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Concentration of an oxidized lead ore from Southeast Missouri

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CONCENTRATION OF AN OXIDIZED LEAD ORE FROM SOUTHEAST MISSOURI

— by —

R. E. Evans

A

THESIS

submitted to the Faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

DEGREE OF

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Approved: Will H Coghill

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PREFACE

This thesis is presented to the Faculty of the School of Mines and Metallurgy of the University of Missouri in partial fulfillment of the work required for the degree of Master of Science in metallurgy.

The results of the investigation embodied herein were obtained from work carried on at the Mississippi Valley Experiment Station of the United States Bureau of Mines, working in cooperation with the Missouri School of Mines and Metallurgy, Rolla, Missouri.

ACKNOWLEDGMENTS

The writer wishes to express his indebtedness to Mr. Will H. Coghill, Supervising Engineer of the Mississippi Valley Experiment Station of the United States Bureau of Mines for his supervision and helpful suggestions; to Mr. Fred DeVaney, Associate Metallurgist of the same station, with whom the writer was associated, for his guidance and advise; to Mr. S. R. B. Cooke, Research Fellow, for help in petrographic work; and to Messrs. O. W. Holmes and Albert Ollar, Chemist and Junior Chemist of the State Mining Experiment Station and

the Mississippi Valley Experiment Station of the United States Bureau of Mines, respectively, who made the chemical analyses required by the investigation.

INTRODUCTION

In the main ore bodies of the Southeast Missouri Lead Belt the lead occurs as galena disseminated in dolomite. The concentration in the mills is by tabling and flotation. The grade of the concentrates and the recovery of the galena are excellent. However, in certain areas of some of the mines ore has been developed that does not concentrate so readily. Because of its reddish brown color this ore is known locally as "red ore", and the presence of oxidized lead has been suspected.

The purpose of this investigation was to determine the extent to which oxidized lead minerals were present in the ore, to ascertain the manner in which they interfered with normal flotation practice, and to devise, if possible, a satisfactory method of concentration.

SCOPE OF WORK DONE

Petrographic examination revealed the presence of lead carbonate, cerussite, and in much smaller proportion lead sulphate, anglesite. A staining method and chemical method were employed to determine the percentages of these minerals. Results of these tests confirmed the opinion of mill operators that the ore was considerably oxidized.

Gravity concentration tests were made. These showed that much of the galena and some of the oxidized minerals were amenable to regular mill "gravity" methods.

Numerous flotation tests were made using a feed of approximately two per cent of lead, which was composed of combined table middlings and tailings, and classifier slimes. The use of customary flotation reagents gave very poor lead recoveries.

The effect of soluble salts on the flotation process was investigated and found of no particular importance .

Sulphidizing agents were then employed in flotation. As good results were obtained by the use of sodium sulphide, tests were made in order to find the correct time for its addition to the circuit and the right amount for most satisfactory concentration.

After excellent results had been secured in the flotation of a single charge of ore, it was desired to ascertain whether the return of the "oxidized-mineral-bearing" froth to the primary flotation circuit would exert any harmful effects upon the sulphide flotation. A series of "lock" tests demonstrated that this concentrate (oxidized lead minerals) might be returned without any pyramiding in the circuit or deleterious effects on the sulphide flotation.

Combined results of gravity and flotation concentration indicated that the ore could be efficiently treated along with, and in the same manner as, the regular sulphide ores, providing sulphidizing were performed in the scavenger circuit.

DESCRIPTION OF ORE

Iron stain caused by the oxidation of some of the iron minerals to limonite gave the sample a brownish color. The lead content was 6.80 per cent, and a cursory examination showed that most of the lead was galena. Small amounts of sphalerite, siderite, and pyrite were present. The chief gangue mineral was dolomite, with smaller amounts of calcite and glauconite.

