Abstract: A direct heat kiln process for the production of phosphoric acid from phosphate ore utilizing a reductant process in combination with a carbon source, silica and heat. The process employs air control to control the burning rate of the product gasses from the kiln bed in order to control the overhead temperature in the kiln and the kiln bed temperature. In order to keep the reaction temperature at the lower ranges to prevent melting. The kiln feed ball constituents are co-ground and finely ground to lower the required bed temperature to minimize melting.
ROTARY KILN PROCESS FOR PHOSPHORIC ACID MANUFACTURE

This application claims the benefit of U.S. Provisional Application No. 60/577,286, filed on June 4, 2004; and U.S. Provisional Application No. 60/648,360, filed on January 28, 2005.

This application incorporates by reference the entire specification and disclosure of U.S. Provisional Application No. 60/577,286, filed on June 4, 2004; and Provisional Application No. 60/648,360, January 28, 2005.


FIELD OF THE INVENTION

The present invention relates to the carbothermic kiln process for producing high quality phosphoric acid from high silica fluorapatite or hydroxyapatite ores.

BACKGROUND OF THE INVENTION

Evolution of kiln technology for a number of processes over the last thirty years with large scale commercial kiln operations using reducing beds and over bed air porting for level temperature control provides a basis for development of a kiln based process for producing phosphoric acid (KPA). The process promises attractive economics, expanded phosphate ore utilization, a high quality concentrated phosphoric acid product, and a smaller environmental footprint.

In 2002 the world phosphate industry produced about 135,000,000 mt (metric ton) of phosphate rock with an average P$_2$O$_5$ content of 32.6% P$_2$O$_5$ (2). Most of it was converted to various grades of phosphoric acid at an average selling price of about $350/mt P$_2$O$_5$ for a world value of about $14 billion per year.

Acid dissolution of phosphate ore (usually sulfuric acid) is, and has been, the major route to phosphoric acid production, but historically the furnace acid process produced a significant fraction, reaching nearly 50% of the total produced in the 1950's. The blast furnace process was a technical success, and was used in two commercial plants around 1930, but was not economic as compared to the furnace acid process due to very large gas volumes and inefficient recovery of heat. Wagaman carried out an engineering study in 1950 that showed that the blast furnace was $5/ton more expensive than the electric furnace process in producing elemental phosphorus and was estimated to cost $66.32/ton at the time (on a P$_2$O$_5$ basis).
This invention relates to a kiln phosphoric acid process ("KPA") for producing high purity phosphoric acid from high silica phosphoric ore sources with limited silica additions to give calcium to silica mole ration in the feed mixture from 0.5 to 1.0. The feed mixture with the phosphate ore, silica and a carbon reductant added is formed into dried agglomerates, pellets or balls, and processed countercurrently in a rotary kiln at about 1180-1300°C.

The carbon and a large amount of heat reduces the phosphate ore forming carbon monoxide and elemental phosphorus vapors reaching one atmosphere vapor pressure at about 1180°C which are blown out of the kiln bed and into the kiln freeboard.

In the freeboard, air is added above the bed to oxidize most of the carbon monoxide and phosphorus, yielding sufficient heat to radiate back into the kiln bed and drive the reduction reaction.

The rotary kiln is an efficient heat transfer device, but a poor mass transfer device, allowing the oxidizing freeboard and reducing bed to co-exist in the kiln.

The process requires very close temperature control and is benefited by overbed air ports. The placement of a shell of high silica and coke on the outside of the agglomerates also extends the operating window for the process to provide a more tolerant commercial operation.

A KPA process uses similar chemistry as practiced in the furnace process, and particularly the blast furnace process. The heat integration can be so complete, that the projected economics are not only significantly better than the furnace process, but also will challenge the wet acid processes with most ore matrix feeds. It appears that the KPA process is going to be kinder on the environment than existing processes.

For many years high purity phosphoric acid has been made by reducing phosphate ore-silica-coke mixtures in an electric furnace (the furnace-phosphate process). In this process, phosphorus and carbon monoxide off gasses are produced. The phosphorus is condensed by direct water-cooling to form liquid phosphorus metal. The phosphorus is then taken to another vessel where it was burned with air in a high temperature furnace and the resulting gaseous phosphorus pentoxide absorbed in a scrubber to form up to 110% phosphoric acid directly. The acid is of high purity and has been preferentially used in detergent and other applications that required high purities.

The very inefficient use of heat in the process, and the considerable amount of high cost electricity required led to the demise of the furnace acid process particularly after 1970, in favor of the wet acid processes based on sulfuric acid reactions with phosphate ore.

The KPA process carries out both the phosphorus reduction reaction (in the bed) and the phosphorus and carbon monoxide oxidation reactions (in the freeboard) in the
same rotary kiln. Early work is set forth in U.S. 2,075,212; 1,630,283; 3,235,330; and 3,241,917. The exothermic heat generated from the freeboard reactions provides the endothermic heat requirement for the bed reactions. The resulting heat integration replaces the electric power used in the furnace process. This idea was originally proposed by Lappel of FMC Corp. in the early 1960's and extended by Robert Hard and the inventor in 1978-82, in a large program at Occidental Petroleum. The theoretical discussion given set forth below shows why these efforts failed to yield a commercial KPA process due to working with the wrong silica levels in the charge to the kiln. In addition, those processes failed to take into account the importance of temperature control along the length of the kiln and importance of feed ball preparations.

The KPA process requires a reasonable “window of operation” where the temperature is hot enough to carry out the reduction reaction at a sufficiently rapid rate, but not so hot that melting and clinkers and kiln refractory interactions occur that would preclude kiln processing.

Heat Utilization Comparison of the Thermal Processes (KPA, Furnace, and Blast Furnace Processes)

To clarify the large economic roll played by heat integration, it must be understood that the dominant reactions which occur in all three thermal processes:

1) Endothermic reduction of phosphate ore (Fluorapatite)
   a) \( \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 9 \text{SiO}_2 + 15 \text{C} \rightarrow 3 \text{P}_2\text{O}_5^\wedge + 15\text{CO}^\wedge + 9 \text{CaSiO}_3 + \text{CaF}_2 \)

2) Exothermic oxidation of phosphorus and carbon monoxide bed off gases with air
   b) \( 3 \text{P}_2\text{O}_5^\wedge + 7.5 \text{O}_2^\wedge + 26.5 \text{N}_2^\wedge \rightarrow 1.5 \text{P}_2\text{O}_{10}^\wedge + 26.5 \text{N}_2^\wedge \)
   c) \( 15 \text{CO}^\wedge + 7.5 \text{O}_2^\wedge + 26.5 \text{N}_2^\wedge \rightarrow 15 \text{CO}_2^\wedge + 26.5 \text{N}_2^\wedge \)

If we consider that the solids on the left side of 1) a) enter the reaction at room temperature and the reaction products are at 1327 °C, and the air used in reactions 2) b) and c) to oxidize the phosphorus and CO, enters the reaction at room temperature and the gaseous products are at 1327 °C, then the amount of heat generated/required in the reactions is given in table 1. Note that the heat generated in the oxidation reactions 2)b) and 2)c) could supply most of the heat required by the reduction reaction 1)a), if they could be coupled. With improvements discussed herein, the reaction to temperature can be reduced down to about 1180 °C, although a temperature of about 1225 °C or higher is preferred.
Table 1. Heat required for reduction of phosphate ore and oxidation of the off gasses. Values were calculated by the inventor from the thermodynamic data compilations of JANAF (10) and USGS Bulletin 1452 (11). The references are identified below.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heat Consequence, MM BTU/mt P₂O₅ (Endothermic)</th>
<th>(Exothermic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Fluorapatite Reduction (kiln bed)</td>
<td>+16,080,000</td>
<td>-6,734,000</td>
</tr>
<tr>
<td>b) Phosphorus Oxidation (kiln freeboard)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c) Carbon Monoxide Oxidation (kiln freeboard)</td>
<td></td>
<td>-5,785,000</td>
</tr>
<tr>
<td>Total</td>
<td>+16,080,000</td>
<td>-12,519,000</td>
</tr>
</tbody>
</table>

How the heat required for the reduction reaction is supplied in each of the three thermal processes.

A. Furnace Acid Process – Here the heat for the fluorapatite reduction is supplied solely by resistance heating in a molten pool by electric power, and the energy generated in burning the phosphorus to P₄O₁₀ is thrown away. Some of the chemical heat, but not the specific heat in the carbon monoxide is occasionally recovered for drying operations outside the furnace. At 4.7 cents per KWH the theoretical heat requirement supplied by electric power costs $221/mt P₂O₅ not counting any furnace heat losses or transformer efficiencies. With actual electrical consumption the cost is ~$298/mt P₂O₅ at 4.7 cents per KWH for the electric furnace process.

B. Blast Furnace Process – All of the heat associated with burning phosphorus with air is discarded and all the specific heat associated with the CO (i.e. 1,400,000 MM BTU/mt P₂O₅) is discarded. The chemical heat in the CO (i.e. – 4,385,000 MM BTU/mt P₂O₅) is partially recovered by burning the CO with more coke to temperatures as hot as the stoves will handle and “blasting” the molten mass to supply the heat required in the reduction reaction in the blast furnace. Waggener (4) gives the coke usage in the blast furnace process to be 4.5 times, and the furnace off gas to be seven times, that of the electric furnace phosphoric acid process. It is the necessity to clean and pressurize large volumes of process off gas and the inefficient recovery of heat from reactions 2)a) and 2)b) that made the blast furnace process even more expensive than the electric furnace, and led to its closure in the late 1930's.

C. KPA Process – All of the heat associated with oxidation of phosphorus and carbon monoxide in the kiln freeboard is directly transferred to the bed using the very high heat transfer rates common in a rotary kiln to supply the heat required for the reduction reaction. In addition, heat can be recouped from the gaseous reaction products in the back
end of the kiln for heating up the incoming solids and lowering the kiln off-gas temperature. Sufficient heat can be removed from the hot solid kiln residue exiting the rotary kiln to dry all of the incoming wet raw materials for grinding, for drying and for preheating the feed balls going into the kiln. Additional heat is generated from burning the carbon volatiles from the ore and green petroleum coke, and from the limited carbon burnout that inevitably occurs with the reducing bed in contact with the oxidizing freeboard.

The result is that the petroleum coke reductant supplies all the heat necessary for the KPA process with only a very modest burner, and consumes only about 1.3 times the theoretical fixed carbon required for the fluorapatite reduction reaction, or about the same amount consumed in the electric furnace process. The efficient heat integration in the KPA process gives a kiln off gas containing about 4.5 wt% phosphorus compared to about 7 wt% in an electric furnace off gas, and 1 wt% in the blast furnace off gas.

Thus the heat integration of the KPA process, coupled with the reasonable capital costs of kiln processing of large quantities of raw materials, promises an attractive phosphoric acid production process, providing carbon burnout from the kiln bed is slow enough for the process to work. The KPA process also has another advantage, it uses less expensive raw materials than the other thermal process.

