Manufacture of Phosphoric Acid by the Volatilization Process[1]

Some Technical Problems

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The production of phosphoric acid by the volatilization method has distinct advantages over the sulfuric acid method—(1) low-grade phosphates can be used, (2) costly filtration and evaporation are obviated by using the Cottrell method of precipitation, and (3) the cost of the thermal energy required should be less than the cost of chemical reagents necessary to effect the same results.

The fuel furnace has been shown to cause volatilization as efficient as the electric furnace, although radiation and heat losses are considerably less in the electric smelting. Such losses, however, can be considerably reduced.

The question of what temperature is best adapted for the volatilization, especially in the fuel furnace, is still only partially answered, since it is dependent upon other factors, such as the lime-silica ratio in the charge, the fineness of division and intimate contact of the reacting materials, the amount of reducing agent present, the time factor, and the type of furnace used. The first of these factors is equally important in both electric and fuel smelting.

Another important problem of commercial importance studied at this laboratory is the determination of the proper P_2O_5 content of the residual slag for the most economic operation. There are a number of others which also offer fields for valuable research.

THE volatilization method of producing phosphoric acid is now an assured commercial success where relatively pure acid and high-grade phosphate products are desired. This method, however, has not become a factor in producing phosphates for fertilizer purposes, but with increased efficiency and a better utilization of the heat units generated by the reactions involved there is little question in the mind of the writer that the process will eventually play an important role in the fertilizer industry. At least one commercial concern in this country is producing phosphoric acid by this general method on quite an extensive scale, and while ferrophosphorus was at first the main product of

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this company the phosphoric acid output has now become a factor of prime consideration.

THEORETICAL CONSIDERATIONS

From a strictly theoretical standpoint the production of phosphoric acid by the volatilization method, using either fuel or electric power as a source of thermal energy, has three distinct advantages over the sulfuric acid method:

(1) It makes possible the use of low-grade and run-of-mine phosphates generally considered unfit for treatment with sulfuric acid.

(2) By using the Cottrell method of precipitation to collect the volatilized phosphoric acid, a concentrated product is obtained directly without involving costly filtration and evaporation steps.

(3) The quantity of electric energy or fuel theoretically required should be an item of expense appreciably less than the cost
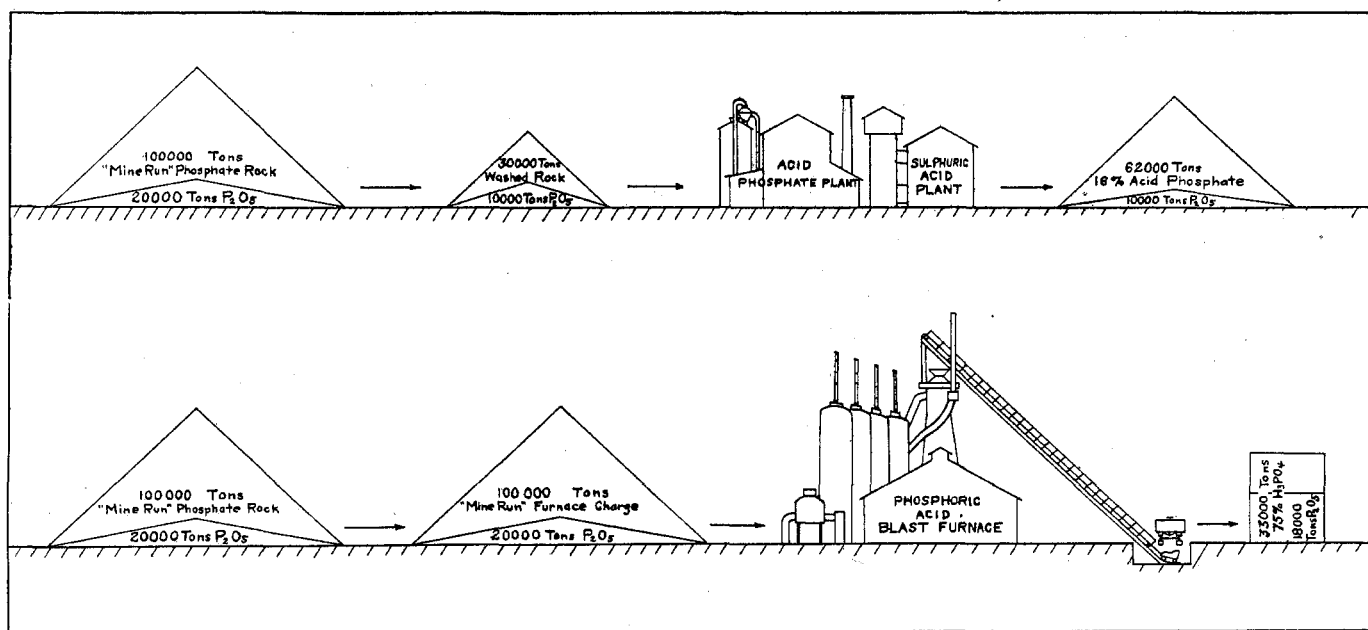

