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THE MINERAL ASSOCIATION IN MANGANESE ORES, WITH

PARTICULAR REFERENCE TO THE PHOSPHORUS-BEARING

MINERALS AND THEIR REMOVAL BY LEACHING METHODS.

By

DANIEL CHALMERS MCLEAN

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

MASTER OF SCIENCE - CHEMICAL ENGINEERING MAJOR

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1941

Approved by _W.T.Schrenk_

Head of the Department of

Chemical Engineering and Chemistry

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iii

CONTENTS

Page

Introduction 1

Domestic Manganese Situation 1

Part I - Mineralogical Investigations 6

Preliminary Work.. 6

Mineralogical Association of the Arkansas Wad Ores 11

Part II - Leaching of Arkansas Wad Ores 21

Preliminary Work.. 21

Batch Leaching 32

Single Batch Leaching............................... 32

Multiple Contact Batch Leaching 34

Counter-current Leaching 35

Miscellaneous Leaching Tests............................ 46

Acid Consumption Tests 46

Wash Tests 46

Hot Leaches 50

Summary of Leaching Data 53

Part III - Volatilization of Phosphorus 66

Conclusions 72

LIST OF TABLES

LIST OF TABLES

LIST OF TABLES

LIST OF GRAPHS

LIST OF DIAGRAMS

INTRODUCTION

The investigation of the phosphate minerals to be described in this paper has for its basic incentive one simple yet highly important fact--manganese is absolutely essential in the production of steel. It is fitting, then, that the sources and economics of this invaluable element be briefly discussed as introduction to this thesis problem.

The Domestic Manganese Situation

Manganese at the present time is the most important strategic metal, not because the United States is lacking in deposits containing this metal, but because the vast resources of manganese ore scattered throughout this country have never been developed. A survey of the literature conducted by the Bureau of Mines in 1934[1] showed that manganese ore bodies occur in about 300 districts scattered throughout 35 states. The manganese content of these ores ranges from 1 per cent to 48 per cent, while the size of the deposits varies from a few hundred tons to several million tons. Recent investigations completed by the United States Geological Survey have disclosed the presence of new reserves of several million tons of ore, so that the United States has sufficient manganese ore to supply her needs for many years if steps are taken immediately to develop these numerous deposits.

The great steel industries in this country each year consume about

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(1) Dean, R. S., DeVaney, F. D., and Coghill, W. H., "Manganese, Its Occurrence, Milling, and Metallurgy", Part I, U. S. Bureau of Mines Information Circular 6768, 34 (1934).

600,000 tons of ferro-grade manganese ore,[2] yet despite the tremendous manganese ore reserves located within our very midst, 95 per cent of this ore is imported from such distant places as Russia, India, South Africa, Brazil, and the Philippine Islands. The answer to this strange state of affairs involves the inevitable economics angle—these foreign countries possess richer ores which can be mined with cheap labor, shipped to this country and sold at prices with which the domestic producer is unable to compete. Several attempts have been made by domestic manganese producers in the last decade to have a sufficiently high protective tariff placed upon manganese ores so that domestic producers could operate at a profit, thus stimulating domestic production. Several embarrassing questions could be asked concerning the final official replies made to each one of these petitions, but political juggling is beyond the scope of this paper. The situation as it now stands is: the protective tariff is lower than it has ever been, and domestic producers of manganese have been accused of being unpatriotic.

Since the outbreak of European hostilities, the manganese question has assumed an entirely different aspect. It is becoming increasingly difficult to obtain foreign ores because of the acute shortage of shipping vessels, and as a natural consequence, prices have soared. The National Defense Committee anticipated this situation, and on June 7, 1939, was authorized by a vote of Congress to spend $100,000,000 over a four-year period for the purchase of strategic materials, of

(2) Ridgeway, R. H. and Davis, H. W., "Manganese and Manganiferous Ores", Minerals Yearbook (1940), p. 571-590.

which manganese ore is required in the largest quantities.[3]   Only
high-grade ore suitable for the manufacture of ferromanganese was
designated as strategic, and the following specifications were made for
three grades of this material:

| | Percentage Composition | | |
	Grade A	Grade B	Grade C
Manganese (minimum)	48	48	48
Iron (maximum)	7	7	7
Silica (maximum)	9	10	7
Phosphorus (maximum)	00.12	0.18	0.15
Alumina (maximum)	3	6	6
Zinc (maximum)	1	1	1

All ore to pass a 6-inch screen and not more than $12\frac{1}{2}$ per
cent to pass thru a 20-mesh screen.

In order to build up stock piles, bids have been awarded at prices
ranging from 45 to 75 cents per unit (a unit is 22.4 pounds of contained
manganese). Within this price range, domestic ores can be marketed
at a profit, and hence a noticeable stir has taken place in domestic
production.

Domestic producers have two major problems with which to contend.
The first is that all of the ores are low grade and hence must be sub-
jected to beneficiating methods. The second is that most all of them
contain harmful impurities which must be removed, and it is with this
phase of the manganese problem that this thesis is most concerned.

Phosphorus is a particularly obnoxious element in the production
of steel. Its effects are adequately described in the following passage:

"Phosphorus is especially noticeable as making steel

brittle, fragile under shock, and unreliable in ductility.

Phosphorus forms a compound with the iron, FeP. This in

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(3) Ridgeway, R. H. and Davis, H. W., op. cit.

turn forms a series of alloys with iron, having a
fusible eutectic containing 10 per cent phosphorus and
90 per cent iron. This eutectic will form in the steel
to the extent of the amount of phosphorus present; that
is to say, 0.1 per cent of phosphorus will result in 0.1
per cent of eutectic. This eutectic melts at a lower
temperature than the remainder of the steel; it is there-
fore apt to be pasty at rolling temperatures and to de-
crease the rolling qualities somewhat, but not so harmful
as sulfur. The phosphorus eutectic migrates to the grain
boundaries during the freezing of steel and produces very
brittle planes of weakness under shock. The effect of
phosphorus, therefore, shows up more especially under the
shock test. Under ordinary static test, the effect of
phosphorus is uncertain and unreliable. Phosphorus is a
dangerous element in steel and is valuable only because
of the hardness which it produces. .... It is
safe practise to have the phosphorus below 0.06 per cent
as a maximum in all structural steel or steel that is to
be subjected to shock or vibration."[4]

Phosphorus is a common ingredient in most domestic ores in per-
centages considerably higher than the minimum allowed in the government
ferro-grade specifications, and its removal is still an unsolved ore-
dressing problem.

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(4) Stoughton, B. and Butts, A., "Engineering Metallurgy", N. Y.,
     McGraw-Hill, 1926, p. 174-175.

The United States Bureau of Mines Experimental Station at Rolla
has recently been conducting an intensive investigation of the amen-
ability of Arkansas used ores to enrichment by standard ore dressing
methods. These Arkansas ores are low grade with the estimated reserves
running into several million tons. They can be concentrated to meet
all Grade B ferromanganese specifications--with the exception of that
of the phosphorus content, but in all cases the phosphorus is so high
as to make the ore worthless under present conditions.

This condition suggested the problem of trying to discover a
method by which the phosphorus could be eliminated, which in turn
called for a positive identification of the phosphorus-bearing com-
pounds. The thesis as finally adopted chose the following lines of
pursuit:

1. A study of standard known manganese and phosphorus minerals
   was to be made in order to become familiar with their properties.

2. The data obtained from this study was to be applied to the
   study of actual manganese ores, especially those from the
   Batesville District in Arkansas.

3. On the completion of the identification work, if the chemical
   composition and interlocking of the phosphorus-containing
   mineral would permit either a mechanical or chemical separa-
   tion from the manganese minerals, the development of a
   practical method of eliminating the phosphorus would be under-
   taken.

PART I - MINERALOGICAL INVESTIGATIONS

PRELIMINARY WORK

Because of the fact that the available optical equipment had not been in use for several years, much time was consumed in the organizing of a microscopical laboratory so that the first part of the work could be carried out.

The machine for polishing opaque mineral mountings was first re-conditioned and re-wired. Three lead laps were re-surfaced and re-grooved, and one new pitch lap made.

A set of fine abrasives was made, the sizes adopted being -10 microns, -3 microns, and -1 micron. These sized particles were obtained by placing thoroughly agitated water suspension of alumina containing sodium silicate as a dispersing agent in a large settling chamber, and siphoning off the top fraction of the suspended solids after a specific time period had elapsed, the time being determined from Stoke's Law computations.[5]

A set of micro-chemical reagents was made by using Short's "Microscopical Determination of the Ore Minerals" as a guide.[6]

The set of 48 mineralogical index liquids was calibrated and corrected to 0.005 intervals of index of refraction.

Miscellaneous repair work to microscope illuminators, adapters, and the camera was also involved.

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(5) Richards, R. H. and Locke, C. E., "Textbook of Ore Dressing",

N. Y., McGraw-Hill, 3d ed., 1940, p. 133.

(6) Short, M. N., "Microscopic Determination of the Ore Minerals",

U. S. Geological Survey Bulletin 914, 2d ed., 1940, 311p.

Polishing Technique

The technique adopted for polishing the bakelite mountings of the various minerals is outlined as follows:

1. Rough surfacing on a glass plate using 500 carborundum.

2. 15-minute run on a lead lap using 500 alumina, water, and a few drops of light lubricating oil.

3. 20-minute run on a lead lap using -10 micron alumina, water, and a few drops of lubricating oil.

4. 45-minute run on a lead lap using -3 micron alumina with soap solution for a lubricant.

5. Final polish on a pitch lap requiring 2 to 3 hours using -1 micron alumina and soap solution.

In polishing the manganese was ores, it was necessary to impregnate the ore particles with a bakelite varnish in order to keep the soft, porous ore grain constituents securely fixed in the bakelite mountings so they could be sectioned and polished to the high degree necessary for microscopic examination. The varnish was made from the bakelite used for mounting the specimens, namely Bakelite Resinoid BR-0217, mixed with ether and acetone in the following proportions:

        25 gm. Bakelite Resinoid
        100 cc Ether
        100 cc Acetone

The ore grains were placed on a watch glass and covered with the impregnating solution. The glass was set aside until the solution had completely evaporated. This evaporation required about four hours. The glass containing the grains was then placed in a drying oven and heated at $105^{\circ}C$ for 24 hours.

The results obtained from this treatment were very satisfactory--

the ore grains on subsequent polishing retaining their true structure
as well as taking an excellent polish.

Bakelite mountings were made of the following minerals and Arkansas
wad ores:

Apatite	Braunite	Magnetite	Arkansas #5
Phosphate Rock	Pyrolusite	Vivianite	
Neotocite	Psilomelane	Arkansas #1	
Bementite	Mangano-calcite	Arkansas #2	
Manganite	Limonite	Arkansas #3	
Hausmannite	Hematite	Arkansas #4	

Cooke gives an excellent description of the bakelite press and the
polishing machine actually used and the methods of operation.[7]

Once the standard minerals were mounted, considerable time was
spent in studying their optical properties, etch reactions, and specific
micro-chemical tests for different constituents.

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(7) Cooke, S. R. B., "Microscopic Structure and Concentratability of
the Important Iron Ores of the United States", U. S. Bureau of
Mines Bulletin 391, p. 9-22 (1936).

CHEMICAL COMPOSITION AND SOME PHYSICAL PROPERTIES OF MORE COMMON MANGANESE MINERALS

Mineral	Composition	Assay, per cent Mn	Specific gravity	Hardness	Color	Structure
Pyrolusite...	MnO_2	60 to 63	4.73 to 4.86	2 to 2.5	Steel-gray or iron-black	Radiating columnar but generally granular massive
Psilomelane..	$4 MnO_2$ Mn, Ba, K, O.nH_2	45 to 60	3.7 to 4.7	5 to 6	Steel-blue to black	Massive, stalactitic, botryoidal.
Manganite	$Mn_2O_3(H_2O)$	62.4	4.2 to 4.4	4	Steel-gray or iron-black.	Usually in radiating crystals.
Hausmannite...	Mn_3O_4	72.1	4.73 to 4.86	5 to 5.5	Black to brownish black	Generally crystalline.
Wad....	Hydrous mixture of oxides	Variable	3 to 4.3	1 to 6	Black or brown	Amorphous or nodular
Rhodochrosite	$MnCO_3$	47.8	3.45 to 3.6	3.5 to 4	Light to dark rose	Usually cleavable; massive to granular.
Rhodonite	$MnSiO_3$	41.9	3.4 to 3.68	5.5 to 6.5	Rose	Commonly massive, cleavable to compact in imbedded grains.
Braunite	$3Mn_2O_3$. $MnSiO_3$	60 to 69	4.75 to 4.82	6 to 6.5	Black or brownish black	Commonly in euhedral crystals, granular.
Bementite	$8MnO.7SiO_2$ 5 H_2O	31.0	3.1	6	Light gray or grayish brown	Fine grained aggregate of plates or fibers.