Petrographic examination showed that some of the lead occurred as carbonate, cerussite, and a smaller amount as sulphate, anglesite. Figure 1 shows replacement of galena by cerussite. The concentric structure is rather characteristic of such replacement. The mineral is undoubtedly cerussite rather than anglesite since it effervesced when treated with dilute nitric acid. Figure 2 was taken

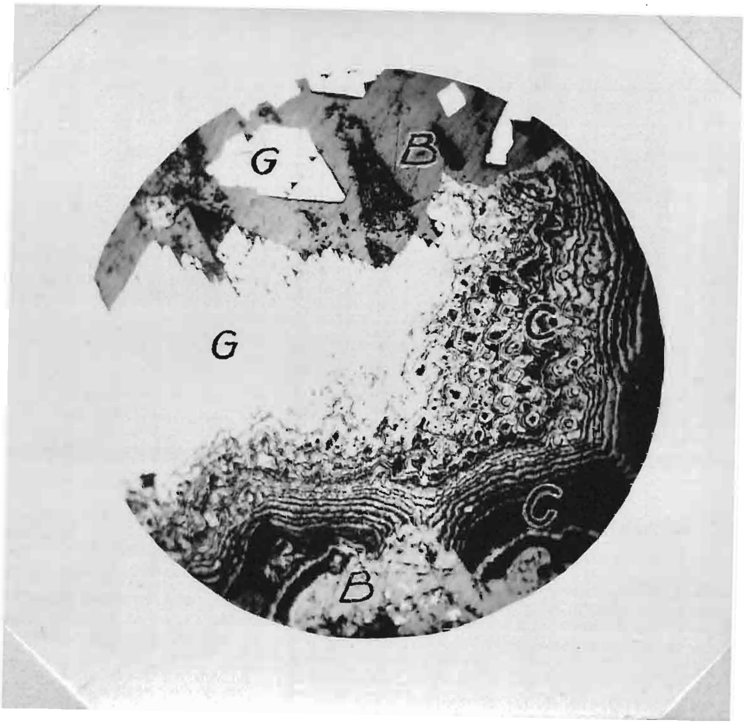

Figure 1. (75 x). Cerussite Replacing Galena.

Cerussite (C); Galena (G); Bakelite (B).

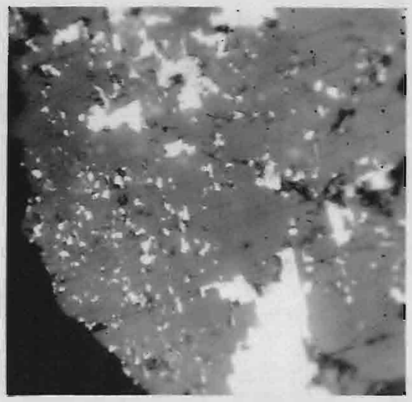

Figure 2A (390 x). Galena Almost Entirely Replaced by Cerussite.

Gray area is cerussite, black area is bakelite, and white area is galena.

at a considerably higher magnification (390 x). Although the concentric structure previously referred to is completely lacking, petrographic examination and microchemical tests clearly proved that the oxidized lead mineral in this specimen is also cerussite.

In order to determine the percentages of cerussite, anglesite, and galena several methods were used. For the purpose of microscopic grain counts a staining method which permitted the ready differentiation of these minerals was employed. Also detailed chemical analyses were made.

The staining method was devised by R. E. Head[1] of the Salt Lake City station of the United States Bureau of Mines. It employs the differential staining or tarnishing of the lead minerals by a slightly alkaline aqueous solution of one per cent of potassium dichromate, or by an aqueous solution of one per cent of chromic anhydride (CrO_3). From grain counts and chemical analyses the estimated distribution of the lead in the lead-bearing minerals was as follows:

Galena	83.4 per cent
Cerussite	13.9
Anglesite	2.7
Total	100.0

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[1] Head, R. E., and Crawford, A. L., A staining method for distinguishing cerussite and anglesite in ores, concentrates, and tailings; U. S. Bureau of Mines Report of Investigations No. 2932, May, 1929.