Fig. 1 (upper)—In the present method of preparing phosphatic fertilizers, only one-half of the phosphoric acid present in the deposit in the form of washed rock reaches the fertilizer factory. This rock is then treated with an equal amount of sulfuric acid and manufactured into acid phosphate, a product containing the same amount of phosphoric acid but in fully twice the bulk

Fig. 2 (lower)—In the furnace method of preparing phosphoric acid, the entire deposit of phosphate may often be utilized, and thus the losses of 50 per cent entailed in washing or purifying the rock eliminated. Assuming a 90 per cent efficiency in the furnace plant, the final product is a liquid containing nearly twice as much phosphoric acid (P_2O_5) as acid phosphate in a little more than one half the weight. This acid may be manufactured into a number of concentrated products suitable for fertilizer use

TABLE I—THEORETICAL HEAT BALANCE OF ELECTRIC FURNACE OF SIMPLE CRUCIBLE TYPE
(Capacity 10 tons P2O5 per day of 24 hours)

Item	Actions Affecting Temperature	Heat Generated (Plus)		Heat Consumed (Minus)	
		Thousands of Kg. Calories per Ton$d$ of P_2O_5	Per cent of Total	Thousands of Kg. Calories per Ton$d$ of P_2O_5	Per cent of Total
1	Absorbed by burden before fusion$a$	...	...	...	...
2	Absorbed by burden in fusing$a$	...	...	...	...
3	Absorbed by endothermic reactions	...	...	4100	36.1
4	Evolved by exothermic reactions	420	3.7	...	...
5	Evolved by oxidation of C to CO	1140	10.0	...	...
6	Evolved by oxidation of this CO to CO_2	2660	23.4	...	...
7	Evolved by oxidation of P to P_2O_5	2850	25.0	...	...
8	Removal of heat by cooling masonry	...	...	1619	14.2
9	Removal of heat by slag$b$	...	...	1707	15.0
10	Removal of heat by evolved gases (at 650° C.)	...	...	2350	20.6
11	Removal of heat by unburned COc	...	...	1600	14.1
12	Heat supplied by electric energy	4306e	37.9	...	...
13	TOTAL	11,376	100.0	11,376	100.0
14	Economy$f$ { Pounds P_2O_5 per kilowatt hour	0.44			
	2000 pounds P_2O_5 per kilowatt year	1.90			
	2000 pounds P_2O_5 per horsepower year	1.43			
	Over-all thermal efficiency, per cent	36.10			

a Included in Item 9.
b Including small amount removed by ferrophosphorus.
c Assuming one-third of Co unburned in furnace.
d Metric ton.
e 5010 kilowatt-hour.
f Production based on 90 per cent recovery of P_2O_5 in furnace charge.

of the sulfuric acid necessary to convert an equivalent amount of phosphate rock into an available form.

The first point may be illustrated in the following sketches, which compare the yield of phosphoric acid (in the form of acid phosphate) actually obtained from a given quantity of run-of-mine phosphate with that which may be recovered where this same quantity of run-of-mine material is treated directly in an electric or fuel furnace. Since in many cases the washing of phosphate rock may be dispensed with where the latter process is employed, the losses of valuable phosphate thus entailed are largely eliminated and a much fuller utilization of phosphate deposits is thus effected.

