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Brine Leaching Tests on Oxidized Ores of Lead

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INTRODUCTION

The oxidized ores of lead have long presented a difficult problem in ore dressing. The two most common of the lead-bearing minerals found in these ores are: (1) cerussite (lead carbonate) and (2) anglesite (lead sulfate). Although many other minerals may be found associated with the above, they are generally of only minor importance, but among them may be mentioned: (1) pyromorphite (lead phosphate), (2) plumbojarosite (basic sulfate of lead and iron), (3) wulfenite (lead molybdate), (4) mimetite (lead arsenate), and (5) crocoite (lead chromate). Some galena is usually found in ores that are largely oxidized -- often as a core surrounded by the oxidized material.

In treating these ores by either gravity methods or by flotation, the chief difficulty encountered is the large amount of slimes formed. The oxidized lead minerals are all relatively soft and easily pulverized by abrasion. Cerussite tends to break into thin flakes that are easily lost in any gravity operation. Not only are these lead minerals themselves easily slimed, but the gangue rock associated with ore of this type is usually altered and contains appreciable amounts of ochreous material.

Of all the oxidized lead minerals cerussite is the most easily recovered by flotation, and satisfactory metallurgical results can be obtained from clean pulps. However, in pulps contaminated with slimes, both the recovery and concentrate grade are likely to be low. Ores containing large amounts of iron or manganese oxides are exceptionally difficult.

Both lead carbonate and lead sulfate are known to be soluble in an acidified brine solution. Previous investigation into the possibility of treating ores containing these minerals by leaching ^{1/} was practically abandoned with the advent of flotation and the subsequent improvement in the metallurgy of the sulfide ores.

Large reserves of oxidized lead ore are known to occur in Idaho; at present these either are not worked at all or only intermittently, and they could become profitable producers if a satisfactory treatment process could be developed. This investigation was undertaken to determine the feasibility of treating some of these higher grade ores by leaching.

TESTING PROCEDURE AND DATA

Most of the tests in this work were made on our Ore Lot No. 66. This ore is composed of highly oxidized material -- the chief lead-bearing mineral is cerussite with small amounts of both anglesite and galena present. Its color

^{1/} Lyon, D. A., and Ralston, O. C., Innovations in the metallurgy of lead, U.S. Bureau of Mines Bull. 157, 1918.

is a brownish-red from the high limonite content. The ore also carries an appreciable amount of barite which tends to lower the grade of any gravity concentrate. Although qualitative tests show some lime and appreciably more magnesia, the gangue material is mostly siliceous. The head sample assayed 11.1% lead.

Before proceeding with the tests, standard solutions of sulfuric acid and sodium hydroxide were prepared. The acid was made to a strength of 474 grams of H_2SO_4 per liter of solution so that 1 cc. of this acid would be equivalent to 1 gram of lead as lead sulfate. The acid was standardized gravimetrically by precipitating a sample with barium chloride and weighing the barium sulfate. The sodium hydroxide was made up to a strength of 7.72 grams of NaOH per liter. One cc. of this base is then equivalent to 1 cc. of the acid in 500 cc. on a 10 cc. sample.

It was thought that, with the standard acid, measured amounts could be added to the brine and its strength would be known. However, this was not quite the case. A check by titrating with the hydroxide showed that the acid strength of the brine was always a little lower than that expected. The brine usually contained a cloudy white precipitate that settled out only very slowly. This was tested and found to be largely magnesium carbonate precipitated from the small amount of magnesium in the table salt and the carbon dioxide dissolved in the distilled water. Since the amount contained was found to vary, it was necessary to determine the acid strength on all tests both before and after agitation.

Except for a slight decrease at first, due to the common ion effect, as sodium chloride is added to water, the solubility of lead chloride increases up to the point of saturation with sodium chloride. For this reason all tests were made with solutions nearly saturated with salt. The ratio of 50 grams of ore in 500 cc. of brine (less 10 cc. to determine the original acid strength) was used for all tests. Each leach was made in a 2.5 liter acid bottle run on the agitating rolls for the desired length of time.

