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Phosphorus Removal From Birmingham, Ala., Calcareous Iron Ores

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Phosphorus Removal From Birmingham, Ala., Calcareous Iron Ores

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CONTENTS

ILLUSTRATIONS

TABLES

PHOSPHORUS REMOVAL FROM BIRMINGHAM, ALA., CALCAREOUS IRON ORES

by

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and I. L. Feld[4]

ABSTRACT

The Federal Bureau of Mines conducted research to develop methods of removing phosphorus from the earthy, calcareous hematite ores of the Birmingham, Ala., iron district while simultaneously improving the grade and recovery of the iron values prior to furnacing. An attempt was also made to identify the phosphorus minerals present in the ores.

The ores contained about 36 percent iron, 12 to 16 percent CaO, 15 to 20 percent hydrochloric acid insolubles, and 0.30 to 0.36 percent phosphorus. Fractions containing 5 to 15 percent phosphorus were isolated from the ores. Collophanite, $Ca_3P_2O_8 \cdot nH_2O$, a member of the apatite group, was the only phosphate mineral identified.

Beneficiation methods using flotation and reduction roasting with magnetic separation yielded good grade iron concentrates, but were not as effective for reducing the phosphorus content of concentrates.

Reduction roasting followed by fine grinding, magnetic separation, and acid leaching gave iron concentrates containing 62.5 percent iron and 0.04 percent phosphorus with an iron recovery of 82.9 percent and a phosphorus rejection of 93.7 percent.

Reoxidation of reduced magnetic concentrates followed by acid treatment gave iron concentrates containing 58.1 percent iron and 0.02 percent phosphorus with 89.6 percent recovery of the iron and 96.5 percent rejection of the phosphorus.

INTRODUCTION

The calcareous iron ores of the Big Seam, Birmingham district, Alabama, remain a major potential reserve of iron ore in the Southeastern United States.

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[1] Metallurgist.
[2] Research geologist (now deceased).
[3] Physical science technician.
[4] Supervisory metallurgist.

Total tonnage in the district has been estimated by Thoenen and coworkers[5] at more than 2 billion long tons. However, these ores are not being mined now because of (1) the high costs of underground mining, (2) the relatively low iron content of mine-run ore, (3) the ore's high phosphorus content, and (4) the availability of higher grade foreign ores in the Birmingham area.

The Bureau of Mines and others have tried to solve these problems, especially the second and third. Although earlier beneficiation studies[6] indicated that some success was obtained in lowering the phosphorus content of iron concentrates produced from Big Seam ores, the conditions required for effective phosphorus removal were not quantified. Mineral identification studies in these earlier research programs failed to identify a significant portion of the phosphorus-bearing component found in the Big Seam ores. A comprehensive study of the occurrence and solubility of phosphorus compounds in several samples of ore from the district and of the solubility of essentially pure phosphate minerals, such as apatite, wavellite, vivianite, etc., was conducted by Hertzog.[7] He found that many mineral and organic acids and various metal salts could be used to solubilize the phosphorus from both the red iron ores and the various species of phosphate minerals studied. However, Hertzog's studies were directed primarily toward obtaining information on the comparative solubilities of the minerals, and the solubilizing action of the reagents. The minimum quantity of reagent required to solubilize the phosphorus in a ton of raw ore or concentrate was not determined.

As a complement to these earlier studies, the Bureau in 1962 initiated an investigation to determine (1) whether the phosphorus-bearing component in these ores could be isolated and identified and (2) the response of the phosphorus to various mineral dressing schemes. Concentration and recovery of the iron values was an adjunctive study, since it was recognized that removal of the phosphorus alone would not suffice to make the ores of the district an important source of the Nation's iron reserves.

ACKNOWLEDGMENT

Appreciation is expressed to these companies for their cooperation in providing samples for this study and for their cooperation in previous studies of Birmingham district iron ores: U.S. Pipe and Foundry Company, Republic

[5] Thoenen, J. R., A. H. Reed, Jr., and B. H. Clemmons. The Future of Birmingham Red Iron Ore, Jefferson County, Ala. BuMines Rept. of Inv. 4988, 1953, p. 13.

[6] Cook, S. R. B. Microscopic Structure and Concentrability of the Important Iron Ores of the United States. BuMines Bull. 391, 1936, 121 pp.

Phillips, W. B. Notes on Magnetization and Concentration of Iron Ores. Trans. AIME, v. 25, 1895, pp. 399-423.

Thoenen, J. R., A. H. Reed, Jr., and B. H. Clemmons. The Future of Birmingham Red Iron Ore, Jefferson County, Ala. BuMines Rept. of Inv. 4988, 1953, pp. 64-71.

[7] Hertzog, E. S. A Study of the Occurrence and Amenability to Leaching of the Phosphorus Compounds in Some Red Iron Ores of Alabama. BuMines Rept. of Inv. 3294, 1935, 9 pp.

Steel, Tennessee Coal and Iron Division of U.S. Steel, and Woodward Company, a division of the Mead Corporation.

SOURCES OF ORE

A suite of calcareous ore samples, representing ore from various mines which had operated within the past 10 years, was chosen as being representative of calcareous ore found in the Big Seam, the major ore horizon mined in the district. The samples were obtained from (1) the Ruffner No. 2 mine of U.S. Pipe and Foundry Company at the northeast end of the district, (2) the Spaulding mine of Republic Steel in the center of the district, (3) the Ishkooda mine of the Tennessee Coal and Iron Division of U.S. Steel, also located approximately in the center of the district, and (4) the Pyne mine of Woodward Iron Company at the southwestern end of the district. Locations of those mines are shown in figure 1.

