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Future Prospects of Elemental Phosphorus and Furnace Acid

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Future Prospects of Elemental Phosphorus and Furnace Acid

Travis P. Hignett
Director of Chemical Development
Tennessee Valley Authority
Muscle Shoals, Alabama 35660

I have approached the task of preparing this paper with sadness occasioned by the death of my good friend Dr. Vincent Sauchelli who was originally invited to speak on this subject. Dr. Sauchelli has long been an inspiration and guiding spirit in the world of fertiliser technology, and he will be sorely missed.

I do not know what Dr. Sauchelli would have said on the subject of the prospects of elemental phosphorus as a fertiliser material. As far as I know, he had not made any substantial start on preparation of his paper. So I shall have to take full responsibility for the content of this paper.

The recent shortage of sulfur and high prices have stimulated interest in the electric-furnace process for producing phosphoric acid for fertiliser production. Sulfur supplies are now ample, and prices are receding. We have experienced two cycles of sulfur shortage and high prices in less than 20 years. Although the future trend is difficult to foresee, most observers expect that the long-range trend will be toward higher prices even though the present trend is downward. The cost of electricity on the other hand has been generally toward lower levels, and nuclear engineers predict that the trend will continue as advanced nuclear reactors now under development are brought into commercial use.

In the past, low-cost electricity has depended on low-cost fuel or hydroelectric generation; in the future it is expected that low-cost electricity may be produced in almost any location where the demand is sufficient to warrant construction of a large-scale nuclear-powered plant. So it seems appropriate to examine the present and future prospects of increased use of the electric-furnace process for supplying phosphatic fertilisers.

Advantages of Electric-Furnace Process

The electric-furnace process produces elemental phosphorus, a highly concentrated material which is equivalent to 229% P_2O_5. Advantage may be taken of this concentrated material to minimize transportation, storage, and handling costs. One ton of elemental phosphorus is equivalent to 7 to 10 tons of phosphate rock or 5 tons of triple superphosphate. Elemental phosphorus is noncorrosive and may be stored and handled in plain steel equipment. It can be pumped in liquid form at moderate temperatures. Precautions must be taken since elemental phosphorus is toxic and ignites spontaneously on contact with the air.

Elemental phosphorus can be readily converted to phosphoric acid of any desired concentration. The conversion process is not complicated and does not require a large-scale plant for economical operation.

The process is versatile. A wide range of phosphorus-containing compounds can be produced that are useful for agriculture, industry, and national defense. Fertilisers produced by the furnace process are highly concentrated. For example, ammonium polyphosphate (15-62-0) is now being produced at the Tennessee Valley Authority plant.

Certain types of low-grade phosphate rock can be used economically in the electric-furnace process. This is an advantage when the low-grade rock is economically mineable as in Tennessee or

the western United States or when high-grade rock is unavailable or expensive.

Disadvantages of Electric-Furnace Process

The investment cost for the electric-furnace process is substantially higher than for the wet process including the cost of facilities for producing sulfuric acid from elemental sulfur. When sulfuric acid must be produced from pyrites, gypsum, or anhydrite, the investment costs may be about the same.

Like other chemical and metallurgical processes, the electric-furnace process is amenable to improved economics through engineering advancements and increased scale of operation. The state of development of the furnace process is less advanced than that of the wet process, so more rapid obsolescence is likely. Present electric-furnace technology may be compared with ammonia production technology 20 years ago. In large modern wet-process plants, as much as 85% of the production cost of phosphoric acid is the cost of raw materials—sulfur and phosphate rock—so the impact of further technological advances on economics is likely to be small.

The electric-furnace process requires skills and technology that are foreign to the fertiliser industry. Those of us who are accustomed to dealing with molten slag, carbon monoxide, and elemental phosphorus may forget how terrifying these hazardous materials may be to the uninitiated. Skilled operators and trained technologists are necessary to the successful operation of an electric-furnace plant. Some difficulty in attaining good operation and full production can be anticipated while skills are being developed.

Standard technology for utilization of wet-process phosphoric acid in production of fertilisers does not always work well with furnace acid. For instance, the production of diammonium phosphate by the usual methods is difficult because the product does not granulate well in the absence of impurities that are associated with wet-process acid. In this case the difficulty can be overcome by addition of a small amount of phosphate rock to the phosphoric acid. Perhaps a better solution is to produce ammonium polyphosphate rather than diammonium phosphate.

Economic Comparisons

In assessing the future prospects of elemental phosphorus for use as a fertiliser intermediate, a common approach is to compare the cost of a given fertilizer product made by the elemental phosphorus route with the cost of the same fertiliser made by the wet-process phosphoric acid route. This approach may be accepted with some reservations. The reservations are that elemental phosphorus is suitable for making food- and feed-grade phosphates and industrial phosphates as well as higher analysis fertilisers that would be difficult or impossible to make from wet-process acid. These considerations are difficult to evaluate and may be regarded as secondary factors to be considered only if the primary economic comparison is close.

