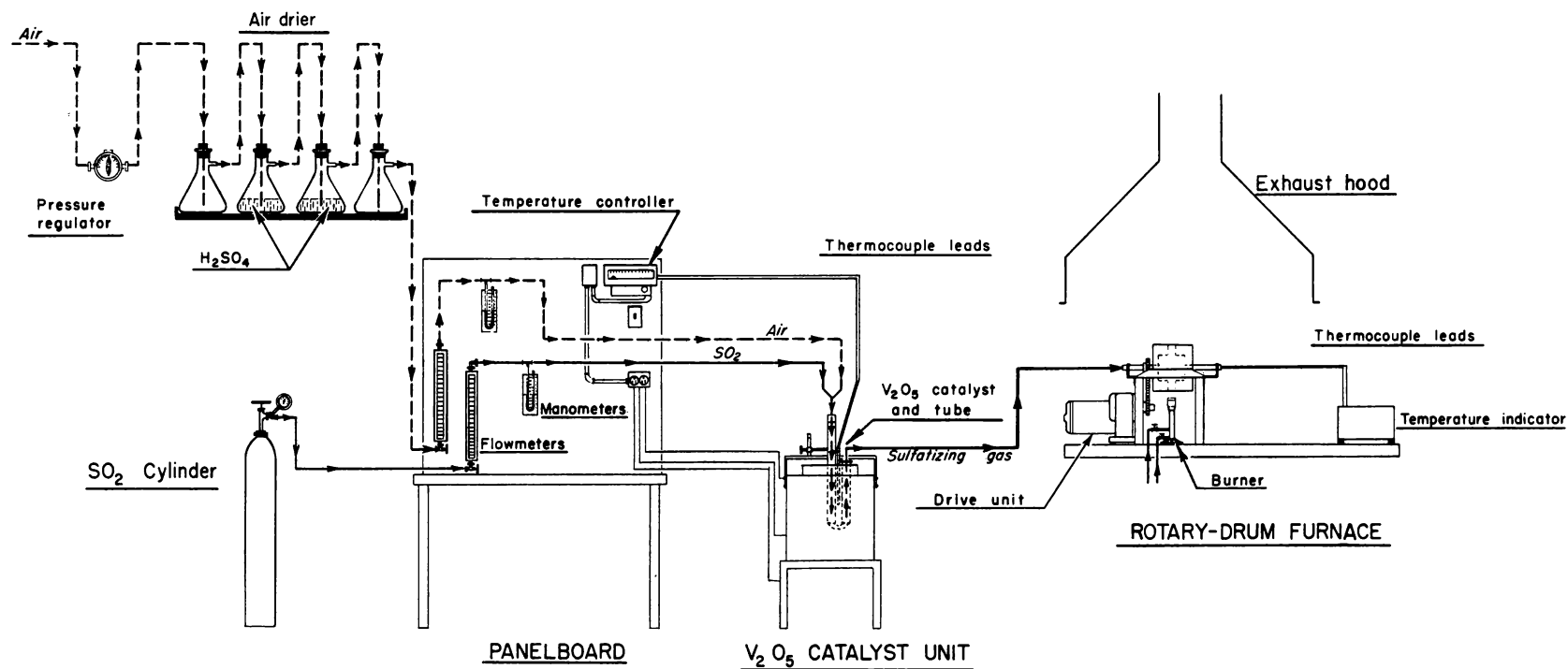


FIGURE 5. - Schematic View of Bench-Scale Sulfatizing Apparatus.