Stable Reducing Bed in Contact With an Oxidizing Freeboard

Lapple, in the early 1960’s described two processes (US 3,235,330 and 3,241,917) showing how carbothermic reduction in a countercurrent rotary kiln, generally similar in arrangement to that used in the present process, which requires only cheap carbon energy that is used with high heat efficiency to produce high concentration phosphoric acid. This gave promising economics, particularly for making high purity acid.

By the 1960’s Lapple concluded from operations like calcining petroleum and coal coke, direct iron ore reduction, and synthetic rutile production that the oxidation of carbon from a kiln bed was slow due to a slow mass transfer rate between the freeboard and the bed of a kiln. Since then several direct iron ore reduction processes and synthetic rutile plants have been commercialized (12). The ilmenite reduction plant now operating successfully for over twenty years in Norway (1) is particularly relevant as it has a reducing bed where iron metal is formed and uses over bed air to affect a level temperature profile in the kiln, as will be required in the KPA process. It is anticipated that the size of a commercial KPA kiln will be similar to the Norwegian ilmenite kiln. This high level of heat transfer and low level of mass transfer of the KPA process is compared to that which occurs in existing commercial lime and ilmenite reduction kiln processes.
Critical role of silica to window size

Lapple (U.S. 3,235,330 and 3,241,917) (FMC) and the early Megy/Hard work at Occidental (U.S. 4,351,809; 4,351,813; 4,389,384; 4,397,826) invested considerable effort to develop a kiln based phosphoric acid process, as they recognized the economic advantages of the heat integration possible in a rotary kiln. The following explains why these efforts failed commercially, and why the current effort has been successful in the lab sized pilot plant tests. It explains why the Hard breakthrough (9) in the last six months of the Occidental work in 1982 was successful in a test in a three foot diameter pilot kiln that made several thousand pounds of phosphoric acid (61% P₂O₅), carried out under the inventor’s direction (13). Lapple attempted to run the process with limited silica so that cement could be made from the spent kiln residue. In the latter part of his reduction Ca₂SiO₄, and finally CaO from the fluorapatite are produced as the phosphorus is reduced and volatilizes from the kiln bed. In the early work at Occidental, more silica was added so that all the CaO released as the phosphorus volatilizes would first form CaSiO₃ and then Ca₂SiO₄ in the residue. Enough silica must be present to react with all of the CaO liberated from the fluorapatite to form CaSiO₃ to avoid melting problems that preclude kiln operation.

In practice, however, the low silica levels advocated by Lapple required a relatively high kiln operating temperature of about 1550°C to obtain high yields. The low silica was recommended because Lapple envisioned making cement clinker simultaneously from the calcium silicate residue. Although the feed mixture and the final (phosphorus removed) composition were relatively refractory, a composition was reached during the course of the reduction where monocalcium silicate and fluorapatite were near eutectic composition, which substantially melts about 1380°C (depending on impurity level in the ore formulation). Thus, a substantial fraction of the kiln charge melted resulting in clinker formation and kiln wall charge interactions, which precluded successful commercial operation of the Lapple patents. At the high temperature required for substantially complete phosphorus extraction, unwanted side reactions also become important and limit the effectiveness of the process.

The underlying cause of the problem can most readily be appreciated by a thermodynamic analysis of the three reactions occurring in the three thermal processes, which indicate the temperature to which the raw materials must be heated to affect the phosphorus reduction when various levels of silica are available to form reaction products. We consider the reaction products all at unit activity (i.e. pure CaF₂, CaSiO₃, Ca₂SiO₄, and CaO) and the CO and P₂ off gas at an activity equal to their partial pressure in the off gas, then the free energy of the reduction reaction operative at different silica levels in the feed
mixtures is given in figure 1 (15). The thermodynamic data is supplied by JANAF (10), USGS (11), and Bureau of Mines (16) to calculate the lines in figure 1.

When the free energy for the reaction goes negative, then the reaction can proceed, which happens at 1269 °C for the excess silica case (high SiO₂) of the later Hard process, 1269°C (theoretical, but actually lower in practice) for the present process, 1387 °C for the silica limited case later in the reaction in the early Occidental process and in the middle of the Lapple process (mid SiO₂), and 1527 °C in the no silica case operative in the latter stages of the Lapple process (low SiO₂). Even though the early Occidental work and the Lapple work had to go to higher temperatures to carry out the reduction, it was not clear that melting would be a problem. Both the feed mixture and the calcium silicate product appeared to be solids at the required temperature based on phase diagram analysis, and from commercial observations in phosphate ore nodulizing kilns and cement manufacture. It is only when one calculates what happens when the reaction is part way complete that the problem of melting in the bed is understood. There is some limited silica present in the Lapple process, and somewhat more in the early Occidental KPA process. During the early part of the reduction the reaction proceeds at the lowest temperature and makes a CaSiO₃ product. As all the silica is consumed, Ca₂SiO₄ must form in the product according to the mid SiO₂ equation shown in figure 1, which requires a 118 °C hotter reaction temperature. The problem is that the CaSiO₃ makes a eutectic with fluorapatite as shown in figure 2. The eutectic melts at a pure component temperature of 1420 °C, and significantly less with the CaF₂, Al₂O₃, and MgO impurities present in the kiln feed (actually about 1280 °C as shown in discussing of the operating window work below.

Figure 2 shows that a eutectic between CaSiO₃ and Tricalcium Phosphate is responsible for melting in Lapple and early Occidental processes when part of the phosphorus had reduced and volatilized from the kiln charge (17).

From the feed silica levels specified in the Lapple patent and the early Occidental work, it is calculated that 53% and 70% of the charge melts respectively at the CaSiO₃ – Ca₃P₂O₈ eutectic where the temperature must jump by 118 °C to continue the reduction reaction (18). The result is that clinkering and refractory interactions preclude further reduction in the kiln for these processes. Conclusion: With excess silica, analysis suggests an operating window should be present.

In Phase I, no experiments were run where the silica was less than that required to convert all of the CaO and MgO released from the fluorapatite reduction reaction, plus any that was present as dolomite or calcium carbonate, completely to CaSiO₃ and MgSiO₃. The thermodynamic analysis, Lapple’s experience, and the work at Occidental, confirm that the KPA process is not commercially possible with less silica. If more silica than this minimum is added, the melting point in the residue from the reduction reaction is not
improved...until the eutectic between CaSiO$_3$ and SiO$_2$ is passed. Then additional silica begins to make the residue more refractory as can be ascertained by analysis of the phase diagram given in figure 3 (18). I have indicated the reaction pathway in each of the processes on the figure.

Figure 3. The lines show change in composition in the kiln residue for each of the processed discussed in this section. The "present process" is one with sufficient silica. The residue gets more refractory as additional silica beyond the eutectic composition is added, as in the "Hard" process for example (18).

In hindsight, one of the reasons that the critical need of having enough silica was not recognized is that it is so against intuition. Anyone with experience in the cement industry or electric furnace phosphate industry "knows" that if you want to make the charge more refractory (less molten) you reduce silica...not increase it. Thus, it is clear why the Laplace and early Occidental work failed in the commercial sense.

Operating Window

The temperature above which the phosphorus reduction reaction proceeds in phosphate ore/silica/coke mixtures and the temperature at which melting of those mixtures occurs, are important to the electric furnace and blast furnace processes. Waggaman (4) speaks to the limited temperature range between them in his book written over 50 years ago, when he was discussing the plausibility of thermal processes for producing phosphoric acid from a solid charge. There does not appear to be any solid data on the temperatures versus silica level in the composition range of interest to the KPA process. It may be, that the data presented below, represent the first time this data has been obtained in this detail.

The Laplace processes have led to a series of processes (including this subject process) based on carbothermic reduction in a rotary kiln, which differ principally in the amount of silica added to the kiln feed. Different minerals form the residue, which result in different operating temperature requirements for the phosphorus extraction reaction, and different melting behavior. The reactions occurring to extract the phosphorus from the ore, and the typical raw material feed mixtures for each of the carbothermic processes follows:

<table>
<thead>
<tr>
<th>Carbothermic Kiln Phosphate Processes</th>
<th>Lapple</th>
<th>Megy/Hard</th>
<th>Hard</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Material Component</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ore (parts Ca$_3$(PO$_4$)$_2$ basis)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Silica (parts SiO$_2$ basis)</td>
<td>0.65</td>
<td>1.14</td>
<td>6.45</td>
<td>2.15</td>
</tr>
<tr>
<td>Coke (parts fixed carbon basis)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Calcium to silica molar ratio</td>
<td>3</td>
<td>1.7</td>
<td>0.35</td>
<td>0.9</td>
</tr>
</tbody>
</table>

8
If more acidic silica is added to the ore-coke formulation, the reaction occurs at a lower operating temperature. Thus, if a calcium/silicon mole ratio of two is used in the ore feed, then dicalcium silicate forms in the reaction products, "pulling" the basic calcium oxide away from fluorapatite at a kiln temperature of about 150°C less than the Lapple composition (i.e. 1400°C).

Hard and the present inventor developed a process based on this mid-silica addition level (USP 4,351,809 and USP 4,351,813) and a significant pilot plant program was run to develop the process around 1980. The actual calcium to silica mole ratio used in this development program was about 1.7. This level of silica addition was chosen after preliminary testing of many compositions and raw materials by thermo gravimetric analysis (TGA) laboratory tests, which were conducted sometimes under nitrogen and sometimes with carbon monoxide sweep gasses. The lab data suggested that high phosphorus extractions were possible, while the pellet retained integrity from melting at this silica addition level.

However, in over two years of scale up tests to pilot plant level in batch and continuous pilot plant equipment, limited yields in the 40-50% range were obtained before clinkering and wall interaction problems were encountered from melting precluding higher temperature operation.

It was then realized that the lab TGA tests were giving optimistically biased results for the phosphorus extraction temperature required in the kiln. The phosphorus reduction reaction off gasses (CO and P₂) were being diluted by the sweep gasses allowing the reaction to proceed at a lower temperature. Since the phosphate reduction reaction produces a lot of off gas, dilution of the partial pressure of these reaction products lowers the “apparent” reaction temperature significantly (i.e. 75-125°C in the lab TGA tests).

In the commercial kiln bed there is no sweep gas, and therefore no “driving” of the reaction. The off gas partial pressure must exceed one atmosphere and literally “blow” out of the bed in the commercial process.

In the mid-silica formulation the eutectic between calcium monosilicate reaction product and fluorapatite forms later in the reduction at about 45-50% phosphorus extraction, right where the pilot tests were running into melting problems. The 1380°C
"melting point" of the "eutectic" composition during the reduction was below the required phosphorus extraction temperature (i.e. 1400°C) after all the raw silica was used up, and further reaction with additional calcium oxide liberated from the reduction reaction had to react with monocalcium silicate to form dicalcium silicate.

Due to the melting problem encountered with the mid-silica composition, Hard conceived of running with silica rich compositions (USP 4,389,384). Sufficient silica to form monocalcium silicate, and an excess silica to a specification of calcium to silica mole ratio of less than 0.5. At this formulation the silica addition was approximately the same weight as the phosphate ore. Excess silica was available to aid in the extraction of the calcium from fluorapatite as it was reduced, plus a substantial excess to dilute and make the residue from the phosphorus reaction more refractory.

