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A. W. Fahrexwald, Director

METALLURGICAL TESTS ON THE MANGANESE BEARING SANDS

OF

PAYETTE COUNTY, IDAHO

By

Lewis S. Prater, Associate Metallurgist

University of Idaho

Moscow, Idaho

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INTRODUCTION

The sample on which these tests were made was from Sand Hollow in Payette County, Idaho, approximately 15 miles southeast of Weiser. The deposit occurs in the Payette formation. The testing project was undertaken to determine the commercial possibilities of several methods of extracting the manganese.

In the general classification of manganese ores, the highest grade manganese dioxide is termed battery ore and is used for the manufacture of dry cells. Relatively small tonnages are required for this. By far the largest consumption of manganese is in the steel industry where an average of 12.5 pounds is required for each ton of steel. This is generally added as ferromanganese or spiegeleisen. Ore for making ferromanganese must be over 45% manganese--usually about 48% manganese. The ratio of manganese to iron is specified as not less than 7 to 1. Silica should be under 10% and phosphorus under 0.2%. Ore in which the manganese to iron ratio is too low for ferromanganese may be utilized for making spiegeleisen.

A sample of approximately 75 pounds of ore was received at the laboratory. It was designated as Ore Lot No. 78. In general appearance, it is a black colored, friable sandstone. The sand grains are largely quartz and mica along with other nonmetallic silicates. The manganese oxide is the cementing material, binding the grains of gangue mineral together. None of the manganese is present as nodules. As received at the laboratory, there was no moisture in the ore.

Partial analysis of the head sample showed:

Mn = 6.8%
Fe = 2.8%
CaO = 0.8%

Qualitative tests for lead, zinc and copper were all negative.

BENEFICIATION TESTS

Grinding and Flotation

The entire sample was crushed to minus one inch. One half was reserved, and the other half was crushed to pass 8 mesh. The head sample for assay and the testing portions were obtained from this.

For the first tests a sample of 2000 grams was ground in the laboratory ball mill and split four ways. One portion was taken for a sizing-assay test. The results are given in Table I.

Table I

Metallurgical Results of Screen Analysis

Size (Mesh)	Weight (Grams)	% Weight	Assays of Products						
			Size	Weight (Grams)	% Weight	% Fe	Fe Distri- bution	% Mn	Mn Distribu- tion
+48	5.6	1.1							
48/65	26.5	5.5	+65	32.0	6.6	2.6	7.1	3.6	3.7
65/100	82.0	16.9							
100/150	72.0	14.8	65/150	154.0	31.7	1.4	18.5	4.9	24.0
150/200	81.5	16.8							
200/325	69.0	14.2	150/325	150.5	31.2	1.1	14.2	6.2	29.7
-325	149.0	30.7	-325	149.0	30.7	4.7	60.2	9.0	42.6
Compos- ite	485.5	100.0	Compos- ite	485.5	100.0	2.4	100.0	6.48	100.0

Flotation tests were made on the other 500-gram samples from grind No. 1. Both soap flotation and cationic reagents were tried with no apparent success. Without desliming, flotation is very sluggish, and since the slimes are high in manganese, they cannot be economically discarded. The various flotation products were examined under the microscope. This proved that there was little or no mineral segregation made by flotation. No assays were made on the products. These tests conclusively proved that flotation is not applicable to the problem.

Differential Grinding

Because the ore is very friable, and the higher values are found in the fines, the possibility of concentration by differential grinding was suggested. To avoid grinding the quartz as much as possible, this test was made in the laboratory pebble mill. Starting with a charge of 1000 grams of ore, the pulp was deslimed after grinding five minutes. The sands were returned for a second grinding period followed by desliming. This process was repeated until four grinds had been completed. The results of the test are given in Table II.

Table II

Metallurgical Results of Differential Grinding

Product	Weight	% Weight	% Fe	Fe Distri- bution %	% Mn	Mn Distri- bution %
Slime No. 1 (5 min. grind)	39.0	3.9	6.9	10.6	22.8	13.4
Slime No. 2 (5 min. grind)	20.0	2.0	6.4	5.1	20.7	6.2
Slime No. 3 (10 min. grind)	20.5	2.1	5.2	4.2	17.8	5.6
Slime No. 4 (15 min. grind)	41.5	4.2	4.6	7.6	15.1	9.4
Sands	872.5	87.8	2.1	72.5	5.0	65.5
Composite	993.5	100.0	2.54	100.0	6.7	100.0

Although some concentration of the manganese can be accomplished by grinding and desliming, it is impossible to produce a commercial product by this method. It should be mentioned here that the sands in the ore contain a very large amount of mica. In grinding, these become extremely small flakes that settle slowly in water. Their presence would also make air classification difficult.