Effect of Increasing Acid Strength -

In the first series of tests, the effect of increasing acid concentration in the brine on the lead extraction was determined. The conditions under which each test was run were as follows:

- 1) 50 grams of ore crushed to minus 20 mesh
- 2) 490 cc. of acidified brine
- 3) Leaching time = 16 hours
- 4) Head sample assay = 11.1% Pb.

The metallurgical results of this series are given in Table I.

TABLE I.

Effect of Varying Acid Strength on Leaching Raw Ore

Test No.	Wt. of Tailing Grams	% Pb in Tailing	Pregnant Solution Assay Gms Pb/l.	% Pb. Extrac- tion	Grams of H ₂ SO ₄		Acid* Equiv. Con- sumed	Acid** Effic- iency %	Grams of Acid con- sumed per gram of Pb extracted
					Applied	Consumed			
9	47	11.0	----	6.85	2.09	2.09	0.795	8.6	5.5
10	45	8.2	----	33.7	4.70	4.70	1.79	18.7	2.53
11	45	4.1	----	66.8	9.72	9.47	3.60	18.6	2.55
12	43	3.1	8.56	76.0	14.7	11.38	4.34	17.4	2.72
13	43	2.9	9.34	78.5	20.4	12.22	4.64	17.7	2.68
14	43	2.3	9.28	82.2	26.5	12.8	4.87	16.8	2.82

* 1 acid equivalent = 0.474 grams of H₂SO₄ per gram of lead in the ore.

** acid efficiency = $\frac{\text{theoretical amount of acid required for lead recovered}}{\text{actual amount of acid consumed}} \times 100$

The preliminary tests on this ore indicate that the acid consumption is going to be high. As increasing amounts are added it is all consumed until about 3.5 acid equivalents of the lead in the ore have been applied. Beyond this as higher concentrations are applied the consumption continues to rise but at a slower rate. Fig. I is a plot of the amount of acid consumed from brines containing varying original concentrations of acid.