With the effect of excess silica the reaction to form monocalcium silicate was operable over the entire range of the reduction reaction, with the partial pressure of the carbon monoxide and phosphorus exceeding one atmosphere sufficient for commercial kiln operation at about 1280°C, and the temperature of melting problems becoming important only at temperatures greater than about 1425°C.

Thus, a window for commercial operation existed, and this process was demonstrated to produce high quality phosphoric acid at commercial yields in a three-foot pilot kiln in 1982, as described by the inventor at the XVII Congreso Mexican de Quimica Pura y Aplicada (Rev. Soc. Quim. Mex. 27, No. 3, Mayo-Junio 1983).

The high-silica Hard process is particularly applicable to run-of-mine high silica ores which have had the clays removed, and if necessary a small amount of beneficiation to adjust the chemistry to the correct silica composition. In this way the cost of beneficiation can be largely avoided. The amount of carbon required stoichiometrically to remove the phosphorus from the ore dictates the amount of heat, which is generated in the freeboard when the phosphorus and carbon monoxide are burned. The heat produced is enough to supply the heat required by the phosphorus extraction reaction in the bed with enough left over to heat all the silica in the high silica formulation to reaction temperature. In other words, the large amount of silica present in the high silica formulation absorbs heat that would otherwise be problematic if it was not present. Naturally, a high silica feed composition requires a larger kiln for a given P$_4$O$_{10}$ yield as compared to a lower silica feed.

The high silica Hard process produces a high quality phosphoric acid at high concentration (i.e. 70%), and therefore avoids cost in concentration and purification of merchant grade wet acid produced in the sulfate process.

The kiln carbothermic processes also solve the major environmental problems associated with existing commercial wet acid processes, namely "gyp piles" and the
The major waste from the kiln carbothermic processes is agglomerates of calcium silicate, which are thought suitable for landfill. In light of projected cost, quality, and environmental advantages, it is surprising that the Hard process has not been commercialized.

The subject patent applies to the processing of ore, which has a limited amount of silica, and to kiln processes where the air content and freeboard temperature along the length of the kiln are controlled.

SUMMARY OF THE INVENTION

In some run-of-mine phosphate ores there is not sufficient silica suitable for the Hard process (U.S. 4,389,384 and 4,397,826). One embodiment of the present process has the advantages of the Hard process, but with a somewhat smaller kiln size and grinding requirement, and with a much smaller silica requirement. In this embodiment, the calcium to silica molar ratio in the kiln feed is set at about 0.4 to about 1.0, preferably about 0.4 to about 0.7. Since there is sufficient silica in the solids to react with all of the calcium liberated by the phosphorus reduction forming monocalcium silicate the process requires a relatively cold 1280°C kiln operation, similar to the hard high silica process. Unfortunately, the process unavoidably encounters the phosphate-monocalcium silicate eutectic melting condition at about 65% phosphorus extraction, with significant melting above about 1320 °C (theoretically 1380°C) depending on minor impurity levels in the ore charge mixture.

This still leaves an operating window of about 100°C. Although the operating window is less than the Hard process, through the use of the following strategies, it is sufficient for practical commercial operation.

As the feed agglomerate in the form of pellets or balls is heated in the kiln bed, the outside layer of the pellets first reaches reaction temperature and evolves phosphorus and carbon monoxide until it reaches the critical composition of 65% reacted where melting can occur in the feed agglomerate. Once the reaction becomes more complete the more refractory monocalcium silicate shell forms and the critical composition moves further into the pellet as the temperature increases inwardly in the pellet where the feed agglomerate is contained and prevented from clinking or refractory agglomeration reaction. Thus, the critical issue is to get past the 65% phosphorus extraction level on the outside of the agglomerate.

This is accomplished by using the following methods:

1. Over bed air in a ported kiln is used in conjunction with close temperature measurement down the length of the kiln to control the temperature to a slow ramp in the
1. The critical 1275-1320°C range for a kiln feed having a calcium to silica molar ratio of from 0.8 to 1.0.

2. The agglomerate pellet is prepared with an outer coating of high silica and coke. This preserves a reducing environment in the agglomerate and provides a melt resistant surface. This can be conveniently accomplished commercially when the agglomerate pellet is produced in a balling drum by adding the coating in a reroll section of the balling drum.

Figure 4A is a phase diagram (Fig. 661; System CaO, SiO₂, 3CaO·P₂O₅; C=CaO; P=P₂O₅; S=SiO₂) showing the melting behavior of various CaO, SiO₂, and P₂O₅ mixtures which was prepared by Wojciechowska, et al., detailing the critical eutectic compositions encountered in the kiln solids during the reduction of phosphorus in each of the process discussed above. The composition of the ore charge to the kiln for each of the four processes is different mixtures of silica with calcium phosphate, Ca₃(PO₄)₂, as shown along the composition line that joins the calcium phosphate composition point to the pure silica point. As the phosphorus is reduced with carbon forming phosphorus vapor, which volatilizes from the agglomerate, the composition of the residue changes along a straight line projected away from the 100% P₂O₅ point of the phase diagram, as has been overlaid on the diagram with notation.

As the phosphorus is reduced, calcium oxide is released which reacts energetically with silica to form monocalcium silicate. In the Lapple and Megy/Hard processes, all of the silica is used up forming monocalcium silicate before all of the calcium phosphate is reacted with carbon. This is the critical melt problem point. Monocalcium silicate and calcium phosphate are present in the following amounts at the critical melting point encountered in the Lapple and Megy/Hard processes:

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt% at Critical Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSiO₃</td>
<td>34.3%</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>65.7%</td>
</tr>
</tbody>
</table>

We shift our attention now to Figure 2 (Fig. 667; System CaO, SiO₂, 3CaO·P₂O₅; C=CaO; P=P₂O₅; S=SiO₂), which is a phase diagram prepared by Wojciechowska, et al., which shows the melting behavior of calcium monosilicate-calcium phosphate mixtures. This figure shows a eutectic at 16.3% by weight P₂O₅ from calcium phosphate or 35.6 w% Ca₃(PO₄)₂ and 64.4 w% CaSiO₃. Therefore, at the eutectic temperature, the CaSiO₃ will dissolve Ca₃(PO₄)₂ until the eutectic composition results. This temperature is given as 1420°C in Figure 2, but in practice is less due to the effect of impurities in the raw materials, chiefly fluoride, magnesium, aluminum, and sodium. This results in a eutectic
less than the temperature of about 1400°C required to continue to reduce phosphorus when the silica is used up. Combining this information with the composition at the critical point determined above, the calculated molten fraction at the eutectic temperature is 53.3% for the Lapple process, and 70.3% for the Megy/Hard process. It is easy to see why pilot efforts failed with these processes. In both the Lapple and Megy/Hard processes, clinkers and kiln refractory-charge interactions (rings) arise from melting and preclude further extraction of the phosphorus from the ore. Both the Lapple and Megy/Hard processes were not successful commercially because of this problem.

In the Hard process and the present process, sufficient silica has been added so that monocalcium silicate can form from all of the calcium oxide liberated from the phosphorus extraction. Thus, a minimum kiln temperature of about at least 20°C above the reduction reaction temperature (about 1180°C to about 1350°C; high temperature at higher silica addition) is required for the reduction reaction over the entire range of phosphorus extraction. This is sufficiently below the temperature where melting problems in the kiln residue occur in the Hard process, and with more control the present process, that can be successfully carried out commercially.

Environmental issues

By far the largest solid waste stream from the KPA plant is the cooled kiln residue in the form of hard, black balls with a bulk density of about 85 lbs/ft³, produced at the rate of 222,000 lbs/hr for a Florida base case or about 8,600 acre feet for the twenty year life of the plant. To determine whether the kiln residue will pass the TCLP test, as residue from the furnace acid process does, a lab pilot run at 1310 °C for 2 hours with six HL3 composition, ¾” diameter pellets was run. The fired pellets were crushed to pass a 6 mesh screen, and analyzed. The results showed ND (not detectable) for each of the heavy metals on the TCLP list (i.e. silver (< 0.05 mg/l), arsenic (< 0.1 mg/l), barium (< 1.0 mg/l), cadmium (<0.05 mg/l), chromium (<0.05 mg/l), mercury (<0.005 mg/l), lead (<0.1 mg/l), and selenium (<.1 mg/l)). The KPA kiln residue is a combination of calcium silicate (CaSiO₃), with some Sonoite, (Si₂N₂O), Calcium Fluoride (CaF₂), and residual carbon (C), and small ferrophos beads, with most between about 1-20 microns in size distributed throughout the residue. While the TCLP tests suggest the residue could be useful for commercial fill applications, experience with the FMC electric furnace slag suggests otherwise. Due to the low level of uranium and thorium in the residue the residue should be amenable to being land filled, and covered with a thin layer of soil for final closure of the landfill (33).

The other major solid waste stream from the process is wet gypsum sludge from the flue gas desulfurization scrubber on the back end of the process. From data derived
from the lab program it is expected that 3,618 pounds per hour including 45% moisture to be generated from the Florida base case plant. It is expected that this gypsum to be quite pure, so there is some chance of selling it as a byproduct. If not, it will probably be acceptable to place this material on existing gyp stacks from an associated dihydrate plant, or on a separately licensed stack. Note that the gyp production rate expected from the KPA plant is about 1/360th of that of a comparable dihydrate plant.

The off gas from the FGD scrubber from the KPA process must be designed so as to meet particulate, fluoride, sulfur dioxide, and radioactivity standards. The fluoride limit will likely be that of CFR 63.603b, which is for phosphoric acid evaporation plants. This spec gives a limit of 0.24 pounds fluorine per hour in the stack for the Florida base case. The weight of the fluoride in the gas going to the FGD unit is expected to be 1 lb/hr, as only about 5% is expected to volatilize from the kiln bed, and of that in the kiln off gas about 98% is expected to be absorbed in the $P_2O_5$ scrubber. The particulate limit will probably be the same as for phosphorus rock calciners (CFR 63.6036), which is 0.0920 g/M$^3$. Since the scrubbers that remove phosphorus from the off gas are very effective we should not have trouble with the particulate spec.

The $SO_2$ limit will be imposed as an ambient air standard. In this case, a computer model is used to determine the appropriate dilution to be used based on stack flow and height, local area geometry, prevailing winds, etc. to determine the maximum ambient exposure for a given stack $SO_2$ concentration. Since the FGD unit is usually designed for power plants with about two orders of magnitude more $SO_2$, I suspect this hurdle will not be too onerous.

The lab pilot results show the uranium stays with the kiln residue as expected. Although support data has not been developed yet, it is suspected that the thorium stays with the residue as well, and the radium and polonium daughter products pass into the off gas. The polonium is removed in electric furnace process kiln off gas with scrubbers to meet an off gas spec of 2 Ci/yr, as described in CFR 61.120. It is suspected that the spray tower and venturi scrubber of the phosphorus oxide off-gas collection system will remove most of the polonium. Some of the residual polonium may be removed in the FGD scrubber as well.

The drier scrubber for the raw materials drier will be required to meet CFR 63.603c at 0.060 lb/mt feed.