SOME PROPERTIES OF THE COMMON PHOSPHATE MINERALS

Mineral Name and Formula	Specific Gravity	Hard-ness	Color	Refractive Index			
				n			
Collphanite $CaO, P_2O_5, H_2O, CO_2,$ etc.	2.6-2.94	3 - 5	White	1.569 1.594 1.634			
Phosphate Rock $Ca_3(PO_4)_2.H_2O$	2.6-2.9	3 - 5	Varied	1.624			
				Omega	Epsilon		
Apatite $9CaO.3P_2O_5.Ca(F_2, (OH)_2, CO_3, Cl_2)$	3.17-3.23	4.5-5	White green violet-blue	1.649	1.644		
Apatite $9CaO.3(P_iA_5)_2O_5.Ca(F,OH)_2$	3.45	5	"	1.664	B = low		
Manganapatite $9(Ca, Mn)).3P_2O_5.Ca(F, OH)_2$	3.26	5	green	1.656	1.651		
				Alpha	Gamma	Beta	
Dufrenite $2Fe_2O_3.P_2O_5.3H_2O$	3.2-3.4	3.5-4	dull green "	1.830 B = 0.054	1.885 ———	1.8404 1.844	
Triplite $3MnO.P_2O_5.MnF_2$	3.6-3.8	3.5-4.5	pink	1.650 1.665 1.675	1.672 1.682 1.692	1.660 1.673 1.683	
Vivianite $3FeO.P_2O_5.8H_2O$	2.5-2.7	2	green blue	1.579	1.633	1.603	
Wavellite $4AlPO_4.2Al(OH)_3.9H_2O$	2.3-2.5	3 -4	white yellow green	1.525	1.562	1.534	

MINERALOGICAL ASSOCIATION OF THE ARKANSAS WAD ORES

Upon the completion of the first stage of the investigation,
work was immediately started upon the identification of the phosphate
minerals in the Arkansas wad ores. The ores investigated are from typical
manganese deposits, the geological background of which has direct bearing
on this work.

Miser[8] give the following description of wad ores:

"Wad is a dark-brown to black very soft earthy mineral,
which is commonly considered to be an impure hydrous oxide of
manganese. It is associated with more or less iron, silica,
alumina, and water. It is present in many localities in the
Batesville district and at some of these places it exceeds in
quantity the higher grade manganese minerals."

These wad ores occur as irregularly shaped masses in the residual clays
of the Fernvale limestone. The Fernvale limestone is overlain by the
Cason shale, a badly weathered structure quite rich in phosphatic
sandstone. The excessive weathering and mineral dissolution that has
taken place within these structures has produced ideal conditions under
which almost any of the phosphates may have been dissolved and later
re-precipitated, or carried mechanically from the upper stratum to the
manganese ore bodies below. Table I clearly shows the amount of
material that was available for numerous phosphatic depositions at
lower levels.

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(8)   Miser, H. D., "Deposits of Manganese Ore in the Batesville District,
      Arkansas," U. S. Geological Survey Bulletin 734, p. 53 (1922).

TABLE I

ANALYSES OF THE FERNVALE LIMESTONE AND ITS RESIDUAL CLAY AND LOSS OF CONSTITUENTS
IN THE DECAY OF THE LIMESTONE

	Limestone	Clay	Percentage of constituents of the limestone saved in the clay.	Percentage of constituents of the limestone lost from the clay.
Manganese oxide (Mn_3O_4)	4.30	14.92	42.41	57.59
Ferric oxide (Fe_2O_3)	2.33	1.98	10.44	89.56
Alumina (Al_2O_3)	4.16	30.18	88.65	11.35
Lime (CaO)	44.51	3.89	1.07	98.93
Magnesia (MgO)	.30	.26	10.62	89.38
Potash (K_2O)	.35	.96	33.63	66.37
Soda (Na_2O)	.16	.61	46.74	53.26
Water (H_2O)	2.25	10.72	58.37	41.63
Carbonic acid (CO_2)	33.88	None	None	100.00
Phosphoric acid (P_2O_5)	3.02	2.53	10.24	89.76
Silica (SiO_2)	4.10	33.55	100.00	None
	99.36	99.60		

The ores actually studied were from deposits as those described above. Their chemical and screen analyses are shown in Table II. At the time this problem was started, Arkansas 1-1, 1-2, 1-3, 1-4, and 1-5 samples had not been received. All the phosphate mineral indentification work was done upon Arkansas 1, 2, 3, 4, and 5; and the data obtained from them applied to removing the phosphorus from the more recent samples because they were representative of deposits of much greater economical importance. The analyses show that both groups of ore are quite similar in every respect, and that they are all unusually high in phosphorus. Two items of particular interest shown in these analyses are the fairly high percentages of lime and the high percentages of -200 mesh material present.

Prior to the time the microscropical investigation was begun, the ore dressing possibilities of the earlier group of ores had been thoroughly investigated by the Bureau of Mines staff. The phosphorus content of several of the concentrate products obtained are shown in Table IV. In practically every case each ore dressing unit operation would split the phosphorus in a ratio such that the phosphorus content of the concentrate product was as high or higher than that in the original sample even though in several cases as much as 70 per cent of the phosphorus had been diverted into the tailings. The results obtained in several roast tests[9] (shown in Table V) seem to indicate that some

(9)   For a description of magnetic roasting and separation see DeVaney, F. D. and Coghill, W. H., "Beneficiating of Oxidized Manganese Ores by Magnetic Separation of Roasted Jig Concentrates", U. S. Bureau of Mines Rept. of Investigations 2936, p. 2 (1929).

TABLE II

HEADS   ANALYSES OF ARKANSAS ORES INVESTIGATED

Ore	Assay Percentages					
	Mn	Fe	CaO	Insol	SiO_2	P
Arkansas 1	23.95	21.16	7.62	10.56	7.34	2.42
Arkansas 2	31.18	24.90		5.92	3.40	0.22
Arkansas 3	30.34	21.25	0.56	11.62	6.64	0.61
Arkansas 4	32.04	13.56	5.79	13.68	9.32	1.68
Arkansas 5	27.16	23.78	4.11	9.56	7.04	1.45
Arkansas 1-1	28.7	14.0	2.8		12.08	0.88
Arkansas 1-3	25.9	14.1	0.74		18.7	0.44
Arkansas 1-4	26.4	15.9	7.9		10.1	2.06
Arkansas 1-5	27.8	22.2	0.9		6.1	0.55

TABLE III

SCREEN   ANALYSES OF ARKANSAS ORES

Mesh	Weight Per Cent				
	Arkansas 1	Arkansas 2	Arkansas 3	Arkansas 4	Arkansas 5
-10 + 14	7.7	8.9	7.3	8.2	1.1
-14 + 20	7.0	10.2	7.0	7.4	1.1
-20 + 28	6.5	9.5	6.4	7.2	2.8
-28 + 35	6.5	12.4	6.1	7.5	6.7
-35 + 48	6.5	11.6	5.9	8.0	13.2
-48 + 65	6.6	9.4	6.3	6.6	20.7
-65 + 100	6.0	6.6	5.8	5.0	18.2
-100 + 150	4.7	5.3	5.2	4.0	13.5
-150 + 200	3.9	3.9	4.0	3.1	7.6
-200	44.6	22.2	45.0	43.1	15.1
Composite	100.0	100.0	100.0	100.0	100.0

TABLE IV

PHOSPHORUS SEPARATION OBTAINED IN VARIOUS ORE DRESSING PROCESSES

Method	Ore (-65 ∤ 200 M)	Product	Per Cent Phosphorus	Total Phosphorus in Head Sample	Per Cent Total Phosphorus in Product
Float-Sink (gravity)	Arkansas 1	Float on 3.5[a]	8.04	2.42	60
"	Arkansas 2	"	0.19	0.21	38
"	Arkansas 4	"	5.50	1.68	65
"	Arkansas 5	"	5.62	1.45	67
Reduction Roast and Magnetic Separation	Arkansas 1	Non-magnetic portion	2.62	2.42	70
	Arkansas 2	"	0.26	0.22	72
	Arkansas 3	"	0.50	0.61	56
	Arkansas 4	"	1.54	1.68	77
	Arkansas 5	"	1.64	1.45	67
Flotation, Jigging and Tabling		Phosphorus concentration same as in magnetic roast - 70 per cent of total in concentrate, 30 per cent in tailings; percentage of phosphorus in concentrates a little higher than that in head samples.			

a. - Float product on heavy liquid with specific gravity of 3.50.

TABLE V

IRON PHOSPHORUS RELATIONSHIP IN ROASTED MAGNETIC SEPARATION PRODUCTS

Ore	Product	Per cent of Total Iron		Per cent of Total Phosphorus	
		-10 mesh fraction	-200 mesh fraction	-10 mesh fraction	-200 mesh fraction
Arkansas 1	Non-magnetic portion	12.4	31.0	22.2	69.6
Arkansas 2	Non-magnetic portion	9.3	30.6	31.8	71.7
Arkansas 3	Non-magnetic portion	15.9	40.8	36.4	55.5
Arkansas 4	Non-magnetic portion	19.2	50.4	23.0	76.8
Arkansas 5	Non-magnetic portion	6.2	15.6	27.7	67.2

definite relation exists between the iron and the phosphorus mineral since in every finer mesh non-magnetic product the iron and phosphorus content increased in about the same proportions. (In all of these roast tests, the -200 mesh sample was made by grinding the roasted -10 mesh fraction on the bucking board.) One the basis of these data and similar results obtained in numerous other roast tests on wad ores, it was assumed that the phosphorus mineral was either closely interlocked with the iron or that it was present as a molecular mixture with the iron, perhaps in the form of iron phosphide. Analyses of the various screen sizes showed little or no change in the percentages of the various constituents in the different screen size fractions and hence were of little help. Phosphorus analyses on the float-sink[10] products from the various screen sizes were not available.

A study of the opaque mineral mountings showed that the iron and manganese minerals occurred both as free particles and as small grains closely interlocked with each other from -28 mesh on down to the smaller sizes. Phosphate rock particles were detected by microchemical methods and were found to be pebble phosphate particles either surrounded by coatings of manganese oxides or enclosed in a matrix of intimate mixtures of the iron and manganese oxides. The phosphate grains ranged in size from -65 mesh to -200 mesh.

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(10) For description of float-sink tests see Sullivan, J. D., "Heavy Liquids for Mineralogical Analysis," U. S. Bureau of Mines Tech. Paper 381, 1927, 26p.

Several float-sink products of Arkansas 1 and 4 were prepared
and an optical study made of the non-opaque minerals contained in
the float products. At least six non-opaque constituents were found,
two of which were isotropic, three uniaxial, and one rather inde-
finite. One of the isotropic minerals had an index of refraction
very close to 1.47 which identifies it as being either neotocite,
a hydrous manganese silicate, or opal. The indefinite mineral seemed
to have some of the optical properties of bementite, another man-
ganese silicate. Both calcite and quartz were found to be present.

Of the two remaining non-opaque minerals, one was a bi-axial
mineral of low bi-refringence with an index of refraction between
1.640 and 1.650, was colorless, and showed no cleavages. These
properties identify this mineral as being apatite. The other trans-
lucent mineral was an amorphous compound, discolored, isotropic,
having an index of refraction of about 1.620. The optical properties
of this constitutent correspond quite closely to those of the mineral
collophanite, essentially $Ca_3(PO_4)_2 \cdot 2H_2O$, as described by Dana.[11]
This mineral, according to the same authority, is an important con-
stituent of the phosphorites, which are concretionary varieties of
apatite. Because of the amorphous nature of the mineral and also
because of its homogeneous contamination by impurities, it was decided
that this constituent would be best classified as phosphate rock[12]
which is described as an amorphous and colloidal phosphate of indefi-

(11) Dana, E. S. and Ford, W. E., "A Textbook of Mineralogy," Fourth
      Ed., N. Y., Wiley, p. 718-719 (1932).

(12) ibid., p. 706.

nite chemical composition quite commonly known as "bone phosphate." A comparison of this mineral with a powdered sample of a known phosphate rock pebble showed the two to be identical in every respect. Both of these phosphate minerals were found in sizes as large as 65 mesh, but the majority of the particles were in the -150 mesh fraction.

Early preliminary tests showed that the phosphate minerals were easily soluble in dilute acids, which futh r substantiated their identification.

Subsequent experience with these ores together with the fact that spectrographic analysis has disclosed the presence of titanium, thorium, and some of the rare earths indicates the presence of other phosphate minerals such as monazite, (Ce, La, Di) PO_4 with ThO_2, and $Ti_3(PO_4)_4$. There is also the possibility that some of the manganese and iron phosphates shown in Table VI may also be present, since the geological formation in which these ores occur could easily have fostered the synthesis of these compounds. However, none of these minerals were identified under the microscope, and it is very definite that the major portion of the phosphate is in the form of phosphate rock.