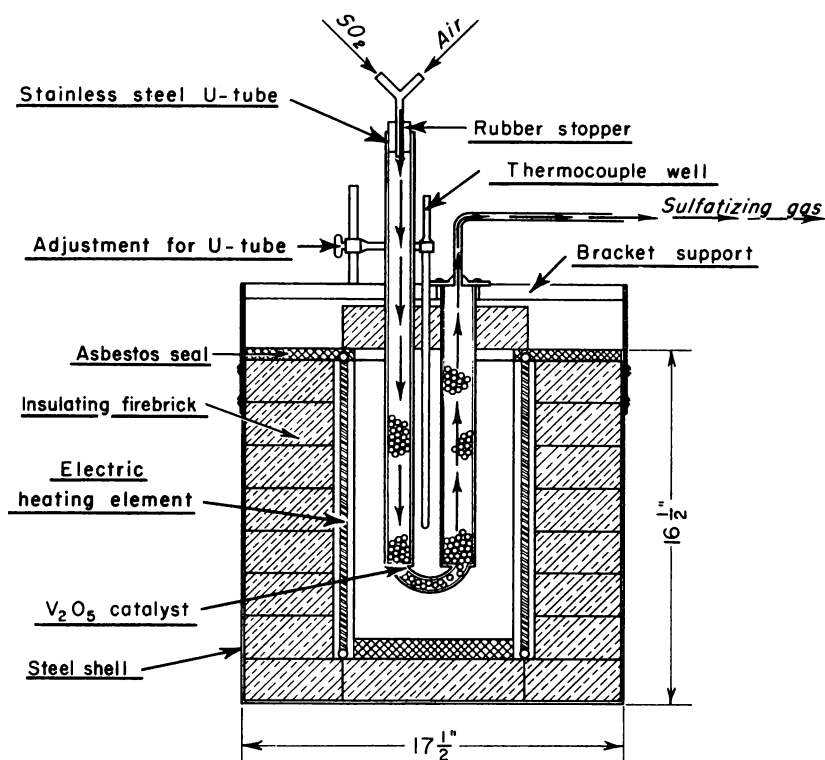


FIGURE 6. - Cross Section of Preheater and Converter Assembly.

which was about  $100^{\circ}$  above that recommended for optimum conversion of sulfur dioxide to the trioxide. Details of the converter and the rotary drum are shown in figures 6 and 7.

A stockpile of mangiferous carbonate slate (sample (A)1) was prepared into minus 3/8- plus 1/4-inch pellets to serve as a standard reference material for the bench-scale sulfatizing studies. Batches of the standard pellets were tested before and during the investigation of the field samples as a control measure. Percentage of sulfatization of manganese in the treated material is a measure of how much manganese is converted to water-soluble manganese sulfate and is determined as follows:

$$\text{Percentage of sulfatization} = \frac{\text{water-soluble Mn}}{\text{total Mn}} \times 100.$$

Percentage of sulfatization, which was determined from 25 tests, using standard pellets, had a standard deviation of less than 1.94 and was indicative of the probable deviation of values for other samples obtained from the field.

Exploratory tests were made with the standard carbonate slate to establish approximate operating conditions. The operating conditions used were not necessarily the most efficient but were selected as those most likely to yield satisfactory results on a wide variety of samples. For example, a gas having a high  $\text{SO}_2$  content (35.7 percent) was used in contrast to the 10 percent  $\text{SO}_2$  used in pilot-plant work, although later tests proved use

The standard procedure consisted of roasting 175 grams of the ore with sulfatizing gas in the rotary drum furnace at  $700^{\circ} \text{C.} \pm 10^{\circ} \text{C.}$  for a period of 7 hours. Drum speed was maintained at 1 r.p.m. and sulfatizing gas was made by passing 0.11 c.f.m. of commercial-grade sulfur dioxide-air mixture (35.7 percent  $\text{SO}_2$ ) through a heated catalyst tube, containing 200 grams of 1/4-inch  $\text{V}_2\text{O}_5$  tablets. The air was bubbled through sulfuric acid to maintain a uniformly low moisture content. To avoid undue cooling of ore in the rotary drum by the sulfatizing gas, the temperature of the catalyst tube was maintained at  $550^{\circ} \text{C.}$ ,