MINERALOGICAL INVESTIGATION OF A TYPICAL ORE

Studies of the suite of samples representing the Big Seam showed that there was little difference in the physical makeup of the samples other than

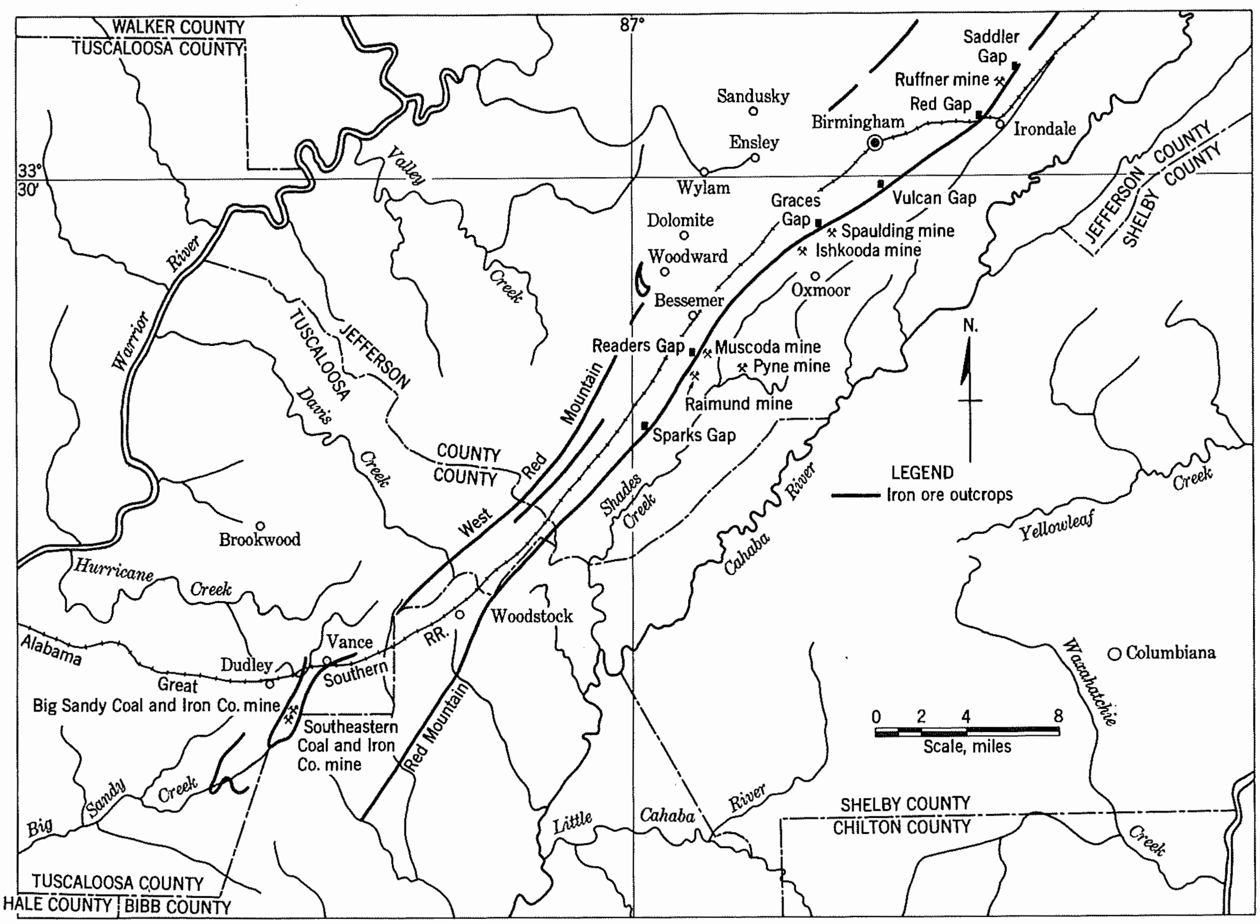

FIGURE 1. - Map of Birmingham district.

the CaO:acid insoluble[8] ratio. Data in table 1 show the results of a sink-float separation made on one of the samples. In this case the sample was wet ground to pass 150 mesh and deslimed by sedimentation techniques at 5 microns. The plus 5-micron fraction was sink-float separated at specific gravities of 2.94, 3.30, and 4.20 using tetrabromoethane, methylene iodide, and thallium malonate-formate, respectively, as the separating medium.

TABLE 1. - Sink-float studies of a typical calcareous ore ground to pass 150 mesh

Product	Weight-percent	Analysis, percent					Distribution, percent				
		Fe	SiO_2	Al_2O_3	CaO	P	Fe	SiO_2	Al_2O_3	CaO	P
Float 2.94...........	29.3	3.0	53.0	0.5	22.8	0.14	2.3	73.9	6.0	58.6	11.4
Sink 2.94, float 3.30	8.3	19.0	15.1	2.7	26.9	1.37	4.3	5.9	9.2	19.6	31.7
Sink 3.30, float 4.20	9.6	37.7	11.7	4.6	12.9	1.07	9.8	5.3	18.1	10.9	28.6
Sink 4.20............	34.2	61.2	4.9	2.8	1.0	.19	56.7	8.0	39.3	3.0	18.0
Composite plus 5-micron............	81.4	33.2	24.0	2.2	12.9	.40	73.1	93.1	72.6	92.0	89.7
Composite minus 5-micron............	18.6	53.4	7.8	3.6	4.9	.20	26.9	6.9	27.4	8.0	10.3
Composite total ore.	100.0	36.9	21.0	2.4	11.4	.36	100.0	100.0	100.0	100.0	100.0

Data in table 1 show that 60.3 percent of the total phosphorus in the ore was isolated into two specific gravity fractions representing approximately 18 percent by weight of the ore. Petrographic analysis of the sink 2.94, float 3.30 fraction showed the presence of collophanite, a hydrated calcium phosphate. Petrographic analysis of the sink 3.30, float 4.20 fraction indicated that if collophanite were present it was too badly stained to be recognized. No other phosphate mineral was identifiable by petrographic means.