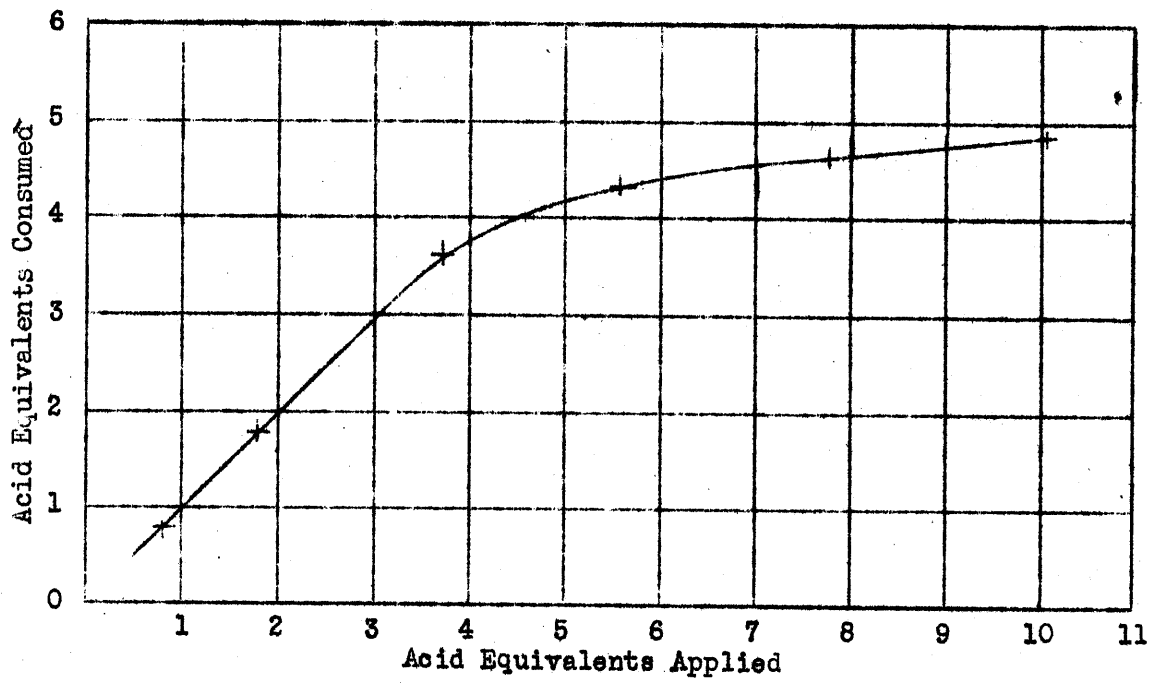


Fig. I. Relationship of Acid Applied to that Consumed

Raw Ore - 11.1% Pb - 16 Hours Leaching

Leaching of Roasted Ore -

Since only fair lead recovery was made on the raw ore in the above tests, it was decided to try the effect of roasting the ore before leaching. The sample was known to contain some galena which is relatively insoluble in the brine and it was believed that this might account for the lead lost in the tailings.

Two series of tests on roasted ore were made; one in which the ore was given an oxidizing roast, and a second in which it was roasted in a chloridizing atmosphere. The roasting was done in batches in the muffle furnace at estimated temperatures of 600°C. For the oxidizing roast the ore was placed in an open crucible and stirred occasionally to allow free access to the air. For chloridizing, the ore was mixed with chloride of lime and heated in the furnace in a covered crucible. It should be noted that when a chloridizing roast is to be followed by leaching, sodium chloride would be more satisfactory than chloride of lime due to the acid consumed by the lime left in the ore. Since none of the roasted samples responded favorably to leaching, however, no tests were made on ore that had been treated this way.

After roasting, the samples were leached, using the same charges and leaching time as on the raw ore. The metallurgical results of these tests are given in Tables II and III.

TABLE II.

Leaching Tests on Oxidizing Roasted Ores

Test No.	Wt. of Tailing Grams	% Pb in Tailings	Pregnant Solution Assay Gms Pb/l.	% Pb. Extraction	Grams of H ₂ SO ₄		Acid Equiv. Consumed	Acid Efficiency %	Grams of Acid consumed per gram of Pb extracted
					Applied	Consumed			
5	49	12.0	----	nil	2.49	2.49	0.87	nil	----
6	49	12.3	----	nil	5.12	5.12	1.79	nil	----
7	48	8.0	----	36.5	10.25	9.50	3.32	11.0	4.3
8	47	6.45	6.17	50.0	15.5	11.9	4.18	12.0	3.94

Roasted ore = 12.1% Pb.