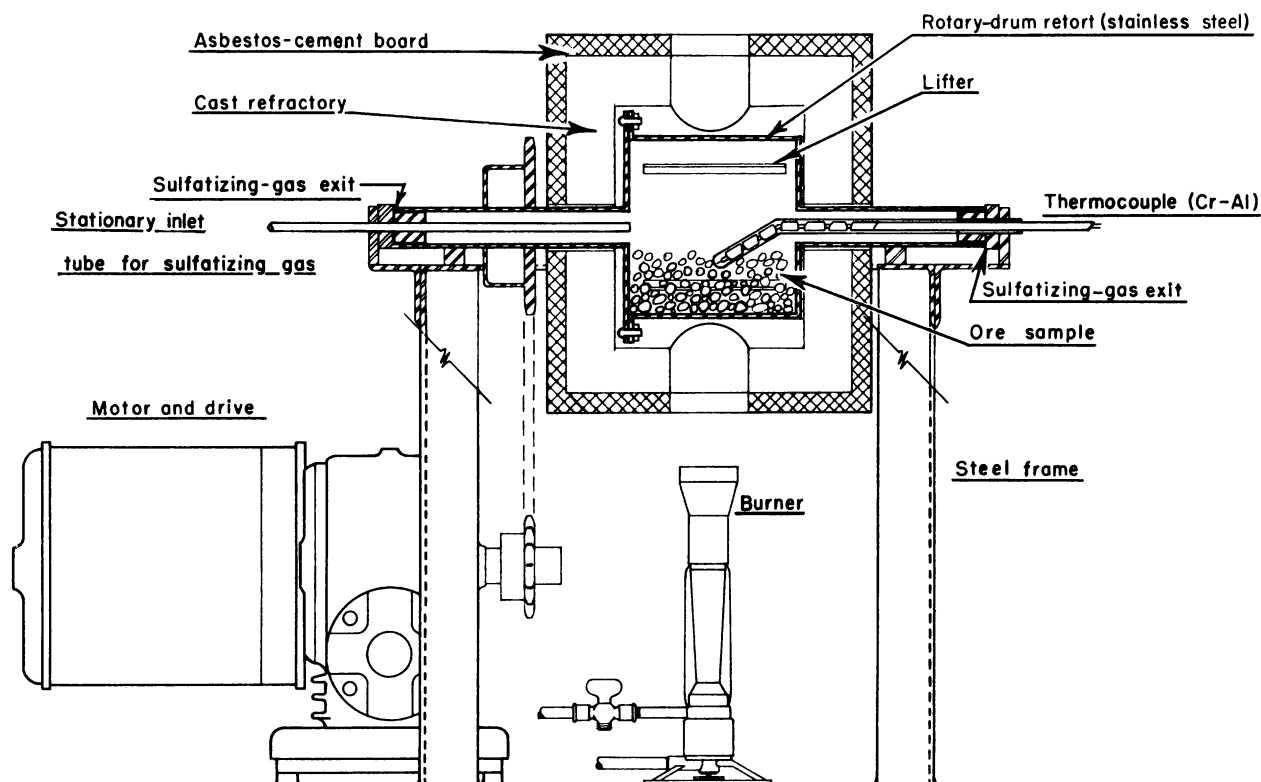


FIGURE 7. - Detail of Rotary-Drum Furnace.

of the richer gas to be unnecessary. The effect of gas composition on sulfatization of the standard carbonate slate pellets is shown in table 10. The effects of temperature and time are shown in tables 11 and 12.

TABLE 10. - Effect of gas composition on sulfatization of standard carbonate slate pellets at 700° C., 7-hour roast

Sulfatizing gas, SO <sub>2</sub> , percent	Sulfatized product, percent		
	Mn, total	Water-soluble Mn	Sulfatization
100.....	8.26	0.31	3.8
61.8.....	6.92	6.18	89.3
46.9.....	6.70	6.06	90.4
35.7.....	6.83	6.32	92.5
30.7.....	6.89	6.43	93.3
18.8.....	7.13	6.55	91.9
9.9.....	7.07	6.52	92.2

Although the batch procedure did not duplicate the shaft furnace technique, the tests were both rapid and reproducible. Several months were required for preparing and treating material in the 20-inch-diameter sulfatizing-shaft furnace in the pilot plant, whereas a batch test could be made in 1 day. Approximately 90 percent of the manganese in the standard pellets was converted to the water-soluble sulfate by either continuous pilot-plant or batch procedures.

