

Volatilization of Phosphorus from Phosphate Rock

I—Experiments in Crucibles and Rotary Kiln¹

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AUTHOR'S NOTE—This is the first of a series of papers describing experiments conducted for the Stockholders' Syndicate of Los Angeles on the volatilization of phosphorus from western phosphate rock mined in southeastern Idaho. The present paper will deal with small experiments in crucibles and will briefly describe a larger scale attempt to volatilize phosphorus in a rotary kiln. The next paper will describe experiments with a small blast furnace charged with coke, phosphate rock, and flux, all in coarse crushed sizes and blasted with oxygen enriched air; and the last paper will be devoted to the development of the elements of design of a large blast furnace, with conclusions as to the probable economic importance of the process.

Acknowledgment is due to L. V. Steck, Ross Cummings, Geo. H. West, and to many others who were associated with the writer throughout this work, and to F. W. Braun, president of the Stockholders' Syndicate.

ROSS, Mehring, and Jones (2) describe an attempt to volatilize phosphorus from mixtures of phosphate rock and sand in the presence of carbon at temperatures below the actual fusion point of the mixture of phosphate rock and sand. They also describe an experiment showing that a high extraction of phosphorus may be obtained from a mixture of phosphate rock and carbon.

Note—Throughout these papers reference will be made to the volatilization of phosphorus, although P_2O_5 is always collected.

A patent was also issued to Guernsey and Yee (1) covering the volatilization of such mixtures in a rotary kiln at temperatures below their point of fusion.

Certainly a method for volatilizing phosphorus in a rotary kiln without fusion held great attraction and the writer, therefore, undertook an independent investigation seeking to confirm these proposals, using western phosphate rock and char made from Rock Springs coal as a reducing agent.

Volatilization in Crucibles

The first step undertaken was the investigation of the variables time, temperature, and mixture in covered crucibles heated in a DeVilbe furnace (coke-fired with forced draft). No. 2 graphite crucibles were employed which usually held 200 grams of charge, but some runs were made with 30-gram charges. The furnace is shown in Figure 1 and the entire outfit in operation is illustrated in Figure 2. It will be noted that temperatures were measured by sighting with a Morse optical pyrometer through a refractory tube directly onto the wall of the crucible.

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Experiments were conducted in covered crucibles for the purpose of determining the effect of the variables time, temperature, and mixture in the volatilization of phosphorus from mixtures of western phosphate rock, char, and silica in varying proportions and sizes.

In the course of this work an interesting phenomenon was observed which might be termed "inhibition of melting by the presence of carbon." If sufficient carbon were present in a mix of phosphate rock and sand which would fuse when carbon was absent or present in usual amount for reduction between 1300° and 1400° C. temperatures as high as 1650° C. could be attained without showing visible signs of fusion. Other conditions being correct, a temperature of 1450° to 1500° C. is required in the reacting materials for rapid and substantially complete elimination of phosphorus.

Experiments to effect volatilization of phosphorus in a rotary kiln from mixtures similar to those tested in the crucibles are described. Owing to insufficient thermal head phosphorus was not volatilized. The low thermal head resulted from the rapid burning of carbon by carbon dioxide to carbon monoxide, a strongly endothermic reaction. Phosphorus was finally volatilized by adding oxygen to the preheated blast.

presence of carbon." If sufficient carbon were present in a mix of phosphate rock and sand which would fuse when carbon was absent or present in usual amount for reduction, between 1300° and 1400° C., temperatures as high as 1650° C. could be attained without showing visible signs of fusion except a few small pellets in a few cases. In the experiments reported, except otherwise noted, all the ingredients of the mix were ground together in a small pebble mill to -200 mesh. The char was mostly made from Rock Springs coal which had been calcined in retorts at about 650° C. The phosphate rock had the following analysis:

	Per cent		Per cent		Per cent
P_2O_5	30.95	Al_2O_3	2.22	SO_3	2.74
CaO	46.15	Fe_2O_3	0.78	Fluorine	3.25
SiO_2	4.66	MgO	0.62	Loss on ignition	8.90

Table I—Effect of Time on Volatilization of Mixes (Temperature, 1550° C.)