LEACHING

The physical nature of the ore and the results of previous tests indicate that leaching will be the most logical method of extracting the manganese. Tests were made to determine the applicability of two methods: (1) leaching raw ore with sulfur dioxide, (2) leaching reduced ore with sulfuric acid.

For all leaching tests the ore was ground to minus 35 mesh. Satisfactory extractions were obtained without requiring excessive leaching times. Finer grinding would be undesirable due to the large amount of slimes formed. Coarser material might be readily leached, but this was not determined in these tests due to the difficulty of accurately sampling coarse ore for the small leach batches.

Acid strengths were determined by titrating with standard sodium hydroxide, prepared so that 1 c. c. was equal to 1.975 grams of H_2SO_4 per liter on a 10 c.c. sample. For the sulfurous acid titrations 1 c.c. of $NaOH$ was equal to 1.290 grams of SO_2 per liter on a 10 c.c. sample. It should be noted that if any sulfuric acid is formed by oxidation of the sulfurous acid the SO_2 determinations by titration would be off. Qualitative tests indicated that only a very small amount of sulfate was present in freshly prepared SO_2 solutions.

In titrating pregnant solutions, the precipitation of hydroxide made accurate identification of the end point difficult. The first indications of hydroxide were taken as the end point rather than the change in color of the indicator. On pregnant solutions, neutralized with ore so that no free acid was present, the pH was determined.

All leaching tests were made by agitating ore and solution in 2-liter reagent bottles on the bottle roller.

Leaching with Sulfur Dioxide

For leaching with sulfur dioxide, the solutions were prepared by bubbling SO_2 gas through distilled water. Solutions could not be completely saturated with SO_2 and used for leaching without having excessive fumes escape to the air. Using a ratio of 100 grams of ore in 250 c. c. of solution, preliminary tests indicated that complete recovery could not be made in one step. To determine the extraction that could be made with excess acid, a 3 stage test was made as follows: Three batch leaches were started together. All were removed after 1-1/2 hours and filtered. The filtrate and residue from No. 1 were saved for assay. The other two residues were returned for a second leaching period of 1-1/2 hours with 250 c.c. of fresh acid added to each. These were again filtered and washed; No. 2 residue and filtrate was saved for assay. The third residue was returned for another leaching period with another 250 c.c. of acid.

Table III

Metallurgical Results of Stage Leaching Tests

Sample	Weight or Volume	Mn Assay	Manganese Content	
			Grams	% of Head Sample
Residue No. 1	94.5 gm.	4.4%	4.16	65.8
Residue No. 2	89.4 gm.	1.7%	1.52	24.2
Residue No. 3	84.9 gm.	0.1%	0.06	1.3
Filtrate No. 1	250 c.c.	9.3 gm./l.	2.32	36.8
Filtrate No. 2	250 c.c.	8.2 gm./l.	2.06	32.6
Filtrate No. 3	250 c.c.	6.5 gm./l.	1.62	25.7

In the above test, about 15 grams of SO_2 were consumed in leaching the 100 gram sample of ore, or 2.4 pounds per pound of manganese. Another test was made to determine if complete extraction could be made in one leaching step. By using more concentrated acid (50.4 gm. SO_2 per liter) and a larger volume (350 c.c.), a slight excess of SO_2 over the total 15 grams consumed was provided in one leach. In this test a tailing containing only 0.06% manganese was produced. Also the SO_2 consumption was only 13.4 grams on the 100 grams of ore.

In the following test a countercurrent leaching procedure was followed to insure complete extraction of the manganese as well as complete consumption of the acid. The flow sheet is diagrammed on page 5.