TABLE 11. - Effect of temperature on sulfatization of standard carbonate slate pellets, 7-hour roast

Temperature, ° C.	Sulfatized product, percent		
	Mn, total	Water-soluble Mn	Sulfatization
600.....	6.44	5.92	91.9
650.....	6.15	5.80	94.3
700.....	6.83	6.32	92.5
750.....	6.99	6.38	91.3
800.....	7.08	6.35	89.7

TABLE 12. - Effect of time on sulfatization of standard carbonate slate pellets at 700° C., 35.7 percent SO<sub>2</sub> gas

Test No.	Time at 700° C., hours	Sulfatized product, percent		
		Mn, total	Water-soluble Mn	Sulfatization
1.....	<sup>1</sup> 0	7.72	3.91	50.7
2.....	1/2	7.26	5.83	80.3
3.....	1	7.08	6.38	90.1
4.....	2	7.08	6.41	90.5
5.....	3	6.89	6.29	91.3
6.....	4	7.02	6.47	92.2
7.....	5	6.89	6.38	92.6
8.....	6	7.02	6.47	92.2
9.....	7	6.83	6.32	92.5

<sup>1</sup>40 minutes was required to reach 700° C. from room temperature, and 700° C. was constant for all tests.

An important feature of the sulfatizing process is that, during continuous-countercurrent treatment in a shaft furnace, excessive amounts of iron sulfate are not formed at operating temperatures of 600° C. to 850° C. in an atmosphere of sulfatizing gas containing approximately 10 percent sulfur dioxide. Manganese is separated from the iron by a water leach, since the iron remains insoluble. The use of relatively larger volumes of a gas, richer in sulfur dioxide, in the batch tests resulted in the formation of appreciable amounts of iron sulfate. A sample of standard carbonate slate treated by the batch procedure contained water-soluble manganese to soluble iron in the ratio of 4 to 1, whereas a sample of the same material treated in the 20-inch-diameter shaft furnace yielded a ratio of 50 to 1. Iron sulfate may be selectively decomposed by roasting in air at temperatures below 700° C. No attempt was made, however, to decompose iron sulfate in the batch samples; extraction of manganese was the most important consideration.

## RESULTS AND DISCUSSION

Sulfatization results for pellets prepared from the first representative part of the carbonate slate and the oxidized samples are shown in tables 13 and 14. The percentage of manganese sulfatized varied from 82.5 to 95.3 in pellets prepared from carbonate slate and from 76.0 to 90.4 in pellets prepared from oxidized material.



TABLE 13. - Sulfatization results for pellets prepared from the first representative part of the unoxidized carbonate slate samples

Sample No.	Sulfatized product, percent		
	Mn, total	Water-soluble Mn	Sulfatization
(A)1.....	6.83	6.30	92.2
(A)2.....	5.73	5.36	93.5
(A)3.....	6.62	5.96	90.0
(A)4.....	4.63	4.34	93.7
(D)9.....	5.63	4.96	88.1
(D)10.....	8.75	7.86	89.8
(E)11.....	7.22	6.08	84.2
(E)12.....	8.85	8.22	92.9
(F)13.....	6.12	5.05	82.5
(F)14.....	8.78	7.62	86.8
(F)15.....	5.76	5.26	91.3
(F)16.....	7.93	6.99	88.1
(F)17.....	6.39	5.92	92.6
(F)18.....	5.92	5.41	91.4
(F)19.....	6.26	5.82	93.0
(F)20.....	5.45	4.97	91.2
(F)21.....	6.17	5.79	93.8
(F)22.....	6.04	5.48	90.7
(F)23.....	6.66	6.35	95.3
(F)24.....	7.80	7.06	90.5
(G)36.....	8.53	7.96	93.3
(H)41.....	5.64	4.94	87.6
(H)42.....	4.97	4.37	87.9
(H)43.....	6.44	5.36	83.2
(H)44.....	5.90	5.36	90.8
(H)45.....	4.82	4.02	83.4
(H)46.....	5.93	5.29	89.2
SP 5 <sup>1</sup> .....	6.04	5.60	92.7

<sup>1</sup>Maroco ramp.

Table 15 shows a total of 93.5 million long tons of potential ore estimated at an average grade of 7.1 percent manganese. An average of 87.4 percent of 5.8 million long tons of manganese may be recovered by sulfatization. This is equivalent to more than 12 million long tons of metallurgical-grade ore, containing 46 percent manganese.<sup>16</sup>

<sup>16</sup>DeHuff, G. L., Manganese: Chap. in Mineral Facts and Problems, Bureau of Mines Bull. 585, 1960, p. 495.