RUN	P_2O_5	TIME Minutes	APPEARANCE OF DISCHARGED MATERIAL
	EXTRACTION Per cent		
50 PER CENT PHOSPHATE ROCK, 50 PER CENT CHAR			
54	69.5	105	Slight shrinkage, black powder
53	68.3	90	
22 ^a	52.7	75	
55	57.8	55	
61	37.1	15	
63 PER CENT PHOSPHATE ROCK, 21 PER CENT CHAR, 16 PER CENT SAND			
66	78.0	15	Shrunk 1/2 to 2/3; black and gray powder
67	82.4	35	
68	92.4	55	
65	95.7	75	
70	97.7	90	

^a Mixed on cloth.

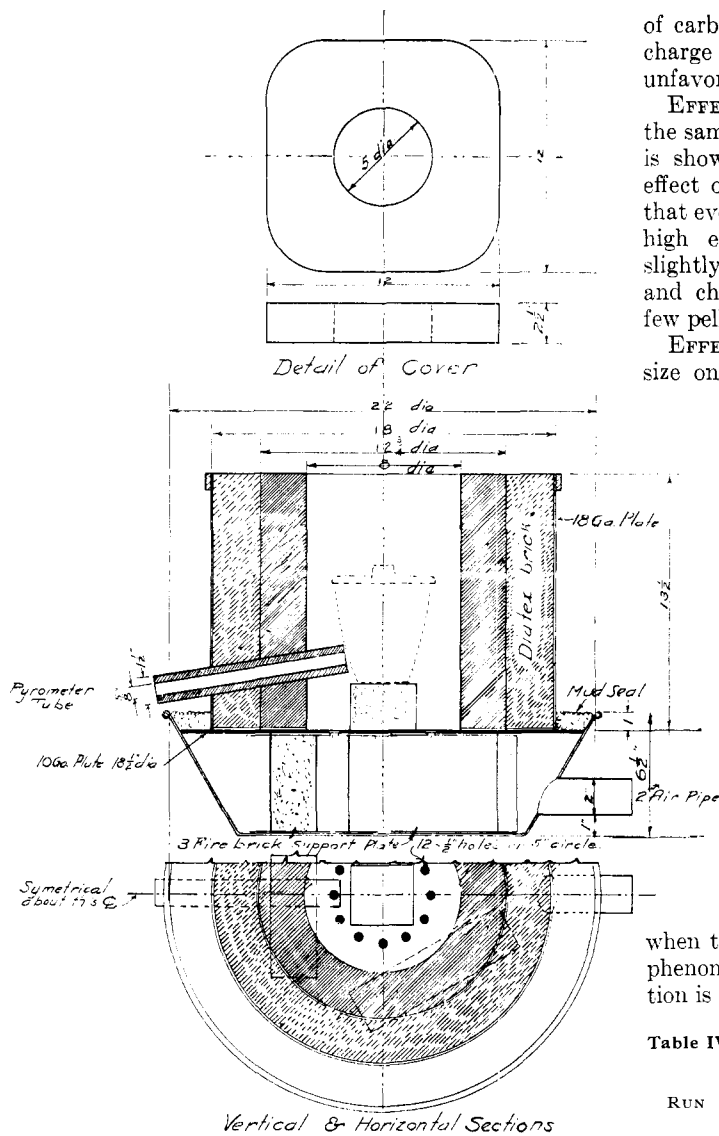
EFFECT OF TIME—Table I shows the effect of time on volatilization of two mixes at 1550° C. It is noteworthy that the mixture of phosphate rock and char, in spite of the large amount of the latter, does not show high extractions. Evidently silica is needed to promote volatilization. To check the action of silica without carbon, several runs were made in which sufficient silica was added to form calcium silicate. (Table II)

Table II—Volatilization of Phosphate Rock and Silica, Carbon Absent

RUN	TIME Minutes	TEMPERATURE ° C.	P_2O_5	CONDITION OF RESIDUE
			EXTRACTION Per cent	
149	75	1650	86.4	Dark green glass
153	60	1450	53.0	Opaque white mass

EFFECT OF COMPOSITION OF MIX—Table II shows the effect of changing the mol ratio $CaO:SiO_2$ in mixes containing an excess of 50 per cent of carbon over the requirements for

¹ Received December 16, 1929.