The chemical analytical method reported by Miller[2] for determining the relative amounts of sulphide and oxidized lead minerals was used. Stated briefly, this method is based on the assumption that the oxides, carbonates, and sulphates of lead are soluble in a ten per cent solution of sodium hydroxide, whereas the lead sulphide and plumbojarosite are insoluble. In the tests performed at Rolla, no plumbojarosite determinations were made. A question may be raised about the absolute chemical correctness of this method, but the results obtained on several labbratory products were in close agreement with microscopic grain counts. Also a fair agreement between these two sets of results and those obtained by a detailed chemical analysis for lead, sulphur, sulphate, carbon dioxide, lime, magnesia, iron, zinc, barium, strontium, and insoluble matter and calculation of the mineral constituents gave added assurance of correctness.

For purposes of comparison, a portion of table concentrates was crushed through 150 mesh and fractionated with a heavy liquid with a density of 3.30. A detailed chemical analysis, a microscopic count of stained grains, and an analysis of oxidized and sulphide lead by the Miller method were used in making a separate estimation of the percentages of lead in the sulphide and oxidized forms. A comparison of these results is given in Table I.

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[2] Miller, Virgil, and Head, R. E., Roasting of carbonate ores/ preliminary to gravity concentration; U. S. Bureau of Mines Technical Paper No. 413, 1928.

Table 1. Distribution of lead in a gravity concentrate.

Product	Method of determination		
	Detailed chemical analysis	Grain count	Analytical method (Miller)
Lead as galena, per cent	79.49	83.33	84.46
Lead as cerussite, per cent	17.20	13.88	15.54
Lead as anglesite, per cent	3.31	2.79	
Total	100.00	100.00	100.00

A screen analysis of the ore crushed to 10 mesh determined the distribution of the oxidized and sulphide lead. These results are given in Table 2, which shows that the oxidized lead minerals slime more than the galena. In the coarsest size, 10 to 20 mesh, only 11.6 per cent of the lead was in the oxidized form, whereas in the finest size, minus 325 mesh, 23.4 per cent of the lead was oxidized.

The natural friability of the oxidized minerals is augmented by their occurrence as replacements at the surface of galena grains or along cleavage planes.

OXIDATION OF THE LEAD MINERALS

From a consideration of the occurrence of the "red" ore, it is not at all surprising that a fair proportion of the galena has been oxidized. The "red" ore is commonly found along water courses and in fissure veins where the action of circulating ground waters exerts considerable effect. A. L. Anderson[3] has the following to say regarding the oxidation of galena:

> "Galena is oxidized in nature either as the result of air-water processes or by attack of ferric sulphate solutions. The simplest reaction and probably the dominant process in nature is the air-water process that is represented by the following equation:
>
> $$PbS + 2O_2 = PbSO_4$$

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[3] Anderson, A. L., The incipient oxidation of galena; Econ. Geol., Vol. 25, pp. 528-548, 1930.

Table 2. Screen analysis of "red" ore crushed to 10 mesh.

Size	Weight, per cent	Assay, per cent			Per cent total			Ratio of oxidized lead to total lead
		Sulphide lead	Oxidized lead	Total lead	Sulphide lead	Oxidized lead	Total lead	
10 to 20 mesh	30.38	4.10	0.54	4.64	23.21	15.26	21.89	0.116
20 to 48 mesh	26.18	5.58	.92	6.50	27.23	22.42	26.43	.142
48 to 100 mesh	11.77	7.85	1.55	9.40	17.22	16.98	17.18	.165
100 to 200 mesh	8.56	6.61	1.72	8.33	10.55	13.70	11.08	.206
200 to 325 mesh	4.90	5.86	1.44	7.30	5.36	6.57	5.56	.197
Minus 325 mesh	18.21	4.84	1.48	6.32	16.43	25.07	17.86	.234
Composite	100.00	5.36	1.07	6.43	100.00	100.00	100.00	.166

This reaction has been demonstrated experimentally by Gottschalk[1] and Buehler and Boswell[2] and Blanchard as checking with conditions actually found in the field, that galena may dissolve without generation of, or attack by, iron-bearing solutions, and commonly does so. In such cases it leaves no limonite. . . . .