TABLE 14. - Sulfatization results for pellets prepared  
from the first representative part  
of the oxidized samples

Sample No.	Sulfatized product, percent		
	Mn, total	Water-soluble Mn	Sulfatization
(B)5.....	6.18	5.05	81.7
(B)6.....	5.29	4.38	82.8
(C)7.....	4.99	4.22	84.6
(C)8.....	5.43	4.85	89.3
(F)25.....	7.67	6.45	84.1
(F)26.....	6.12	4.65	76.0
(F)27.....	2.57	2.29	89.1
(F)28.....	7.41	6.55	88.4
(F)29.....	4.74	4.16	87.8
(F)30.....	2.30	2.05	89.1
(F)31.....	6.67	5.45	81.7
(F)32.....	5.57	4.53	81.3
(F)33.....	4.74	4.22	89.0
(F)34.....	6.06	5.48	90.4
(F)35.....	6.92	6.12	88.4
(G)37.....	10.53	8.81	83.7
(G)38.....	8.94	7.41	82.9
(G)39.....	5.66	4.65	82.2
(G)40.....	9.55	7.74	81.1
(G) <sup>1</sup> .....	1.93	1.71	88.6
(G) <sup>2</sup> .....	11.35	9.43	83.1
(I) <sup>3</sup> .....	5.79	4.56	78.8
SP 6 <sup>4</sup> .....	3.80	3.21	84.5

<sup>1</sup> Fine tails.

<sup>2</sup> Concentrate.

<sup>3</sup> Coarse tails.

<sup>4</sup> Portsmouth.

TABLE 15. - Estimate of manganese recoverable by sulfatization  
from potential resources

Resource	Tonnage, million long tons <sup>1</sup>	Average grade, Mn, percent <sup>1</sup>	Sample No.	Sulfatized Mn, percent	Average	Mn responsive to sulfatization, million long tons
A.....	12.7	6.7	{ (A)1 (A)2 (A)3 (A)4	92.2 93.5 90.0 93.7	} 92.4	0.8
B.....	15.4	6.0	{ (B)5 (B)6	81.7 82.8	} 82.3	.8
C.....	4.5	8.4	{ (C)7 (C)8	84.6 89.3	} 87.0	.3
D.....	6.7	6.5	{ (D)9 (D)10	88.1 89.8	} 89.0	.4

See footnotes at end of table.

TABLE 15. - Estimate of manganese recoverable by sulfatization  
from potential resources (Con.)

Resource	Tonnage, million long tons <sup>1</sup>	Average grade, Mn, percent <sup>1</sup>	Sample No.	Sulfatized Mn, percent	Average	Mn responsive to sulfatization, million long tons
E.....	11.2	7.2	{(E)11 (E)12 (F)13 (F)14 (F)15 (F)16 (F)17 (F)18 (F)19 (F)20 (F)21 (F)22	84.2 92.9 82.5 86.8 91.3 88.1 92.6 91.4 93.0 91.2 93.8 90.7	} 88.6	0.7
F.....	24.7	7.9	{(F)23 (F)24 (F)25 (F)26 (F)27 (F)28 (F)29 (F)30 (F)31 (F)32 (F)33 (F)34 (F)35 (G)36 (G)37 (G)38 (G)39 (G)40 (G) <sup>2 3</sup> (G) <sup>2 4</sup>	95.3 90.5 84.1 76.0 89.1 88.4 87.8 89.1 81.7 81.3 89.0 90.4 88.4 93.3 83.7 82.9 82.2 81.1 88.6 83.1	} 88.4	1.7
G.....	3.6	7.5	{(H)41 (H)42 (H)43 (H)44 (H)45 (H)46	87.6 87.9 83.2 90.8 83.4 89.2	} 84.6	.2
H.....	14.7	6.8	{(H)41 (H)42 (H)43 (H)44 (H)45 (H)46	87.6 87.9 83.2 90.8 83.4 89.2	} 87.0	.9
Total:						
A-H..	93.5	7.1	-	-	87.4	5.8
I....	46.0	10.9	(I) <sup>2 5</sup>	78.8	-	-

<sup>1</sup>From table 2, p. 8.

<sup>2</sup>Samples of processed material from resource areas G and I are not included in the total estimates.

<sup>3</sup>Fine tails.

<sup>4</sup>Concentrate.

<sup>5</sup>Coarse tails.