A combination of more elaborate magnetic and heavy-liquid separation techniques were used to isolate high phosphorus fractions. Data in table 2 present the results of these studies.

TABLE 2. - Phosphorus analyses of concentrates isolated from Big Seam ores

Mine	Percent, phosphorus		Mineral identification
	Analysis	Distribution	(petrographic analysis)
Ruffner............	5.16	3.4	Collophanite
Spaulding..........	15.04	2.1	do.
Ishkooda...........	9.70	8.6	do.
Pyne...............	9.13	.6	do.

The studies showed that only minor amounts of the phosphorus could be isolated as petrographically identifiable phosphorus-bearing compounds; however, collophanite was identified in each of the samples.

PHOSPHORUS REMOVAL STUDIES

Flotation Studies

Although data in table 1 had indicated that little success could be anticipated using physical methods for reducing the phosphorus content of the calcareous ores of

[8] "Acid insoluble" and/or "Insol" as used in this paper is hydrochloric acid insoluble.

the district, a number of flotation tests were made to confirm this conclusion. Test variables included size of grind, quantity and type of collectors and depressants, pH and type of pH modifiers, percent solids, and pulp temperature.

Under the trial conditions, several flotation conditions indicated that a substantial reduction of the phosphorus was obtained in the primary iron concentrate. However, when the iron middlings, lost in rougher flotation, were added to the primary concentrate it was found that, in all cases, the percent phosphorus in the iron concentrate varied directly with iron recovery. From these results it was concluded that flotation was not a promising method for removing the phosphorus without sustaining excessive loss of the iron values.

Reduction Roasting and Magnetic Separation

Early studies[9] of reduction roasting and magnetic separation of numerous ore samples from the Birmingham iron district showed phosphorus rejections of 29 to 49 percent. Most of the tests shown in this study were conducted on samples ground to pass 100 mesh; however, one test series showed the effect of grinding one of the samples to as fine as 300 mesh. Unfortunately, phosphorus analyses in this test series were not discussed. In this part of the present study the effect of extremely fine grinding on phosphorus rejection from reduced ore was studied initially.

A sample of Big Seam calcareous iron ore was reduced to magnetite using natural gas at 700° C as the reductant in an externally fired rotary drum. After cooling, the reduced ore was stage ground in a rod mill to pass 400 mesh. Sink-float and magnetic separations, using a Davis tube magnetic separator,[10] were performed on this sample to determine if the reduction step had any effect upon liberation of the phosphorus. No nonmagnetic product was obtained when treating the sink 4.10 specific gravity fraction. Data in table 3 giving the results of this study show that neither reduction roasting nor magnetic separation of the reduced ore ground to minus 400 mesh effectively increased the phosphorus liberation and rejection from the iron concentrate.

An additional test was made to determine the effect of grinding much finer than 400 mesh. In this case the reduced ore was ground to a product containing less than 13 percent, by weight, of material coarser than 20 microns. Magnetic separation of this material yielded a concentrate with improved phosphorus rejection but recovery of iron was significantly reduced. This magnetic concentrate analyzed 61.1 percent Fe, 8.3 percent insol, 3.0 percent CaO, and 0.19 percent P.

Data from the reduction roasting and magnetic separation studies indicated that some additional treatment such as acid leaching would be required for more effective reduction of the phosphorus content.

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[9] Lee, Oscar, B. W. Gandrud, and F. D. DeVaney. Magnetic Concentration of Iron Ores of Alabama. BuMines Bull. 278, 1927, 75 pp.

[10] Reference to a trade name is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 3. - Sink-float and magnetic separation studies of reduced ore ground to pass 400 mesh

Specific gravity	Magnetic separation product	Weight-percent	Analysis, percent				Distribution, percent			
			Fe	Insol	CaO	P	Fe	Insol	CaO	P
Float 2.94......................	Nonmagnetic	17.2	2.9	32.5	34.4	0.09	1.4	34.2	37.3	4.8
	Magnetic	6.0	17.6	33.0	21.3	.24	2.9	12.1	8.0	4.5
Composite float 2.94............	-	23.2	6.7	32.6	31.0	.13	4.3	46.3	45.3	9.3
Sink 2.94, float 3.30...........	Nonmagnetic	13.4	5.3	23.1	36.2	.47	1.9	18.9	30.6	20.1
	Magnetic	18.3	39.9	15.2	13.1	.72	20.0	17.0	15.1	42.2
Composite sink 2.94, float 3.30..	-	31.7	25.3	18.5	22.9	.62	21.9	35.9	45.7	62.3
Sink 3.30, float 4.10...........	Nonmagnetic	1.5	10.4	20.4	33.0	.59	.4	1.9	3.1	2.9
	Magnetic	4.1	47.4	11.5	9.2	.81	5.3	2.9	2.4	10.5
Composite sink 3.30, float 4.10..	-	5.6	37.5	13.9	15.7	.75	5.7	4.8	5.5	13.4
Sink 4.10.......................	-	39.5	63.0	5.4	1.4	.12	68.1	13.0	3.5	15.0
Composite.......................	-	100.0	36.6	16.4	15.9	.31	100.0	100.0	100.0	100.0
Composite sink 4.10 plus magnetic fractions.........................		67.9	51.8	10.8	6.8	.33	96.3	45.0	29.0	72.2