"Another feature of note is that galena first oxidizes to sulphate and apparently any carbonate that might form does so by replacement of anglesite and never of galena directly. Such conclusions were obtained in all the specimens studied and are in line with similar conclusions made by Wang[3], who found in relation to the alteration of sphalerite, that carbonate never replaces sphalerite directly.

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[1] Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides; Econ. Geol., Vol. 7, pp. 13-34, 1912.

[2] Boswell, P. F. and Blanchard, Roland, Oxidation products derived from sphalerite and galena; Econ. Geol., Vol. 22, pp. 419-453, 1927.

[3] Wang, W. T., The formation of oxidized ores of zinc from the sulphide; Trans. Amer. Inst. Min. Eng., 1915, p. 1001."

CONCENTRATION TESTS

Preliminary examination indicated that much of the galena and some of the oxidized minerals were amenable to gravity concentration. Consideration was given to the fact that in the milling the proportion of the oxidized ore to the sulphide ore would be relatively small, and that the two types of ore should be treated together. The premise was therefore established that the treatment of the oxidized ore must be much the same as now employed on the usual sulphide ore, except that such changes could be made in the flotation circuit that would permit the recovery of the oxidized lead minerals without interfering with the flotation of the galena.

Gravity Concentration

Gravity concentration tests were made on the "red" ore at 10 mesh. The products of classification were treated on a small-size Wilfley table, shown in Figure 3, for clean concentrates. Although possible, no final tailings were made. Since the classifier slimes were higher grade than the usual primary slimes in the mills, the table tailings were reground and added to the slimes for a flotation feed of about the same grade as in commercial practice.

In a representative table test, 75.85 per cent of the lead was recovered in a concentrate assaying 71.84 per cent of lead; the results are given in Table 3.