Conclusion: The major solid waste from the KPA process meets TCLP and contains most of the sulfur and fluoride present in the ore minimizing air pollution issues.
"Process Engineering"

The two critical issues for successful commercial operation of the KPA process are: 1) Can a kiln operate with an oxidizing freeboard in contact with a reducing bed and still leave enough carbon in the bed to reduce the phosphorus at reaction temperature? And 2) Can enough heat be transferred to carry out the reduction reaction in a reasonable time period in a reasonable sized kiln? These questions are addressed below by comparing the KPA carbon burnout limitation with actual carbon burnout observed in the Tyssendal ilmenite reduction plant in Norway, and by comparing the heat transfer required by the KPA process to that obtained in a commercial lime kiln. A summary of results of a pilot plant and commercial plant heat and material balance are discussed.

Loss of Carbon from the Bed by Carbon Burnout

Both iron ore reduction to make DRI pellets, a common feed to steel blast furnaces, and ilmenite reduction to make synthetic rutile and iron are routinely practiced on a large scale in rotary kilns. These processes have reducing beds in contact with an oxidizing freeboard. The fact that large amounts of heat can be generated in an oxidizing freeboard, and transferred to the kiln burden, without whole scale burnout of carbon from the bed, forms the basis for the KPA process. In this section we will estimate how much carbon will burn out of the kiln burden by comparing the KPA kiln to a similar kiln in operation for the last twenty five years at the Tinfos Titan & Iron KS in Tyssendal, Norway, where there is sufficient literature data available to estimate carbon burnout (1).

The Tyssendal kiln performs a different reduction reaction than in the KPA process. Iron ore is reduced by carbon monoxide rather than carbon.

1) Fe₂O₃ + 3 CO⁺ → 2 Fe + 3 CO₂⁺ .........................................................Tyssendal
2) Ca₁₀(PO₄)₆F₂ + 15 C + 9 SiO₂ → 15 CO⁺ + 3 P₂⁺ + 9 CaSiO₃ + CaF₂ ......KPA

Diffusion of the carbon monoxide into ilmenite against the outward diffusion of carbon dioxide is shower than is the outward diffusion of only carbon dioxide from limestone during calcinations, which is limited by heat transfer into the limestone pellets. Fluorapatite, on the other hand, will not be reduced by carbon monoxide but requires, instead, direct contact with carbon.

In the Tyssendal system the iron ore is pelletized and preheated separately from coal which is used as the reductant in the process. One of the primary functions of preheating the balls on the grate in an oxidizing atmosphere was to oxidize the ferrous oxide, (FeO) in the ore to ferric oxide, (Fe₂O₃) prior to entering the kiln. This "opened up the ilmenite" and facilitated the reduction of the ore to iron in the kiln. This preoxidation to
$\text{Fe}_2\text{O}_3$ resulted in more of the carbon being used to reduce the iron than if this step was not performed. Part of the coal is added with the feed and up to 30% is "blown" onto the kiln bed separately up to one-half the way down the kiln. Since the coal is lighter than the ore balls, it tends to ride on top of the bed. Carbon dioxide from the freeboard reacts with the carbon in the bed to form two moles of carbon monoxide, which diffuses into the ore ball to reduce the iron ore to iron. This diffusion step is slow, and is the reason for the large kiln and high loadings (i.e. 15%) used in this process to achieve the 75% metallization goal of this plant. This also accounts for the small ball diameters required by this process.

Since the balls and feed coal are fed countercurrent to the flow of gas in the Tyssendal kiln, most of the volatiles come off of the coal, and are removed in the off gas, before the charge reaches reaction temperature of about 1000 °C. These volatiles in the kiln off gas were burned in an afterburner, and part of the hot off gas tempered with more air, and used to dry, preheat, and oxidize the balls before entering the kiln. Up to 30% of the coal was blown in with the air added for oxidation at the burner end of the kiln. This coal could be blown half way down the kiln. Some of the volatiles from this coal may have reduced some of the iron, but most of it would be swept by the off gas out of the kiln before it could be converted to CO and react with the iron. In the analysis below, it is presumed that none of the volatile organics reduced the iron. Note that nearly all of the volatiles leave coal by 950 °C, which is still below the temperature required to reduce iron ore in the kiln.

In the KPA process the carbon is mixed into the ore ball, and when heated to ~1250 °C, it reacts as rapidly as heat transfers to the reaction site. In this case carbon dioxide and $\text{P}_2\text{O}_{10}$ from the freeboard oxidize the carbon from the pellets. This "burnout" is analogous to the Tyssendal kiln in that it is the rate that CO$_2$ diffuses to the bed that determines the rate of carbon burnout. In this KPA case, however, the bed has a continuing evolution of $\text{P}_2$ and CO coming from the bed helping to maintain reducing conditions there. The $\text{P}_2$ is particularly effective as it will reduce CO$_2$ to CO at 1600 °K, stopping the CO$_2$ from reaching the bed. (The literature refers to elemental phosphorus existing as $\text{P}_2$ and $\text{P}_4$) The KPA kiln is about the same size as the Tyssendal kiln. It is believed that carbon burnout will not be any worse and may be somewhat better, particularly since the residence time is much less in the KPA kiln. The following is a comparison of the proposed KPA kiln with the Tyssendal Kiln.
Table 8. Comparison of Tyssedal Synthetic Rutile Plant Kiln versus KPA Kiln

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Tyssedal</th>
<th>KPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>19’</td>
<td>19’ {Metso quoted 2 ea. 16’}</td>
</tr>
<tr>
<td>Length</td>
<td>234’</td>
<td>250’ {Metso quoted 200’}</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>1170 °C</td>
<td>1280 °C</td>
</tr>
<tr>
<td>Ore Feed/hr</td>
<td>38.22T/hr</td>
<td>111 MT/hr</td>
</tr>
<tr>
<td>Coal Feed/hr</td>
<td>8 MT/hr</td>
<td>14.8 MT/hr</td>
</tr>
<tr>
<td>Char/hr</td>
<td>1.7 MT/hr</td>
<td>0</td>
</tr>
</tbody>
</table>

Carbon Burnout in Tyssedal Kiln

The coal used had a fixed carbon content of 62% and the recycle char, 70%. The theoretical use of carbon to reduce all of the iron in the ore to FeO and 75% of it on to Fe is calculated as follows:

<table>
<thead>
<tr>
<th></th>
<th>#/Hr, in feed</th>
<th>Carbon for 75% Metallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>10,519</td>
<td>+989 lbs/hr</td>
</tr>
<tr>
<td>FeO*</td>
<td>28,189</td>
<td>+2,945 lbs/hr</td>
</tr>
<tr>
<td>Total Carbon for Reduction</td>
<td>+3,934 lbs/hr</td>
<td></td>
</tr>
</tbody>
</table>

*Also oxidized to Fe₂O₃ on high temperature grate before entering the kiln

Carbon Balance

The total weight of fixed carbon in coal and recycle char charged to the Tyssendal kiln is:

In:
- Coal 17,640 x 0.62 = 10,937 lbs/hr
- Char 3,308 x 0.70 = 2,315 lbs/hr
- Total = 13,252 lbs/hr

Out:
- Product +3 mm Char = -4,410 lbs/hr
- Out Product -3 mm Char = -1,000 lbs/hr
- Consumed reducing iron oxide = -3,934 lbs/hr
- Remainder Burned out = 3,908 lbs/hr

In the base case for the 200,000 mt/yr P₂O₅ Florida commercial KPA plant, it is assumed that 4,104 pounds of carbon per hour is burned out of the bed. The rate of burnout in the KPA kiln would be expected to depend on the amount of surface area in the
bed compared to the volume of the bed. As we scale up the KPA process the relative carbon burnout should be reduced in direct proportion to the kiln diameter. The fact that during the Occidental KPA project over twenty years ago, we were able to get over 90% elimination of phosphorus in a 3' diameter batch pilot of the KPA process, suggests that we will do even better when operating in a nineteen foot commercial kiln where we expect the carbon burnout to be six times less. The residence time of the burden in the Tyssendal plant is almost twice as long as we expect the burden to be in the KPA kiln, which also makes us comfortable with the assumption we have made.

10 Heat transfer in the KPA kiln compared to lime kilns

The KPA feed pellets or balls require a certain length of time at the "hold" temperature for the phosphorus reaction to occur. As shown in the "operating window" section (E.3.b) a residence time of approximately 4 hours at 1200 °C, 2 hours at 1225 °C, and about 1 hour at ~1250 °C is required to complete the phosphorus reaction regardless of the excess silica level. In addition, it takes finite time to heat the charge to the hold temperature. With >600 °C off gas temperatures, experience dictates the heat up time for a dry charge with limited low temperature reactions is no more than forty minutes. A heavy loading in a kiln is 15% of the cross sectional area. The bulk density of the residue pellets or balls is 85 lbs/ft³. Therefore, to process the pellets or balls required for the KPA Florida base case plant, the minimum length of a 19' diameter kiln to meet these constraints is given in table 9.

Another design constraint on kiln throughput is the flow rate of gas in the hot zone of the kiln which experience from the cement industry suggests should ideally be less than 28 ft/sec to maximize heat transfer while minimizing dusting (34). The mass and heat balance for the Florida base case plant gives a gas flow in the hot zone of 31 ft/sec according to my calculation. While this is slightly more than the recommended limit given above, it is still less than that common in wet process cement plants (34).

Table 9. Length of KPA kiln necessary to meet processing time constraint

<table>
<thead>
<tr>
<th>Time at temperature</th>
<th>Megy composition</th>
<th>HL3 composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>107'</td>
<td>159'</td>
</tr>
<tr>
<td>2 hour</td>
<td>167'</td>
<td>250'</td>
</tr>
<tr>
<td>4 hour</td>
<td>289'</td>
<td>431'</td>
</tr>
</tbody>
</table>

35 Once the reaction residence time requirement is exceeded, then the reaction proceeds as fast as heat can get to the reaction site. To estimate how rapidly heat can
penetrates to the reaction site, compared the specific heat requirement of the KPA process with the calcination of lime, which has a similar heat transfer requirement.

The Greer Lime facility in West Virginia produces 500 tons/day of lime from a 98% calcium carbonate feed in an 11'6" diameter kiln 170' long. To heat the calcium carbonate to reaction temperature and volatilize the carbon dioxide requires 2,065 BTU/lb CaO. Thus this kiln transfers about 86 MM BTU/hr or 4,873 BTU/ft²-hr. The KPA base case involves transfer of 370 MM BTU/hr in a 19' diameter by 250' long kiln, or 5,223 BTU/ft²-hr.

Kiln processing engineers have suggested using two kilns, each 16' diameter by 200' long for a base case plant, or a single kiln with a 19' diameter by 250' long for the base case.

Conclusion: Carbon burnout is slow enough and heat transfer rapid enough to project reasonable commercial throughputs in a KPA kiln.

**Process Heat and Material Balances**

The mass balance data derived from the Phase I lab program, and the thermodynamic data from the references cited above (11, 12, 16), to create a heat and material balance for the kiln portion a 200,000 mt/yr P₂O₅ plant in Bone Valley, Florida (35). A 90% operating rate and 92% phosphorus yield was assumed. The plant uses a Megy composition feed and produces a phosphoric acid product (75.6%). The kiln off gas is oxidizing with 1% excess oxygen specified. The main results of the heat balance are:

1. The off gas temperature will be 1127 °C, when a small pilot burner is used.
2. There is enough recoverable heat in the kiln residue discharge from the kiln to dry the incoming raw materials, and to also dry and preheat the balls prior to feeding them into the kiln.