This discovery invalidates the theory that the iron and phosphate are closely related. The increase in the phosphate content of the finer mesh roast test products can be explained on the basis of the size distribution of the phosphate minerals. These phosphates would be liberated from the manganese and iron at the -200 mesh size and would naturally go into the non-magnetic portion. This fact can further be substantiated by the results obtained from a float-sink test on one of these ores in which the phosphorus content of the float product on a 3.5 specific gravity liquid from the -65 $+$ 200 mesh portion increased over

that in the float product from the -48 ∤ 65 mesh fraction, while the iron content decreased. The increase in the percentage of the iron in the smaller mesh non-magnetic fractions in the roast tests was due to the liberation in the subsequent crushing operation of the unroasted hematite present in the interior of the -10 mesh particles about which a superficial layer of magnetite had been formed of sufficient magnetic strength to carry the uncrushed particle into the magnetic portion at the larger sizes.

The following is the working data acquired from this phase of the work:

1. The major phosphate-bearing mineral in the wad ores investigated is phosphate rock.

2. This mineral is present in discrete particles ranging in size from -65 mesh to -200 mesh. This size range allows the possibility of a mechanical separation by flotation.

3. Chemically, the phosphate mineral is readily soluble in all dilute acids and apparently can be easily leached out of the ore.

4. Due to the fact that this ore must be floated at -100 mesh in order to get an efficient separation of the manganese from the iron, a sintering machine must be used to fuse the ore into cakes of sufficient size to meet the ferro-grade specifications. This sintering operation affords favorable conditions under which high temperature reactions might be carried out to convert the phosphorus into either some volatile form which could be driven off as a gas, or into a form which would be water soluble or soluble in very dilute acids.

PART II

LEACHING OF ARKANSAS WAD ORES

Preliminary Work

The leaching of high phosphorus iron ores has been attempted previously,[13] but in every case the process was either chemically impossible or economically unsound. One of these investigations was that conducted by Hertzog[14] at the Tuscaloosa station of the Bureau of Mines, during which the solubilities of the various phosphate minerals in dilute aqueous solutions of numerous reagents were determined. The results that he obtained were used as a guide in conducting the preliminary leaching tests, the most useful of which are included in Tables VII, VIII, and IX.

In the first tests conducted it was thought that acids would dissolve too high a percentage of iron and manganese, hence the salt solutions that gave the best dissolution were used. At Dr. Schrenk's suggestion, however, it was decided to try the acids alone, and much better results were immediately obtained. The first leaching results are presented in Table X, and although they are of little value for quantitative purposes, they are entirely responsible for the launching of a major attack upon the leaching of Arkansas wad ores.

(13) Winslow, R. M., "Leaching Iron Ores for Phosphorus," U. S. Bur. Mines Rept. of Investigations 2266, 1921, 4p.

(14) Hertzog, E. S., "A Study of the Occurrence and Amenability to Leaching of the Phosphorus Compounds in Some Red Iron Ores of Alabama," U. S. Bur. Mines Rept. of Investigations 3294, 1935, 9p.

TABLE VI

PARTIAL ANALYSIS OF PHOSPHATE MINERALS USED IN SOLUBILITY TESTS

Mineral	Chemical Name	Formula	Partial Analysis, per cent					
			CaO	Fe_2O_3	FeO	Mn	Al_2O_3	P_2O_5
Phosphate rock	Calcium phosphate	$Ca_3(PO_4)_2.H_2O$	47.79	0.64	0.08		0.83	32.53
Apatite	do.	$CaF.Ca_4(PO_4)_3$	53.58	1.03	.08		0.17	39.53
Dufrenite	Ferric phosphate	$FePO_4.Fe(OH)_3$	.31	67.84	1.26	0.28	.03	19.78
Triplite	Ferrous and manganese phosphate	$(RF)HPO_4$ RaFe and Mn	2.43	5.63	27.26	18.51	.47	31.64
Wavellite	Aluminum phosphate	$4AlPO_4.2Al(OH)_3.9H_2O$	.11	1.17	.13	.08	27.68	22.70
Vivianite	Ferrous phosphate	$Fe_3(PO_4)_2.8H_2O$	4.8C	15.99	17.39			.24	21.32

TABLE VII

SOLUBILITY OF SOME PHOSPHATE MINERALS IN N/4 HNO_3 and N/2 NaOH

Mineral	Chemical Name	N/4 HNO_3	N/2 NaOH
Phosphate rock	Calcium phosphate	100.0	0.4
Apatite	do.	100.0	.0
Dufrenite	Ferric phosphate	1.4	9.1
Triplite	Ferrous and manganese phosphate	99.6	6.1
Wavellite	Aluminum phosphate	.2	96.4
Vivianite	Ferrous phosphate	98.1	98.1

TABLE VIII

SOLUBILITY OF SOME PHOSPHATE MINERALS IN VARIOUS SOLVENTS

Solvents	Per cent of total phosphorus dissolved from					
	Phosphate rock	Apatite	Dufrenite	Triplite	Wavellite	Vivianite
2N KOH	0.0	0.0	52.2	13.5	99.7	
N/2 KOH	.8	.1	7.9	5.4	89.7	
2N NaOH	3.0	.0	73.1	29.2	100.0	
1N NaOH	2.0	1.8	33.2	42.4	96.7	
N/2 NaOH	.4	.0	9.1	6.1	96.4	98.1
N/3 NaOH	.3	.6	9.3	5.8	91.1	96.8
N/4 NaOH	.3	.0	6.5	5.7	87.2	
1N Na₂CO₃	.3	.0	.5	.9	14.7	
1N HCl	98.7	99.9	4.5	99.8	2.1	
N/2 H₂SO₄	100.0	100.0	3.4	100.0	2.6	
N/4 H₂SO₄	100.0	96.2	1.5	100.0	.4	
1N HNO₃	100.0	100.0	7.5	100.0		
N/2 HNO₃	100.0	100.0	2.5	100.0	.9	
N/4 HNO₃	100.0	100.0	1.4	99.6	.2	98.1
N/5 HNO₃	97.3	100.0	1.1	98.5	1.0	
1N H₃PO₄	100.0	59.2	8.5	100.0	7.6	
N/2 H₂SO₃	100.0	67.1	4.0	82.4	.7	
1N Tartaric acid	100.0	50.9	4.0	59.2	2.4	
N/2 NH₄HSO₄	100.0	86.9	1.9	99.3	1.6	
Sat. solution MnSO₄ made N/4 with H₂SO₄	92.7	52.4	5.3	49.5	5.3	
Sat. solution ferric alum made N/4 with H₂SO₄	93.5	15.4	5.7	12.3	6.5	
Sat. solution Mohr's salt made N/4 with H₂SO₄	98.0	36.0	6.6	35.2	5.3	

TABLE IX

* PHOSPHORUS DISSOLVED FROM FLORIDA PHOSPHATE ROCK

BY 1-PERCENT SOLUTIONS OF VARIOUS CHEMICALS

Chemical	Formula	Percent of Total Dissolved
Ammonium persulphate	$(NH_4)_2S_2O_8$	100.0
Ammonium phosphate	$(NH4)_2HPO_4$	0.0
Ammonium bi-sulphate	NH_4HSO_4	95.0
Ammonium sulphate	$(NH_4)_2SO_4$	3.7
Citric acid	$H_3C_6H_5O_7 \cdot H_2O$	90.7
Hydrobromic acid	HBr	100.0
Hydrochloric acid	HCl	100.0
Nitric acid	HNO_3	100.0
Perchloric acid	$HClO_4$	99.9
Sulphuric acid	H_2SO_4	100.0

* See reference (14)

TABLE X

PRELIMINARY LEACHING TESTS USING ONE PER CENT SOLUTIONS AT 25° C. ON NO. 1 AND NO. 4 ARKANSAS ORES

No.	Reagent	Weight of Charge Grams	Mesh	Time	cc of Reagent	Qualitative Tests Filtrate			Agitation	
						P	Mn	Fe		
1	NH_4HSO_4	0.2	-200	36 hrs.	300	None	None	None	None	
2	"	1.0	"	40 min.	"	Strong	Weak	None	Stirrer-180 rpm	
3	$Na_2S_2O_8$	0.2	"	36 hrs.	"	None	None	None	None	
4	"	0.2	"	40 min.	"	Very weak	Very weak	None	Stirrer-180 rpm	
5	HNO_3	1.0	"	40 min.	"	Strong	Fairly strong	Weak	"	"
6	"	1.0	"	2 hrs.	"	Strong	Fairly strong	Weak	"	"
7	"	1.0	-65 $\neq$ 100	40 min.	"	Strong	Very weak	Trace	"	"
8	"	1.0	-48 $\neq$ 65	40 min.	"	Strong	Weak	Trace	"	"
9	H_2SO_4	1.0	-200	" "	"	Strong	Fairly	Weak	"	
10	"	1.0	-65 $\neq$ 100	" "	"	Strong	strong	Trace		
11	"	1.0	-48 $\neq$ 65	" "	"	Strong	Weak	Trace		

Because this leaching operation seemed to have possibilities,
Mr. Shelton assigned Mr. F. W. Hoertel, Junior Analytical Chemist of
the Bureau of Mines to devote his full time to collaborating with the
writer in making a thorough investigation of the leaching possibilities
of these ores. It was decided to concentrate upon Arkansas 1-1 on the
assumption that what would work for one ore would work for all. This
assumption has since proved to be erroneous.

Plans for the leaching program called for tests on Arkansas 1-1
that had been given a one-hour roast in hydrogen at 650° C., then cooled
to room temperature in hydrogen. A number of tests were made leaching
the ore in various strengths of ammonium sulfite, ammonium bisulfite,
citric acid, tartaric acid, sodium carbonate, ammonium carbonate, sodium
chloride, ammonium citrate, and ammonium persulfate at room temperature
and at 70° C. Tests were also made using ammonium sulfite, ammonium bi-
sulfate, ammonium persulfate and sodium chloride solutions which had been
acidified with sulfuric acid with the acidity throughout the test held
constant.

Qualitative tests were run on the leach liquids to determine roughly
the amount of phosphorus, manganese, and iron that had been dissolved.
With all these reagents, however, either no phosphorus was extracted or
the amount was too small to justify quantitative determination.

A series of tests was then run using nitric and sulfuric acids as
leaching reagents. Various strengths were used, but even with very
dilute solutions the presence of manganese monoxide in the roasted ore
resulted in prohibitive extractions of the manganese. Because of the
high manganese extraction in acid solution the leaching of all roasted
products was abandoned.

Preliminary tests were made on Arkansas l-l raw ore using nitric and sulphuric acids. The results of the tests are shown in Tables XI and XII. The high percentage of phosphorus extraction and the low iron and manganese dissolution indicated that both acids were superior to any other reagent tested.

Perchloric acid was tried despite its exhorbitant cost, and the results are shown in Table XIII.

It was thought that a reducing roast with sodium chloride present in the ore might alter the phosphate minerals so that they would become either water soluble or soluble in weak acids. A roast of this kind was made using 1000 grams of ore and 20 grams of commercial sodium chloride. The results of the test, shown in Table XIV, again prove that leaching of roasted products for phosphorus is impractical because of the high solubility of the reduced manganese oxides.

From data obtained in this phase of the work the following conclusions were reached.

1. Sulfuric acid was the best leaching reagent.

2. Roasted products could not be leached economically in acid solutions.

3. The most logical place in the flow sheet for the leaching operation was immediately following flotation. This limited the size of the ore to be leached to minus 100 mesh.

4. Because the reduction roast ignition losses range between 20 and 25 per cent, the maximum percentage of phosphorus in the leach residue should not be greater than 0.16 per cent, thus allowing for an increase in the phosphorus content of the roasted product due to the loss of weight in the roasting process.

TABLE XI

PRELIMINARY LEACHING TESTS ON ARKANSAS 1-1 USING ACID REAGENTS

Leach Number	42	43	44	45
Product Leached, Raw Ore	Ark 1-1	Ark 1-1	Ark 1-1	Ark 1-1
Mesh	-200	-200	-200	-200
Reagent Used	HNO_3	HNO_3	H_2SO_4	H_2SO_4
Reagent Strength, per cent	$2\frac{1}{2}$	5	1	2
Equivalents Present $CaCO_3 - Ca_3(PO_4)_2$	5	10	3	6
Leach Charge, grams solid	25	25	25	25
Leach Charge, milliliters liquid	600	600	600	600
Pulp Density^a - $\frac{L}{S}$	24	24	24	24
Theoretical Acid Required, pounds/ton ore	232	232	171	171
Total Acid Added, pounds/ton ore	1160	2320	528	1056
pH at Start	1.0	0.6	1.5	1.5
pH at End	1.6	1.3	2.0	2.1
Time of Leach, hours	2	2	2	2
Temperature of Leach, $^\circ$C.	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls
Leach Residue, grams	22	22.5	24	23.5
Charge Recovered, per cent	88	90	94	94
Charge Lost in Leach, per cent	12	10	6	6
Extractions,				
Mn, per cent of total	2.9	3.3	2.4	3.1
Fe, per cent of total	4.4	5.2	2.2	3.5
P, per cent of total	71.0	75.0	67.7	76.3
Phosphorus in Leach Tails, per cent	0.31	0.28	0.35	0.29

a. The term "pulp density" as used in all tables is the weight ratio of liquid to solids.