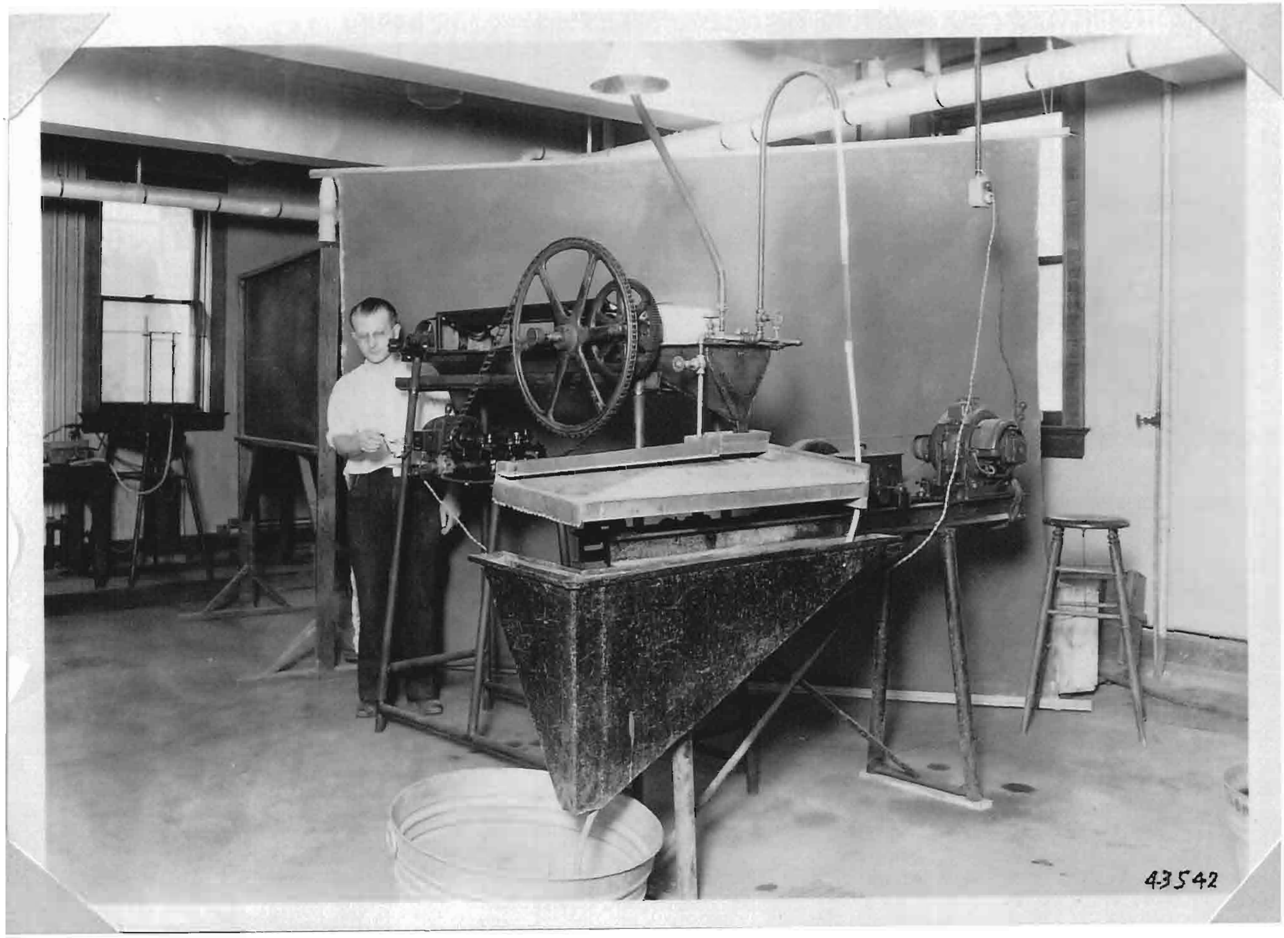

Figure 3. Wilfley Laboratory Concentrating Table and Mechanical Feeder.

Table. 3. Gravity concentration test on classified "red" ore crushed to 10 mesh.

Product	Weight, per cent	Assay, per cent lead	Per cent total lead
Table concentrate	7.43	71.84	75.85
Table middling (tailing) . .	71.94	.96	9.81
Classifier slime	20.63	4.89	14.34
Composite	100.00	7.04	100.00
Head sample		7.05	

Approximately 15 per cent of the lead in the concentrate was oxidized.

Flotation

Proportional parts of table middling (tailing) and classifier slime constituted the flotation feed. This feed had a tenor of approximately two per cent of lead. Tests were made on 500-gram samples in a flotation cell of the mechanical agitation type. Generally the charge was ground to 100 mesh; however, a few tests were made at 150 mesh and at 200 mesh. Slightly better grades of rougher concentrates and slightly lower lead tailings were obtained by the finer grinding but the extra grinding was not warranted.

The grinding was done by stages in water with flint pebbles. Pulp density in flotation was 20 per cent of solids by weight.

Inasmuch as soluble salts affect flotation, tests were made to ascertain the kind, amount, and possible effects of the soluble salts in the oxidized ore. A charge of flotation feed was ground in the presence of distilled water. Subsequently, this water contained the following soluble salts: 17.5 p.p.m. (parts per million) of bicarbonate alkalinity as sodium bicarbonate; 44.3 p.p.m. of lime; 56.0 p.p.m. of magnesia; and 86.4 p.p.m. of sulphate. None of these seemed excessively high. However, flotation tests were made in which all grinding was in distilled water, the ore was thoroughly washed in distilled water, and distilled water was used in flotation. Since only slightly improved results were obtained, soluble salts were given no more consideration; they had given the water a trace of alkalinity.

Varying the amount of soda ash as a conditioning agent with potassium ethyl and amyl xanthates did not affect the grade of tailing materially. Sodium silicate as a conditioning agent was of slight value; the grade of rougher concentrate was improved somewhat, but the lead content of the tailing was higher. To disperse gangue the flotation feed was conditioned with gum arabic. The grade of the concentrate was improved, but gum arabic was abandoned because the tailing was too high.

Several tests were made with mono-ammonium phosphate with several of the xanthates. This conditioning agent, which has been used commercially on lead carbonate ores, did not give better tailings and reduced the grade of the concentrates.