The second point, the saving in handling and transportation charges which may be brought about where a relatively concentrated product is obtained, is illustrated in the following sketches, drawn to scale, which show the amount of car space occupied by equivalent quantities of phosphoric acid in several types of finished products.
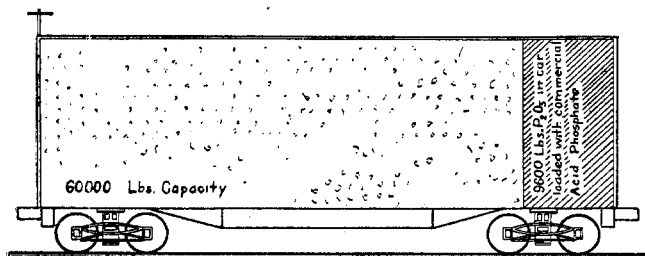

FIG. 3

A car loaded to capacity (60,000 pounds) with 16 per cent acid phosphate (standard phosphate fertilizer of today) contains only 9600 pounds of actual phosphoric acid (P_2O_5). Yet transportation and handling charges must also be paid on 84 per cent of gypsum and other impurities contained in this product.

It will be noted that by producing, instead of the ordinary acid phosphate containing 16 per cent of soluble P_2O_5, double acid phosphate containing 45 per cent of P_2O_5, or 75 per cent liquid phosphoric acid containing over 50 per cent of P_2O_5, or monoammonium phosphate containing over 60 per cent P_2O_5 besides an appreciable amount of nitrogen, a great reduction in the annual freight bills for fertilizer materials might readily be brought about.

The third point, the economy in the thermal energy where the volatilization process is employed, has perhaps not been given the thorough study and consideration which it deserves. In Table I the heat balance of a simple electric crucible furnace is shown. While certain assumptions have been made in making up this table, the figures are considered conservative as far as they show the relative quantities of heat generated and heat consumed in a furnace of this type.

The various items are based on the assumption that the furnace has a capacity of 10 tons of P_2O_5 per day, that sufficient coke is present in the charge to reduce completely the phosphoric acid to elemental phosphorus, and that the ratio of silica to lime is approximately the same as that in calcium metasilicate ($CaSiO_3$). Under these conditions the over-all furnace reactions are exothermic; in other words, if no sensible heat were lost in the evolved gases, in unburned carbon monoxide, by radiation through the walls of the furnace and in the slag which is tapped off, the reaction when started should go to an end without power consumption.

It is impossible, of course, to eliminate entirely any of these losses, and some of them can only be partially reduced. The heat units contained in the slag tapped off are almost entirely wasted and certain loss of heat by radiation through the walls of the furnace is unavoidable, although by the use of the highest grade refractories it might be considerably lowered. Items 10 and 11 in this table, however—namely, the removal of heat by evolved gases and by unburned carbon monoxide—could be cut down very greatly if proper regenerative apparatus were employed, and it will be noted that the sum of these two items is 34.7 per cent of the total heat consumed, and only 3.2 per cent below the quantity of thermal energy supplied to a furnace of this type by electric power. Therefore, with proper equipment designed to conserve a large amount of this avoidable loss of heat, it seems quite possible that the electric energy required for the pyrolytic process might be reduced to a point where its cost would be less than that of the sulfuric acid required for rendering an equivalent quantity of phosphate rock available.

ELECTRIC vs. FUEL FURNACE FOR THE VOLATILIZATION OF PHOSPHORIC ACID

The two types of furnaces so far proposed for decomposing phosphate rock and volatilizing its phosphoric acid content are
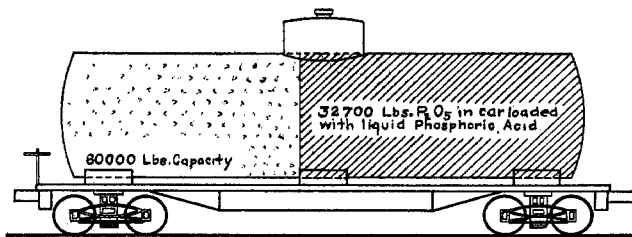

FIG. 4

A car loaded to capacity (60,000 pounds) with liquid phosphoric acid (75 per cent H_3PO_4) manufactured by the pyrolytic or furnace process contains 32,700 pounds of actual P_2O_5, or nearly three and one-half times as much as that in a car of acid phosphate.