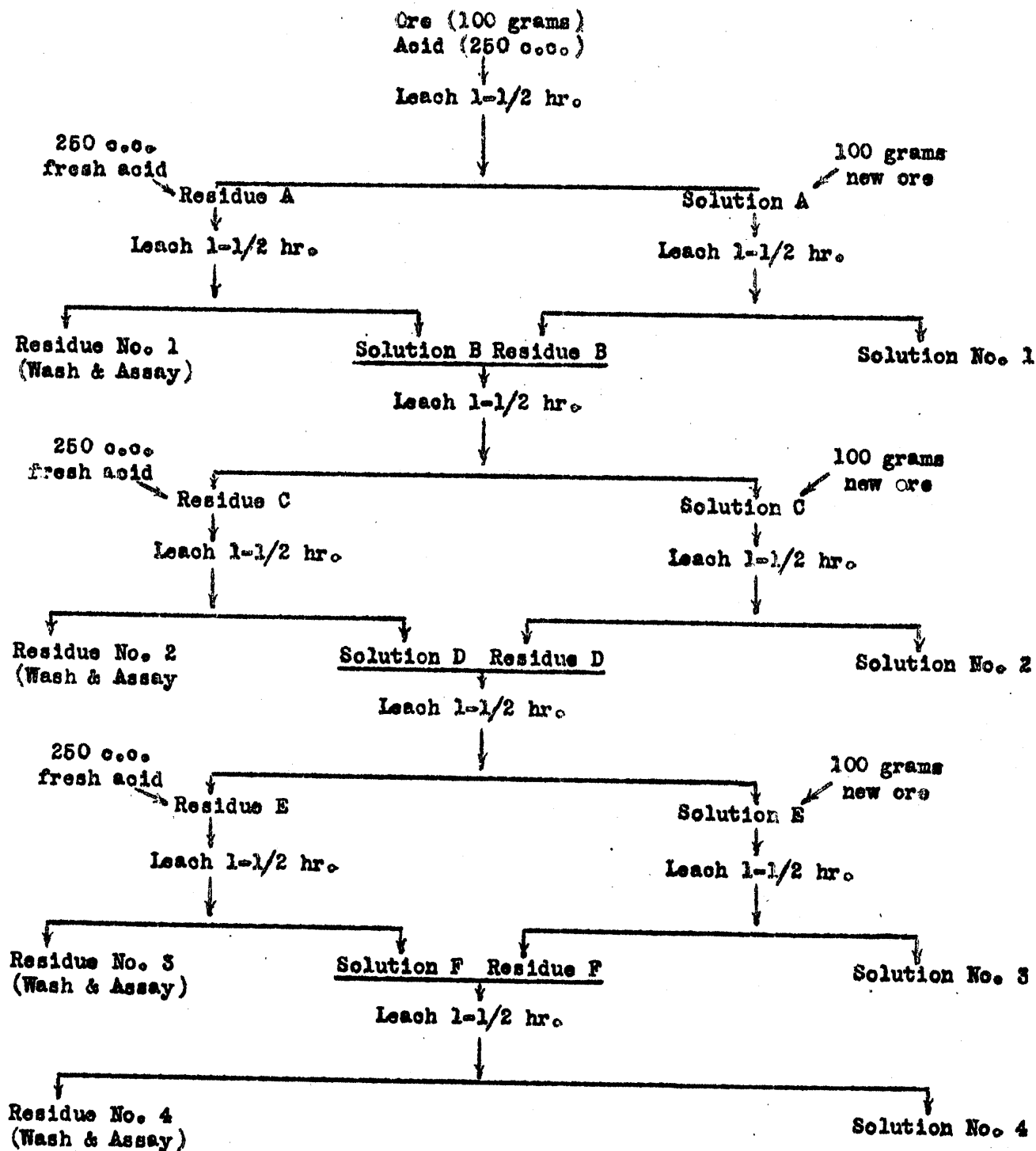


Fig. 1 - Countercurrent Leaching Scheme

In the test tabulated on page 6, the countercurrent leaching scheme was followed, using acid containing 49 grams of SO_2 per liter. The pregnant solutions were evaporated, and the evaporated residue was then calcined at about 950°C .

Table IV
Metallurgical Results of Countercurrent Leaching Test

Sample	Weight	Fe Assay %	Fe Content (Grams)	Fe Distribution	Mn Assay %	Mn Content	Mn Distribution
Residue No. 1	85.0	2.0	1.70	29.8	0.0	0.0	0.0
Residue No. 2	83.6	2.1	1.75	31.1	0.0	0.0	0.0
Residue No. 3	85.6	2.5	1.97	25.6	0.3	0.26	1.1
Residue No. 4	98.8	2.9	2.87	34.6	0.0	6.33	27.4
Calcine No. 1	6.28	0.0	0.0	0.0	60.5	3.71	19.1
Calcine No. 2	8.49	0.0	0.0	0.0	58.5	3.61	15.0
Calcine No. 3	7.58	0.0	0.0	0.0	58.6	4.43	19.1
Calcine No. 4	9.69	0.0	0.0	0.0	59.1	5.73	23.3
Composites			2.29	100.0		24.52	100.0

As indicated in the flowsheet, the leaching of residue No. 4 was not completed, but it and solution No. 4 were included in the results for a metallurgical balance. From the appearance of the tests, it was apparent that the ratio of acid to ore would have had to be increased to maintain a balance.