Production of Magnetic Concentrates by Magnetic Flocculation

In the course of sizing studies of ground, reduced ore it was found that magnetic flocculation could be used to produce concentrates equivalent in iron grade and recovery to those produced by magnetic separation techniques. For example, data in table 4 compare the results of sizing reduced ore pulps which had been ground for 25 minutes in a rod mill with dispersing agents. After preliminary sizing at 20 microns the plus 20 micron fractions were reground an additional 25 minutes, to pass 400 mesh, and resized at 20 microns. In one case the reduced ore pulp was not subjected to a magnetic field, and in the other case, a small hand magnet was used to magnetize the ore pulp prior to sizing. For comparison, the results of stage grinding the reduced ore to pass 400 mesh and recovering the magnetite in a Davis tube magnetic separator (composite concentrate, table 3) are also shown in the table.

TABLE 4. - Results of treating reduced ore by grinding, sizing, magnetic flocculation and magnetic separation

	Dispersed pulp	Magnetic flocculation	Magnetic separation[1]
FIRST GRIND (25 MINUTES)			
Minus 20 micron:			
Weight, percent	38.6	22.3	-
Analysis, percent:			
Fe	24.4	4.3	-
Insol	17.3	20.5	-
CaO	25.7	39.1	-
P	.32	.31	-
SECOND GRIND (25 MINUTES)			
Minus 20 micron:			
Weight, percent	24.5	9.6	-
Analysis, percent:			
Fe	33.3	6.1	-
Insol	19.7	29.6	-
CaO	16.7	31.0	-
P	.37	.34	-
Minus 400 mesh, plus 20 micron:			
Weight, percent	36.9	68.1	67.9
Analysis, percent:			
Fe	49.5	51.4	51.8
Insol	13.2	11.8	10.8
CaO	8.9	7.2	6.8
P	.32	.35	.33
Distribution, percent:			
Fe	51.0	95.8	96.3
Insol	29.7	52.0	45.0
CaO	19.0	29.5	29.0
P	35.5	70.3	72.2

[1]Composite magnetic concentrate from table 3.

As a result of these studies magnetic flocculation was used as a simplified magnetic separation method to prepare several pounds of concentrate for acid leaching studies. However, in this case, three 25-minute grinds were used in a similar treatment to that described. The dispersed minus 20-micron slimes were combined and the composited results of this test are shown in table 5.

TABLE 5. - Results of preparing magnetically flocculated concentrate for acid leaching studies

Product	Weight-percent	Analysis, percent					Distribution, percent				
		Fe	Fe(+2)	Insol	CaO	P	Fe	Fe(+2)	Insol	CaO	P
Magnetic...	62.0	55.3	20.9	9.7	4.5	0.30	95.8	95.2	37.8	18.2	62.0
Nonmagnetic	38.0	4.0	1.7	26.0	33.1	.30	4.2	4.8	62.2	81.8	38.0
Composite	100.0	35.8	13.6	15.9	15.4	.30	100.0	100.0	100.0	100.0	100.0

A Davis tube magnetic separation test of the magnetic product of table 5 failed to improve materially the grade of iron concentrate or the phosphorus rejection.

Acid Leaching of Magnetic Concentrate

Acid leaching studies made of the concentrate shown in table 5 indicated that effective reduction of phosphorus was achieved, but large quantities of acid were required. Leach tests were made using chemically pure hydrochloric acid, sulfuric acid, and nitric acid as the leaching agents. Leaching tests were conducted on 10-gram samples at 33 percent solids with a reaction time of 3 minutes. Preliminary tests had shown that a reaction time of 3 minutes was as effective as 10 or 30 minutes. No effort was made to control or record the reaction temperature. A standard laboratory bottle shaker was utilized to agitate the sample vigorously during reaction.

Data in tables 6, 7, and 8 present the results of the leaching studies when using 1, 2, and 3 times the stoichiometric requirements of HCl, H_2SO_4 and HNO_3 to react with CaO content of the magnetically flocculated concentrate. After leaching, the samples were filtered and washed to remove soluble salts and the washed residue was dried and weighed. A sample of the leached residue was reserved for analysis and the remainder of the sample was repulped for magnetic separation studies using the Davis tube separator. These magnetic separation studies of the leach residues were made to determine if leaching would effectively release additional insoluble material for rejection by magnetic separation.

Data in tables 6, 7, and 8 show that the acid requirements for effective reduction of the phosphorus content were more than the stoichiometric requirement for the CaO reaction. The data show that essentially all of the CaO must be solubilized before the acids will react with the phosphorus-bearing compound. Although results in table 7, showing the effect of H_2SO_4 leaching, might tend to contradict this statement, the CaO remaining in these leach residues resulted from the formation of insoluble Ca sulfate, most of which was removed by the magnetic separation step.