Vertical & Horizontal Sections
Figure 1—DeVilbe Furnace

reduction in accordance with the nominal equation of the reaction:

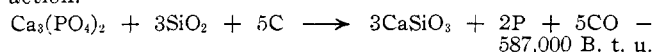


Table III—Effect of Varying Lime-Silica Ratio on Volatilization of Mix Containing 50 Per Cent Excess Carbon in Each Charge (Temperature, 1500° C., time, 45 minutes)

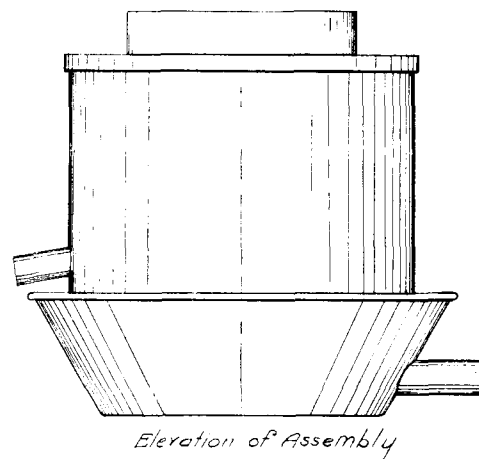
RUN	CaO:SiO ₂	P ₂ O ₅ EXTRACTION Per cent	CONDITION
159	2:3	96.8	Hard button; no fines
136	1:1	98.4	Fused and separated from char
160	3:2	96.5	Soft lump, gray and black, sintered
161	2:1	85.0	Soft black lump
162	3:1	68.0	Fine black powder, some sintering

These data show that both carbon and silica are necessary for high extraction, although there appears to exist no requirement for a precise stoichiometric relation between lime and silica. This might be inferred from the fact that both silica alone and carbon alone will produce partial volatilization. When carbon is present in excess, evidently all P₂O₅ is reduced to phosphorus, and this assists the reaction between the silica and the lime; at the same time the carbon attacks the rock independently. Thus in the presence of a surplus of carbon substantially complete elimination of phosphorus is attainable with relatively small amounts of silica. Table III also shows that when only so small an excess of 50 per cent

of carbon is present over the requirements of reduction the charge becomes fused, but this does not affect volatilization unfavorably.

EFFECT OF TEMPERATURE—The effect of temperature upon the same mixes used for the experiments described in Table I is shown in Table IV. This table brings out clearly the effect of excess carbon in inhibiting fusion. It also shows that even at 1600° C. carbon alone is not sufficient to cause high extraction, and only at 1650° C. does extraction slightly exceed 90 per cent. In the phosphate rock, sand, and char mix the residues were all powdery, except for a few pellets.

EFFECT OF GRAIN SIZE—Table V shows the effect of grain size on the phenomenon of "inhibition of melting." Only



when the entire charge is ground finer than 200 mesh is the phenomenon observed. It is also shown that the volatilization is somewhat assisted by a coalescence of the particles.

Table IV—Effect of Variable Temperature on Volatilization of Mixes (Time, 75 minutes)

RUN	TIME IN FURNACE Minutes	TEMPERATURE ° C.	P ₂ O ₅ EXTRACTION Per cent	APPEARANCE OF DISCHARGED MATERIAL
103 ^a	78	1300	61.1	Loose black powder
111 ^a	78	1300	42.2	
44	85	1400	27.4	
38	80	1450	39.7	
13	96	1500	38.1	
22	85	1550	52.7	
27	85	1800	67.2	
34	120	1650	91.5	
46 ^b	75	1400	72.7	63 PER CENT PHOSPHATE ROCK, 21 PER CENT CHAR, 16 PER CENT SAND Gray and black powder, some gray pellets of rather hard material
69	75	1450	91.1	Black with gray surface
64	75	1500	93.9	Black with gray surface, some + 150 mesh
65	75	1550	95.7	Black with gray surface, some + 150 mesh

^a Thirty-gram charge.
^b Mixed by hand.