Tests were made to fine some type of collector more suitable than the xanthates. Among those tried were various types of Aerofloat, G. N. S. No. 17, Flotation Oil No. 400 (National Turpentine Products Co.), and thiocarbanilid. Tests with these collectors indicated that as a class the xanthates were undoubtedly the best. Either ethyl or amyl xanthate is satisfactory as a collector, but, due to its more widespread use and lower cost, the ethyl xanthate is probably preferable. Consequently, all subsequent tests were made with potassium ethyl xanthate.

Several frothers were used with ethyl xanthate, but cresylic acid, commonly used in the district, was found to give the most satisfactory size of bubbles and stability of froth. The best preliminary results were with 0.16 pounds of potassium ethyl xanthate and 0.48 pounds of cresylic; the results appear in Table 4.

The inability to make low-grade tailing led to the use of sulphidizing agents. Various amounts of sodium mono-sulphide ($Na_2S \cdot 9 H_2O$) were used to condition the ore before flotation. Three pounds per ton was found most desirable. This reagent gave a better tailing and a satisfactory concentrate.

In early tests the pulp was conditioned for 15 minutes in the flotation cell before the addition of the collector. Results soon indicated, however, that the sodium sulphide should be added to the cell immediately before the addition of the collecting agent. A test in which three pounds per ton of sodium sulphide, 0.48 pounds of ethyl xanthate, and 0.48 pounds of cresylic acid were used gave a rougher concentrate about 19 per cent of lead, a recovery of 84 per cent, and a tailing assaying 0.30 per cent of lead. For comparison with the best results without sulphidizing, the test with sodium sulphide is given in Table 5. Sodium sulphide increased the recovery of lead approximately 16 per cent.

Table 4. Flotation test without sulphidizing.

Product	Weight, per cent	Assay, per cent lead	Per cent total lead
Concentrate	6.41	23.86	67.97
Tailing	93.59	.77	32.03
Composite	100.00	2.25	100.00

Table 5. Flotation test with entire feed sulphidized.

Product	Weight, per cent	Assay, per cent lead	Per cent total lead
Concentrate	7.60	18.84	83.77
Tailing	92.40	.30	16.23
Composite	100.00	1.71	100.00

Later tests, however, showed that for the best results by sulphidizing as much as possible of the sulphide lead should be floated with ethyl xanthate and cresylic acid. After which the oxidized lead may be floated with sodium sulphide, additional xanthate and cresylic acid. The tailings by this scheme were 0.08 per cent lower than tailings from the test in which the entire flotation feed was sulphidized. The added recovery was about 5.5 per cent.

The conclusion was reached that the sulphidizer should be added to the scavenger machine. The advantage of sulphidizing in the scavenger is brought out by Table 6.

The ultimate gain by the introduction of sodium sulphide and the use of it in the scavenger treatment was great; the grade of tailing was reduced from 0.77 to 0.22 per cent of lead.

To determine whether the "oxidized" concentrates as shown in Table 6 could be cleaned satisfactorily by returning the scavenger froth to the rougher flotation feed, a series of lock tests was made. The reagents were the same as in the batch test reported in Table 6. The oxide-bearing froth from each test was added to the next new charge and re-floated with the new feed. The results of this series are given in Table 7. They show that when the oxidized minerals have been sulphidized and floated they can be re-floated and cleaned with the sulphide. The small amount of sodium sulphide carried by the oxide-bearing froth is not detrimental to the flotation of the galena in the new feed. This is indicated by the small amount of oxide-bear-

Table 6. Flotation test in which sulphidizing was confined to the scavenging treatment.

Product	Weight, per cent	Assay, per cent lead	Per cent total lead
Galena concentrate	6.87	17.60	66.36
"Oxidized concentrate". . . .	2.92	14.23	22.76
Tailing	90.21	.22	10.88
Composite	100.00	1.82	100.00

Table 7. Flotation lock test in which sulphidizing was confined to the scavenging treatment.