TABLE 6. - Effect of leaching with hydrochloric acid and magnetic separation of the leached material

HCl (pounds per ton).....	Heads	304		608		912	
Treatment................	[1]1	[2]2	[3]3	2	3	2	3
Weight, percent[4].........	62.0	57.7	52.5	53.9	48.8	52.2	47.5
Analysis, percent:							
Fe.....................	55.3	58.4	60.8	59.6	62.6	59.6	62.5
Fe^{+2}..................	20.9	18.5	21.1	17.7	18.9	16.9	18.0
Insol..................	9.7	9.7	7.0	9.7	6.7	9.9	6.6
CaO....................	4.5	1.5	1.1	.4	.3	.2	.2
P......................	.30	.31	.26	.11	.06	.06	.04
Fe(S.F.)...............	50.6	51.0	55.0	51.1	56.2	50.8	56.1
P:Fe...................	.0054	.0053	.0043	.0018	.0010	.0010	.0006
Distribution, percent:[5]							
Fe.....................	95.8	94.1	89.2	89.7	85.3	86.9	82.9
Fe^{+2}..................	95.2	78.5	81.5	70.1	67.8	64.9	62.9
Insol..................	37.8	35.2	23.1	32.9	20.6	32.5	19.7
CaO....................	18.2	5.6	3.8	1.4	1.0	.7	.6
P......................	62.0	59.6	45.5	19.8	9.8	10.4	6.3

[1]Magnetic flocculation and desliming.
[2]Acid leaching and filtering of magnetically flocculated concentrate.
[3]Acid leaching and magnetic separation of magnetically flocculated concentrate.

[4]$$\mathrm{Fe(S.F.)} = \frac{100\ (\mathrm{Fe,\ pct})}{100 + 1.78\ (\mathrm{insol,\ pct} - \mathrm{CaO,\ pct})}$$

[5]Based on total ore.

TABLE 7. - Effect of leaching with sulfuric acid and magnetic separation of the leached material

H_2SO_4 (pounds per ton)...	Heads	165		330		495	
Treatment................	[1]1	[2]2	[3]3	2	3	2	3
Weight, percent[4].........	62.0	59.9	52.9	59.3	51.3	59.0	51.7
Analysis, percent:							
Fe.....................	55.3	56.4	61.4	56.1	62.6	55.5	62.3
Fe^{+2}..................	20.9	17.6	21.3	16.3	20.4	15.0	19.1
Insol..................	9.7	8.9	6.9	9.0	6.8	8.9	6.9
CaO....................	4.5	2.8	.9	2.9	.3	3.2	.2
P......................	.30	.30	.26	.08	.06	.05	.06
S......................	([5])	1.04	.04	1.38	.04	1.61	.04
Fe(S.F.)...............	50.6	50.9	55.5	50.6	56.1	50.4	55.6
P:Fe...................	.0054	.0053	.0042	.0014	.0010	.0009	.0010
Distribution, percent:[4]							
Fe.....................	95.8	94.4	90.7	92.9	89.7	91.5	90.0
Fe^{+2}..................	95.2	77.5	82.9	71.1	77.0	65.7	72.6
Insol..................	37.8	33.5	23.0	33.6	21.9	33.0	22.4
CaO....................	18.2	10.9	3.1	11.2	1.0	12.3	.7
P......................	62.0	59.9	45.8	15.8	10.3	9.8	10.3

[1]Magnetic flocculation and desliming.
[2]Acid leaching and filtering of magnetically flocculated concentrate.
[3]Acid leaching and magnetic separation of magnetically flocculated concentrate.
[4]Based on total ore.
[5]Not analyzed.

TABLE 8. - Effect of leaching with nitric acid and magnetic separation of the leached material

HNO_3 (pounds per ton)...	Heads	288		576		864	
Treatment................	[1]1	[2]2	[3]3	2	3	2	3
Weight, percent[4].........	62.0	57.5	53.8	55.9	51.9	55.7	52.9
Analysis, percent:							
Fe.....................	55.3	59.3	61.6	60.0	62.6	60.0	62.2
Fe^{+2}..................	20.9	20.5	21.7	19.5	21.5	19.0	20.6
Insol..................	9.7	9.4	7.1	9.6	6.9	9.4	7.1
CaO....................	4.5	1.0	.9	.4	.4	.3	.3
P......................	.30	.32	.25	.07	.05	.06	.05
Fe(S.F.)...............	50.6	51.6	55.4	51.5	56.1	51.6	55.5
P:Fe...................	.0054	.0054	.0041	.0012	.0008	.0010	.0008
Distribution, percent:[4]							
Fe.....................	95.8	95.2	92.6	93.7	90.8	93.4	91.9
Fe^{+2}..................	95.2	86.7	85.8	80.2	82.0	77.8	80.1
Insol..................	37.8	34.0	24.0	33.8	22.5	32.9	23.6
CaO....................	18.2	3.7	3.1	1.5	1.3	1.1	1.0
P......................	62.0	61.3	44.8	13.0	8.7	11.1	8.8

[1]Magnetic flocculation and desliming.
[2]Acid leaching and filtering of magnetically flocculated concentrate.
[3]Acid leaching and magnetic separation of magnetically flocculated concentrate.
[4]Based on total ore.

These data also indicate a substantial improvement in the concentrate iron grade with acid leaching alone. However, magnetic separation of the residues was necessary for the self-fluxing iron content of the concentrates to be notably improved. The data show that the iron content of the leached concentrate increased as the CaO content was reduced; however, the fact that the acid insoluble did not increase, similarly, as the CaO content was reduced could not be explained.

Since these results showed that substantial acid consumption was necessary for effective phosphorus removal, modifications to leaching, such as reoxidizing the magnetic concentrates prior to leaching, were investigated.

Leaching of Magnetic Concentrates After Reoxidation

Several hundred grams of the magnetically flocculated concentrate product were reoxidized in the externally fired rotary drum used for the reduction of the ore. The sample was brought to 950° C under an air sweep and held at this temperature for 15 minutes. Results of the leaching studies on the oxidized concentrate at acid concentrations in the range used on the reduced concentrate product showed that, while excellent phosphorus extractions were obtained, iron losses were high. As a consequence, studies of low acid concentrations were initiated.