The above results indicated that good extraction of the manganese can be made by countercurrent leaching. The iron rejection in the residues is almost complete. Acid consumption was complete; the pH of pregnant solutions ranged from 2.0 to 5.5.

Maximum Manganese Content of Solutions

In order to cycle the SO_2 for leaching it is necessary to crystallize the manganese sulfate and calcine the crystals to produce manganese dioxide and SO_2 . For economic evaporation the manganese content of the pregnant solution should be as high as possible. In all previous tests no attempt has been made to saturate the solution with manganese sulfate. The following test was started with 250 c.c. of acid and 100 grams of ore. After leaching and filtering, the filtrate was again saturated with SO_2 and applied to a new bath of ore. This process was repeated until four leaches had been completed. An excess of ore was purposely provided in all leaches, no attempt being made at complete extraction of the manganese. The leach residues were combined into one sample for assaying.

The solutions filtered readily, and no evidence of crystallization appeared after standing two hours. On standing overnight, however, some manganese sulfate precipitated. The filtrate was then evaporated to dryness and calcined at approximately 900° C. The metallurgical results of this test are summarized below.

Table V
Metallurgical Results of Stage Leaching (Excess Ore)

Product	Volume or Weight	Fe Assay %	Fe Content (Grams)	Mn Assay %	Mn Content (Grams)
Calcine	33.77 grams (from 395 c.c. of solution)	0.0	0.0	57.2	19.3
Residue	509.5 grams	2.2	11.2	5.2	16.5

Manganese content of solution = 49 grams per liter

Another stage leaching test was made following the same procedure as outlined above except that an excess of acid was provided for each leach. Only 1/2-hour leaching periods were used in this test, and the results indicated that no advantage is gained from longer intervals. The data is given in Table VI.

Table VI
Metallurgical Results of Stage Leaching (Excess Acid)

Product,	Volume or Weight	Fe Assay %	Fe Content (Grams)	Mn Assay %	Mn Content (Grams)
Calcoine	48.0 grams (from 372 c.c. of solution)	2.0	0.92	57.0	28.2
Residue No. 1	64.0 grams	2.2	1.41	0.14	0.09
Residue No. 2	66.0 grams	2.4	1.58	0.60	0.40
Residue No. 3	66.5 grams	2.3	1.53	0.50	0.33
Residue No. 4	64.0 grams	2.2	1.41	0.70	0.45
Residue No. 5	70.0 grams	2.5	1.75	1.0	0.70
Residue No. 6	68.0 grams	2.5	1.70	1.7	1.16

Manganese Content of Solution = 70.5 grams per liter

Impurities

The data obtained shows that the manganese is leached by SO_2 in preference to the iron. When there is an excess of ore present in the leaches, the amount of iron going into solution is very small. Some iron is dissolved, however, when the acid is in excess. In a countercurrent flowsheet (see Table IV), where the pregnant solution is neutralized with an excess of ore, little trouble should be had with iron.

Qualitative tests on the evaporated filtrate residue for zinc, lead, and copper were all negative.

The ore contains only 0.8% CaO . Whether or not this would be enough to build up crusts of calcium sulfate to block valves, et cetera, in plant operation can not be predicted from these batch tests.

No determinations of the dithionate content of solutions were made. Excessive amounts would cause evolution of SO_2 in evaporation. Dithionate content will depend largely on proper control of the pH in leaching and neutralizing.

Eliminating the sulfur from the calcined product will be difficult. Samples that were calcined at 900-950° C. for several hours still contained a large amount of sulfate. Continued ignition over the Bunsen burner lowered this somewhat, but it is doubtful if a satisfactory product for making ferromanganese could be produced by calcination only. The sulfate in the calcoine is water soluble, however, and it is assumed that there is no sulfide sulfur present to interfere. Data are given below.

Table VII
Elimination of Sulfur from Calcoine by Water Leaching

Calcoine Product	As Calcined		Calcoine Water Leached	
	% S present as sulfate	% Manganese	% S present as sulfate	% Manganese
Test No. 15	5.6	57.2	0.16	69.4
Test No. 16	3.9	57.0	0.06	67.6

Leaching Reduced Ore with Sulfuric Acid

Tests were also made to determine the possibility of using sulfuric acid to leach reduced ore. Preliminary tests showed that the unreduced ore was insoluble in dilute sulfuric acid, confirming the original mineralogical analysis. Reduction and leaching is the procedure followed by the U. S. Bureau of Mines in their process for preparing electrolyte for the production of electrolytic manganese. Only the leaching step, to determine the extraction that might be expected, was covered in these tests. The impurities in the ore should be easily removed from the electrolyte by the Bureau of Mines purification steps.