Table V—Effect of Various Grain Sizes of Mix Composed of 63 Per Cent Phosphate, 21 Per Cent Char, and 16 Per Cent Sand (Time, 60 minutes; temperature, 1550° C.)

RUN	GRAIN SIZE ^a Mesh	P ₂ O ₅ EXTRACTIONS Per cent	CONDITION OF RESIDUE
88	- 35 + 48	94.1	Button in bottom, fines black
82	- 48 + 65	97.0	
83	- 65 + 100	97.6	
84	- 100 + 150	96.2	
85	- 150 + 200	96.8	
94	- 150 + 200	94.1	
86	- 200	92.6	Powdery mass, powder and "shot"

^a All components of mix of these sizes.

An experiment was subsequently tried in which the rock and sand were ground to -200 mesh but the char was rather

coarse. Coalescence in this case was partly inhibited, but not to the same extent as when all the material was -200 mesh.

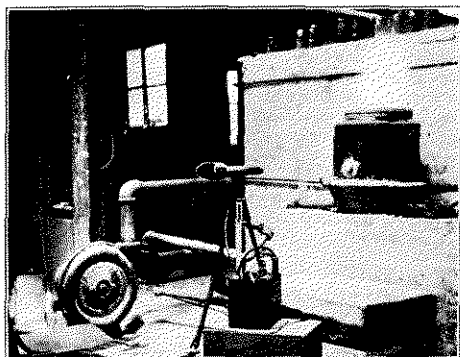


Figure 2—Deville Furnace in Operation with Optical Pyrometer in Position to Determine the Temperature in the Furnace

Volatilization in Rotary Kiln

An attempt was made to effect volatilization of phosphorus in a rotary kiln from mixtures similar to those tested in the crucibles. A photograph of the kiln is shown in Figure 3 and a cross-sectional sketch in Figure 4. The kiln was fired with a standard oil burner using distillate. The general idea of the operation was to employ a large excess of carbon so that a reducing atmosphere would be maintained in the charge. In a typical run the feed was made up as follows:

	Pounds
Non-coking coal	40
Char from same	40
Coking coal	20
Phosphate rock	71.5
Silica	28.5

The presence of the coking coal made the charge lump up to some extent, which it was thought might aid in reduction.

The P_2O_5 content of the carbon-free feed was 22.4 per cent. The phosphate rock was ground so that 59 per cent was -200 mesh. The silica was all -200 mesh and the coal and char were about -10 mesh. Temperatures were read by an optical pyrometer sighted through a small hole in the firing hood. For 2 hours during the run temperatures were held at 1450° C. with the fuel on. Checks made immediately after the oil was shut off showed 1400° and 1368° C. At no time during the run was any material discharged from the kiln which was low in P_2O_5 . The metallurgical results of this run, which are typical of the seven runs, are shown in Table VI, and show practically no volatilization of phosphorus, as may be gathered from the fact that, of the total phosphorus in the feed, 76.7 per cent was found in the kiln discharge and 15.7 per cent in the flue dust. (Fusion was never complete but small masses of semi-fused material were present in the discharge from the kiln.)

The other experiments with the rotary kiln may be very briefly summarized. The negative results of seven runs led to the supposition that the flame did not have a sufficient thermal head. Therefore, the air for combustion was preheated to about 371° C., but still with negative results. As

a last resort oxygen was added to the preheated air for combustion, giving 52 per cent of oxygen by weight in the blast. When the flame was on, the reading on the optical pyrometer was 1750° C., when the flame was off, it was 1650° C. Under these conditions a viscous slag was produced, which did not run freely from the kiln but contained only 0.9 per cent P_2O_5 . Obviously, the conditions under which this slag was produced were entirely impractical, because no kiln lining could stand up for more than a few hours, but this proved that if the thermal head of the flame was made high enough phosphorus could be volatilized in a rotary kiln.