Results of leaching studies of the reoxidized concentrate, which contained 0.31 percent P, with low acid concentrations are shown in table 9. Leaching conditions in this case were the same as those used on the reduced concentrate, that is, 3 minutes contact time, ambient temperature, and 33 percent solids.

Data in table 9 show that acid leaching of the magnetically flocculated concentrate after reoxidation effectively reduced the phosphorus content of the iron concentrate with much lower acid concentrations than were required for the reduced material.

TABLE 9. - Results of leaching reoxidized magnetically flocculated concentrate with HCl, H_2SO_4, and HNO_3

Type acid	Pounds per ton[1]	Leach residue weight, percent	Analysis-percent, P	Extraction-percent, P
Leach feed......	-	100.0	0.31	-
HCl.............	25	98.7	.26	17.2
Do............	50	97.6	.14	55.9
Do............	75	96.8	.06	81.3
Do............	100	96.5	.03	90.7
H_2SO_4...........	25	99.0	.29	7.4
Do............	50	98.4	.25	20.6
Do............	75	97.4	.19	40.1
Do............	100	97.1	.13	59.3
HNO_3............	25	99.1	.29	7.3
Do............	50	98.5	.25	20.6
Do............	75	97.8	.17	46.4
Do............	100	97.3	.11	65.5

[1]Pounds per ton, based on concentrate.

A series of tests was made to determine the minimum reoxidation temperature at which the phosphorus could be extracted at low acid concentrations. Hydrochloric acid was used in this series of tests since the data in table 9 indicated that it was the most effective of the three acids in reducing the phosphorus content. In these tests the magnetically flocculated concentrate was reoxidized in the rotary drum at temperatures of 700°, 800°, 900°, and 1,000° C. An air sweep of the drum was used in each case and the samples were held at these temperatures for 1 hour. Data in table 10 show the effect of leaching the reoxidized samples.

Data in table 10 also show that phosphorus extraction was directly related to both acid concentration and reoxidation temperature. CaO extraction was directly related to acid concentration through 800° C and inversely related to reoxidation temperature. The relationship of the CaO to acid concentration above 800° C was not clearly understood; however, it appeared that the CaO formed an insoluble compound as the temperature increased. The solubility of the iron was negligible in all cases, for example, 0.7 percent extraction of the iron was the highest recorded. Attempts to study extraction at a reoxidation temperature of 1,100° C failed as slagging occurred. Magnetic separation of the samples, as had been used to reduce the insoluble content of the leached reduced material, was not possible in this case since the iron was reoxidized to the nonmagnetic ferric state.

TABLE 10. - Effect of reoxidation temperature on extraction of CaO and P using HCl as leaching agent

Reoxidation temperature, ° C	HCl, lb/ton[1]	Leach residue weight, percent	Analysis, percent		Extraction, percent	
			CaO	P	CaO	P
Leach feed.....	-	-	5.4	0.33	-	-
700..........	50	97.9	3.3	.34	40.5	0
700..........	100	95.7	2.3	.26	59.2	24.6
700..........	150	94.0	1.3	.08	77.4	77.2
700..........	200	93.3	.9	.06	84.4	83.0
Leach feed.....	-	-	5.1	.34	-	-
800..........	50	97.3	3.8	.31	27.5	11.3
800..........	100	95.2	2.8	.14	47.7	60.8
800..........	150	94.1	2.3	.05	57.6	86.2
800..........	200	93.5	1.8	.04	67.0	89.0
Leach feed.....	-	-	5.1	.34	-	-
900..........	50	98.6	3.7	.20	28.5	42.0
900..........	100	95.5	3.0	.03	43.8	91.6
900..........	150	95.3	2.9	.03	45.8	91.6
900..........	200	95.2	2.9	.02	45.9	94.4
Leach feed.....	-	-	5.0	.32	-	-
1,000........	50	97.6	3.7	.12	27.8	63.4
1,000........	100	96.7	3.2	.03	38.1	90.9
1,000........	150	96.6	3.2	.02	38.2	94.0
1,000........	200	96.6	3.4	.02	34.3	94.0

[1] Pounds per ton, based on concentrate.

Leaching of Magnetic Concentrates Reoxidized in the Presence of $CaCl_2 \cdot 2H_2O$

At the time this study was being made, a fellowship research study,[11] which resulted in a patentable[12] process, was being conducted at the Tuscaloosa Metallurgy Research Laboratory on the use of calcium chloride and other compounds as aids in effectively reducing the phosphorus content of brown iron ores.

On the basis of the results from this fellowship research, a series of tests was made to determine the effect of using $CaCl_2$ in the reoxidation step on the calcareous red ores. The reduced concentrate was prepared by grinding, magnetic flocculation and magnetic separation of the magnetically flocculated concentrate. This magnetic concentrate represented a weight recovery of 61.4 percent and contained 53.8 percent Fe, 9.9 percent insoluble, 6.5 percent CaO, and 0.34 percent P. Iron recovery was 93.8 percent; and insoluble, CaO, and P rejections were 62.9, 76.4, and 32.7 percent, respectively. Samples of this concentrate with and without a 10-percent addition of $CaCl_2 \cdot 2H_2O$ were reoxidized at 1,000° C for 1 hour in the rotary drum, using an air sweep. The

[11] Lampkin, W. M. Removal of Phosphorus From a South Alabama Brown Iron Ore Concentrate by Pyro-Hydrometallurgical Techniques. University of Alabama, 1965, 70 pp.