TABLE XII

PRELIMINARY LEACHING TESTS ON ARKANSAS 1-1 USING ACID REAGENTS

Leach Number	50	51	52	53
Product Leached, Raw Ore	Ark 1-1	Ark 1-1	Ark 1-1	Ark 1-1
Mesh	-200	-200	-200	-200
Reagent Used	HNO_3	HNO_3	H_2SO_4	H_2SO_4
Reagent Strength, per cent	½	3/4	2	3
Equivalents Present	1	1½	5	7.5
Leach Charge - grams solid	25	25	25	25
Leach Charge - milliliters liquid	500	500	500	500
Pulp Density - $\frac{L}{S}$	20	20	20	20
Theoretical Acid Required, pounds/ ton ore	232	232	171	171
Total Acid Added, pounds/ton ore	232	290	855	1282
pH at Start	1.8	1.5	1.7	1.6
pH at End	2.6	1.9	2.2	2.2
Time of Leach, hours	2	2	2	2
Temperature of Leach, °C.	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls
Leach Residue, grams	24	24	21.5	23.0
Charge Recovered, per cent	96	96	86	92
Charge Lost in Leaching, per cent	4	4	14	8
Extractions				
Mn, per cent of total	1.3	1.6	2.3	2.7
Fe, per cent of total	0.3	1.5	3.0	3.5
P, per cent of total	44.5	55.0	77.5	82.5
Phosphorus in Leach Tails, per cent	0.51	0.46	0.27	0.24

TABLE XIII

PRELIMINARY LEACHING TESTS ON ARKANSAS 1-1 USING PERCHLORIC ACID

Leach Number	54	55	56	57
Product Leached, Raw Ore	Ark 1-1	Ark 1-1	Ark 1-1	Ark 1-1
Mesh	-200	-200	-200	-200
Reagent Used	$HClO_4$	$HClO_4$	$HClO_4$	$HClO_4$
Reagent Strength, per cent	$\frac{1}{2}$	1	$1\frac{1}{2}$	3
Equivalents Present	0.67	1	1.66	3.34
Leach Charge - grams solid	25	25	25	25
Leach Charge - milliliters liquid	500	500	500	500
Pulp Density	20	20	20	20
Theoretical Acid Required, pounds/ton ore	411	411	411	411
Total Acid Added, pounds/ton ore	275	413	686	1370
pH at Start	2.5	2.0	1.8	1.5
pH at End	2.6	2.0	1.7	1.9
Time of Leach, hours	3	3	3	3
Temperature of Leach, °C.	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls
Leach Residue, grams	24	22.5	23	23
Charge Recovered, per cent	96	90	92	92
Charge Lost in Leaching, per cent	4	10	8	8
Extractions				
Mn, per cent of total	0.42	0.58	0.58	2.14
Fe, per cent of total	0.04	1.00	1.40	3.0
P, per cent of total	66.3	69.0	53.0	69.0
Phosphorus in Leach tails, per cent	0.29	0.27	0.23	0.19

TABLE XIV

PRELIMINARY ACID LEACH TESTS ON ARKANSAS 1-1 ROASTED WITH SODIUM CHLORIDE

Leach Number	46	47	48
Product Leached	Special Roast with	NaCl	
Mesh	-200	-200	-200
Reagent Used	H_2O	1 per cent H_2SO_4	5 per cent H_2SO_4
Reagent Strength, per cent		1 per cent	5
Leach Charge, grams solid	25	25	25
Leach Charge, milliliters liquid	500	500	500
Pulp Density	20	20	20
pH at Start	9.5	2.5	0.9
pH at End	9.2	4.2	1.8
Leach Residue, grams			9.5
Charge Recovered, per cent			38.0
Charge Lost in Leaching, per cent			62.0
Extractions			
Mn, per cent of total	More than 28 per cent		
Fe, per cent of total			8.3
P, per cent of total			95
Phosphorus in Leach Tails, per cent			0.104

5. All experimental leaching should be done in capped glass

bottles agitated on motor driven rolls.

BATCH LEACHING

Single Batch Leaching

Because of the simplicity of the single batch leaching process,
this method was tried first. A series of tests was scheduled of the
following type:

Per cent acid   1   1   1   1   1   1   1

Pounds of acid per ton of ore   50   75   100   125   150   175   200

Each series was run using acid strengths of 0.5, 1.0, 1.5, 2.0, 2.5,
3.0 and 5.0 per cent, all at room temperature. All samples were raw ore
which had been quartered, crushed to minus 100 mesh and rolled. The
samples were prepared in 10 to 15-pound lots by the laboratory mechanics
of the Bureau of Mines staff. About 500 tests of this type have been
made, the major portion of this work being done by Mr. Hoertel and Mr.
O. R. Waldron, Junior Metallurgist of the Bureau of Mines. Miscellane-
ous single batch tests were also made using acid strengths ranging from
0.25 to 10 per cent in amounts of from 50 to 2200 pounds of acid per
ton of ore. The results from these tests are shown in Figure 1. The
significant facts derived from this investigation are:

1. High pulp dilutions with strong acids produced the lowest
phosphorus content in the residues.

2. Low pulp dilutions with strong acids produced the highest
phosphorus content in the residues.

3. The lowest percentage of phosphorus that could be obtained
consistently in pulp dilutions lower than about 7 was 0.20

FIGURE 1.

REDUCTION OF PHOSPHORUS CONTENT IN ORE

BY SINGLE BATCH LEACHING OPERATIONS
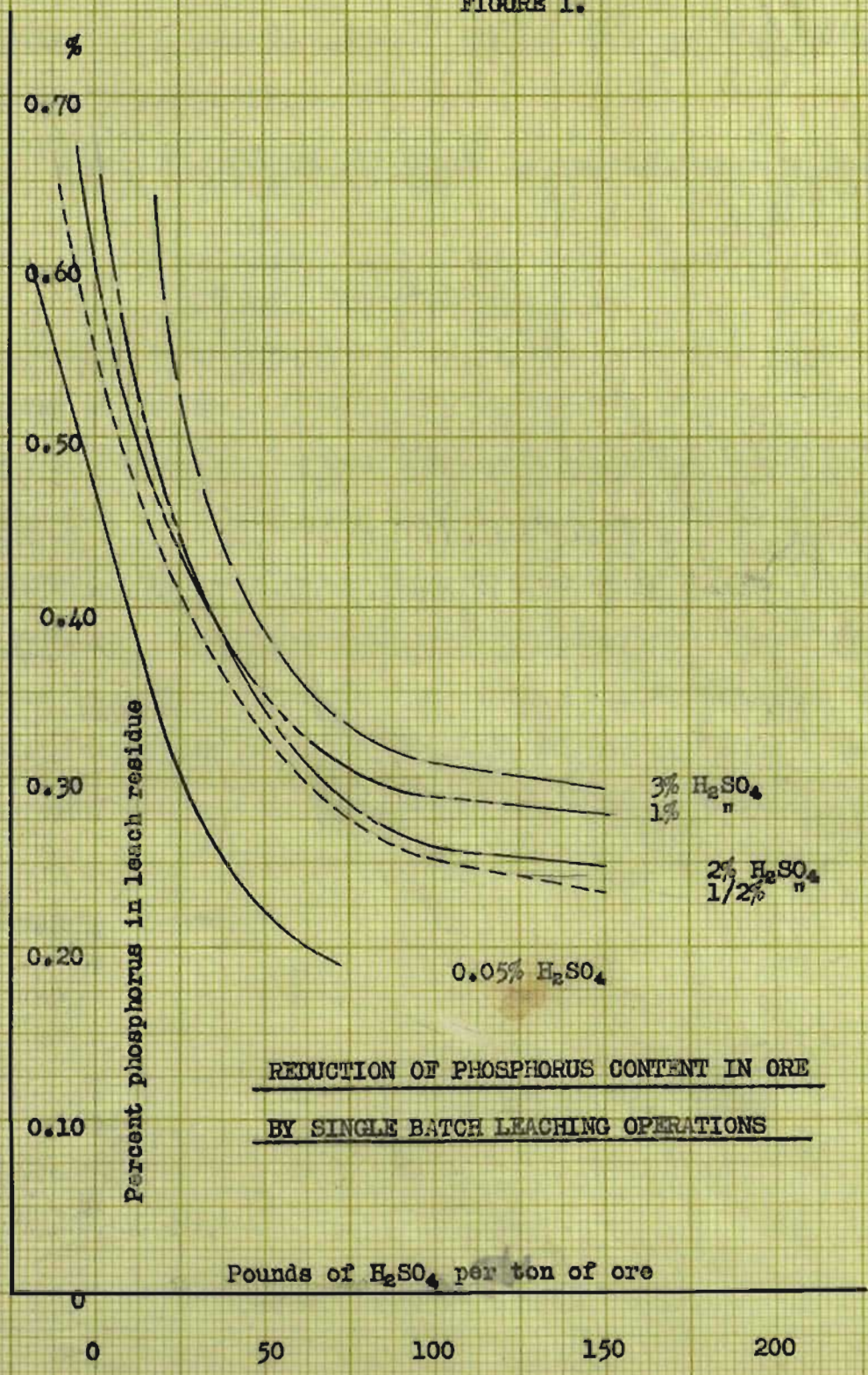
per cent. Several isolated cases produced ferro-grade products, but the results could not be reproduced.

The term "pulp dilution" is used to express the ratio of liquids to solids in the leaching mixture. This is the ratio by weight and is expressed by the equation

$$\frac{\text{Weight of liquid in leach tank}}{\text{Weight of Ore in leach tank}} = \text{pulp dilution} = \text{pulp density (in table)}$$

Multiple Contact Batch Leaching

Multiple contact batch leaching using 0.5 to 0.05 per cent acid solution was investigated by Hoertel and Waldron. A given volume of dilute acid equivalent to about 100 pounds of acid per ton of ore was divided into equal portions of about 10 pounds of acid per ton of ore. Each portion was added to the ore, rolled for a given time, filtered, and rejected. Another fresh portion was added to the ore and the process repeated until the total amount of acid had been used. Tests were run using 0.05, 0.1, 0.25, 0.4, and 0.5 per cent acids. The best result obtained was 0.25 per cent phosphorus in the residue.

The remainder of the work described in this paper was done entirely by the author.

COUNTER-CURRENT LEACHING

Several designs for counter-current systems were devised and double runs made. The results are shown in Tables XV to XX. All but one of the systems produced residues sufficiently low in phosphorus to meet ferro-grade specifications as is shown in the following tabulation:

| System	Test Number	Phosphorus in residue, per cent	Pulp Dilution	Acid Discarded pounds per ton of ore
1	64	0.16	17	631
2	84	.153	17	704
	86	.169	17	682
3	107	.086	10	595
	110	.092	10	567

With the exception of a few isolated cases in the single batch tests, these were the only ferro-grade products obtained. The subsequent roasting and magnetic separation still left the leach residues of ferro-grade quality with one exception, as may be noted by the following:

Test	Phosphorus in leach residue, per cent	Phosphorus in roasted non-magnetic product, per cent
64	0.16	0.12
66	.16	.18
84	.16	.09
86	.17	.19
107	0.086	.12) Numerous .16) values were .13) obtained by .12) varying the .10) roasting .11) conditions
110	0.092	.13) .10) " .10)

DESIGNS FOR COUNTER-CURRENT SYSTEMS

SYSTEM 1

Flotation Concentrates   Partially Used Acid

1st Stage

(Pulp)

Pressure Filter

Spent Acid

Partially Leached Ore

Fresh Acid - 1%
375 lbs./ton of
Ore Entering the
1st Stage

2nd Stage

(Pulp)

Pressure Filter

Leached Ore
to Reduction Roast
and Magnetic Separation

Partially Used Acid

SYSTEM 2

Partially Used Acid   Flotation Concentrates

1st Stage

(Pulp)

Pressure Filter

Spent Acid

Partially Leached Ore

Fresh Acid - 1%
400 lbs./ton of
Ore entering the
1st Stage

2nd Stage

(Pulp)

Pressure Filter

Partially Used Acid

Leached Ore
to Reduction Roast
and Magnetic Separation

DESIGNS FOR COUNTER-CURRENT SYSTEMS

SYSTEM 3

Flotation Concentrates   Used 1% Acid

1st Stage

(Pulp)

Add Water
Dilute to 1%

Pressure Filter

Spent Acid

Partially
Leached
Ore

Used 2% Acid

2nd Stage

Add Water
Dilute to 2%

(pulp)

Pressure Filter

Used Acid

Partially
Leached
Ore

Fresh Acid - 3%
268 lbs./ton of
Ore entering the
1st Stage

3rd Stage

(Pulp)