A mass balance for an 8,000 st/yr P₂O₅ pilot plant was prepared based on raw materials available in Soda Springs, Idaho (34). This flow sheet was based on an HL3 composition. The balance required an additional 16% more heat in the kiln to supply the specific heat necessary to bring the additional silica in this formulation to reaction temperature. This heat requirement was obtained by recouping more heat from the back end of the kiln. The kiln off gas, in this case, is 900 °C, 200 °C cooler than in the base commercial case, thus reducing the cooling tower load cooling the phosphoric acid circulating in the hydrators and venturi scrubbers.
References
18. ibid, fig. 669.
22. Simplot Industrial Products, Product Data Sheet, Silica Sand #100.


34. JDC, Inc, 8,000 T P₂O₅/yr, 92% yield, 90% op rate, Drawing 0417-101.

35. JDC, Inc, 200,000 T P₂O₅/yr, 92% yield, 90% op rate, Drawing 0408-100, 6/10/04.


37. Gerrard, A.M.; Guide to Capital Cost Estimating; Fourth Edition; IchemE; Rugby,UK; Chapter 4.5; p. 38-39

38. Jebson, R.S.; Capital Cost Estimation for chemical Engineering Projects; Paper #407; Institute of Food Science, Nutrition & Human Health; Massey University; Palmerston North, New Zealand.


BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a thermodynamic analysis of the phosphorus reduction reaction;
Figure 2 is a temperature phase diagram of the system CoO-SiO₂-3CaO·P₂O₅;
Figure 3A is a TGA graph of KPA onset temperature;
Figure 4 is a KPA temperature operating window;
Figure 4A is a diagram on feed ball melting;
Figure 5 is a flow diagram of preparation steps for the feed balls for the kiln of Figure 7;
Figure 6 is a graph of weight loss of kiln phosphate feed balls v. temperature;
Figure 7 is a side plan view of a direct heated rotary kiln for the present process;
Figure 8 is a graph of the operating window for the KPA process with respect to temperature;
Figure 9 is a flow diagram of the treatment of the kiln product off gas from the kiln of Figure 7;
Figure 10 is a graph of the thermodynamic evaluations of several potential pellet reactions;
Figure 11 (intentionally omitted);
Figure 12 is a TGA graph showing weight loss with respect to temperature;
Figure 13 is a phase diagram of the compositions of refractory materials tested.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring to Figure 7, a rotary direct-heat kiln 10 is shown having a kiln cylindrical shell 12, a front end 14 (also called the lower end, the solid discharge end, the air inlet end), and a back end 16 (also called the upper end, product end, solid feed end). The front end if fitted with a kiln firing hood having a burner 18 fed by an air line 20 and a fuel line 22. The kiln firing hood also has a solids discharge 26. In addition, but not shown, the kiln firing hood can have an auxiliary air supply. The back end of the kiln has a gaseous product manifold 29 to collect the gaseous product which is discharged through the product at off gas of vent 30 to be treated to recover the product, in this case P₂O₅, and a feeder 28 for feeding feed balls into the kiln. Along the length of the kiln there will be a plurality of air ports 38 used to control the amount of air being supplied to the head space or overhead or over bed space of the kiln in order to control the process temperature as described below. The kiln is lined with refractory brick which will not be affected by the burning gasses in the kiln, the product gasses and the hot feed balls.

Referring to Figure 5, a system for preparing feed balls is shown. As will be explained herein, preferably the silica carbon source, petroleum coke for example, and phosphate ore are co-ground in a grinder. Depending upon the composition of the ore, the
balls can be made from cleaned or washed phosphate ore, and/or from beneficiated ore, depending upon the clay composition and silica composition of the ore. Optionally, water and a binder, such as bentonite, can be added to the grinder. Some phosphate ores can be ground and bailed dry, others require water. In addition, some phosphate ores require binders and others no binders to produce feed balls. The ground material is passed to an agglomerator 52 to form balls or pellets having a diameter from 3/8 to 3/4 inches in diameter. Optionally, the outer shell of the balls can be coated with a coating of coke and/or coke and silica. The balls are passed from agglomerator to a dryer 54 which can be heated with the hot kiln solid residue or from the hot gasses the product off gas after removal of the product to form dried hot feed balls. The dried feed balls which are hot can be passed directly to the kiln 10 or they can be placed in storage and utilized later.

Referring to Figure 9, product off gas from the kiln is passed to a cyclone separator 60. Air is also introduced into the cyclone separator to complete any burning of gaseous elemental phosphorus. The gas products and the solid products are separated in the cyclone separator and the off gas solids drop out the bottom of the cyclone. Product gas is passed through line 62 and passed to a wetted wall spray tower 64. The product gas passes countercurrently through the wetted ball spray tower with the spray fluid which comprises phosphoric acid and water. The bulk of the P$_2$O$_5$ reacts with the water in tower 64 to produce phosphoric acid and the majority of the phosphoric acid product is collected in tower 64 and passes out line 68 to storage. The moist off gas containing droplets of phosphoric acid passes through line 70 to venturi scrubber 72. In the venturi scrubber 72, the moist droplets of phosphoric acid in the product stream from line 70 are trapped and collected and are passed to storage through line 74. The off gas from scrubber 76, which contains fine droplets of phosphoric acid, is passed through line 76 into demister or screening tower 78 wherein the off gas passes through a plurality of fine screens wherein to trap the droplets on the screens where they coalesce on the screening material and drop out the bottom and are passed to storage product line 80. The off gas which is now cooled down and is virtually free of any phosphoric acid and only has small residual values of fluorine and sulfur is primarily made up of air and carbon monoxide and carbon dioxide. The off gas pass through line 82 where it is treated to recover any residual fluorine values and residual sulfur values. The off gas is then vented to the air without effecting the environment.

Referring back to Figure 7, the kiln is normally operated in steady state to ensure product quality control, to operate and efficiently as possible, to reduce all the phosphate values and to preserve the life of the kiln. The formation of clinkers on refractory lining or the burning out of the refractory lining can have a disastrous result on the kiln and can destroy the kiln. Kilns are massive structures and can be 30 feet in diameter and 400-500
teet in length. They are rotated with large electrical motors. The kilns are supported by a series of support rings (not shown) which rest on rollers on piers. A large kiln can require a large electric motor such as a 3000-horsepower electric motor.

The feed balls are introduced into the feeder 28 either at ambient temperature or elevated temperature. Once in the kiln, when the kiln is in a steady state operation, the feed balls are brought up to the reaction temperature in the heating zone 34. To start a cold kiln the burner is used to heat the incoming air to heat up the kiln and the kiln bed. After they reach the reaction temperature, the feed balls are maintained at a fairly constant temperature range within 60°C, preferably within about 40°C along the length of the reaction zone 36. The reduction of the phosphate ore in the feed balls is extremely endothermic and requires a great deal of heat to release the elemental phosphorus, normally designated as P₄ or P₂. The elemental phosphorus is in a gaseous state at the reaction temperature and escapes from the feed balls because of their porous nature and goes into the overhead or head space of the kiln. Typically in cross section, the kiln is filled with from 5 to 15% solids with the overhead comprising 95 to 85% of the volume of the kiln. Silica and carbon are involved in the reduction and byproducts include a large amount of carbon monoxide and a large amount of calcium silicate. The calcium silicate remains in the feed balls whereas the carbon monoxide reports to the overhead together with the elemental phosphorus. In the overhead, the elemental phosphorus and the carbon monoxide are burned with the oxygen from the air supplied to the kiln to produce P₂O₅ and carbon dioxide. These two burning reactions are very exothermic and produce more than enough heat energy to heat up the feed balls, maintain the feed balls at the reaction temperature, and supply enough energy to carry out the reduction reaction. The heat transfer in the kiln is primarily through radiation. The heat from the burning of the elemental phosphorus and carbon monoxide is radiated in to the overhead gas, the kiln refractory lining and the top of bed. During operation, the refractory lining releases heat to the bed and the overhead gas. The overhead temperature in the reaction zone 36 is typically between 1200 and 1500°C, preferably between 1200°C and 1350°C.

Once the feed balls reach the reaction temperature, the reduction proceeds. If the balls are heated to temperature in excess of 1225°C, the reaction proceed rapidly and releases most of the elemental phosphorus and carbon monoxide within 10 to 15 minutes of the feed balls reaching the reaction temperature. This is only the case when the phosphate rock, silica and carbon source are intimately mixed and the carbon source is finely ground, such as to 80% -200 mesh and all the air is introduced into the front end of the kiln. Preferably the constituents are co-ground and finely ground to ensure intimate contact. By permitting the reduction to proceed between 1180 and 1320°C at the reaction site in the feed balls, melting is virtually eliminated, side reactions are minimized and S, F,
Na and K values remain substantially with the balls. At high silica levels, such as used by Hard, the reaction temperature can be allowed to exceed 1400°C without melting concerns. If all the carbon monoxide and elemental phosphorus were allowed to react promptly upon being released from the kiln bed, the temperature above that portion of the bed releasing the elemental phosphorus and carbon monoxide would quickly heat up to excessive temperatures, far in excess of 1225°C. Once the inventor recognized this rapid progression of the reduction at the reaction temperature, the inventor recognized that to prevent excess melting, side reactions and release of S, F, Na and K values, and to obtain 90% plus yields of P, the burning of the elemental phosphorus and the carbon monoxide in the overhead had to be controlled so that the burning occurred along substantially the entire length of the reaction zone 36 to maintain a relatively constant bed temperature to allow the reduction to proceed along the entire reaction zone to ensure complete reduction of the phosphate values in the ore. If all the air was introduced to the front end of the kiln, it would be impossible to control the burning and the temperature of the bed over the reaction zone. Uncontrolled burning would cause a zone of fire or hot zone where the elemental phosphorus and carbon monoxide is being released from the bed. Thus, the reduction and the burning must occur in a controlled manner along the entire length of the reaction zone 36 in the kiln. This requires that only a portion of the required air for burning be introduced into the front end and that the bulk of the air required for the burning be introduced by ports placed along the length of the kiln as shown in Figure 7. By controlling the burning in the overhead, the bed temperature and the reduction reaction rate in the feed balls can be controlled. In this way, the reduction can be controlled and maintained at a uniform rate along the reaction zone 36. This prevents melting, avoids hot spots or zones of fire, and permits complete reduction of the phosphate values in the ore. Ideally, the reaction would take place along the entire reaction zone 36 so that the last of the reduction was completed just prior to discharge. This is not feasible and the reduction is completed at least 5 or 10 feet before the end of the kiln.