From a superficial view it would seem that the principal difference in inputs is that the furnace process requires electricity, whereas the wet process requires sulfur or sulfuric acid. If this were the only difference, a comparison would be simple. The wet process requires about 0.95 short tons of sulfur per short ton of P_2O_5 recovered as phosphoric acid. The electric-furnace process requires about 5300 kilowatt-hours on the same basis. So the wet process would be preferable whenever 0.95 ton of sulfur costs less than 5300 kilowatt-hours; with sulfur at $40 per ton and electricity at 7.2 mills per kilowatt-hour, costs would be about equal. Unfortunately, the problem is much more complicated.

Another approach is to compare actual costs in existing plants. This method has two drawbacks. First, actual costs are not easy to obtain, and second, the two processes are not in an equal state of development.

I have no doubt that the average production cost of electric-furnace phosphoric acid in the United States is substantially higher than the average cost of wet-process phosphoric acid. Electric-furnace plants are geared to supply the market for phosphates for industrial, detergent, and animal feed, a relatively small market compared with fertilisers. Only excess furnace acid is marketed for fertiliser use. There are 13 plants in the United States that produce elemental phosphorus in 36 individual furnaces (1). The total capacity is about 650,000 short tons of elemental phosphorus per year, an average of about 18,000 tons of

phosphorus per furnace per year, or an equivalent of about 41,000 tons of P_2O_5 per year. Assuming an average consumption of 12,000 kilowatt-hours per ton of phosphorus, the average power input rating would be about 27,500 kilowatts. While some companies have built large furnaces ranging in capacity from 50,000 to 70,000 kilowatts, most plants, including TVA's, contain small, obsolete furnaces that would be quite uneconomical for fertiliser production. Thus, the production costs in present plants do not reflect presently available technology, much less future technology.

In examining prices of wet-process acid, we find that, in the last 2 years, prices f.o.b. Florida plants have ranged from $90 to $120 per short ton of P_2O_5, depending on market conditions and other factors. Delivered prices in the midwestern area are generally about $30 higher ($120 to $150/ton) regardless of whether the acid is produced in Florida or in other locations. Sales of elemental phosphorus have ranged from about $280 to $380 per short ton, equivalent to $122 to $166 per ton of P_2O_5, usually on a delivered basis. Again, the variations are caused by market conditions, terms of contract, and quantity involved. Since the cost of conversion of phosphorus to phosphoric acid is about $10 per ton of P_2O_5, these data again indicate that the present cost of furnace acid is generally somewhat higher than wet-process acid. One may speculate that the lower end of the price range for both wet-process acid and elemental phosphorus may be close to production costs.

An effort was made to compare the economics of the wet and furnace processes on the basis of new, modern plants of 600 tons of P_2O_5 per day capacity in a Florida location (2). The estimates assumed that the electric-furnace plant would consist of three 45,000-kilowatt furnaces. This was a conservative assumption since the desired capacity could be attained with two larger furnaces. The results of the estimates indicated that the investment cost would be $16.5 million for the wet-process plant and $35.1 million for the electric-furnace plant. The estimated production cost of wet-process phosphoric acid assuming a delivered sulfur cost of $35 per short ton was $79.38 per short ton of P_2O_5. For the electric furnace the estimated production cost was $76.32 with 3-mill electricity, or about $81.65 with 4-mill electricity. The exact cost of electricity to such a plant in Florida is not known, but has been reported to be about 4 mills. (Costs in Tennessee are in the range of 4.0 to 4.5 mills.)

A disadvantage of the electric-furnace process is its high investment cost. In the previously mentioned estimate, addition of 20% return on the investment to production costs would yield sums of $96 per short ton of P_2O_5 for the wet process and $111 for the electric-furnace process with 3-mill power or $116 with 4-mill power. On the other hand, a substantial saving could be realized by transporting elemental phosphorus to the market area and converting it to fertiliser there rather than transporting the finished fertiliser. One ton of elemental phosphorus is equivalent to about 5 tons of triple superphosphate, so a saving of nearly $20 per ton of P_2O_5 would result if elemental phosphorus rather than triple superphosphate were shipped from Florida to the Midwest. It was estimated (3) that the delivered cost of ammonium phosphate fertiliser in the Midwest, including 20% return on investment, would be about equal if the power cost for the electric furnace were 4 mills and sulfur cost were $34 per ton. This estimate did not take into account the value of the higher analysis and more versatile products such as ammonium polyphosphate (15-62-0) that can be made from electric-furnace superphosphoric acid.