the electric arc furnace and a modification of the blast or open-hearth furnace. The first type is the only one which has yet been applied in a commercial way, but whichever is used the process is based on the same fundamental principles. The main function which the electric arc furnace performs is to furnish high temperatures in a localized zone, and it permits the maintenance of strictly reducing conditions during the smelting operation. It has been conclusively demonstrated that where similar temperatures and reducing conditions are obtained in a furnace heated by fuel a volatilization of phosphoric acid fully as efficient as that obtained in the arc furnace can be brought about.
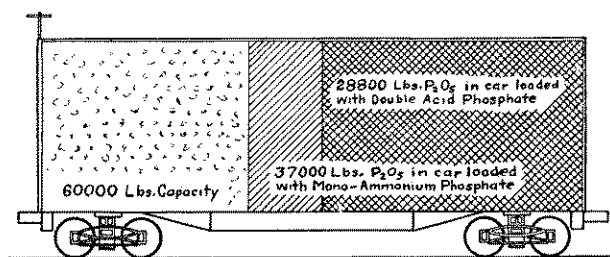

FIG. 5

A car loaded to capacity (60,000 pounds) with either double acid phosphate or monoammonium phosphate contains from 28,800 pounds to 37,000 pounds of actual P_2O_5, or from three to four times as much as that in a car of acid phosphate. By shipping phosphoric acid (P_2O_5) in these concentrated forms an annual saving of from \$8,000,000 to \$9,000,000 in freight charges alone might be eventually affected on this fertilizer ingredient.

Each method, however, has its own chemical and mechanical problems. In electrical smelting, where oxidation is not depended upon to generate the necessary heat, the highest temperature is confined to a relatively narrow zone, and since only a minimum amount of air is introduced, few gases are generated except from the constituents in the charge. It is readily seen, therefore, that radiation and heat losses in evolved gases are considerably less than in smelting by means of fuel, where the introduction of air is necessary to burn the fuel and furnish the high temperature required. In the latter case large volumes of nitrogen, water vapor, carbon monoxide, and carbon dioxide are produced, which carry in latent and sensible form an immense amount of thermal energy, which must be extracted in order to obtain an efficiency approximating that obtained in the electric furnace. Fortunately, modern furnace practice has given to us recuperative and regenerative apparatus which has proved highly effective in recovering the heat evolved in
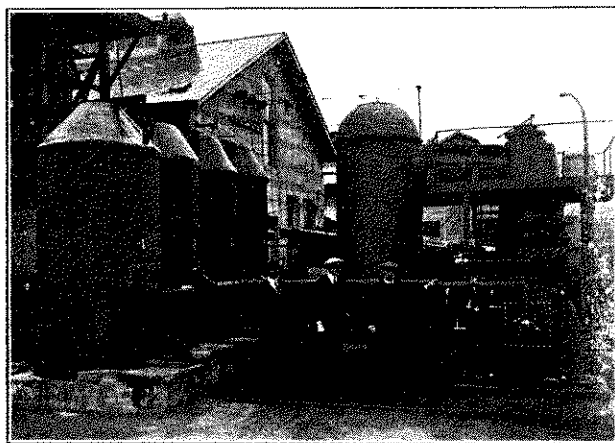

FIG. 6—GENERAL VIEW OF SMALL OIL BURNING FURNACE FOR THE VOLATILIZATION OF PHOSPHORIC ACID. ARLINGTON, VA

fuel smelting, and therefore it seems that much of this energy may be utilized.

It would appear that one of the first and most important problems to be solved in connection with the pyrolytic process is the determination of the temperature best adapted to bring about the volatilization of phosphoric acid from mixtures of phosphate rock, silica, and carbon, but, while much work has been done along this line, considerable doubt still exists regarding the minimum temperature required. The reason for this is that the temperature necessary for complete volatilization is dependent on a number of other factors, such as the lime-silica ratio in the charge, the fineness of division and intimate contact of the reacting materials, the quantity of carbon or reducing agent present, the time factor, and the type of furnace employed. Probably this problem is more strictly applicable to the fuel furnace than to the electric arc furnace, since in the latter type it is hardly possible to work at anything below a smelting temperature.