[12] Feld, I. L., Thomas W. Franklin, and W. M. Lampkin. Process for Removing Phosphorus From Iron Ores. U.S. Patent 3,402,041, Sept. 17, 1968.

material reoxidized in the presence of $CaCl_2 \cdot 2H_2O$ was hygroscopic after cooling and picked up moisture readily. Data in table 11 show comparative analyses of the reoxidized samples. Also included in this table is an analysis of the sample oxidized in the presence of $CaCl_2 \cdot 2H_2O$ and then washed with water to remove the soluble hygroscopic material.

TABLE 11. - Analyses of samples reoxidized at 1,000° C with and without 10 percent $CaCl_2 \cdot 2H_2O$

$CaCl_2 \cdot 2H_2O$	Analysis, percent				
	Fe	Insol	CaO	P	Loss on ignition (110° C)
None............	54.4	10.3	6.1	0.35	0
10 pct..........	46.3	8.3	9.7	.31	3.4
10 pct, washed..	54.4	9.5	7.6	.35	0

Leaching tests of the two reoxidized samples using HCl and a contact time of 3 minutes at ambient temperature gave the results shown in table 12. The approximate 10 to 12 percent difference in weight recovery between the samples was a result of the soluble hygroscopic material being removed as was indicated in table 11.

TABLE 12. - Comparison of leaching results on samples reoxidized with and without 10 percent $CaCl_2 \cdot 2H_2O$

HCl, lb/ton	Leach residue weight, percent	Analysis, percent				Extraction, percent			
		Fe	Insol	CaO	P	Fe	Insol	CaO	P
REOXIDIZED (no $CaCl_2 \cdot 2H_2O$)									
Leach feed....	100.0	54.4	10.3	6.1	0.35	-	-	-	-
50.........	96.9	55.6	10.2	5.0	.19	1.0	4.0	20.6	47.4
100.........	95.7	56.6	10.2	4.1	.07	.4	5.2	35.7	80.8
200.........	95.1	56.8	10.1	4.1	.04	.7	6.7	36.1	89.1
REOXIDIZED (10 percent $CaCl_2 \cdot 2H_2O$) NOT WASHED									
Leach feed....	100.0	46.3	8.3	9.7	0.31	-	-	-	-
50.........	85.1	55.0	9.9	7.1	.05	0	0	37.7	86.3
100.........	84.8	55.2	9.7	7.3	.03	0	.9	36.2	91.8
200.........	83.5	55.2	9.7	7.1	.03	.4	2.4	38.9	91.9

Data in table 12 show that the use of $CaCl_2 \cdot 2H_2O$ in the reoxidizing step was an effective method of reducing the acid requirements for phosphorus extraction. As a result of these initial studies additional tests were conducted to determine the minimum requirement of $CaCl_2 \cdot 2H_2O$ in the oxidizing step, to quantify the HCl requirements at the minimum $CaCl_2 \cdot 2H_2O$, and to investigate the effect of concentrate particle size on the acid requirement.

Studies of three different sized magnetic concentrates were made. Concentrate Number 1 had a size consist of 1.8 percent by weight of plus 200-mesh material, 43.0 percent by weight of 200 to 400 mesh, and 55.2 percent by weight of minus 400 mesh. Concentrate Number 2 was prepared by ball mill grinding a portion of concentrate Number 1 for an additional 25 minutes to yield a minus 400-mesh product, which was magnetically separated in a Davis tube separator. Concentrate Number 3, also a portion of concentrate Number 1, was ball mill ground for 75 minutes and magnetically separated in a Davis tube separator.

Samples of each of the three concentrates were mixed with the equivalent of 6, 15, 30, 60, and 120 pounds of $CaCl_2 \cdot 2H_2O$ per ton of leach feed and reoxidized at 1,000° C for 1 hour in the rotary drum using an air sweep. For control purposes a sample from each concentrate was also reoxidized without any $CaCl_2 \cdot 2H_2O$. After oxidation the samples were thoroughly mixed, and leaching studies were initiated using 12.5, 25, and 50 pounds of HCl per ton of leach feed. Results of these studies are presented graphically in figure 2.

KEY

Analysis, pct

	Fe	Insol	CaO	P	Fe(S.F.)
○ Concentrate No. 1	54.2	10.0	6.3	0.35	50.8
△ Concentrate No. 2	55.5	10.0	4.9	0.32	50.9
□ Concentrate No. 3	57.4	9.2	3.8	0.30	52.4