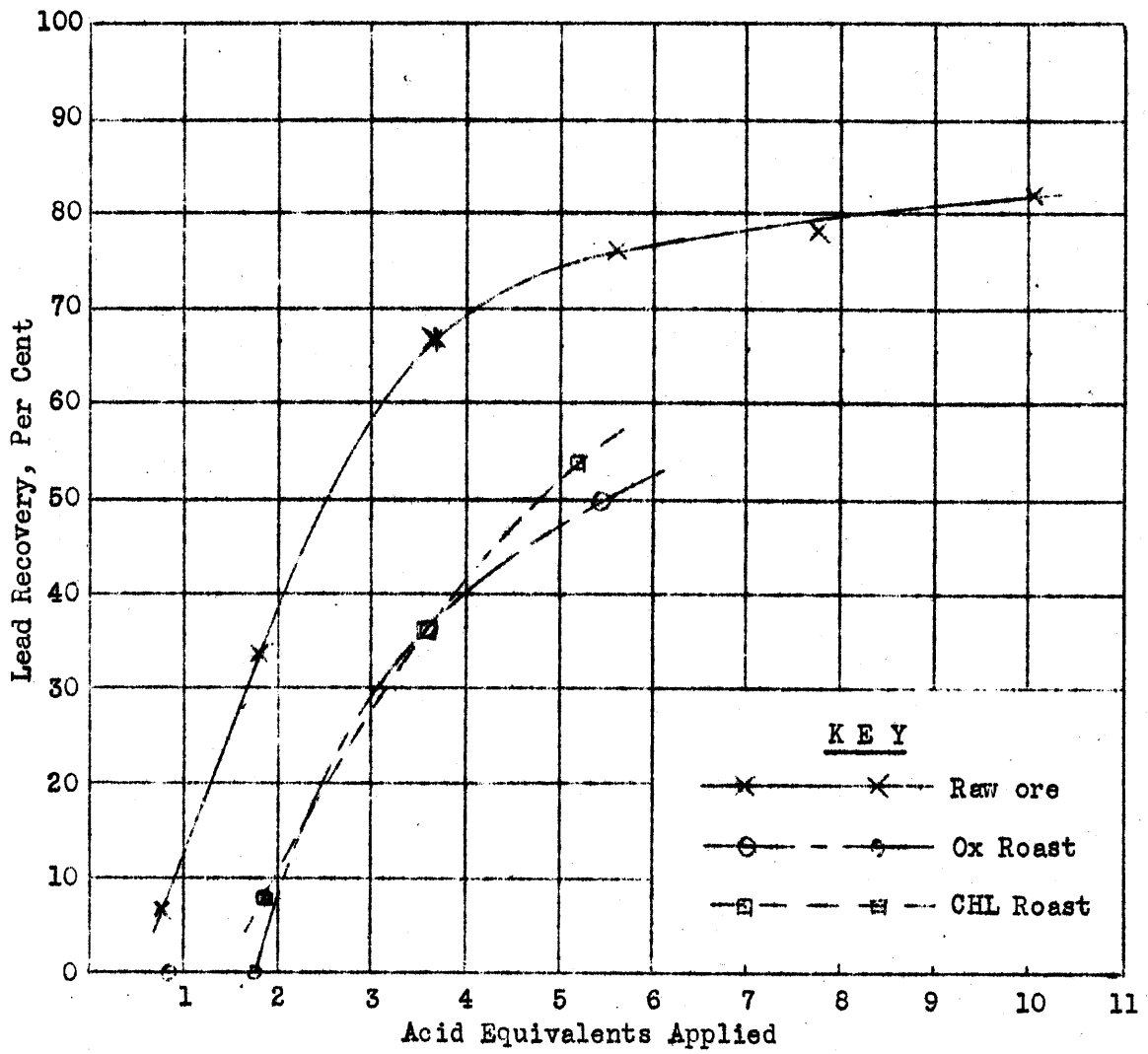


Fig. II. Effect of Acid Concentration on Lead Recovery

TABLE III.

Leaching Tests on Chloridizing Roasted Ore.

Test No.	Wt. of Tailing Grams	% Pb in Tailings	Pregnant Solution Assay Gms Pb/l.	% Pb. Extrac-tion	Grams of H ₂ SO ₄		Acid Equiv. Con-sumed	Acid Effic-ieny %	Grams of acid con-sumed per gram of Pb extracted
					Applied	Consumed			
15	48	10.75	----	7.8	4.90	4.90	1.84	4.3	11.1
16	49	7.25	----	36.6	9.45	9.10	3.42	10.6	4.45
17	48	5.4	6.21	54.0	13.65	13.1	4.93	11.0	4.31

Roasted ore = 11.2% Pb.

The data from Tables I, II, and III are plotted in Fig. II., giving a comparison of the metallurgical results to be expected. The lead recovery made on the raw ore was so much higher than that made on either roasted sample that all succeeding tests were made on unroasted material.