Upon further recent study and testing, the inventor began to realize that this process was primarily a solid phase process and that interaction of external gasses reactants from outside the balls played a minor role in the reduction reaction. Thus, the inventor began to realize that possibly the intimate mixing by co-grinding of the constituents (phosphate rock, silica and a carbon source) as well as the reduction of the carbon source to very fine particles, especially particles 80% less than 200 mesh was preferable. Normally constituents are ground separately because of their difference in hardness. But the inventor realized that if they could be co-ground, that the mixing would even be more intimate and thus enhance the reduction reaction. This would also cause the find grinding of the constituents and not just the carbon source. By enhancing the
reduction reaction; the inventor discovered that the reaction temperature can be lower thus minimizing melting. This was totally unexpected. If the balls begin to melt, the outside of the balls can become sticky, clinkers can form and this becomes a serious problem in the operation of the kiln. Clinkers can bring a kiln operation to a grinding halt. The inventor surprisingly successfully co-ground the carbon source, petroleum coke, silica, and the phosphate ore together. The inventor found that by making balls of this co-ground composition ground to 80% minus 200 mesh, that the balls were much more reactive at a given temperature than courser ground balls or balls that were made up of separately ground constituents.

The inventor also discovered that if all the carbon burned out of the feed balls during the kiln processing, the balls become sticky. Thus, the inventor discovered that not only must the air be controlled to maintain a uniform temperature along the reaction zone of the kiln, it is also important to heat the balls up quickly to prevent carbon burn out before reduction takes place.

By controlling the bed temperature and by reducing the required bed temperature by fine grinding and intimate contact of the feed constituents, melting is avoided and side reactions, such as Senoite are minimized. In addition, the release of S values, F values into the overhead gas and the release of Na and K values from the feed balls are minimized.

The KPA process is preferably run so that in the heating, sufficient oxygen is supplied to burn elemental phosphorus and carbon monoxide to heat the bed up at a gradual rate preferably between 20 and 40 minutes from the starting temperature which can be ambient temperature up to 500°C for the feed balls up to the reaction temperature of between about 1180°C and about 1350°C. The reduction takes place in the reaction zone of the kiln preferably in about 40 minutes to about 80 minutes, although longer and shorter periods may be utilized, depending upon the selected reaction temperature. The process is run with about a 1% excess of O₂ in the air to burn the elemental phosphorus, carbon monoxide and any organic volatiles in the feed ball constituents.

In the preferred embodiment of the present invention, the calcium oxide silicon dioxide molar ratio is maintained between 0.4 and about 1.0, preferably between about 0.44 and about 0.7 which establishes the molar ratio of the fluorapatite phosphate ore and the silica used to make up the feed balls. An excess of carbon source is employed in the feed balls, that is the molar ratio of carbon source to phosphorus in the feed balls is greater than about 2.5. To minimize melting, even in this lower temperature KPA process, the amount of aluminum oxide is maintained at less than 2% by weight and the magnesium oxide is maintained below 0.5% by weight of the phosphate ore. These values can be increased if a low reduction temperature is selected. Surprisingly, it does not appear that
the amounts of sodium or potassium in the phosphate ore have much effect on the overall process, including melting characteristics of the feed balls. Preferably, the reaction is carried out so that the temperature in the bed is between about 1225 and about 1270°C. Most preferably from about 1240 to 1250°C. At the high silica levels, i.e. Hard process, the reaction temperature in the bed can exceed 1400°C. It has been found that a reaction temperature in the bed of about 1180°C, the reaction take about four hours to completely reduce all the phosphate in the feed balls. At about 1225°C the reduction reaction takes about two hours to reduce all the phosphate in the ore. At a temperature between about 1240 and about 1270°C (up to about 1320°C at high silica levels), the reduction reaction takes about one hour to reduce all the phosphate in the phosphate ore. Reaction temperatures above 1400°C are possible with high silica levels, but side reactions become a problem. At a reaction temperature of about 1425°C, the reduction takes about 15 minutes to complete. Although not fully confirmed, the inventor believes that the overhead temperature and the temperature at the surface of the refractory material is normally about 20 to 30°C above the reaction temperature at the reaction site. It is difficult to measure temperatures in a direct heat rotary kiln because of the high temperatures involved and because of the intense radiation from the burning and from the hot bed and hot refractory walls.

Whether wet grinding or dry grinding is to be carried out, and whether wet ground material or dry ground material can be utilized to produce balls, will depend upon the phosphate ore. For Idaho phosphate ore, the inventor has found that dry grinding is more economical and wet ball formation appears to be needed employing bentonite as a binder in the amount of about 0.7% by weight to form hard feed balls which can survive the tumbling and hot environment of a rotary kiln.

It appears that at least 95% of the phosphate value in the phosphate ore can be recovered as phosphoric acid with about 2% of the phosphate being retained in the residual feed balls as ferrophos. If the iron content of the phosphate ore can be reduced further, less phosphorus will be lost as ferrophos.

The co-grinding of the ore constituents and fine grinding of the coke is found to be very beneficial for all KPA processes. The co-grinding, the intimate mixing and the fine reduction of the feed ball constituents, especially the carbon source, not only speeds up the reaction rate within the feed ball, but also lowers the reaction temperature. This improvement can be utilized in the older KPA process, such as the Lapple process, the Megy/Hard process, and the Hard process described herein. It is also useful for the KPA processes described by Hokanson et al. in pending U.S. Applications No. 10/315,842, filed on December 10, 2002, and 10/894,297, filed on July 19, 2004.
The controlled burning of the elemental phosphorus and the carbon monoxide in the head space which leads to temperature control within the head space and thus in turn leads to control of the reaction rate within the feed balls can also be utilized in other KPA processes besides the process described herein. If all the air supplied from one end of the kiln, the kiln will form a fire zone or hot zone which will be like a closed loop because as the temperature in the head space raises, the temperature of the bed at that point will rise causing the reaction rate increase driving more elemental phosphorus and carbon monoxide in the head space which will be burned by the oxygen in the air causing the bed temperature to increase further which could lead to melting and to clinker formation, serious side reactions, and the release of S values, F values, Na values, and K values from the balls. It is only through the controlled burning of the elemental phosphorus and the carbon monoxide along the length of the reaction zone of the kiln that the reaction rates of the reduction can be controlled and this requires a uniform bed temperature along the reaction zone so that the reduction takes place along the reaction zone. This also ensures complete reduction of phosphate values in the balls. This also permits a greater pass through of feed through the kiln, such as 200 to 300% increase in pass through.

The step of ensuring that there is enough carbon in the feed balls to both ensure the completion of the reduction reaction of the phosphate ore, but also to ensure that there is enough carbon available to prevent sticking of the balls and sticking of the balls to the kiln lining.

The carbon source can be charcoal, coal, coal coke, petroleum coke (pet coke), and the like. Petroleum coke has been found suitable even though it contains appreciable amounts of S values. When the bed temperature is maintained below 1350°C, most of the S values remain in the solid kiln residue. All carbon sources, with the possible exception of charcoal, contains S values of from about 1% to about 8% by weight. Thus, the Megy/Hard and Hard processes were carried out with carbon sources containing S.

It appears that washed phosphate ore can be used in the process and beneficiated is not required thus eliminating tailing pond discharges. The ore may have to be blended (washed ore with some beneficiated ore) to maintain the aluminum and magnesium values below certain values described herein.

EXAMPLE 1

Phosphate ore with high dolomite content is screened from run-of-mine ore in central Florida and has a silica content of 15% as it comes from the screens. Silica sand is added in the amount of 3 parts silica (96% basis) to 10 parts ore (40% CaO, 25% P₂O₅, 3% MgO), and 2 parts petroleum coke (75% fixed carbon). This mixture is ground to 80% - 150 mesh in an open circuit ball/mill. The ground ore is mixed with appropriate amounts
of binder and water and formed into balls (nominally 3/8" diameter) in a balling drum, with a
mixture of 70% fine silica and 30% coke sufficient to form a 10 mil coat is added near the
discharge of the balling drum. The balls are dried and preheated to 300°C in a grate drier
using heat recouped from the solids discharged from the hot end of the kiln.

The balls are then processed in a counter current rotary kiln. After startup, essentially all the fuel originates from the coke in the balls. The kiln is equipped with porting to supply over bed air in such a way as to have a flat controllable temperature profile. The off-gas from the kiln passes first into a refractory lined cyclone to remove gas born dust and condensates from the kiln. Air is added at this point to complete any oxidation required in the off-gas, and then the P₂O₅ scrubbed therefrom, first in a wetted wall spray tower and finally in a venturi scrubber. Residual phosphoric acid mist droplets are removed by demisters and finally acidic sulfur and fluorine acid vapors are scrubbed before releasing the off-gas to the environment.

The solid discharge from the kiln is suitable for landfill and the phosphoric acid produced is of high quality at 70% concentration and greater than ninety percent yield.

OPERATIONAL TEST RUNS
The TGA Tests

Indeed obtaining clear information proved quite a challenge due to experimental and theoretical difficulties encountered:

1. The temperature range where the "operating window" lies is above that of a common nichrome furnace. A furnace with molybdenum, silicon carbide, or other high temperature elements less commonly available is required.

2. Platinum thermocouples or instrumental furniture are destroyed by even small amounts of phosphorus vapor, which forms P₂P₂, which particularly attacks the grain boundaries (19). Platinum is almost universally used in TGA/DTA equipment, which is frequently used to determine high temperature melting and reaction data. An old standard treatise for analytical chemistry warns of this problem. Furman (20) states, "It should be noted that the presence of reducing substances, such as carbonaceous materials, in melts containing phosphates, leads to destruction of the platinum. In general, oxidation states of phosphorus lower than the phosphate should never be allowed to come in contact with heated platinum." In spite of the inventor's experience with phosphorus chemistry, he did not know of the problem, and proceeded to unknowingly destroy about $8,000 worth of platinum early in his work, which put the program under financial pressure, and increased the time it took to get the data.
3. After obtaining tungsten thermocouples and graphite/ceramic furniture for the TGA/DTA system, and setting up to run under strictly reducing atmospheres to protect them, the DTA was not useful for obtaining melting information. Very small samples are used in the TGA/DTA system to minimize heat transfer resistance and allow reactions and phase transitions to happen very rapidly. It was found in later studies (see below) the rate limiting step in the KPA reaction involves mass transfer within the pellet, not heat transfer to the pellet, or into the pellet. Therefore, the reaction is tens to hundreds of minutes, even when the sample size is very small. This made separating—the reduction reaction from melting phenomena difficult, even at slow scan rates. A second feature of the reaction discussed below is that a large amount of amorphous material is formed as a reaction product, which does not have a distinct melting point. The gradual melting over a temperature range is difficult to quantify in a DTA scan. A third complication is that there are high temperature reactions that occur after the phosphorus is evolved as described below, which interfere with the thermal indication of melting in the DTA equipment. Fortunately the TGA data gave a quantitative indication of the weight loss in the residue which indicates the amount of phosphorus reduction versus time and temperature and could be conveniently used to acquire reaction rate data.

The TGA Screen Tests for Reaction Onset Temperature

Once the TGA was operational, preliminary TGA tests were run to get a feel for how high the temperature must be to accomplish the phosphorus reduction and removal from the pellet. The “Megy”, “Eutectic”, and “Hard” raw material formulations had low, medium and high silica content respectively. Each composition was run to yield TGA data on a Netzsch SGA 409C/CD instrument. The runs were conducted as follows.

1. A weighed amount (about 27-29 milligrams) of one of the formulations was placed in a small TGA crucible and mounted on the scale shaft in the TGA unit. A tight graphite lid with a pinhole is fitted onto the crucible.