In the foregoing table, an additional estimated 46.0 million long tons of potential ore is shown for I. Recovery of manganese by sulfatization from this deposit was limited to old mill tailings, the only material available for testing. This material responded to sulfatization, and although the tailings are not necessarily representative of the remaining deposit, the manganese recoverable from this area might increase the estimate of ferrograde product by 50 percent.

Tables 16 and 17 show the results of sulfatizing the second representative part of the samples as a mixture of coarse ore and pellets. The minus 6-mesh material, which was ground, pelletized, and recombined with the minus 3/8-inch plus 6-mesh coarse ore, was separated after sulfatization for individual appraisal of these two components.

Twenty of the 28 treated samples of coarse carbonate slate and only 3 of the 22 coarse oxidized samples contained over 50 percent of the manganese as the water-soluble manganese sulfate. This fact points out the advantage of testing batch samples in pellet form rather than as coarse ore to evaluate the response of the manganese minerals to sulfatization. It does not necessarily imply that pelletization of all Cuyuna materials would be required for possible commercial application of the procedures.

TABLE 16. - Sulfatization results for the coarse ore and pellet mixtures prepared from the second representative part of the unoxidized carbonate slate samples

No.	Sample	Sulfatized product, percent		
		Mn, total	Water-soluble Mn	Sulfatization
(A)1.....	A <sup>1</sup> .....	7.15	5.71	80.0
	B <sup>2</sup> .....	6.92	6.15	88.9
(A)2.....	A.....	7.06	4.20	59.5
	B.....	5.24	4.70	89.7
(A)3.....	A.....	6.87	4.61	67.1
	B.....	6.26	6.02	96.2
(A)4.....	A.....	4.29	2.81	65.5
	B.....	4.64	4.34	93.5
(D)9.....	A.....	6.21	1.69	27.2
	B.....	5.45	4.76	87.3
(D)10.....	A.....	8.93	5.96	66.7
	B.....	8.13	7.59	93.3
(E)11.....	A.....	7.88	2.83	35.9
	B.....	7.34	6.20	84.5
(E)12.....	A.....	9.54	7.63	80.0
	B.....	9.05	8.30	91.7
(F)13.....	A.....	6.78	2.59	38.2
	B.....	6.20	5.30	85.5
(F)14.....	A.....	8.49	7.30	86.0
	B.....	8.60	7.87	91.5
(F)15.....	A.....	7.10	3.86	54.4
	B.....	6.41	5.94	92.7

See footnotes at end of table.

TABLE 16. - Sulfatization results for the coarse ore and pellet mixtures prepared from the second representative part of the unoxidized carbonate slate samples (Con.)

No.	Sample	Sulfatized product, percent		
		Mn, total	Water-soluble Mn	Sulfatization
(F)16.....	A.....	7.89	6.09	77.2
	B.....	7.91	7.33	92.7
(F)17.....	A.....	6.46	5.57	86.2
	B.....	6.46	5.91	91.5
(F)18.....	A.....	5.80	4.81	82.9
	B.....	5.88	5.28	89.8
(F)19.....	A.....	6.61	3.54	53.6
	B.....	6.38	5.68	89.0
(F)20.....	A.....	5.72	4.05	70.8
	B.....	5.55	4.97	89.5
(F)21.....	A.....	6.71	4.68	69.7
	B.....	6.39	5.61	87.8
(F)22.....	A.....	6.42	4.28	66.7
	B.....	6.19	5.46	88.2
(F)23.....	A.....	8.16	4.76	58.3
	B.....	7.06	6.63	93.9
(F)24.....	A.....	11.32	3.86	34.1
	B.....	8.81	7.01	79.6
(G)36.....	A.....	7.37	6.21	84.3
	B.....	7.83	7.17	91.6
(H)41.....	A.....	5.66	2.23	39.4
	B.....	5.69	5.18	91.0
(H)42.....	A.....	5.18	2.02	39.0
	B.....	4.91	4.49	91.4
(H)43.....	A.....	6.63	2.17	32.7
	B.....	6.15	5.45	88.6
(H)44.....	A.....	6.08	3.66	60.2
	B.....	5.90	5.44	92.2
(H)45.....	A.....	5.18	.90	17.4
	B.....	4.70	4.13	87.9
(H)46.....	A.....	6.17	4.34	70.3
	B.....	5.90	5.27	89.3
SP 5 <sup>3</sup> .....	A.....	5.18	4.18	80.7
	B.....	5.47	5.10	93.2

<sup>1</sup> Coarse ore component (minus 3/8-inch plus 6-mesh).