Flotation and Leaching -

Since the conversion of any unoxidized galena to a soluble form by roasting did not prove to be successful, it was decided to test the possibility of a combination of flotation followed by leaching of the flotation tailings. Two tests were outlined -- one in which only the mineral that could be floated with a xanthate and frother was removed by flotation, and a second in which as much of the lead as possible was recovered by flotation using a sulfidizing agent and xanthate for collecting. It was found that only a very small weight of concentrate was collected when no sulfidizing agent was used in the flotation circuit and that it was so badly contaminated with slimes that its grade was no higher than the head sample.

For these tests a 2000-gram sample of minus 10 mesh ore was ground for 13 minutes in the laboratory ball mill, and then split into 500-gram samples for flotation. After drying, weighing, and sampling, the products, the tailings were broken up to pass 20 mesh and leached, following the same procedure as used on the raw ore. Parallel tests were made on the high lead and low lead tailings as outlined below.

Test 18

Flotation

Ore = 1/4 of 2000 gram grind
 Sodium Silicate = 0.5 lb/ton (approx.)
 Na₂CO₃ = 4.0 lb/ton
 Z-5 = 0.4 lb/ton
 Fine oil = 0.1 lb/ton
 Frothing time = 6 minutes

} condition 3 minutes

TABLE IV.

Metallurgical Results of Flotation Test

Product	% of Weight	Pb Assay %	Pb Distribution %
Conct. (18-1)	7.7	10.05	6.6
Tailing (18-2)	92.3	11.8	93.4
Composite	100.0	11.6	100.0

TABLE V.

Leaching of Flotation Tailings (18-2)

Test No.	Leaching Time (Hours)	Wt. of Tailing Grams	% Pb in Tailing	Pregnant Solution Assay Gms Pb/l.	Recoveries %			Grams of H ₂ SO ₄		Acid Equiv. Consumed	Grams of Acid consumed per Gm. of Pb.extr.
					of Lead in Flot. Tail. by Leaching	of Total Lead		Applied	Consumed		
						by leaching	leaching and flotation				
18-3	2	45	5.0	----	61.8	57.9	64.5	9.02	8.93	3.20	2.45
18-4	4	44	5.05	----	62.4	58.2	64.8	9.02	8.98	3.21	2.44
18-5	16	45	4.95	----	62.4	58.2	64.8	9.05	9.05	3.23	2.46
18-6	2	45	4.0	8.55	69.9	65.2	71.8	15.9	10.7	3.83	2.56
18-7	2	44.5	3.7	8.95	72.6	67.8	74.4	22.7	11.3	4.05	2.58
18-8	16	43	2.4	9.71	82.2	76.6	83.2	15.9	11.4	4.08	2.40
18-9	16	42	1.6	10.4	88.4	82.6	89.2	22.8	12.3	4.40	2.42

-1-A

Test No. 19

Flotation

Ore = 1/4 of 2000-gram grind
Sodium Silicate = 0.5 lb/ton (approx) } condition 3 minutes
Na₂CO₃ = 4.0 lb./ton

Z-5 = 0.8 lb./ton }
Na₂S = 4.0 lb./ton } added in 4 stages

Pine Oil = 0.14 lb./ton
Frothing time = 22 minutes

TABLE VI.

Metallurgical Results of Flotation Test

Product	% of Weight	Pb Assay %	Pb Distribution %
Conct. (19-1)	19.1	36.3	57.8
Tailing (19-2)	80.9	6.27	42.2
Composite	100.0	12.0	100.0

TABLE VII.