Pressure Filter

Leached Ore to
Reduction Roast and
Magnetic Separation

TABLE XV

3-STAGE COUNTER-CURRENT LEACH ON RAW ARKANSAS 1-1 USING NITRIC ACID

Leach Number 42A	1st Stage	2nd Stage Residue	3rd Stage Residue
Product Leached	Ark. 1-1 Raw	from 1st Stage	from 2nd Stage
Mesh	-200	-200	-200
Reagent Used	HNO_3	HNO_3	HNO_3
Reagent Strength, per cent	2.5	2.5	2.5
Equivalents Present	5	2.5	2.5
$(CaCO_2 - Ca_3(PO_4)_2$			
Leach Charge - grams solid	25		
Leach Charge - milliliters liquid	600	300	300
Pulp Density - L/S	24	12	12
Theoretical Acid Required, pounds/ton ore	260	260	260
Total Acid Added, pounds/ton ore	1300	650	650
Time of Leach, hours	1	1	1
Temperature of Leach, $^{\circ}$C.	25	25	25
Agitation	Rolls	Rolls	Rolls
Leach Residue, grams			18
Charge Recovered, per cent			72
Charge Lost in Leaching, per cent			18
Extractions			
Mn, per cent of total	3.5	0.74	.39 = 4.7
Fe, per cent of total	2.5	1.5	.7 = 4.5
P, per cent of total	82	5.7	8.8 = 91
Phosphorus in Leach Tails, per cent			0.199

TABLE XVI

3-STAGE COUNTER-CURRENT LEACH ON RAW ARKANSAS 1-1 USING SULFURIC ACID

Leach Number 42-B	1st Stage	2nd Stage	3rd Stage	
Product Leached	Ark 1-1 Raw	Residue from 1st Stage	Residue from 2nd Stage	
Mesh	-200	-200	-200	
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	
Reagent Strength, per cent	1	1	1	
Equivalents Present	2.66	1.3	1.3	
$CaCO_3 - Ca_3(PO_4)_2$				
Leach Charge - grams solid	25			
Leach Charge - milliliters liquid	600	300	300	
Pulp Density	24	12	12	
Theoretical Acid Required, pounds/ton ore	200	200	200	
Total Acid Added	460	230	230	
Time of Leach, hours	1	1	1	
Temperature of Leach, $^{\circ}C$.	25	25	25	
Agitation	Rolls	Rolls	Rolls	
Leach Residue, grams			20	
Charge Recovered, per cent			80	
Charge Lost in Leaching, per cent			20	
Extractions				Total
Mn, per cent of total	2.3	0.59	0.32	3.2
Fe, per cent of total	1.98	2.0		
P, per cent of total	78.5	8.6	3.2	90.3
Phosphorus in Leach Tails, per cent			0.198	

TABLE XVII

COUNTER-CURRENT LEACHES ON FLOTATION CONCENTRATES OF ARKANSAS 1-1

Leach Number	63	64 Residue	65	66 Residue
Product Leached	F-465	from 63	5F-F461-0	from 65
Mesh	-100	-100	-100	-100
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, per cent	1	1	1	1
Equivalents Present				
$(CaCO_3 - (PO_4)_2$	2	2	2	2
Leach Charge - grams solid	120		120	
Leach Charge - milliliters liquid	2000	2000	2000	2000
Pulp Density	17	17	17	17
Theoretical Acid Required, pounds/ton ore	200	200	200	200
Total Acid Added, pounds/ton ore	375	375	375	375
Acid Consumed, pounds/ton ore	110	9	105	5
Residual Acid, pounds/ton ore	265	366	260	370
pH at Start	1.3	1.3	1.3	1.3
pH at End	1.5	1.4	1.5	1.3
Time of Leach, minutes	30	30	30	30
Temperature of Leach, °C.	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls
Leach Residue, grams		115		115
Charge Recovered, per cent		95		95
Charge Lost in Leaching, per cent		5		5
Phosphorus in residue, per cent (computed)		0.16		0.16
Per cent Phosphorus in non-magnetic roast product		0.12		0.18

TABLE XVIII. COUNTER-CURRENT LEACHES ON FLOTATION CONCENTRATES OF ARKANSAS 1-1

Leach Number	83	84	85	86
Product Leached	F476	Residue from 83	F473	Residue from 85
Mesh	100	100	100	100
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, per cent	1	1	1	1
Equivalents Present				
($CaCO_3 - Ca_3PO_4$)	2	2	2	2
Leach Charge - grams solid	88		113	
Leach Charge - milliliters liquid	1520	1520	1920	1920
Pulp Density	17	17	17	17
Theoretical Acid Required, pounds/				
ton ore	200		200	
Total Acid Added, pounds/ton ore	400	400	400	400
Acid Consumed, pounds/ton ore	71	25	115	3
Residual Acid, pounds/ton ore	329	375	285	397
Time of Leach, hours	1	1	1	1
Temperature of Leach, °C.	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls
Leach Residue, grams		84		106
Charge Recovered, per cent		95		95
Charge Lost in Leaching, per cent		5		5
Phosphorus in Leach Tails, per cent		0.153		0.169
Phosphorus in non-magnetic portion				
of roasted leach tails		0.09		0.19

| | ANALYSES OF PRODUCTS | | | |
| | Assay Percentages | | | |
Product	Mn	Fe	P	SiO_2
F-476 Unleached heads	40.1	13.5	(1.2 (0.74	3.4
Leached Residue	43.42	13.51	0.153	2.46
F-473 Unleached heads	37.5	14.7	1.1	5.5
Leached Residue	39.96	15.81	0.169	5.40

TABLE XIX

3-STAGE COUNTER-CURRENT LEACH ON FLOTATION CONCENTRATES OF ARKANSAS 1-1

Leach Number	105	106	107
Product Leached (Flotation Test No.)	F-490	Residue 105	Residue 106
Mesh	100	100	100
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4
Actual Reagent Strength	1	2	3
Equivalents Present $CaCO_3 - Ca_3(PO_4)_2$	1	6	9.5
Leach Charge - grams solid	210		
Leach Charge - milliliters liquid	2100	1180	830
Pulp Density $\frac{L}{S}$	10	5.6	
Theoretical Acid Required - pounds/ton ore	200	56	28
Total Acid Added - pounds/ton ore	200	252	268
Acid Consumed - pounds/ton ore	87	37	22.7 = 147 lbs. total
Residual Acid - pounds/ton ore	113	215	245
pH at Start	1.3	1.3	1.3
pH at End	1.5	1.3	1.3
Time of Leach, hours	1	1	1
Temperature of Leach, °C.	25	25	25
Agitation	Rolls	Rolls	Rolls
Leach Residue, grams	200	200	200
Charge Recovered, per cent	95	95	95
Charge Lost in Leaching, per cent	5	5	5
Extractions			
Mn, per cent of total	0.97	0.37	0.24 = 1.58 total
Fe, per cent of total	0.62	0.71	0.77 = 2.10 total
P, per cent of total	77.0	9.9	2.8 - 89.9 total
Phosphorus in Leach Tails			0.086
Phosphorus in non-magnetic portion of roasted leach tails			0.10) for roasts at 0.11) various 0.12) temperatures 0.16)

TABLE XX.   3-STAGE COUNTER-CURRENT LEACH ON FLOTATION CONCENTRATES OF ARKANSAS 1-1

	108	109	110
Leach Number	108	109	110
Product Leached (Flotation Test No.)	F-489	Residue from 108	Residue from 109
Mesh	100	100	100
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, per cent	1	2	3
Equivalents Present ($CaCO_3 - Ca_3(PO_4)_2$)	1	5	10
Leach Charge - grams solid	210		
Leach Charge - milliliters liquid	2100	1180	830
Pulp Density $\frac{L}{S}$	10	6	4
Theoretical Acid Required, pounds/ton ore	200	56	28
Total Acid Added	200	252	265
Acid Consumed, pounds/ton ore	100	39.6	33.4 = 173 lbs. total acid consumed
Residual Acid, pounds/ton ore	113	215	232
pH at Start	1.3	1.3	1.3
pH at End	1.3	1.3	1.3
Time of Leach, hours	1	1	1
Temperature of Leach, °C.	25	25	25
Agitation	Rolls	Rolls	Rolls
Leach Residue, grams			200
Charge Recovered, per cent			95
Charge Lost in Leaching, per cent			5
Extractions, Mn, per cent of total	1.32	0.48	0.32 = 2.10 total
Fe, per cent of total	0.60	0.95	0.82 = 2.37 total
P, per cent of total	77.5	11.1	2.4 = 91.0 total
Phosphorus in Leach Tails			0.092
Phosphorus in non-magnetic portion of roasted leach tails			0.13) for roasts at 0.10) various 0.10) temperatures

ANALYSES OF PRODUCTS.

Product		Assay Percentage			
		Mn	Fe	P	SiO_2
F-489	Unleached Heads	39.2	13.1	1.0	4.5
	Leached Residue	41.0	14.6	0.092	4.7

Test 86 could probably be brought up to ferro-grade by altering the roasting conditions. As may be seen from the assays of the roasted products in Tests 110 and 107, the roasting conditions affect the final percentage of phosphorus.

The roasting and magnetic separation work was done by Messrs. J. D. Bardill and R. B. Fisher, Associate and Assistant Metallurgist respectively of the Bureau of Mines.

Since in these counter-current systems these tests represent only the initial runs, they are actually tests on multiple contact batch processes; and although the product obtained from the various leaching systems met qualifications the amount of acid rejected was too great to make these process commercially feasible. The original designs, of course, called for the utilization of the acids from one stage in the next stage, with filtration of the sludge between stages. It has been found in commercial practice, however, that filtering manganese ore is almost impossible,[15] hence these systems were not investigated further and all future efforts were devoted to the development of a method wherein filtration would not be necessary.

No other leaching scheme tried has produced results comparable to those obtained in this series of tests, but if these systems--in the multiple batch form--were used in ferromanganese production the cost of the leaching operation would be exhorbitant. The current price for sulfuric acid is $0.009 per pound. Each of these systems required

(15) Norcrosse, F. S., "Development of Low-Grade Manganese Ores of Cuba," A. I. M. E. Tech. Publication No. 1188, p. 8 (1940) - Mining Technology 4, May, 1940.

about 800 pounds of acid per ton of ore making the cost of leaching reagent alone about $7.20 per ton of ore. This compared with an overall operating margin of about $5.00 per ton is entirely out of the question.

Significant factors to be noted from this series are the high pulp densities, the large excesses of acid, and the fact that all of the leach heads were flotation concentrates.

Duplicate three-stage counter current tests, similar to System 3 were made in which the 3-per cent acid was added in the third stage in amount equivalent to 150 pounds of acid per ton of ore, with settling and decanting used in place of filtering between stages and after the third stage. Nine samples were subjected to this method which gave the following percentages of phosphorus in the residue: 0.187, 0.276, 0.225, 0.279, 0.212, 0.251, 0.248, 0.212, and 0.220.

In each stage of this system there was an intermixing of used and new solution, and the pulp dilutions were all relatively low. None of the residues were sufficiently low in phosphorus to be of value.

MISCELLANEOUS LEACHING TESTS

Acid Consumption Tests

Acid consumption tests were run for the purpose of determining optimum leaching periods. The results of the tests are shown in Tables XXI and XXII. Most of the acid was consumed within the first 20 minutes with low percentages of iron and manganese being extracted. The phosphorus analyses showed that there is no advantage in leaching for a period exceeding 10 minutes, while the percentage of iron and manganese dissolved varies directly as the time of contact. The manganese and iron extractions for the longer leaching periods in this series were much lower than those from most of the other leach tests. The average extraction value for both manganese and iron after an hour leach is about 2.5 per cent. The results, however, show the general trend. (See figure 2).