Nielsen,[2] Peacock,[3] and Guernsey and Yee[4] all state that phosphorus or phosphoric acid can be evolved either completely or in part from mixtures of phosphate rock, silica, and carbon at temperatures ranging from 1150° to 1350° C. The writer and his co-workers have found in both laboratory and large-scale experiments that a partial evolution of P_2O_5 is obtained from briquetted mixtures of phosphate rock, silica,
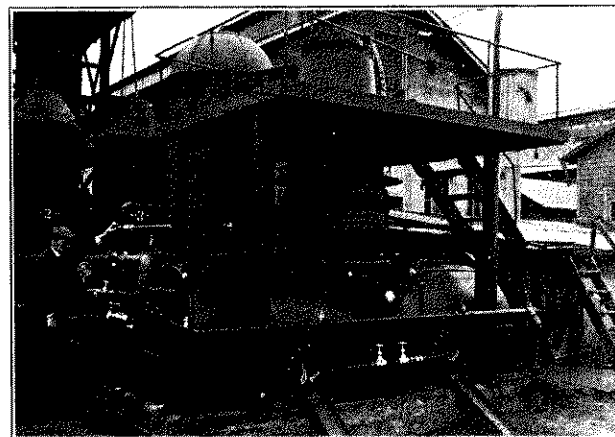

FIG. 7—A CLOSER VIEW OF THE FURNACE PROPER SHOWING THE EQUIPMENT FOR WATER-COOLING THE FURNACE, OIL BURNERS, AND CINDER NOTCHES

and coke at temperatures appreciably lower than the fusing points of such mixtures, and considerably below the temperatures attained in the arc furnace; but in no case where such briquetted charges were exposed directly to the flame did complete evolution of the P_2O_5 take place until the temperature was raised sufficiently high (1500° to 1600° C.) to reduce the mass to a fluid slag.

Whether or not it is commercially practicable to drive off the greater part of the P_2O_5 from such mixtures at temperatures below their fusing points under the conditions existing in direct fired furnaces or kilns yet remains to be proved, but if this can be accomplished without unduly prolonging the time factor, it may simplify the furnace design and materially reduce the cost of production.

The writer's experience has been that, in order to bring about the nearly complete volatilization of P_2O_5 from briquetted charges of phosphate rock, silica, and coke, and at the same time insure the working conditions necessary to make such a process continuous, a very fluid slag must be

[2] *Ferrum*, **10**, 97 (1913).
[3] *Am. Fertilizer*, **39**, 63 (1913).
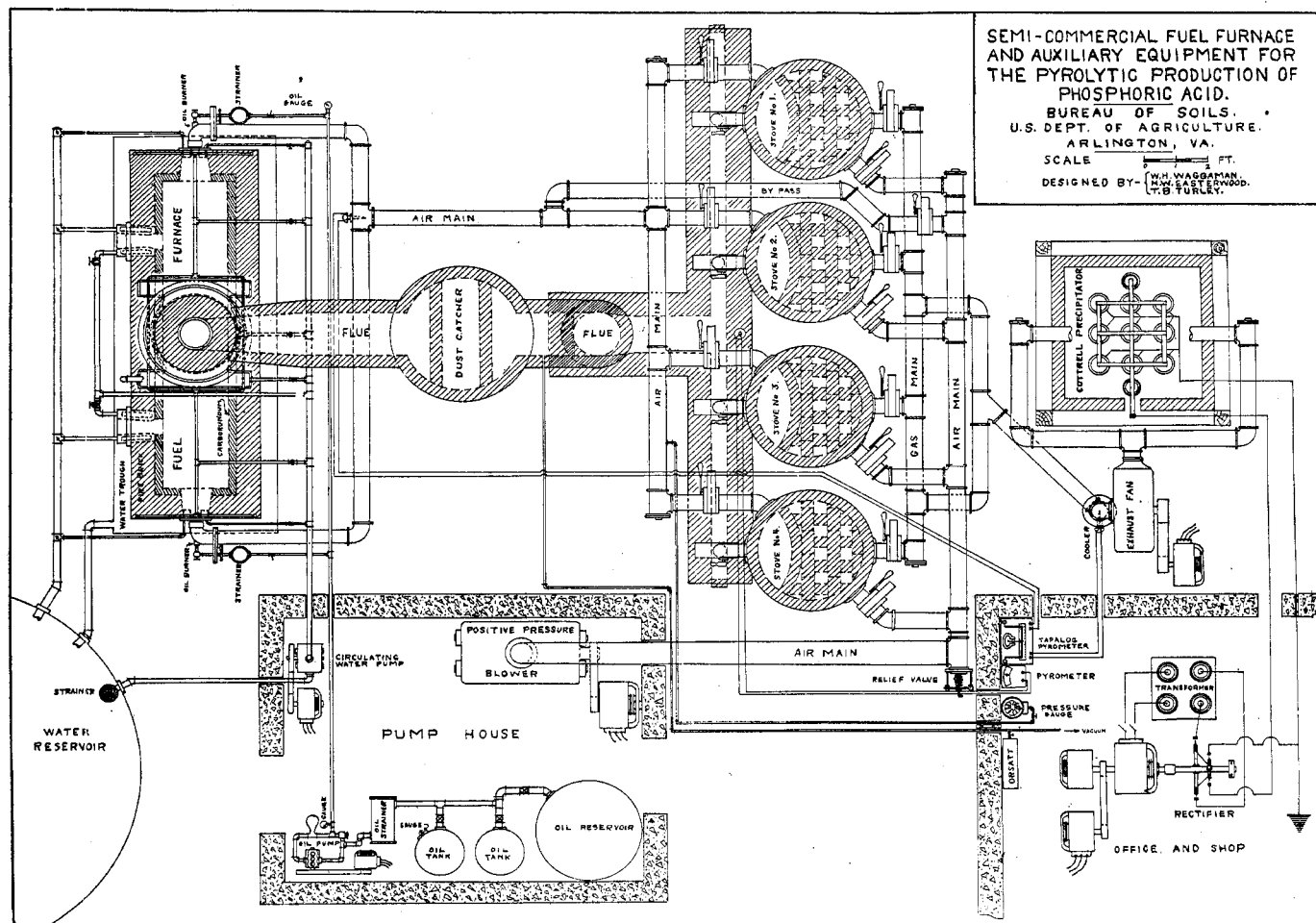[4] U. S. Patent 1,422,699 (1922).