Leaching of Flotation Tailings (19-2)

Test No.	Leaching Time (Hours)	Wt. of Tailing Grams	% Pb in Tail-ing	Pregnant Solution Assay Gms Pb/l.	Recoveries %			Grams of H ₂ SO ₄		Acid Equiv. Consumed	Grams of Acid Consumed per Gm. of Pb Extracted
					of Lead in Flot. Tail. by Leaching	of Total Lead		Applied	Consumed		
						by Leaching	Leaching and Flotation				
19-3	2	48	4.95	----	24.0	10.1	67.9	8.33	8.33	5.6	11.1
19-4	4	48	4.90	----	24.9	10.5	68.3	9.05	8.97	6.05	11.5
19-5	16	48	4.70	----	28.1	11.8	69.6	9.07	9.05	6.10	10.25
19-6	2	49	3.5	2.92	45.3	19.1	76.9	15.8	10.55	7.15	7.37
19-7	2	49	3.3	3.03	47.9	20.2	78.0	21.6	11.0	7.45	7.40
19-8	16	46	2.1	4.31	68.6	29.0	86.8	15.9	11.5	7.80	5.45

From the above results, it can be pointed out that leaching stops as soon as the acid in the brine is all consumed. In those tests in which the acid concentration in the pregnant brine was reduced to practically zero, the same recovery was made in 2 hours as in 16. Also the grade of the tailing made from the feed material containing 11.8% Pb was the same as that from the 6.27% head. The results also indicate that nothing is gained by recovering part of the lead by flotation since the final tailings ran almost the same in lead as those from the ore treated only by leaching under similar conditions.

Leaching Time and Fineness of Grind -

In the final tests on this ore, parallel runs were made on ore ground to minus 100 mesh and on ore crushed to minus 20 mesh. The same original acid concentration was used in all tests but the time of leaching was varied from 2 to 48 hours. The ratio of 50 grams of ore to 490 cc. of acidified brine that had been used in all previous tests was followed through this series. The data obtained from these tests is given in Tables VIII and IX.

TABLE VIII.

Effect of Leaching Time on Minus 20 Mesh Ore

Test No.	Leaching Time Hours	Wt. of Tailing Grams	% Pb in Tailing	Pregnant Solution Assay Gm Pb/l.	% Pb Extraction	Grams of H ₂ SO ₄		Acid Equiv. Consumed	Acid Efficiency %	Grams of Acid Consumed per Gm of Pb Extracted
						Applied	Consumed			
21-1	2	44	4.8	7.50	62.9	16.0	9.07	3.45	18.8	2.55
21-2	4	44	4.1	7.67	67.6	16.0	9.81	3.73	18.1	2.61
21-3	8	44	3.7	8.25	71.2	16.0	10.4	3.95	18.3	2.58
21-4	16	44	2.9	8.75	77.0	16.0	11.05	4.20	18.3	2.58
21-5	24	44	2.55	9.15	80.0	16.0	11.40	4.34	18.6	2.55
21-6	48	42	2.0	10.0	85.5	16.0	11.70	4.45	19.8	2.39

TABLE IX.

Effect of Leaching Time on Minus 100 Mesh Ore

Test No.	Leaching Time Hours	Wt. of Tailing Grams	% Pb in Tailing	Pregnant Solution Assay Gm Pb/l.	% Pb Extraction	Grams of H ₂ SO ₄		Acid Equiv. Consumed	Acid Efficiency %	Grams of Acid Consumed per Gm of Pb Extracted
						Applied	Consumed			
22-1	2	44	4.25	7.65	66.7	16.0	9.72	3.69	18.3	2.59
22-2	4	44	3.75	7.95	70.2	16.0	10.2	3.88	18.1	2.62
22-3	8	45	3.30	8.50	73.7	16.0	10.8	4.11	18.2	2.60
22-4	16	44	2.60	9.05	79.6	16.0	11.3	4.31	18.6	2.55
22-5	24	44	2.25	9.45	82.4	16.0	11.65	4.43	18.8	2.52
22-6	48	42	1.70	10.1	87.5	16.0	12.0	4.57	19.5	2.43