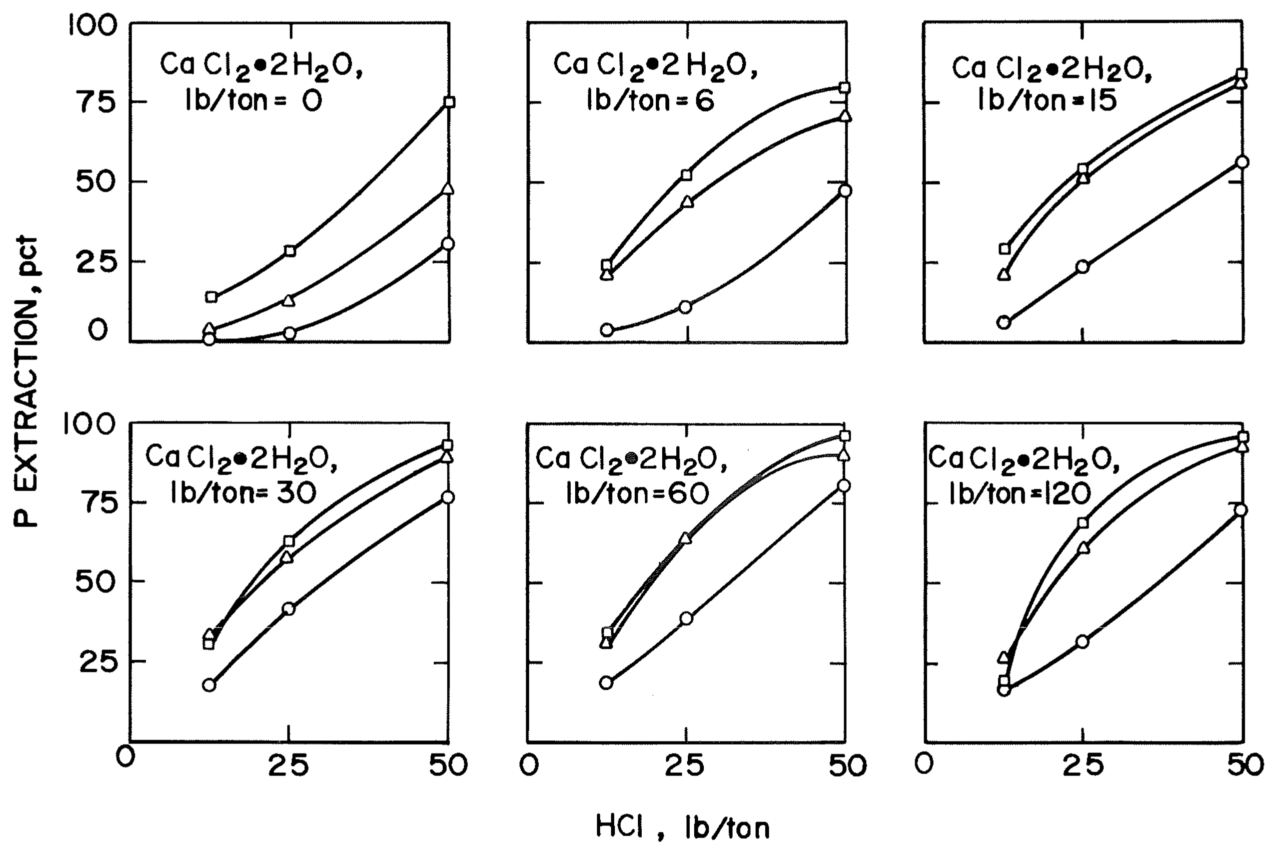

FIGURE 2. - Effect of $CaCl_2 \cdot 2H_2O$ used in reoxidation and hydrochloric acid for leaching on phosphorus extraction.

Phosphorus extraction data were based on leaching of the concentrates and do not refer to total ore basis.

Data in figure 2 show that phosphorus extraction was primarily a function of the quantity of acid used. However, the use of up to about 30 pounds $CaCl_2 \cdot 2H_2O$ per ton of leach feed effectively improved phosphorus extraction at all acid concentrations. The use of more than 30 pounds $CaCl_2 \cdot 2H_2O$ per ton of leach feed did not show any substantial improvement in phosphorus extraction. The effect of size of grind on phosphorus extraction was inconclusive since the finer sized concentrates contained less CaO and P; however, there does appear to be substantially greater phosphorus extraction between the concentrate containing approximately 50 percent plus 400-mesh material (concentrate Number 1) and concentrate Number 2 which was ground to pass 400 mesh.

Data in table 13 show the results of reoxidizing the three concentrates with 30 pounds $CaCl_2 \cdot 2H_2O$ and leaching with 50 pounds HCl per ton.

TABLE 13. - Results of reoxidation studies using 30 pounds $CaCl_2 \cdot 2H_2O$ and leaching with 50 pounds HCl per ton

Concentrate number	Pounds per ton		Weight[1] recovery, percent	Analysis, percent			Distribution, percent	
	$CaCl_2 \cdot 2H_2O$	HCl		Fe	Fe(S.F.)	P	Fe	P
1	30	50	57.8	56.3	52.1	0.09	92.4	16.8
2	30	50	58.0	57.1	51.3	.03	94.1	5.6
3	30	50	54.3	58.1	53.7	.02	89.6	3.5

[1] Based on total ore.

Results of these studies demonstrated that best phosphorus extraction from magnetic concentrates was obtained when $CaCl_2 \cdot 2H_2O$ was used as an additive during reoxidation and HCl was used for leaching.

CONCLUSIONS

Numerous flotation studies and reduction roasting followed by fine grinding and magnetic separation studies showed that phosphorus rejection by these methods was not technically feasible without sustaining high iron losses.

Reduction roasting followed by fine grinding, magnetic separation or magnetic flocculation, acid leaching, and secondary magnetic separation yielded iron concentrates containing 62 percent Fe and 0.04 percent phosphorus, with iron recoveries of 82 to 90 percent and phosphorus extraction of 90 to 93 percent; however, acid requirements were high.

Reduction roasting followed by fine grinding, magnetic separation or magnetic flocculation, reoxidation of the magnetic concentrates, either with or without $CaCl_2 \cdot 2H_2O$ as an additive, gave the most effective phosphorus extractions with high recovery of the iron values. Concentrates containing 57 to 58 percent Fe and 0.03 percent P with iron recoveries of 90 to 94 percent and phosphorus extractions of about 95 percent were obtained when using 30 pounds $CaCl_2 \cdot 2H_2O$ per ton of concentrate in the reoxidation step and 50 pounds HCl per ton of concentrate as the leaching agent.

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