2. After evacuation and backfill with argon three times to remove all traces of oxygen and water vapor which would otherwise destroy the tungsten thermocouple, a flow rate of 50 cc/min of argon is established over the sample crucible, the sample is heated at high rates to 1100 °C, and then at 5 °C/minute to 1330 °C.

3. The weight of the pellet is plotted in % of total sample weight as the ordinate, and temperature is plotted as the abscissa.
The data from all three runs are superimposed and shown in figure 3a. These data show an onset temperature of \(~1224\ ^\circ\text{C}\), where the reduction reaction significantly increases in rate. Note that this onset temperature \((1224 \ ^\circ\text{C})\) is somewhat less than the value calculated from thermodynamic data above \((1269 \ ^\circ\text{C})\). More recent data indicates that the onset temperature appears to be between 1170 and 1180\(^\circ\text{C}\). The reason is likely that the reaction products are in a different crystal form and the calcium fluoride is likely mixed into the calcium silicate product which would lower its activity to less than one. A major observation is that the excess silica present in the “eutectic” and “Hard” compositions, do not affect the reaction onset temperature, which is the same in all three cases.

**The Method Used to get the upper melting curve**

Over 125 lab pilot runs of the KPA process, using \(\frac{1}{8}''\) and \(\frac{3}{4}''\) diameter pressed pellets containing different candidate ore/silica/coke ratios, fired at different hold temperatures, for different lengths of time, were used to define the “operating window”. Since only one run at one time/temperature combination could be run each day, nearly five months was spent acquiring the data presented below. If the DTA would have been effective in getting the melting data, then it could have been acquired in a couple of weeks.

Getting data that was relevant to a commercial kiln bed required paying strict attention to the gases sweeping the test pellet in the lab. This critical item is discussed in the section following before the “operating window” data is presented.

**The “sweep gas”effect**

The phosphate reduction reaction with excess silica is:

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 9 \text{SiO}_2 + 15 \text{C} \rightarrow 15 \text{CO}^\Delta + 3 \text{P}_2^\Delta + 9 \text{CaSiO}_3 + \text{CaF}_2
\]

As indicated above, at unit activity for the solid reaction products (CaSiO\(_3\) and CaF\(_2\)) and with activities equal to their partial pressures for the gaseous components (CO and P\(_2\)), the thermodynamic analysis shows the free energy of reaction is zero at 1269 \(^\circ\text{C}\). In a kiln very little gas from the freeboard enters the bed, particularly with CO and P\(_2\) gas being generated within the bed and evolved from the bed at a rapid rate.

What about in the lab simulation of the KPA process? If sweep gas is allowed to dilute the CO and P\(_2\) at the reaction site, the temperature at which the reaction proceeds will be lowered. It can be calculated by how much from thermodynamic analysis. The inventor calculated that if the partial pressure at the reaction site is reduced by \(\frac{1}{2}\) by sweeping it with an inert gas, then the reaction will proceed at a 50 \(^\circ\text{C}\) lower temperature. This large effect is due to 18 moles of off gas forming for every mole of fluorapatite reacted. Thus, to simulate a kiln bed in the lab, the reaction site must be bathed in its own
*off-gas, and the off-gas cannot be swept away with an inert gas. Since this is a log function, each additional reduction of the off gas partial pressure by \( \frac{1}{2} \) will result in lowering the reaction temperature by an additional 50 °C. For the TGA experiments, tight fitting graphite lids, with pinholes, covering the sample were used. KPA lab pilots used graphite crucibles with graphite lids.

The Lab Pilot Runs

These experiments were run by mixing ground phosphate ore, silica, and petroleum coke intensively; first dry, and then with 8% moisture to form a well mixed slightly damp paste. The mixtures were pressed into \( \frac{1}{2} '' \) or \( \frac{3}{4} '' \) pellets in stainless steel dies at \(~35,000\) psi pressure. The resulting pellets were dried under a nitrogen sweep at \(~120\) °C overnight. The resulting pellets had a true density of about 125 lbs/ft\(^3\).

To run an experiment, a pellet was weighed and placed on a \(~2\) gram bed of highly calcined – 60 mesh carbon, in an ATJ graphite crucible \( 1\frac{1}{2}'' \) diameter x \( 1\frac{1}{2}'' \) deep (inside dimensions) with a \( \frac{3}{4}'' \) wall. The crucible was placed in a box furnace with molybdenum furnace elements, and a second graphite crucible placed on top of the first closing it off from the atmosphere. The box furnace was a Del Tech Inc DT-31-5BL-AE-888-C furnace system. The furnace was then closed. There was a fiber seal in the furnace door that kept air from entering the furnace, but the refractory picked up some air or water vapor from the air when the furnace was open, and despite the nitrogen purge described below, we would loose a few tenths of a gram of graphite from the crucibles each run from oxidation.

A sweep of approximately three liters/minute of high purity nitrogen was passed through the furnace for the duration of the run. The temperature profile for a run was programmed as follows:

1. Ramp sample to 100 °C at 20 °C/minute.
2. Hold for six hours to remove as much air and water vapor from the furnace as possible.
3. Ramp to the test temperature at 20 °C/minute.
4. Hold at the test temperature for the test time.
5. Ramp back to room temperature at 20 °C/minute.

After the run the following data was taken:
1. The fired residual weight of the pellet.
2. If not melted, the dimensions of the fired pellet.
3. Color of the pellet.
4. Observation of pellet melting.
5. Observation of graphite bed powder sticking to pellet.
In some cases chemical or instrumental analysis was made of the fired pellets as follows:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chemical analysis (Leco for gases, ICP, wet)</td>
<td>Phosphorus removal - Elements that volatilized</td>
</tr>
<tr>
<td>2. XRD</td>
<td>Crystal form in residue pellet</td>
</tr>
<tr>
<td>3. EDAX</td>
<td>Element distribution in pellet</td>
</tr>
<tr>
<td>4. TCLP</td>
<td>Reaction mechanism</td>
</tr>
<tr>
<td>5. Acid reactivity</td>
<td>Environmental assessment</td>
</tr>
<tr>
<td>6. Grinding</td>
<td>Odor assessment</td>
</tr>
<tr>
<td>7. Density</td>
<td>Integrity of residue pellet</td>
</tr>
<tr>
<td></td>
<td>Residue density</td>
</tr>
</tbody>
</table>

The results as they apply to “operating window” size are set forth below. Other issues will be discussed in the sections that follow. The 20 °C ramp rate used in the tests is close to that which occurs in a commercial kiln.

**Raw Materials**

Phosphate ore from Rasmussen Ridge mine, just outside Soda Springs, Idaho, which had been washed and sized to − ¼” in the Agrium wash plant and wet ground to 40% less than 200 mesh in the Agrium wet mill was used in all the tests run during phase I. The ore was dried at 110 °C in air. The material passing a 200 mesh screen was used in all the Phase I tests and is referred to as Conda Ore (21).

Silica from a Soda Springs Simplot source was ground in a ceramic mortar and pestle to -200 mesh. The grinding was difficult, and the product was contaminated with alumina from the grinding. After the first few runs, a fine Simplot sand fraction from their Overton, Nevada plant was obtained and screened using the -200 mesh fraction for most of the runs in this Phase I study (22).

Green Petroleum coke was from the Chevron facility in Pascagoula, Alabama. It was typical shot coke that was part of a large ocean shipment sent to Europe. It was ground in a disc mill and the -200 mesh screen fraction was used in all the Phase I experiments (23).

A chemical analysis of these raw materials is given in table 2.

**Table 2.** Analysis of raw materials used in KPA lab pilot runs
<table>
<thead>
<tr>
<th>Raw Mat, wt.%</th>
<th>Al₂O₃</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>Mn</th>
<th>Fe₂O₃</th>
<th>S</th>
<th>K</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Ti</th>
<th>V</th>
<th>Zn</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conda Ore*</td>
<td>1.724</td>
<td>29.7</td>
<td>42.08</td>
<td>0.0513</td>
<td>0.7192</td>
<td>0.465</td>
<td>0.5999</td>
<td>0.5475</td>
<td>12.29</td>
<td>0.0674</td>
<td>0.0651</td>
<td>0.0228</td>
<td>2.87</td>
</tr>
<tr>
<td>Simplot Silica</td>
<td>2.551</td>
<td>0.1</td>
<td>0.0308</td>
<td>0.0062</td>
<td>0.2459</td>
<td>0.007</td>
<td>1.181</td>
<td>0.0637</td>
<td>97.26</td>
<td>0.1372</td>
<td>0.0015</td>
<td>0.345</td>
<td>87.47</td>
</tr>
<tr>
<td>Green Pet Coke**</td>
<td>0.009</td>
<td>0.011</td>
<td>0.01</td>
<td>6.15</td>
<td>0.0136</td>
<td>0.0136</td>
<td>0.335</td>
<td>0.8747</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The mineral breakdown of the ore is fluorapatite- 74.55%, Silica- 12.29%, Muscovite- 3.74%, Dolomite 2.17%
  Albite- 2.03%, Organic- 3.09, Sulfides -FeS and minor sulfides.(24)
** Green pet coke also contains 3.31% hydrogen and 1.94% nitrogen. (all petroleum coke [pet coke], coal coke, and coal contains, normally in the range of from 2% to 8% by weight)

The compositions receiving the greatest study differed in their silica content as follows:

<table>
<thead>
<tr>
<th>Formulation name</th>
<th>“Megy”</th>
<th>“Eutectic”</th>
<th>“HL3”</th>
<th>Hard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica level</td>
<td>low</td>
<td>medium</td>
<td>high</td>
<td>higher</td>
</tr>
<tr>
<td>Parts -200 mesh Conda Ore</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Parts -200 mesh Simplot SiO₂</td>
<td>0.4850</td>
<td>0.6535</td>
<td>1.05</td>
<td>1.2</td>
</tr>
<tr>
<td>Parts -200 mesh Green Shot Coke</td>
<td>0.1971</td>
<td>0.1971</td>
<td>0.1971</td>
<td>0.1971</td>
</tr>
</tbody>
</table>

Results

A graph showing the weight loss of the pellet versus the temperature at which the pellet was fired is given in figure 4 for thirty five "HL3" pellets. The flag on each of the data points shows the time the pellet was held at the firing temperature. Half inch diameter pellets are shown as dots and ¾" pellets have a circle drawn around them. If there is a second number indicated in the flag, it is the percent phosphorus eliminated from the pellet as determined by chemical analysis.

The ordinate shows the weight loss the pellet gave up during the furnace treatment in percent of feed pellet weight. The abscissa gives the temperature in degrees Centigrade at which the pellet was held. The lower dashed line in the figure 4 is the weight loss calculated to occur from the sum of the various low temperature reactions described herein. The reaction off gas from these low temperature reactions is 2.8% of the feed weight for the pellet. The upper dashed line shows the additional weight loss of phosphorus and CO which are expected from the reduction of the contained fluorapatite, and totals 19.68% of the original weight of the pellet for an HL3 feed composition. This weight loss comprehends the ~2% of the phosphorus which is formed in the KPA process but stays in the kiln residue forming ferrophos. The curve in the figure is the approximate weight loss obtained in a two hour hold time versus temperature.
This curve shows that weight loss consistent with the reduction of all of the phosphorus occurs at \( \approx 1225 \) °C in two hours. A typical fired pellet at lower temperatures or for short duration is black in color and retains the sharp edges of the input pellet. They are shrunk about 8% in all dimensions, leaving a true density of \( \approx 125 \) lbs/ft³, which is the same as the input pellet. The residue pellet is hard as a rock requiring multiple blows in a mortar and pestle to break down. Iron and other metals remain in the kiln residue.