Wash Tests

The data obtained in the acid consumption tests suggested the possibility of using 10-minute washes instead of long periods of agitation as a method of removing the same amount of phosphorus with lower accompanying manganese and iron extractions. Four series of tests were run, using a multiple contact batch process. The procedure was to leach the ore for 10 minutes with intermittent shaking, allow the ore to settle out (about 30 minutes), decant the supernatant liquid, and add fresh acid. After the final leach 600 cc. of water were added before settling and decantation. The ore was then washed with another 600 cc. of water, allowed to settle, the wash water decanted and the residue transferred to a pan and dried on a sand bath. Two tests were

TABLE XXI

LEACHING TEST

ACID CONSUMPTION TEST ON ARKANSAS 1-1

Leach Number	Mc-40	41	42	43	44	45	46
Mesh	100	100	100	100	100	100	100
Reagent used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent strength, per cent	1	1	1	1	1	1	1
Equivalents present							
$CaCO_3 - Ca_3(PO_4)_2$	1	1	1	1	1	1	1
Leach charge - grams solid	25	25	25	25	25	25	25
Leach charge - milliliters liquid	225	225	225	225	225	225	225
Pulp density - $\frac{L}{S}$	9	9	9	9	9	9	9
Theoretical acid required, pounds/ton	200	200	200	200	200	200	200
Total acid added, pounds/ton	200	200	200	200	200	200	200
Acid consumed, pounds/ton	93	94	99	130	103	108	108
Residual acid, pounds/ton	107	106	101	70	97	92	92
pH at start							
pH at end							
Time of leach, minutes	10	20	30	60	90	120	180
Temperature of Leach, $^{\circ}$C	25	25	25	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls	Rolls	Rolls	Rolls
Phosphorus in leach tailings, per cent	0.195	0.192	0.178	0.167	.201	.187	.195

TABLE XXII

ACID CONSUMPTION DATA

Time Minutes	Test 1					Test 2		
	Acid Consumed pounds/ton	Per cent Extraction				Acid Consumed pounds/ton	Per cent Manganese Extracted	Phosphorus in Residue
		Mn	Fe	P				
10	158					93	0.34	0.195
20	111	0.42	0.46	64.5		94	0.52	0.192
30	120	0.42	0.40	62.5		99	0.48	0.178
60						130	0.66	0.167
75	117	0.58	0.39	64.0				
90						103	0.62	0.201
120	127	0.58	0.86	63.3		108	0.66	0.187
180						108	0.73	0.195

Test 1 - 380 pounds acid per ton of ore added - 1 per cent solution

Test 2 - 200 pounds acid per ton of ore added - 1 per cent solution

FIGURE 2.

ACID CONSUMPTION DATA
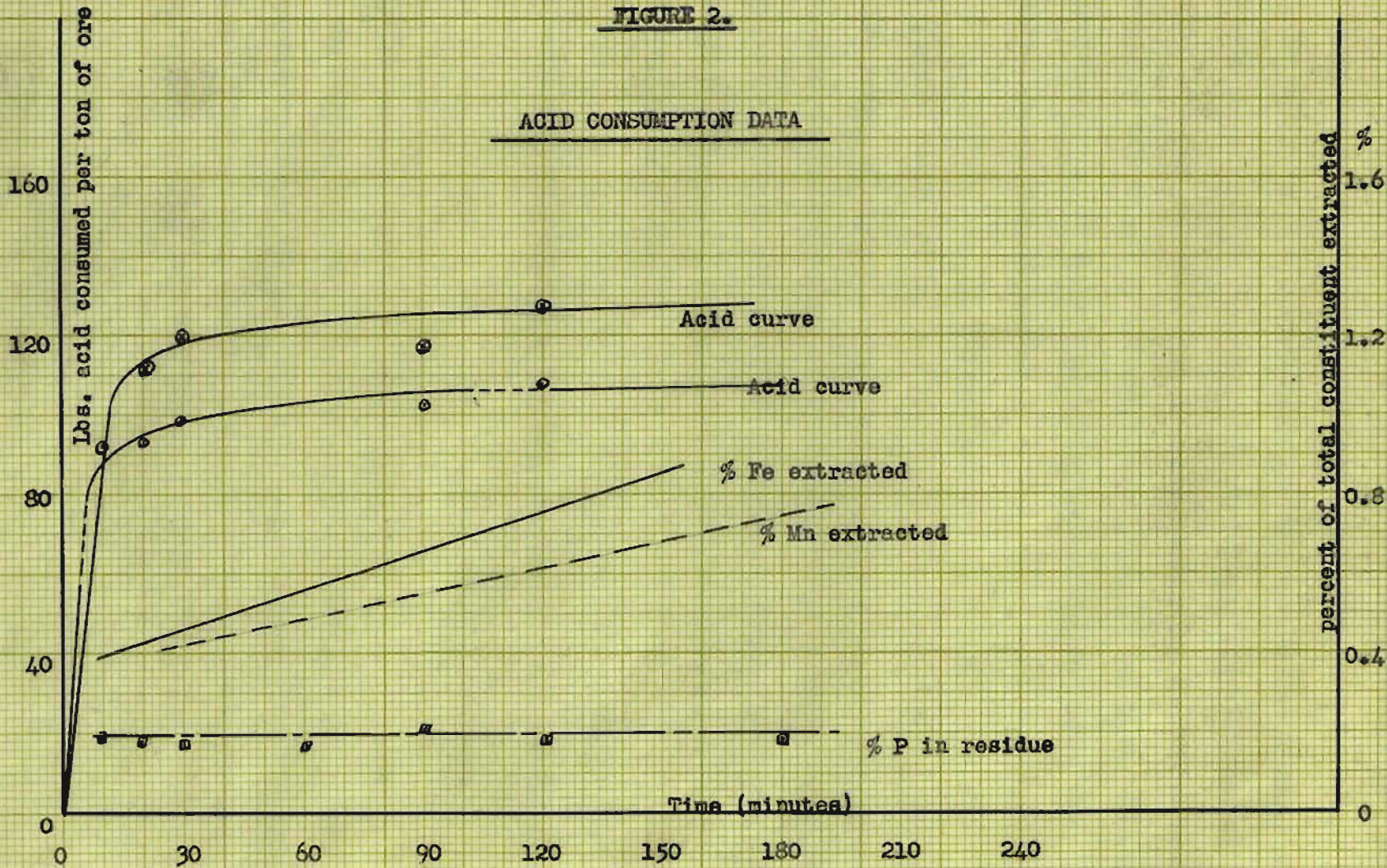
made with solutions at 85° C., the rest at room temperature. The data
for these tests are shown in Tables XXIII and XXIV.

The analytical results indicate that the wash method is fully as
efficient as methods in which one hour was allowed for each contact
period. For some unknown reason the acid consumption in these tests was
much higher than in any of the other leach tests at the same acid con-
centrations. The hot leaches seemed to give better extraction and
prompted further investigation.

Hot Leaches

Several additional hot leaches using one per cent acid solutions
and 150 pounds of acid per ton of ore were made. The heat was intro-
duced into the leaching solution by bubbling steam at 212° F. through
it while it was being agitated by an electric stirrer. The temperature
attained in every leach was 95° C. The phosphorus analyses on the
residues were as follows:

	Arkansas 1-1	Arkansas 1-5
Phosphorus in leach residue, per cent	0.26	0.415
	.30	.482
	.237	.485
	.273	.457
		.481
Phospherus in head sample, per cent	.88	.554

The results from this set of tests were very discouraging, with
the phosphorus values in these residues even worse than those obtained
with cold leaches. Lack of time prevented the investigation of phos-
phorus dissolution at temperatures other than 95° C.

TABLE XXIII

WASH TESTS ON RAW ARKANSAS 1-1

	Mc-57	Mc-58	Mc-59	Mc-63	Mc-64	Mc-65
Leach Number	Mc-57	Mc-58	Mc-59	Mc-63	Mc-64	Mc-65
Mesh	100	100	100	100	100	100
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, percent	1	1	1	1	1	1
Leach Charge, grams solid	50	50	50	50	50	50
Leach Charge, milliliters liquid	112	(112 (112	(112 (112 (112	224	(224 (112	(224 (112 (112
Theoretical Acid Required, pounds/ton ore	200	200	200	200	200	200
Total Acid Added, pounds/ton ore	50	100	150	100	150	200
Acid Consumed, pounds/ton ore	49.5	97.0	143	92	137	183
Residual Acid, pounds/ton ore	0.5	3.0	7.4	8	13	17
Time of Washes, 10-minute periods	1	2	3	1	2	3
Temperature of Leach, °C.	25	25	25	25	25	25
Agitation - Hand Shaking						
Phosphorus in Leach Tails, per cent	0.549	0.284	0.209	0.273	0.231	0.206

TABLE XXIV

WASHING TESTS ON RAW ARKANSAS 1 AND 1-1

Leach Number	Mc-60	Mc-61	Mc-62	Mc-66	Mc-67
Product Leached	Ark 1	Ark 1	Ark 1	Ark 1-1	Ark 1-1
Mesh	100	100	100	100	100
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, per cent	1	1	1	1	1
Leach Charge, grams solid	50	50	50	50	50
Leach Charge, milliliters liquid	223	(223 (223	(223 (223 (223	224	(224 (112
Theoretical Acid Required, pounds/ton ore	300	300	300	200	200
Total Acid Added, pounds/ton ore	100	200	300	100	150
Acid Consumed, pounds/ton ore	95.5	185.5	278	91	134
Residual Acid, pounds/ton ore	4.5	14.5	22	2	16
Time of Leach, 10-minute periods	1	2	3	1	2
Temperature of Leach, °C.	25	25	25	85	85
Agitation	Rolls	Rolls	Rolls	Rolls	Rolls
Phosphorus in Leach Tails, per cent	1.60	0.847	0.538	0.304	0.227
Phosphorus in Leach Heads, per cent	2.42	2.42	2.42	0.88	0.88

Summary of the Leaching Data

The several ferro-grade products obtained in the counter-current systems used, while not produced by processes which are commercially feasible, prove that enough of the phosphatic material in the ore is sufficiently soluble in dilute acids to permit the reduction in phosphorus content necessary. (See Table XXV) All of these low phosphorus residues were made from flotation concentrates, whereas all other tests were run on raw ore. It may be that the flocculation of the ore brought about in the flotation cell or the presence of traces of the flotation reagents are beneficial to the leaching operation. The other important factors associated only with the counter-current series are the high pulp dilutions used and the large excesses of acid.

Three points of unusual interest were brought out in this leaching investigation: first, the phosphorus was more soluble in dilute acids than it was in strong acids; second, filtering between stages seemed to be beneficial while no results were obtained by decantation and third, hot leaches at 95° C. were worse than the cold leaches. In discussing this with Dr. Schrenk, it was suggested that perhaps the trouble might be due to the leach solutions being saturated with calcium sulfate.

There is much evidence to support the fact that the leach solutions are saturated with this salt. As shown in the ore analyses in Table II, there is 2.8 per cent of CaO as $CaCO_3$ in Arkansas 1-1, which is more than enough soluble calcium to produce supersaturation in the volumes of solutions usually employed in a leach test. (See Figures 3 and 4). It was often observed that clear filtrates from leach residues precipitated a white crystalline solid after standing for an hour which

TABLE XXV

PHOSPHORUS REDUCTION IN SAMPLES TREATED

Test No.	Product (Flotation Number)	Percentage of Phosphorus				
		Raw Ore	Flotation Concentrates	Leach Residue	Non-Magnetic Roasted Portion (Final concent- rats)	Ferro-grade Specifica- tions (Grade B)
64	465	0.88	Not reported	0.16	0.12	0.18
66	461	0.88	Not reported	0.16	0.18	0.18
67	465	0.88	Not reported	0.13		0.18
68	461	0.88	Not reported	0.27		0.18
84	476	0.88	1.20 0.74	0.15	0.09	0.18
86	473	0.88	1.1	0.17	0.19	0.18
107	490	0.88	1.1 0.77	0.086	0.12) analyses 0.16) from 0.13) varied 0.12) roasting 0.10) condi- 0.11) tions	0.18
110	489	0.88	1.20 0.863	0.092	0.13) 0.10) ditto 0.10)	0.18

FIGURE 3.

SOLUBILITY OF CALCIUM SULFATE IN
AQUEOUS SULFURIC ACID AT 25° C.

FIGURE 4.