Test Number	Product	Weight, per cent	Assay, per cent lead	Per cent total lead
1	Sulphide concentrate	5.45	20.90	80.52
	Tailing	94.55	.29	19.48
	Composite	100.00	1.41	100.00
2	Sulphide concentrate	6.28	26.20	87.10
	Tailing	93.72	.26	12.90
	Composite	100.00	1.89	100.00
3	Sulphide concentrate	9.17	18.94	89.68
	Tailing	90.83	.22	10.32
	Composite	100.00	1.94	100.00
4	Sulphide concentrate	9.67	16.40	70.58
	Oxidized concentrate	3.90	12.28	21.34
	Tailing	86.43	.21	8.08
	Composite	100.00	2.25	100.00
Composite	Sulphide concentrate	7.71	19.80	81.11
	Oxidized concentrate	1.08	12.28	7.02
	Tailing	91.21	.24	11.87
	Composite	100.00	1.88	100.00

ing froth from the fourth charge, which is no larger than the amount expected from a single batch test, and which shows no pyramiding of oxidized minerals in the circuit. The grade of concentrates and of tailings decreased in the last two tests. Probably the change was due to accumulated reagents in the circuit. The control of this condition is solely a matter of adjustments of reagents.

Summary of Concentration Results

The combined results by classification and tabling of 10 mesh ore, flotation of the reground table tailings and slimes, and sulphidizing in the scavenging cell are summarized in Table 8. In this table the flotation concentrates are analogous to the froth produced in the rougher flotation cell of a mill circuit where the scavenger concentrates are returned to the roughing cells. In practice this froth would be recleaned. A recovery of 97.12 per cent of the lead was in a combined gravity and flotation concentrate. Only 2.88 per cent of the total lead remained in the tailings, which had a tenor of 0.24 per cent of lead.

Table 8. Composite gravity and flotation test.

Product	Weight, per cent	Assay, per cent lead	Per cent total lead
Table concentrate	7.43	71.84	75.82
Rougher flotation concentrate	7.75	19.33	21.30
Tailing	84.82	.24	2.88
Composite	100.00	7.04	100.00

SUMMARY AND CONCLUSIONS

(1) With the deposits of disseminated galena in the Southeast Missouri Lead Belt bodies of ore characterized by a reddish brown color are found. The presence of much of this ore in the mill feed results in an added tailing loss.

(2) A detailed examination of this "red" ore showed that it was oxidized. Lead carbonate, cerussite, and lead sulphate, anglesite, were present. Of the total lead content of the ore, approximately 83 per cent was galena, 14 per cent cerussite, and 3 per cent anglesite.

(3) Chromate staining methods for the microscopic differentiation of galena, cerussite, and anglesite were investigated and found to be helpful. A special analytical method for the determination of oxidized and sulphide lead was used and found to give results in fair agreement with those obtained from grain counts and detailed chemical analyses.

(4) A screen analysis of the ore showed that the oxidized lead minerals slimed more freely than the galena.

(5) Tests showed that a large portion of the coarser galena and some of the oxidized lead minerals were recoverable by table concentration.

(6) Flotation tests with the usual combination of reagents employed in galena flotation permitted approximately 30 per cent of the lead to be lost in the tailing. No greater improvement

could be made on these results by changing the alkalinity of the pulp, the use of sodium silicate, gum arabic, or mono-ammonium phosphate. Of the collectors used, the xanthates seemed to give the best results while cresylic acid served satisfactorily as a frother.

(7) The use of sodium sulphide increased the percentage of recoverable lead in the flotation circuit. The addition of sodium sulphide to the scavenger circuit gave higher recoveries than if the sodium sulphide be added to the rougher circuit. The use of sodium sulphide permitted a loss of only 11 per cent of the lead in the flotation circuit as compared to 30 per cent when it was not used. Series tests showed that the oxide-mineral froth from the scavenger circuit could be returned without injurious results to the roughing circuit for recleaning.

(8) Concentration tests indicate the possibility of efficiently treating the oxidized ore in the same manner as, and along with, the regular sulphide ores, providing sulphidizing is done in the flotation scavenger circuit. Tests in the laboratory gave an overall recovery of lead of 97.12 per cent, and a tailing 0.24 per cent of lead.

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