Table VI—Attempt to Volatilize Phosphorus in Rotary Kiln without Fusion

PRODUCT	PER CENT OF C-FREE FEED	PER CENT OF TOTAL P_2O_5 IN FEED	P_2O_5 IN EACH PRODUCT (C-FREE BASIS)	
			Per cent	
Kiln discharge	61.1	76.7	28.1	
Flue dust	16.1	15.7	21.9	
Stack loss and unaccounted for (by diff.)	22.8	7.6	7.4	

Discussion and Conclusions

It is possible to effect substantially complete volatilization of phosphorus in covered crucibles heated in a coke furnace without fusing the charge when the mix is of phosphate rock, sand, and carbon all ground to less than 200 mesh, and when carbon is present in considerable excess. Neither carbon nor silica alone is sufficient to effect complete volatilization at 1550° C. If grinding is coarser than -200 mesh, the charge fuses and this tends somewhat to assist volatilization.

Charges of ground phosphate rock, silica, and excess carbon were heated in an oil-fired rotary kiln to temperatures between 1400° and 1450° C. without effecting any volatilization of phosphorus worth recording. The phosphate rock-silica part of the charge became semi-fused and coalesced into porous masses. Judging from the results of the crucible experiments one would have expected some volatilization to occur, and its almost complete absence is rather surprising. The explanation follows from the fact that the carbon dioxide of the flame permeates the porous charge and the endothermic reaction between carbon and carbon dioxide is so rapid that the

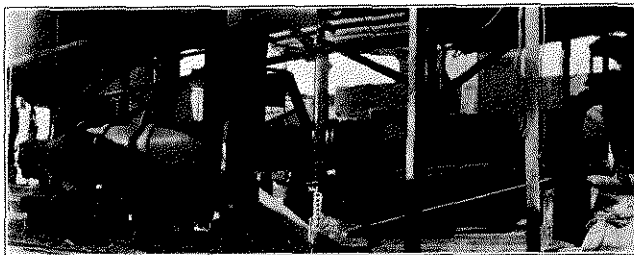


Figure 3—Rotary Kiln

net result of the combustion in the kiln was the burning of carbon to carbon monoxide. This combustion with air at room temperature does not furnish a high enough thermal head to effect the strongly endothermic reaction of volatilization of phosphorus, which was shown by the crucible experiments to require a temperature around 1500° C., which is in excess of that resulting from the combustion of carbon to carbon monoxide.

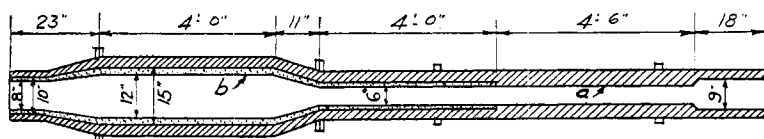


Figure 4—Longitudinal Section of Rotary Kiln

Complete volatilization was effected in the rotary kiln by increasing the thermal head of the flame by use of oxygen-enriched air for combustion, but the wall of the kiln became so hot that it would be rapidly destroyed. No known lining could stand these conditions in practical operation.

The volatilization of phosphorus involves a reaction which absorbs much heat and which must be carried out at a high temperature. For practical working, therefore, a large supply of heat at a very high temperature must be brought to bear

upon the reaction. This does not mean that the reacting materials themselves must be heated more than to about 1500° C., and possibly temperatures as low as 1400° to 1450° C. may suffice when the materials are fully melted, but in order to force heat to flow rapidly into these materials the source of heat must have a considerably higher temperature. This explains why the electric furnace is so effective for the volatilization of phosphorus.

The most promising outlook for volatilization of phosphorus with fuel is therefore in the coke-fired blast furnace with oxygen-enriched blast.