SOLUBILITY OF CALCIUM SULFATE IN
PHOSPHORIC ACID SOLUTIONS AT 25° C.
(J.Phys. Chem. 10, 629 (1910))
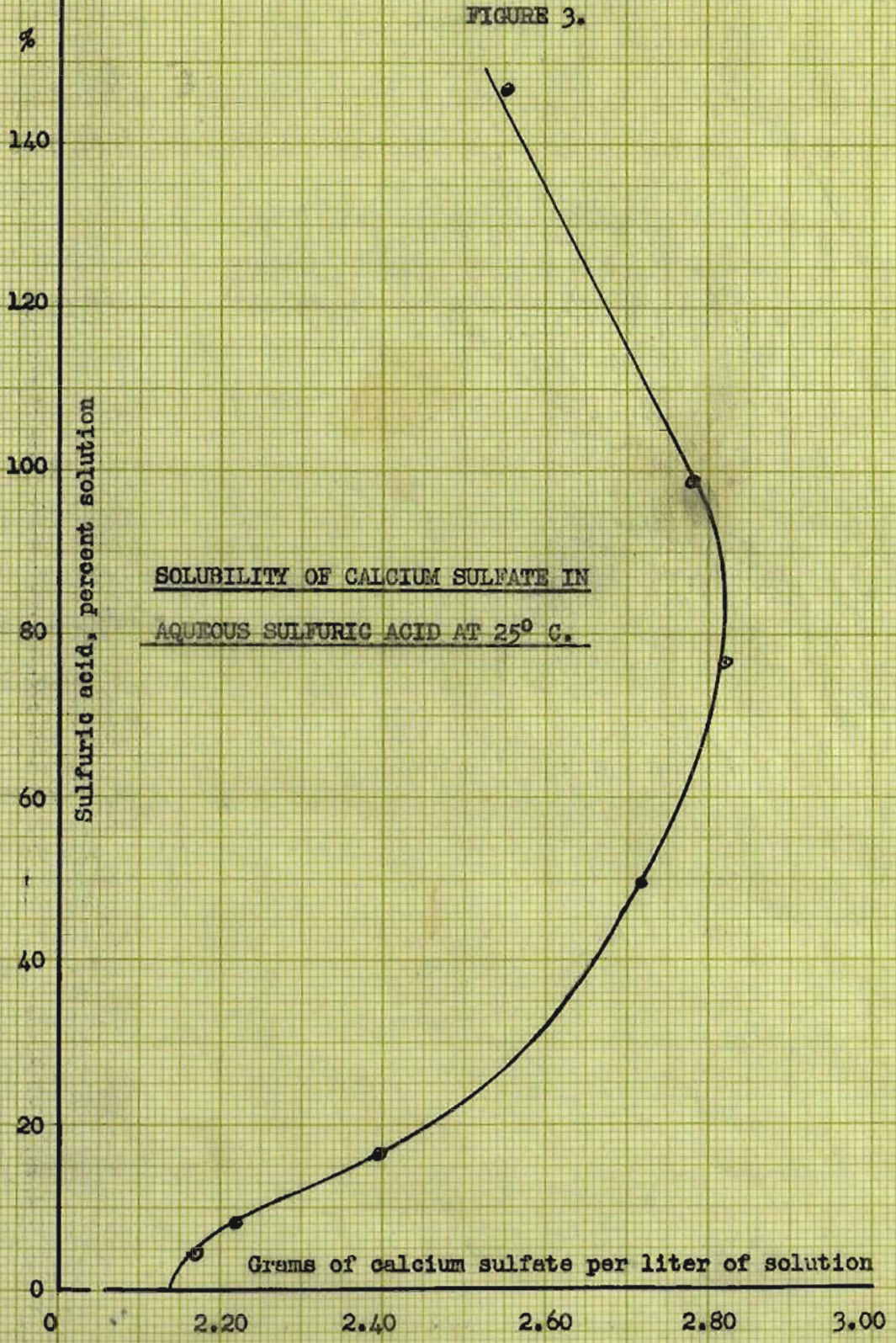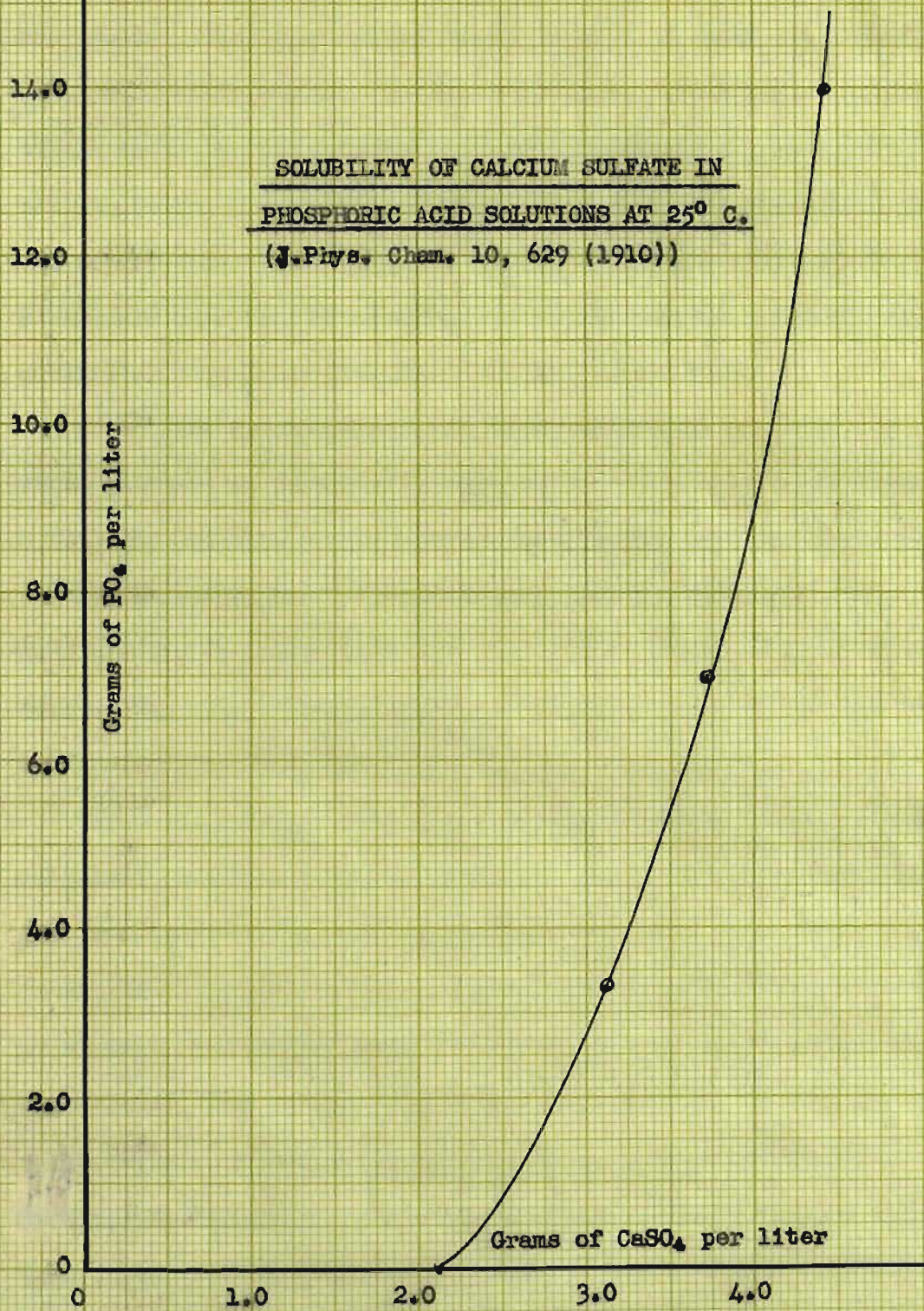
was highly insoluble in all acids. Every ferro-grade product that was obtained came from solutions which had very high pulp dilutions, large excesses of acid, and which had been filtered between stages, hence the calcium sulfate was either easily carried in solution or completely eliminated by filtration. On the other hand, however, most of the single batch leaches contained too little solution to carry all of the calcium sulfate present in solution, hence when the saturation point was reached, it is possible that an impervious layer of calcium sulfate film could form over the surface of the undissolved phosphate rock particles, thus preventing their further dissolution.

This line of reasoning would also account for the fact that strong acids were not as effective as weak acids. Every strong acid leach had a low pulp dilution so that despite the increased solubility of calcium sulfate in strong acid, there was still enough calcium present to produce a saturated solution in much shorter time than was required in the more dilute pulps, thus preventing a larger portion of the phosphorus from going into solution.

From the data collected by Hoertel and Waldron, several tables of computations were made in an effort to correlate the numerous factors involved so as to find the controlling factor in the leaching operation. In almost every case each variable was either a straight line function of another with a third being held constant, or else they were power functions of the type normally expected. One plot of per cent phosphorus in the residue versus pulp dilution (Figure 5) suggested that the controlling factor was the pulp dilution, which varied inversely as the per cent phosphorus remaining in the residue. Although several low phosphorus values had previously been obtained at high pulp dilutions, subsequent

leaches at very high pulp dilutions which were made to check with this curve could produce results no lower than 0.19 per cent phosphorus. This indicates that both the percentage extraction and the pulp dilution are secondary to some other factor as yet undetermined. One thing that was quite apparent from several of the plots was that low acid concentrations were fully as effective as high concentrations as long as there was sufficient acid present to keep the pulp acidic.

As is shown in Figure 6, the amount of phosphorus extracted from these ores varies from 19 to 90 per cent which is definite proof that some one insoluble phosphate mineral constituent is not responsible for the phosphorus in the residue consistently ranging between 0.20 and 0.22 per cent. There is evidently something taking place in the leach solution which is either preventing the phosphorus from going completely into solution, or is re-precipiting the phosphorus in some insoluble form. Two agents may be responsible for either of these conditions: first, the presence of colloidal slimes, which would accelerate the precipitation of either sulfate or phosphate salts that had exceeded their respective saturation values; and second, the presence of metallic ions which would re-precipitate the dissolved phosphates as insoluble salts. Both types of agent are present in these solutions. A third mechanism which would account for the incomplete dissolution of the phosphorus is the decomposition of soluble salts of the phosphates into fairly insoluble forms, a phenomenon quite characteristic of the compounds of this puzzling element.

Most of the ore used in the leach tests contained a large percentage of material that would pass thru a 400-mesh screen, hence the leach solutions were loaded with very fine slimes. Both the filtering operation and flotation seemed to eliminate these to a great degree, and they

FIGURE 6.
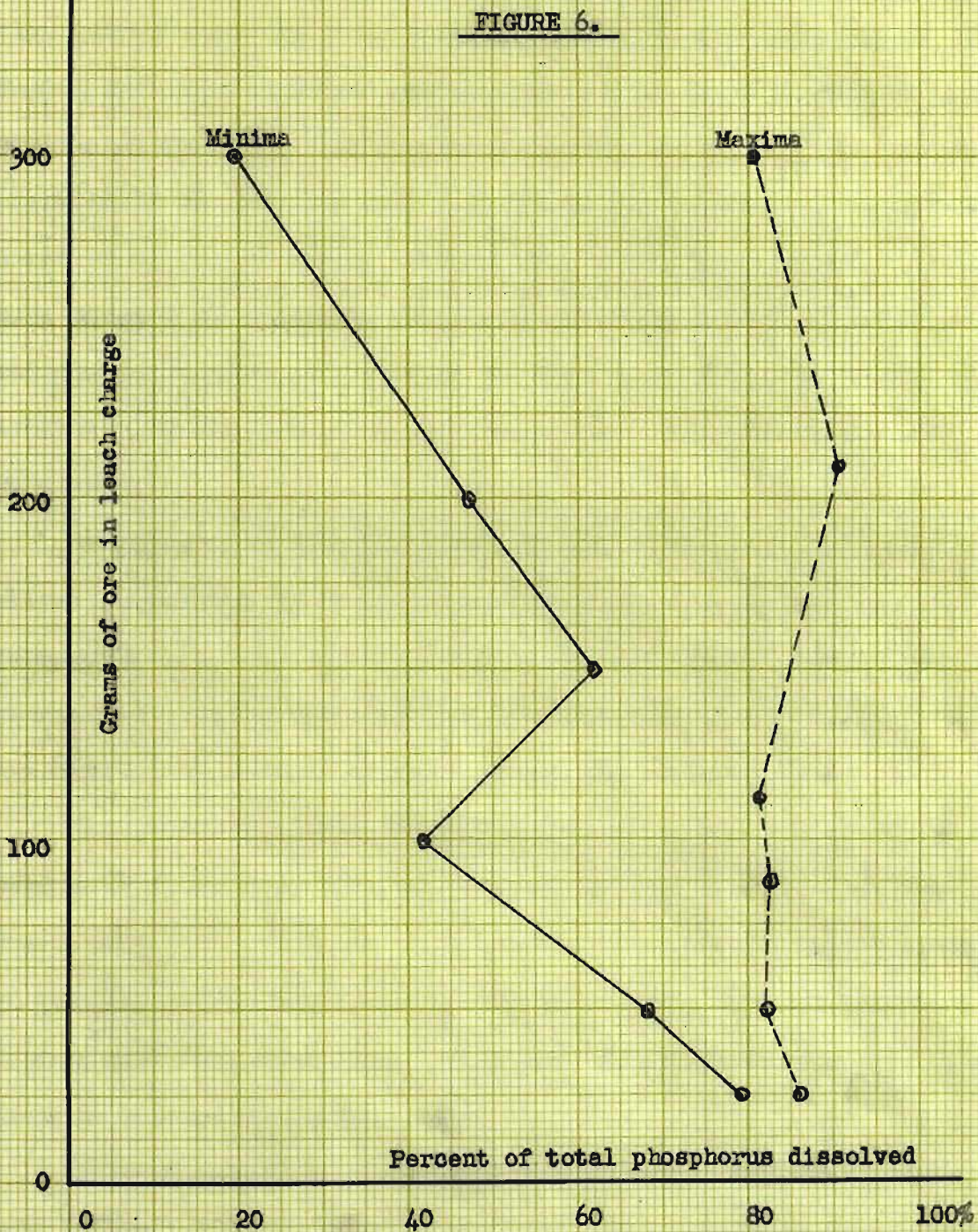
VARIATION IN THE PERCENTAGE OF PHOSPHORUS DISSOLVED

FROM ARKANSAS WAD ORE 1-1

were usually associated with low phosphorus residues. Since the majority
of the phosphate rock is in the minus 150-mesh fraction, and since these
fine particles are the ideal locations for incipient precipitation, it is
logical to assume that the calcium sulfate film theory previously mention-
ed is a plausible one, and should be investigated thoroughly. No deter-
minations of calcium were ever made in the leach solutions, hence this
theory could not be checked with the data available at present. However,
both Figure 2 and 3 showing the solubility of calcium sulfate in sulfuric
and phosphoric acids make evident the fact that there is more than enough
calcium to produce saturated solutions, hence their effects are to be
expected.