FIG. 8

produced, for even under reducing conditions a viscous acid slag tends to retain or hold the phosphorus either in solution or in chemical combination, whereas this element may be readily boiled out of such a slag when it becomes very molten. Moreover, the successful operation of either the open-hearth or blast furnace depends upon the production of a slag which will flow freely from the tap holes when the smelting operation is completed.

In Figs. 6 and 7 are shown views of the small oil-burning furnace and its auxiliary equipment at Arlington Farm, Va., where experiments on a semicommercial scale are being conducted, and in Fig. 8 a plan view of the entire plant is shown.

The determination of the silica-lime ratio in the phosphate charge best adapted to the rapid volatilization of P_2O_5 is a problem equally important in both electric and fuel smelting. The writer and his co-workers have conducted a number of experiments with a view to determining the mixtures which will give a rapid evolution of phosphorus and yet yield a slag sufficiently fluid to admit of its being readily tapped from the furnace.

The details of these experiments will be published shortly in a bulletin of the U. S. Department of Agriculture. In a general way, however, it was found that at a definite temperature (1600° C.) the more acid slags give up their P_2O_5 content the quickest, but when the ratio of silica to lime in the mixtures is increased beyond 61 : 39 the melting point of the resultant slags increases to such an extent as to introduce serious difficulties in the tapping operation. Furthermore, these more acid mixtures involve the addition of so much silica that the phosphate content of the mass is considerably diluted, so that any advantage gained in the more rapid evolution of phosphorus is largely offset by the greater bulk of relatively valueless material which must be raised to a smelting temperature.

This brings up another important point which is of considerable commercial importance—namely, how low the P_2O_5 content of the residual slag should be reduced for the most economic furnace operation.

While it has been proved beyond question that the P_2O_5 can be eliminated almost entirely from the slag either in the electric or fuel-fired furnace, the recorded data showing what proportion of the total heat energy is required to drive off the last few per cent of this acid are as yet rather incomplete. Obviously, it would be poor economy to consume large amounts of power or fuel for the sake of freeing the slag entirely from P_2O_5, when the bulk of it may be driven off with considerable rapidity.

OTHER PROBLEMS

There are a number of other important problems in connection with this process, such as the possible commercial utilization of the slag or furnace residue and the effect at high temperature of P_2O_5 and other volatilized products on refractory linings and metal parts used in construction of a furnace plant. Some of these problems are partially solved and others have been scarcely attacked. It seems probable that most of them will be worked out in large-scale operations and an economic balance eventually established, but there is a field here for valuable laboratory research which may perhaps save considerable time, money, and energy.