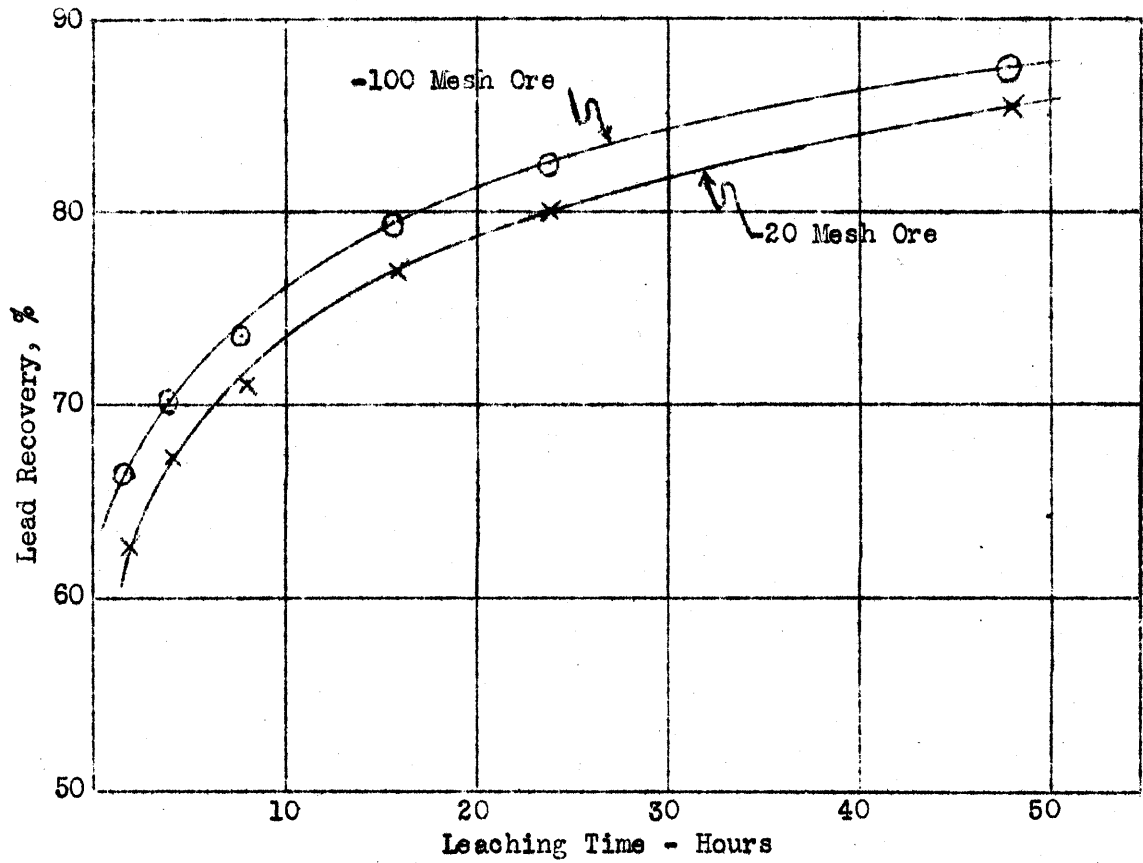


Fig. III. Relationship of Lead Recovery to Leaching Time

Raw Ore - 11.1% Pb - 6.1 Acid Equivalents Applied

Reference to the above tables and to Fig. III shows that both the lead recovery and the weight of acid consumed are slightly higher when the ore is ground to 100 mesh. The weight of acid consumed per gram of lead recovered remains constant throughout the entire series of tests, however. The tests would also indicate that, even though a slightly higher recovery can be made on the minus 100 mesh ore, fine grinding before leaching would be uneconomical.