Literature Cited

- (1) Guernsey and Yee, U. S. Patent 1,422,699 (July 11, 1922).
- (2) Ross, Mehring, and Jones, *IND. ENG. CHEM.*, **16**, 563 (1924).

Loss of Mercaptan Sulfur in Naphtha by Use of Inorganic Salts and Caustic Soda¹

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THE literature dealing with the reactions of known mercaptans in hydrocarbons as solvent is not extensive, most of the work having to do with the removal of mercaptans from the refining viewpoint. The reaction that seems to have been studied more than any other is that which involves sodium plumbite, lead sulfide, and caustic soda, or the doctor and the resulting lead sulfide.

Wendt and Diggs (?) discuss the reactions of sodium plumbite and ethyl and cetyl mercaptans. Simultaneously Wood, Lowy, and Faragher (8) give a detailed study of sodium plumbite and isoamyl and isobutyl mercaptans, showing that disulfides are formed. Morrell and Faragher (5) studied ethyl, *n*-butyl, isoamyl, heptyl, and benzyl mercaptans with different combinations of lead sulfide, doctor, caustic soda, sulfur, and oxygen. The use of alcoholic doctor for complete removal of mercaptans has been recommended by Faragher, Morrell, and Monroe (4), using ethyl, *n*-propyl, *n*-butyl, isoamyl, and benzyl mercaptans. Youtz and Perkins (9) have suggested the addition of lead sulfide to the alcoholic doctor for the same purpose. Birch and Norris (2) have studied the removal of mercaptans with caustic soda using ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and isoamyl mercaptans dissolved in naphtha. They show that alkali removes the lower mercaptans almost completely and less of those with increasing molecular weights. Wood, Lowy, and Faragher (8) also studied the effect of aluminum trichloride on isoamyl, mercaptan, copper oxide on isoamyl and *n*-propyl mercaptans, sulfuric acid on isoamyl, *n*-amyl, and isobutyl mercaptans, and

This paper describes a study of the removal of low-boiling mercaptans from various naphthas by inorganic salts and sodium hydroxide. The experiments indicate that the removal of a mercaptan from a naphtha is dependent upon the reagent used, the molecular weight and configuration of the mercaptan. The solvent also plays some part, but just what has not yet been fully determined.

sodium hypochlorite on isoamyl and isobutyl mercaptans. Waterman and Heimel (6) studied the effect of sodium hypochlorite on thiophenol and Birch and Norris (1) studied ethyl, isopropyl, and isobutyl mercaptans with the same reagent.

Of the mercaptans studied it will be noted that but one secondary aliphatic mercaptan, isopropyl, has been used. The branched-chain aliphatic mercaptans are represented by isobutyl and isoamyl. The present knowledge of the chemistry of the mercaptans in a hydrocarbon solution (or naphtha) is based upon studies of these with the hope that the information thus gained will be applicable to all mercaptans. Whether this holds or not can only be decided after much experimental work.

This paper describes the results of a study of the removal of mercaptans by inorganic reagents and sodium hydroxide. The mercaptans studied are ethyl; normal and iso-propyl; normal, iso-, and secondary butyl; and normal, iso-, and secondary amyl (pentathiol-2). These include four primary straight-chain, two primary branched-chain, and three secondary straight-chain mercaptans. All are rather low boiling—that is, from ethyl at 35° C. to *n*-amyl at 124° C. The higher boiling mercaptans in naphtha will be discussed in later papers.

Materials Used

The naphthas used are described in another paper (page 249 this issue), the numbers being the same throughout. Ethyl, isobutyl, and isoamyl mercaptans were used as purchased from the Eastman Kodak Company. The others were prepared as part of this project and the method of preparation and constants will be published later.

The samples were made up by weight, the mercaptans being sealed in small bulbs for weighing. The samples were then analyzed by the silver nitrate titration method (3) and frequently checked to see if any decomposition had occurred. There was no opportunity to check this work by the use of the lamp sulfur.

¹ Received January 21, 1930. This paper contains results obtained in an investigation on "A Study of the Reactions of a Number of Selected Organic Sulfur Compounds" listed as Project 28 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

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