For these tests the ore was also crushed to minus 35 mesh. Sulfuric acid containing 49 grams of H_2SO_4 per liter was used for leaching. Preliminary tests indicated that a ratio of 100 grams of ore to 250 c.c. of acid would be satisfactory. With less ore, appreciable free acid remained after leaching. With more ore only a slight increase was noted in the total weight of manganese dissolved.

Reduction

These tests have proved that the manganese extraction by leaching depends upon the completeness of the reduction of the manganese dioxide. Considerable difference was noted in the metallurgical results of the tests due to variations in reduction. In the first tests, fuel oil was used as the reducing agent. The ore was moistened with the oil and heated in a covered dish or crucible to approximately $750^{\circ}C$. Most of the reductions were made in the electric pot furnace, but one batch was reduced in an oil fired muffle with a reducing atmosphere in the muffle. No improvement in results was noted.

In later tests, powdered charcoal was used as the reducing agent. Its reducing power was about equal to the fuel oil; its only advantage was the elimination of the smoke and fumes given off by fuel oil. In the tests that are summarized below, it will be noted that incomplete extraction of the manganese was obtained with only one reduction. Re-leaching residues with fresh acid did not materially increase the recovery. However, if the leach residue was reduced a second time and then leached, very satisfactory extractions were obtained. It should be noted that these batch reductions were made without stirring the charge. In a hearth roaster, the charge would be rabbled and exposed to the reducing gases much better. These tests proved that satisfactory reduction could be made with either fuel oil or charcoal with sufficient exposure.

The tests tabulated below illustrate the necessity of complete reduction. In test No. 3 (Table VIII) 100 grams of ore that had been reduced with fuel oil were leached with 250 c.c. of acid. The solution was filtered off and designated as No. 1. The residue was washed and sampled. The sample was designated as residue No. 1, and the remainder was returned for a second leach with fresh acid. The results follow.

Table VIII

Metallurgical Results - Leaching Reduced Ore with Sulfuric Acid - Single Reduction

Product	Weight or Volume	Mn Assay	Mn Content
Residue No. 1	9.0 grams	2.3%	0.20 gram
Residue No. 2	73.5 grams	1.6%	1.18 gram
Solution No. 1	250 c.c.	13.5 gm./l.	4.35 grams
Solution No. 2	250 c.c.	1.4 gm./l.	0.35 gram

In test No. 11, a charge of 105 grams of raw ore was reduced with fuel oil and then leached, following the same procedure as outlined above except that the residue from the leach No. 1 was reduced again before the second leach. These data are given below.

Table IX

Metallurgical Results - Leaching Reduced Ore with Sulfuric Acid - Double Reduction

Product	Weight or Volume	Mn Assay	Mn Content
Residue No. 1	7.3 grams	2.0%	0.15 gram
Residue No. 2	83.0 grams	0.15%	0.12 gram
Solution No. 1	250 c.c.	19.7 gm./l.	4.93 grams
Solution No. 2	250 c.c.	6.2 gm./l.	1.55 gram

Results comparable to the above two tests were obtained when the ore was reduced with charcoal, but the data will not be included here.

Countercurrent Leaching

Following the same flowsheet as outlined for the countercurrent leaching test with SO_2 , a test was made using reduced ore and sulfuric acid. Charcoal was used for reduction--10 grams for sample No. 1 and 5 grams for each of the others. Each batch of 100 grams of ore was reduced separately. In this way no sample stood for any length of time before charging, limiting as much as possible any reoxidation of the manganese. Each sample was reduced only once. The results are given in Table X.