The Electric Reduction Company of Canada is operating two 60,000-kilowatt furnaces in Newfoundland and plans a third furnace (4). Florida phosphate rock and low-cost hydroelectric power are used. Elemental phosphorus is being shipped to England in ocean tankers. It was estimated that phosphorus from this plant could be delivered in England for about $200 per ton which is equivalent to $87 per ton of P_2O_5.

Hoechst-Vlissingen is operating a 60,000-kilowatt furnace in The Netherlands, and a second furnace is under construction. Florida phosphate rock is used in this plant. No cost information is available. It is not known whether any phosphorus will be offered for fertiliser use from either of these plants. The primary market is for products of higher value than fertilizer.

Four large furnaces of 50,000 and 60,000 kilowatts' capacity have been built in or near Chimkent in South Kazakhstan (USSR), and additional furnaces of 72,000 kilowatts' capacity are planned in the immediate future (5). A design for a 100,000-kilowatt furnace is being considered.

This operation is based on large deposits of low-grade phosphate rock in the Karatan Basin. It was reported (5) that calculations indicated that the electric-furnace method would have about the same investment cost as the wet process, but a 30% lower production cost. No details of the estimate were given; perhaps the production of sulfuric acid from sources other than elemental sulfur was involved in the case of the wet process. The output of these furnaces is intended mainly for fertiliser. Shipment of elemental phosphorus to fertiliser-consuming areas 2000 to 3500 kilometers distant is planned. Substantial savings in transportation costs are expected. Future projects may be based on Siberian phosphate deposits where there are enormous resources of cheap hydroelectric power.

Requirements for the Electric Furnace

Phosphate Rock– –An important advantage of the electric furnace is its ability to use low-grade rock. Most of the phosphorus production in the United States is based on low-grade Tennessee and western rock (23 to 27% P_2O_5) which is unsuited to use in the wet process, but can be mined at low cost. Silica is a desirable impurity up to a SiO_2:CaO weight ratio of about 0.85 since this ratio is required to produce a fluid slag. Larger proportions of silica can be tolerated at the expense of increase in electrical energy consumption per unit of phosphorus. Alumina is not objectionable up to a level of 5 or 6% and perhaps higher. Iron oxide in the phosphate rock causes formation of ferrophosphorus which is an economic disadvantage, as it decreases the recovery of elemental phosphorus. However, moderately high contents of iron oxide, up to 3 or 4% Fe_2O_3, are economically tolerable if the cost of the rock is low enough and causes no technical problems. Calcium and magnesium carbonates in the phosphate rock are economically disadvantageous, as they must be fluxed with additional silica forming extra slag which increases electrical energy consumption.

The charge for the electric furnace must be in lump form. No exact definition of an optimum size is available. A closely sized charge such as 0.5 to 1 inch is generally regarded as technically optimum, but in practice, a compromise usually is struck between cost of preparation and technical considerations. For instance, a charge ranging from 6 mesh to 1.5 inches can be tolerated.

If a lump rock of the desired particle size is available which does not decrepitate in the furnace, it may be used directly in the furnace without preparatory treatment, particularly if it is low in volatile matter. Florida hard rock has been successfully used in TVA and other furnaces, and a hard Montana rock was used in a TVA pilot-plant furnace. Screened Florida pebble ranging from 6 mesh to 0.5 inch is used in some furnaces in the United States and England. If such rock is available, a substantial saving in investment and operating cost may result. It appears likely that high-grade Indian rock from the Udaipur area would be suitable for direct use if properly sized since it is hard, thermally stable, and low in volatile matter.

In most cases, some type of charge preparation is required to agglomerate the phosphate rock, calcine it, and indurate the agglomerates. For instance, in the Vlissingen plant the Florida pebble is finely ground, mixed with a clay binder (about 5%), pelletized in inclined pans, and calcined in a grate kiln. Carbon monoxide gas from the furnaces is used as fuel.

Coke–Metallurgical coke is commonly used as a reducing agent. It should have about the same size range as the phosphate rock. If wet, it should be dried.

As metallurgical coke is expensive and not always available, there has been some interest in alternative sources of reducing carbon. Coke made by the "Chemcoke" process is used in some plants in Tennessee. The process consists of burning part of the coal on a moving grate to carbonize the remainder; the volatile matter evolved is burned in a boiler to generate steam. Coal that is not suited for making metallurgical coke can be used, and substantial savings are possible when low-cost coal is available.

Briquetted char from carbonization of low-grade coal has been used quite successfully in Idaho. Calcined anthracite coal is used in England. Petroleum coke should be suitable if prepared in lumps or briquets of the proper size and strength and if the sulfur content is not too high. Information on the effect of high sulfur content is lacking; in one test, semianthracite coal containing 3.5% S was used in a TVA furnace without

apparent adverse effect. TVA has used high-fixed carbon bituminous coal to supply 25 to 50% of the carbon in the electric-furnace charge. The practice causes some difficulty with disposition of tarry material in pipelines and in the condenser, but these difficulties are tolerated when the economic advantage is sufficient.