The presence of iron and manganese ions in the leach solutions
allows the possibility of the formation of several manganese and iron
phosphates as well as double phosphate salts of these metals. The com-
pounds that would be the most troublesome and the most likely to form
are ferric phosphate and manganous dihydrogen orthophosphate.

Ferric orthophosphate, $Fe_2(PO_4)_2 \cdot xH_2O$, is reported to be easily
soluble in dilute mineral acids excepting aqueous solutions of phos-
phoric acid.[16] Since the final sulfuric acid concentrations in many
of the leaches have been quite low, it is possible that precipitation
of this salt from these dilute phosphoric acid solutions may have taken
place in several instances.

Manganous tetrahydrogen phosphate, $MnH_4(PO_4)_2$, is a very soluble
salt and one of the most logical compounds to be expected in the leach

(16)   Comey, A. M., "A Dictionary of Chemical Solubilities," Second Ed.,

       N. Y., MacMillan, 1921, p. 694.

solution. However, with less than 20 grams of this salt to 100 grams of water, decomposition takes place similar to that of calcium monophosphate:

$$CaH_4(PO_4)_2 = CaHPO_4 + H_3PO_4$$

$$MnH_4(PO_4)_2 = MnHPO_4 + H_3PO_4$$

MnHPO_4 is reported easily soluble in concentrated acids,[17] which would lead one to believe that it is fairly insoluble in dilute acids, especially phosphoric acid. If this assumption is true, this is another means by which phosphorus may be being re-precipitated from solution.

As for the third mechanism mentioned, Armsby[18] has shown that if sulfuric acid reacts with an excess of calcium orthophosphate, after five minutes 93 per cent of the theoretical amount of phosphoric acid will be formed. If the solution is allowed to stand, however, the amount of soluble phosphate decreases rapidly so that at the end of 30 minutes only 36 per cent of the theoretical amount of the phosphoric acid is in solution. The following equations are given to explain this phenomenon:

$$Ca_3(PO_4)_2 + H_2SO_4 = CaH_4(PO_4)_2 + CaSO_4$$

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4CaHPO_4$$

It is quite possible that these same reactions are taking place in the leach solutions with the ultimate formation of the fairly insoluble calcium dihydrogen phosphate. Figure 7 shows the solubility of this salt in aqueous solutions of phosphoric acid, with the curve extrapolated to

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(17) Comey, A. M., p. cit., p. 698.

(18) Armsby, H. P., "On the Reaction of Sulfuric Acid upon Tri-calcic Phosphate," Amer. Journ. Sci. 12, 3. Series, p. 46-48 (1876).

FIGURE 7.

14.0

12.0

10.0

Grams H_3PO_4 in 100 cc. of solution

Grams $CaHPO_4$ possible from 68% of total P in 25 gms. ore

Grams $CaHPO_4$ possible from 68% of total P in 100 gms. ore

8.0

SOLUBILITY OF $CaHPO_4$ IN AQUEOUS

PHOSPHORIC ACID

25° C.

6.0

4.0

Maximum concentration of H_3PO_4 obtained in leach solutions

2.0

Average value of concentration of H_3PO_4 in leach solutions

Grams of $CaHPO_4$ dissolved by H_3PO_4

0

0   2.0   4.0   6.0   8.0   10.0

bring it into the range of the phosphoric acid strengths resulting from the leaching of the manganese ores. If this extrapolation is correct, this curve shows very definitely that the presence of even small amounts of this salt are potential sources of trouble.

Armsby also found that the conversions of the monocalcium phosphate to the dicalcium phosphate was accelerated by an increase in temperature, which phenomenon would explain the high phosphorus residues obtained in the hot leaches.

Erlenmeyer[19] says that $CaH_4(PO_4)_2$ is decomposed into $CaHPO_4$ when the ratio of water to the weight of monocalcium phosphate is less than 700:1, hence this decomposition is also a function of pulp dilution. This too would check with the results obtained in this paper since most of the low pulp dilutions produced high phosphorus residues. Erlenmeyer also reports that decomposition takes place at $50°$ C. which further substantiates Armsby's findings and again fits in with the results obtained in this paper.

Any or all of these theories proposed to explain the faulty leaching of these manganese ores are very plausible, yet much more detailed research work would have to be done in order to prove any one of them.

If the trouble encountered is due to functions of the leach solution stimulated either by slimes, metallic ions, or decompositions, the best way of eliminating it is to remove the leach solution from the ore as fast as it dissolves the phosphorus from the ore. This can be done by leaching the ore directly on a filter, passing dilute acid solutions thru the ore once without any recirculation whatsoever. A

(19) Comey, A. M., op. cit., p. 687.

test of this type was made on Arkansas 1-1 in which 500 pounds of acid per ton of ore in a one-half per cent solution was filtered thru the ore. A residue containing 0.17 per cent was obtained, thus showing that this method has possibilities.

PART III

VOLATILIZATION OF PHOSPHORUS

The successful elimination of impurities such as lead and copper from manganese ores has been accomplished by adding sulfuric acid and sodium chloride to the ore and then roasting at high temperatures, during which process chlorides of the impurities are formed which volatilize at the roasting temperature. Since phosphorus forms several chlorides and oxychlorides which are quite volatile at relatively low temperatures (300° C.) it was hoped that the phosphorus might be removed from this ore by similar methods.

The following ore charges were made and treated as follows:

Sinter A - 100 grams of ore, 10 grams sulfuric acid (1.84), 4 per cent NaCl - charge was roasted at 950° C. for 4 hours, cooled slowly for 4 hours to 150° C., then quenched in water.

Sinter B - 14 pounds of ore charge containing 12 per cent water and 10 per cent coke - sintered in a Dwight-Lloyd type laboratory machine.

Sinter C - 14 pounds of ore charge containing 12 per cent water, 10 per cent coke, and 4 per cent NaCl - sintered in the laboratory machine.

Sinter D - 14 pounds of ore charge containing 10 per cent coke, 1.35 pounds of sulfuric acid (1.84), and 12 per cent water - sintered.

Sinter E - 14 pounds of ore charge containing 10 per cent coke, 1.35 pounds sulfuric acid, 12 per cent water, and 4

per cent NaCl - sintered.

Analyses of the sintered products obtained are shown in Table XXVI. These indicate that under ordinary roasting and sintering conditons the phosphorus is not converted into a volatile compound.

When these sinters were washed thoroughly in a small amount of water, a trace of water-soluble phosphates could be found, but the amount was insignificantly small.

Several tests were run to determine whether or not these special sintering operations had rendered the phosphate mineral any more soluble in dilute sulfuric acid. The results of these tests are shown in Tables XXVII, XXVIII, and XXIX. It is apparent from the high phosphorus in the leach tails that the sintered product is not amenable to phosphate leaching with dilute acid.

TABLE XXVI

ANALYSES OF SINTERS

Sinter	Assay Percentages				
	Mn	Fe	P	SiO2	Insol
Sinter A (NaCl.H₂SO₄)	28.41	14.6	0.82	—	—
			0.91	—	—
Sinter B (plain)	30.11	15.6	0.85	17.08	—
" (fused portion)	28.77	16.0	0.95	14.0	—
Sinter C (NaCl)	29.33	14.9	0.81	14.08	18.04
Sinter D (H₂SO₄)	29.55	14.3	0.94	13.74	23.00
" (fused portion)	29.00	14.1	0.81	15.56	26.80
Sinter E (NaCl.H₂SO₄)	29.09	16.5	0.85	14.48	18.70
Heads Analyses	26.7	12.0	0.88	12.08	

TABLE XXVII

LEACH TESTS ON SINTERED PRODUCTS OF ARK 1-1

Leach Number	Mc-30	Mc-31	Mc-32	Mc-51	Mc-52
Product Leached-Ark 1-1	Sinter C	Sinter B	Sinter B	Sinter[a] A	Sinter A
Mesh	uncrushed	uncrushed	uncrushed	uncrushed	uncrushed
Reagent Used	H_2SO_4	H_2SO_4	H_2O	H_2SO_4	H_2SO_4
Reagent Strength, per cent	0.25	0.25		1	1
Leach Charge - grams solid	124	124	50	35	35
Leach Charge - milliliters liquid	500	500	500	200	400
Pulp Density $\frac{L}{S}$	4	4		5	10
Theoretical Acid Required, pounds/ton	200	200		150	300
Total Acid Added, pounds/ton	50	50			
Acid Consumed, pounds/ton	50	50		145	252
Residual Acid, pounds/ton	0	0		5	48
Time of Leach, hours	5	5	5	1	1
Temperature of Leach, °C.	25	25	25	25	25
Agitation	Rolls	Rolls	Rolls	Rolls	Rolls
Charge Recovered, per cent	98	98	100	98	98
Extractions of Mn, per cent of total				6.17	11.6
Phosphorus in Leach Tails, per cent	0.788	0.853	.811	2.32	2.18

a. The plain sinter was made from Arkansas 1-4 with a heads analysis of 2.06 per cent
    phosphorus.

TABLE XXVIII

LEACH TESTS ON SINTERED PRODUCTS OF ARKANSAS 1-1

Leach Number	Mc-53	Mc-54	Mc-55	Mc-56
*Product Leached	Sinter B	Sinter C	Sinter D	Sinter E
Mesh	Uncrushed	Uncrushed	Uncrushed	Uncrushed
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, per cent	1	1	1	1
Leach Charge - grams solid	25	25	25	25
Leach Charge, milliliters liquid	(200	(200	(200	(200
	(100	(100	(100	(100
Theoretical Acid Required, pounds/ton ore	300	200	200	200
Total Acid Added, pounds/ton ore	300	300	300	300
Temperature of Leach, °C.	25	25	25	25
Phosphorus in Leach Tails, per cent	2.16	0.763	0.749	0.875

*Sinter B was made from Arkansas 1-4 with a heads analysis of 2.06% P.

Each sample was washed for five minutes in 200cc of 1 per cent acid, the acid decanted off,
100 cc of fresh 1 per cent acid added and sample washed for another five minutes. Acid was
then decanted, sample washed twice with cold water.

TABLE XXIV

LEACHING OF SINTER BY PERCULATION METHODS - ARKANSAS 1-1

Leach Number	Mc80	Mc81	Mc82	Mc83
Product Leached	Sinter A	Residue from 80	Sinter C	Residue from 82
Mesh	Uncrushed	Uncrushed	Uncrushed	Uncrushed
Reagent Used	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Reagent Strength, per cent	$\frac{1}{2}$	3	$\frac{1}{2}$	3
Leach Charge, grams solid	100		100	
Theoretical Acid Required, pounds/ton ore	200		200	
Total Acid Added, pounds/ton ore	100	125	75	125
Acid Consumed, pounds/ton ore	30	36.5	67	
Time of Leach, minutes	30	15	30	15
Temperature of Leach, °C.	25	25	25	25
Agitation	None	None	None	None
Extractions of Mn, per cent of total	2.1	2.46	2.8	
Phosphorus in Leach Tails, per cent		0.783		0.769
Phosphorus in Leach Heads, per cent		0.953		0.841

Acid was percolated through sinter at fairly rapid rate with continuous

re-circulation for periods of time noted.

CONCLUSIONS

The conclusions that can be drawn from the data obtained in this research problem narrow down to the following major considerations:

1. The most abundant phosphate mineral in the Arkansas wad ores investigated in this work is phosphate rock, with apatite the second most important phosphorus-bearing constituent.

2. These phosphate minerals are sufficiently soluble in dilute acids under the proper conditions so that they can be leached to produce a residue which will meet ferro-grade B specifications.

3. Leach residues containing as low as 0.09 per cent phosphorus can be produced at a cost of approximately $7.50 per ton, but the process is economically impossible.

4. Ultimate methods of leaching the ore must either use filtration in a counter-current system, or a stabilizing reagent must be discovered which will allow the phosphate to go completely into solution and remain in a soluble form until the leach solution can be removed from the ore.

5. Leaching directly on a filter seems to have possibilities.

6. Sintered products are not amenable to leaching methods because of their fused condition.

7. Phosphorus cannot be volatilized from the ore by ordinary methods in the Dwight-Lloyd type laboratory sintering machine.

Although a large amount of work has been done upon this problem and some ferro-grade products produced, an economically sound method for removing phosphorus from the Arkansas wad ores still remains to be developed. This paper has shown that the phosphorus can be removed from

the ore, and the writer is confident that the Bureau of Mines Staff
which is continuing the work will find a practical solution to the
problem in the very near future.

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INDEX