Table X

Metallurgical Results of Countercurrent Leaching Reduced Ore with Sulfuric Acid

Sample	Weight or Volume	Fe Assay	Fe Content (grams)	% Fe Distribution	Mn Assay	Mn Content (grams)	% Mn Distribution
Residue No. 1	86.6 gm.	2.1%	1.82	17.8	1.5%	1.30	6.4
Residue No. 2	86.0 gm.	2.4%	2.06	20.1	2.9%	2.50	10.3
Residue No. 3	84.5 gm.	2.7%	2.28	22.3	3.0%	2.54	10.5
Residue No. 4	90.0 gm.	3.6%	3.24	31.6	3.5%	3.15	13.0
Solution No. 1	202 c.c.	0.0	0.0	0.0	20.1 gm./l.	4.06	16.8
Solution No. 2	230 c.c.	0.18 gm./l.	0.04	0.4	15.1 gm./l.	3.48	14.4
Solution No. 3	238 c.c.	0.17 gm./l.	0.04	0.4	15.7 gm./l.	3.74	15.4
Solution No. 4	280 c.c.	2.7 gm./l.	0.76	7.4	12.3 gm./l.	3.44	14.2
Calculated Head	-----	2.56%	10.24	100.0	6.05%	24.21	100.0

Effect of Ammonium Sulfate on Leaching

In order to obtain satisfactory deposits of electrolytic manganese, the electrolyte must carry about 135 grams of ammonium sulfate per liter. One test was, therefore, made to determine if this concentration of ammonium sulfate would affect the leaching step. The extraction obtained was equally as good as those obtained in the tests without ammonium sulfate in solution.

CONCLUSIONS AND RECOMMENDATIONS

Beneficiation of this ore to a grade of commercial value by any method of concentration appears to be impossible. It can be graded upward by differential grinding but not enough for commercial use, and manganese recovery by any such method would be low.

Satisfactory extraction of the manganese can be made by leaching with either sulfur dioxide or sulfuric acid. Reference to the tabulated data indicates higher recovery with sulfur dioxide. The success of leaching with sulfuric acid would depend on more complete reduction of the manganese dioxide before leaching than it was possible to attain by single batch reductions. This should not prove exceptionally difficult.

Not all the variables were run down in these tests. To do so would require extensive investigation. This work was done largely to determine the manganese extraction that might be expected and also to determine if there were any impurities or other obvious reasons why leaching would be impossible. More work would be required to determine the best ratio of grind to leach^{ing} time. In these tests satisfactory extraction was obtained on minus 35 mesh ore in one-half to one hour's leaching. Finer grinding would obviously be objectionable due to the large amount of slimes that would be formed, as well as the additional cost of grinding. Coarser material might be leached to an advantage if it were possible to handle it in the thickeners, filters, et cetera, in plant operation. More tests would be required to determine optimum solution strengths and ratio of ore to acid. Some of these data could be obtained only in a pilot plant.

In a plant operation, batch leaching would probably be most satisfactory since the pH of the pregnant solution must be closely controlled. For leaching with sulfur dioxide, it would be necessary to bubble the gas directly into the leaching tank or agitator, as it would obviously be impossible to charge water with sufficient SO_2 and then apply this to the ore. If this were attempted, excessive SO_2 fumes would be given off, and the pregnant solution would be very low in manganese.

The best method of handling the leached pulp would have to be determined in a pilot plant. Washing in countercurrent thickeners would probably be most satisfactory. The volume of solids would appear to be excessive for filtering, although filtration would have to be provided following purification of solutions.

No apparent difficulties should arise from impurities in the ore. The selection between manganese and iron in leaching is very definite in the data of all tests. When solutions are neutralized with excess ore, iron rejection is almost complete. In leaching reduced ore with sulfuric acid, only traces of impurities can be tolerated in the purified electrolyte. The data of these tests would indicate that solutions suitable for producing electrolytic manganese could be made. For leaching with SO_2 the finished product is manganese dioxide. Somewhat higher impurity content could be tolerated in the pregnant solutions. As noted above, the elimination of the sulfur will be most difficult. Qualitative tests showed that the ore contained only a trace of phosphorus.

These tests would indicate that technically it is possible to obtain very satisfactory extraction of the manganese from these sands. From the economic side, however, exploitation of a deposit of such low grade would require a very low cost operation.

For several reasons the ore is naturally adaptable to a leaching process.

1. The manganese dioxide is the cementing material, binding the gangue grains together. There are no large nodules of pyrolusite or psilomelane that would be slow in dissolving.

2. Grinding costs would be low. The ore is very friable, and grinding only to the natural size of the quartz sand grains should be sufficient.

3. If reduction, followed by sulfuric acid leaching, were to be used, drying costs prior to reduction should be low. This is an appreciable item on some bad type ores.

4. Due to the sandy nature of the ore, settling rates would be high in thickening. In one test the ore and solution were allowed to stand overnight. The filtering rate on this sample was very slow. In all other tests where solutions were filtered after one-half to one and one-half hour's leaching, filtering rates were very fast.

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