<sup>2</sup> Pellet component (minus 6-mesh material ground to minus 65-mesh and rolled into minus 3/8- plus 1/4-inch pellets).

<sup>3</sup> Maroco ramp.

TABLE 17. - Sulfatization results for the coarse ore and pellet mixtures prepared from the second representative part of the oxidized samples

No.	Sample	Sulfatized product, percent		
		Mn, total	Water-soluble Mn	Sulfatization
(B)5.....	A <sup>1</sup> .....	7.35	1.62	22.0
	B <sup>2</sup> .....	6.30	5.08	80.6
(B)6.....	A.....	7.16	3.37	47.1
	B.....	5.41	4.84	89.5
(C)7.....	A.....	8.08	2.98	36.9
	B.....	6.61	5.26	79.6
(C)8.....	A.....	7.02	3.33	47.4
	B.....	5.46	5.00	91.6
(F)25.....	A.....	11.32	3.18	28.1
	B.....	10.16	8.11	79.8
(F)26.....	A.....	9.43	2.87	30.4
	B.....	4.71	3.89	82.6
(F)27.....	A.....	4.28	1.77	41.4
	B.....	3.49	2.79	79.9
(F)28.....	A.....	8.87	4.54	51.2
	B.....	7.83	6.88	87.9
(F)29.....	A.....	5.65	2.76	48.8
	B.....	5.13	4.24	82.7
(F)30.....	A.....	2.51	1.53	61.0
	B.....	2.20	2.02	91.8
(F)31.....	A.....	8.63	3.98	46.1
	B.....	6.67	5.53	79.9
(F)32.....	A.....	7.65	2.88	36.8
	B.....	3.86	3.24	83.9
(F)33.....	A.....	11.02	4.07	36.9
	B.....	8.29	7.13	86.0
(F)34.....	A.....	10.34	4.86	47.0
	B.....	6.73	6.12	90.9
(F)35.....	A.....	8.14	4.59	56.4
	B.....	6.70	5.94	88.7
(G)37.....	A.....	9.41	4.50	47.8
	B.....	9.34	8.80	94.2
(G)38.....	A.....	8.45	2.67	31.6
	B.....	8.70	7.15	82.2
(G)39.....	A.....	4.10	1.08	26.3
	B.....	5.66	5.02	88.7
(G)40.....	A.....	9.98	2.61	26.2
	B.....	9.57	7.94	83.0
(G) <sup>3 4</sup> .....	.....	1.93	1.71	88.6
(G) <sup>5</sup> .....	A.....	10.17	4.10	40.3
	B.....	11.18	9.44	84.4
(I) <sup>6</sup> .....	A.....	5.15	2.26	43.9
	B.....	5.78	4.77	82.5
SP 6 <sup>7</sup> .....	A.....	5.09	2.10	41.3
	B.....	5.02	4.39	87.4

<sup>1</sup>Coarse ore component (minus 3/8-inch plus 6-mesh). <sup>2</sup>Pellet component (minus 6-mesh material ground to minus 65-mesh and rolled into minus 3/8- plus 1/4-inch pellets). <sup>3</sup>No coarse ore component. Fines from tailings pond (ground to minus 65-mesh and rolled into minus 3/8-plus 1/4-inch pellets).

<sup>4</sup>Fine tails. <sup>5</sup>Concentrate. <sup>6</sup>Coarse tails. <sup>7</sup>Portsmouth.



## CONCLUSIONS

1. A revised estimate of potential ore resources for the North range of the Cuyuna district showed that in the central and southwestern parts there are approximately 140 million long tons of potential manganiferous ore (averaging 8 percent manganese and 33 percent iron). Of this total, the materials tested were believed representative of 94 million long tons, averaging 7 percent manganese.

2. A bench-scale procedure was developed to test the response of both coarse and pelletized manganiferous materials to sulfatization.

3. The tests suggest that an average of 87.4 percent or 5.8 million long tons of manganese may be recovered by sulfatization from the 94-million-ton potential resource. This is equivalent to more than 12 million long tons of metallurgical-grade ore, containing 46 percent manganese.