Silica—Silica is added to the charge in such proportions as to form a fluid slag. The usual SiO_2:CaO weight ratio is about 0.85, although higher and lower ratios have been used successfully. The main requirements for the siliceous material are a reasonably high silica content and a particle size similar to that of the rest of the charge. Sized gravel containing 90 to 95% SiO_2 is the most common source. Crushed, sized siliceous rock (sandstone or quartzite) may be used. If lump materials are not available, silica sand may be agglomerated with the phosphate rock. The Tennessee phosphate ore and some of the western ores are nearly self-fluxing so that little silica is needed.

Byproducts—The byproducts of the electric-furnace process are slag, carbon monoxide gas, and ferrophosphorus. Small amounts of fluorine are evolved and collected in the condenser liquor or precipitator dust, but the amounts are not sufficient to warrant consideration as a byproduct.

The slag may be used as a substitute for crushed rock for road building or concrete aggregate. Little income can be expected from this use except in areas where suitable rock is scarce (such as Florida or The Netherlands). When the slag has a low alumina content (less than about 7%), it is suitable for use as an agricultural liming material. The P_2O_5 remaining in the slag (1 to 2%) is available to crops. In tests in Hawaii a substantial increase in yield of sugarcane resulting from application of slag was attributed to its silicon content. For agricultural purposes the slag is granulated with water to produce a sand-sized product. Since limestone is cheap and readily available in most locations, little income can be expected from agricultural sales of slag. When suitable areas are available, disposal may be moryeconomical than utilization. Disposal in mined-out areas is an example.

The carbon monoxide gas from the furnaces is commonly used as fuel for calcining or nodulizing the charge and for drying coke and silica. The quantity is usually sufficient for these purposes although there may be some excess or deficiency, depending on the amount of drying to be done and the thermal efficiency of the charge preparation system. When the charge is not calcined, utilization of the excess gas may be a problem. Small amounts of phosphorus in the gas render its combustion products corrosive to heat exchange surfaces in most types of boilers. However, in England the gas is used to produce steam in a special type of boiler that has a low thermal efficiency. Removal of the traces of phosphorus (and sulfur compounds) is generally considered too expensive. For the same reason, utilization of the carbon monoxide to make ammonia synthesis gas has not been considered economical.

The ferrophosphorus typically contains 23% P, about 70% Fe, and small percentages of silicon, manganese, vanadium, chromium, and other metals, depending on the ore composition. It is usually sold to the steel industry. There is a substantial demand in the European steel industry where the phosphorus content of the ferrophosphorus is recovered in basic slag. However, value of the ferrophosphorus is not very high.

Any great increase in production of ferrophosphorus might cause the supply to exceed the present demand. Various methods of utilizing ferrophosphorus have been developed, and some of these methods might be economical if a large quantity became available.

Location—Obviously the main consideration in selecting a location for an electric-furnace operation is the cost of electricity and phosphate rock. The proximity to the market area is less important since the high concentration of elemental phosphorus minimizes transportation cost. If a location can be found where both phosphate rock and electricity are cheap, so much the better. If not, it may be a problem to decide whether to transport the rock or accept a higher electricity cost.

From 7 to 10 tons of phosphate rock is required per ton of phosphorus produced. If the cost of transporting the rock is $5 per ton, for example, the cost per ton of phosphorus would be $35 to $50. So the cost of electricity would have to be 3 to 4 mills lower than at the mine to offset the cost

of transporting the rock. Of course, many other factors will enter into the choice of a location.

Electric phosphorus furnaces may be operated at reduced load or shut down entirely for several hours without any ill effects other than loss of production. Some plants in Europe are operated at reduced loads when power demands for other purposes are high. The TVA furnaces have been operated on a peak-sharing schedule. Naturally the economics of such an operation would require careful evaluation.

Special Considerations for India

The fact that India does not have adequate reserves of sulfur is a point favoring the furnace process. On the other hand, low-cost electricity is not abundant, and present sites of low-cost electricity are distant from presently known phosphate deposits.

The phosphate rock deposits near Udaipur are well suited for both the wet process and electric-furnace process. If a part of this phosphate rock can be provided in lump form, and if it can be shown that this material can be used directly in the furnace, this circumstance would constitute a distinct advantage for the furnace process. I do not have sufficient information on the composition, quantity, and prospective mining cost of other Indian deposits to comment.

In conclusion, it is my opinion that the electric-furnace process will become an important means for producing phosphatic fertiliser in the future. This is my personal opinion with which some of my colleagues, both in TVA and other organizations, may disagree. Whether the electric furnace should be used in India in the near future is a question that I cannot answer. I hope this paper will help in some small way to indicate what sort of information is needed for a decision.

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