Tests on Ore Lot No. 65 -

A series of four tests, using various acid strengths, was made on a second oxidized ore (Ore Lot No. 65). This sample was from the tailings dump of an old gravity concentration mill. In general appearance the ore is a light gray color containing a large amount of finely-divided clay-like material, but only a small amount of limonite. Qualitative tests showed that it also contains appreciable amounts of both lime and magnesia. This ore does not carry any unoxidized galena -- the chief lead-bearing mineral is cerussite. The head sample assayed 6.5% lead.

The same procedure as outlined for the previous tests was followed in this series. Leaching time was 16 hours for all tests. The metallurgical results of this series are given in the following table.

TABLE X.
Results of Brine Leaching on Ore Lot No. 65

Test No.	Wt. of Tailing Grams	% Pb in Tailings	Pregnant Solution Assay Gms Pb/l.	% Pb. Extrac-tion	Grams of H ₂ SO ₄		Acid Equiv. Con-sumed	Acid Effic-ency %	Grams of acid con-sumed per Gram of Pb Extracted
					Applied	Consumed			
1	46	2.48	----	64.9	1.49	1.49	0.97	66.8	0.71
2	45	0.97	----	86.5	3.10	3.10	2.01	43.1	1.10
3	41	0.93	----	88.3	6.20	6.13	3.97	22.1	2.14
4	41	0.80	5.74	89.5	8.40	7.59	4.92	17.6	2.70

The above data shows that this ore responds more favorably to leaching than the other. As increasing amounts of acid are added to the brine, the lead recovery rises rapidly at first and then levels off. The acid consumption continues to rise, however, with practically all being consumed in the range of concentration tested. This indicates that something other than the lead minerals is consuming acid but that most of the lead is being extracted first.

SUMMARY

Tests have been made on two oxidized lead ores from Idaho to determine the recovery that may be expected from a leaching process using an acidified brine (sodium chloride) solution as the solvent. The results showed that if the ore is composed largely of the oxidized lead minerals, satisfactory extraction of the lead can be made but that the acid consumption is high.

With the first ore treated (Lot No. 66), as the original acid concentration in the brine was increased the amount of lead extracted was also increased. As larger amounts of acid were added to the leach, all was consumed up to a certain point. Beyond this as the original acid concentration was increased, the amount consumed rose only slightly. It was found that with this ore approximately 2.5 lb. of H_2SO_4 were consumed for every pound of lead recovered. This varied only slightly for all recoveries over 50 per cent.

On Ore No. 65, an extraction of 86.5% of the lead was made with an acid consumption of 1.1 lb. of sulfuric acid per pound of lead recovered. Additional acid was all consumed with only a slight increase in recovery. To raise the lead extraction to 89.5 per cent required 2.7 lb. of acid per pound of lead dissolved.

Leaching stops as soon as the acid in the brine is consumed. When an excess of acid is present, however, the lead recovery continues to rise, rapidly at first and then slowly, as the time of leaching is increased up to 48 hours.

The tests indicated that little is to be gained by crushing finer than 20 mesh. Slightly higher recoveries were made with minus 100 mesh ore, but there was not enough improvement in the results to warrant the cost of finer grinding.

It was also shown that the total recovery from a combination of flotation followed by leaching of the flotation tailings was no better than that made by leaching alone.

Roasting the ore before leaching is unsatisfactory. The benefit that is gained by converting any small amount of galena present to the sulfate is more than offset by the lead carbonate that is calcined to less soluble compounds.

No cyclic leaching tests were made in this series nor were the methods of precipitating the dissolved lead from solution investigated. However, either of two precipitation schemes may be applied, namely, electrolytic and precipitation with lime. Although the electrolytic would probably be the most satisfactory from an operating standpoint, the original cost would be high. If lime is used, careful control of the acidity must be maintained. A large excess would mean a high consumption of both acid and lime. Any free acid in the solution to be precipitated would be thrown down as calcium sulfate and lost.

The results of these tests would indicate that the acid consumption is the main factor which will determine its applicability to the treatment of an ore. Only those ores that do not contain an excessive amount of lime or other acid-consuming substance would be amenable to this process.