At higher temperatures and longer times the pellet acquires a white shell that becomes sticky toward carbon powder as can be observed with the \( \frac{1}{2}'' \) pellet at four hours at a 1330 °C hold temperature, and both pellets at twelve hours at a 1330°C hold temperature. At this point the weight loss exceeds that explained by the low temperature reactions and the phosphorus reduction reaction combined, and increases with longer reaction times. This "weight loss excess", is due to high temperature reactions, which are discussed herein. At about 1360°C, depending on impurity level in the feed pellet, we notice that the sharp edges begin to round. At 1380 °C a low impurity pellets shows significant melting at this silica level. The effect of impurities on melting is discussed herein. Above 1360 -1380 °C, depending on the level of impurities, melting sets in.

**Megy and Eutectic compositions**

A graph of the "Megy" and "Eutectic" compositions weight loss versus temperature is shown in figure 6. At this reduced silica level melting in the residue occurs at a lower temperature of about 1280 °C. This is only 55 °C hotter than the temperature required for carrying out the reduction reaction in two hours. Several experiments where the charge was held for four hours were carried out to see if that would open up the window. Indeed, the pellet can be fully reduced at about 1200 °C in four hours or about 25 °C less than in two hours.

The temperature reaction curve against silica level in the formulation the result is shown in Figure 6. Weight loss from "Megy" pellet lab pilot runs (left) and "Eutectic" pellets (right), with examples of pellets both just before and after melting was observed.

A graph of the "Eutectic" composition is shown in figure 7 and is very similar to the Megy composition. Figure 7 shows the weight loss data from the "Eutectic" composition lab pilot runs.

If we combine the data from each of the graphs to show the upper temperature melting curve and the lower temperature reaction curve against silica level in the formulation, the result is shown in figure 8.

Figure 8 shows the operating window for the KPA process

**Conclusion**: The operating window is adequate for commercial KPA operation particularly with the high silica formulation.
Low temperature reactions occurring within the kiln bed

The chemistry of the phosphate ore used in the Phase I experiments was analyzed by Agrium (21). Knudsen gives a detailed mineralogy of the Idaho Meade Formation Ore (24). It is mostly fluorapatite, with some magnesium, aluminum, and sodium cations and carbonate anions substituted in the mineral. In addition there is some dolomite (CaMg(CO₃)₂), Muscovite (KAl₂(AlSi₃)O₁₀(OH)₂), and other minor clays present. Iron is present mostly as FeS and small amounts of other sulfides are present (i.e. Zn, As, Cu, Hg, Pb, etc.) Some organic material is also present. In order to understand the weight loss observed in the lab KPA pilot runs, and to construct a mass and heat balance for the KPA process the inventor has attempted to estimate what reactions occur while the ore is being heated to the reaction temperature. The conclusions are as follows:

1) Bound water in Muscovite is released to the kiln freeboard at a temperature below which it would react with carbon to form CO or CO₂.

2) Calcium carbonate, whether within the fluorapatite mineral or as calcite (CaCO₃) or dolomite reacts with silica and carbon as follows:

\[ \text{CaCO}_3 + \text{C} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + 2 \text{CO}^\text{=} \]

This is a simplification because a ratio of CO and CO₂ are formed, but at the temperature of the above reaction around 900 °C it is mostly CO.

3) Magnesium carbonate either within the fluorapatite mineral or in dolomite reacts at a lower temperature and forms magnesium silicate. For this reaction the CO/CO₂ assumption was made the other way:

\[ \text{MgCO}_3 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{CO}_2^= \]

Green coke has volatiles, nitrogen and sulfur to consider in low temperature reactions. Coke also contains fixed sulfur. Volatiles are organics (mainly CH₄) that volatilize < 950 °C. Most volatiles have left the coke by 950 °C. The carbon that remains is termed "fixed carbon", and will remain as a solid in inert atmosphere even if graphitized at ~2500 °C. The coke used had 1.81% nitrogen and 6.81% sulfur. A significant fraction, but not all of the nitrogen will volatilize from the coke by the time the reduction reaction gets under way at 1224 °C. Most of the sulfur will stay in the coke volatilizing in the 1300 °C – 1700 °C range with time (25). The fact that most of the S in the feed remains in the kiln residue is a blessing. In an experiment, dried green coke was heated to 1224 °C for two hours. A total of 16.22% of the weight was lost including 95% of the hydrogen (3.08% of the weight of the dry feed coke), 17% of the sulfur (6.81% of the dry feed coke), and 64% of the nitrogen (1.81% of the dry feed coke).

The Conda ore also contains a small amount of organic material. I assumed 60 % of the organic in the ore was volatile (CH₄), and 40 % was fixed carbon in the weight loss
calculations given above, and in the mass balance calculated in the process engineering for the process.

Conclusion: The low temperature reactions result in ~2-3 % loss of volatiles from the dried feed pellet depending on the fraction of phosphate ore verses silica in the pellet.

Completeness of the Phosphorus Removal from the kiln burden

When fluorapatite is reduced, phosphorus metal vapor and carbon monoxide gases form which blow out of the pellet into the gas around the pellet when they exceed one atmosphere pressure. The kiln is operated basically at atmospheric pressure. About 2% of the phosphorus in the feed pellet stays behind in the residue. Examination of the residue shows that the residual phosphorus is entirely associated with iron, which also remains in the residue as a ferrophos phase. As shown in an EDAX scan and qualitative analysis, other minor metals present in the phosphate ore, like Cr,V, and Ti are also present in the "ferrophos phase". A Zeiss LEO 982 FE-SEM was used for high-resolution imaging. The system is equipped with an Oxford INCA EDS that was used for qualitative elemental mapping analysis. Operating conditions consisted of 20 KeV for SEM imaging, and 20 KeV, EDS analyses consisted of 10K counts per second rate and total count 1.5 hours for each map area. The EDS analyses are limited to elements with atomic weights heavier than boron. Photomicrographs of high-resolution secondary electron (se) images and backscattered electron (bse) images were obtained as digital images and stored in electronic format.

This chemistry is similar to that observed in ferrophos from the electric furnace process. The difference is that here the ferrophos is in small beads, usually less than -325 mesh, and averaging perhaps 10 microns or less in diameter, encapsulated in the calcium silicate residue. What a nice thing environmentally to have the ferrophos part of the inert calcium silicate residue.

Conclusion: From analysis of the phosphorus and iron in the fired pellets it is found that the ratio of moles of iron per mole phosphorus is between 1.0 and 1.8. Hanson (26) reports that although Fe₂P is the dominant binary between iron and phosphorus, FeP is stable at these temperatures if the partial pressure of phosphorus is high enough. The encapsulation of the small "ferrophos" beads in solid CaSiO₃ as the phosphorus is evolved results in at least some of the iron surviving as FeP and the rest Fe₂P. Note that there does not seem to be any particular barrier to getting the last of the free phosphorus out of the pellet (that not associated with ferrophos). The analytical data shows all the free phosphorus is out in two hours at 1225 °C, and the weight loss data show all of the free phosphorus removed in four hours at ~1200 °C. In other words, there does not appear to
be any special "slow step" in removing the last say 10% of the free phosphorus, but rather just the smooth completion of the "slow step" in the reaction, which is described herein.

High temperature reactions occurring within the kiln bed

**Fluorapatite Reduction**

The primary high temperature reaction is the fluorapatite mineral reduction in the presence of silica with carbon. This reaction proceeds according to the reaction:

\[ \text{Ca}_{10} (\text{PO}_4)_6 \text{F}_2 + 9 \text{SiO}_2 + 15 \text{C} \rightarrow 3 \text{P}_2^\wedge + 15 \text{CO}^\wedge + 9 \text{CaSiO}_3 + \text{CaF}_2 \]

To gain additional insight into the nature of the reaction products, the residue of several lab pilot runs were analyzed by XRD (x-ray diffraction). The special applications X-ray diffractometer is a Philips X'Pert MPD system with a vertical \( \theta-\theta \) goniometer (220 mm radius). The X-ray source is a long-focus, ceramic X-ray tube with Cu anode. Normal operating power is 45 kV, 40 mA (1.8 kW). The focusing optics consist of programmable divergence, anti-scatter, and receiving slits, incident and diffracted beam slitter slits, a curved graphite diffracted beam monochromator, and a proportional counter detector. The principal application of this setup is phase analysis of powder specimens. For ambient X-ray diffraction measurements, the Multi-Purpose Sample Stage supports typical cavity-type powder mounts and will also accommodate monolithic specimens of a wide variety of sizes and shapes.

Three fired HL3 pellets and one eutectic pellet were analyzed with the results shown in table 3. The high amount of amorphous phase is to be noted. It is of a calcium silicate composition, but not crystalline. In the HL3 pellet residues silica grains survive, but in the eutectic pellet residue all silica is in the CaSiO\(_3\) or amorphous phase. No fluorapatite is observed in these fully reacted pellets. Note that cristobalite, quartz, and tridymite are three different crystalline forms of pure SiO\(_2\), and Ca\(_3\)(SiO\(_3\))\(_3\), pseudowollastonite, and CaSiO\(_3\) are three different forms of calcium silicate.

A separate XRD analysis of the Conda fluorapatite raw material used in the pellet formulation shows no amorphous material, with a semi quantitative analysis of \( \sim 45\% \) fluorapatite, \( \sim 50\% \) quartz, and \( < 5\% \) muscovite and dolomite.

**Volatility of feed pellet elements**

It is of particular importance in developing the KPA process to determine where the minor components of the raw pellet go when fired. A determination whether the residual carbon present in the residue pellet is that predicted by the reduction reaction was also made. It was decided to find out more about the Si\(_2\)N\(_2\)O that the XRD result suggested was present in our residue on occasion.
Table 3. Phases identified in fired pellets by XRD.

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<td>Yes</td>
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<tr>
<td>Composition</td>
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<td>HL3</td>
<td>HL3</td>
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<table>
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</tr>
<tr>
<td>Quartz</td>
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<tr>
<td>Tridymite</td>
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<tr>
<td>Ca₃(SiO₃)₃</td>
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<tr>
<td>Pseudowollastonite</td>
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</tr>
<tr>
<td>Si₃N₂O</td>
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<tr>
<td>CaF₂</td>
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To make these determinations, the raw pellet and fired residue pellet from several different experiments were analyzed. The results are summarized in table 4. The DCP and ICP was used to conduct the majority of the metallic element analysis. It is semi quantitative, with a nominal accuracy of about +/- 10% on major elements and +/- 50% at levels near the sensitivity limit. Sample prep can add additional error. Table 4 shows how much of a component in the feed is volatilized from the residue.

**Senoite (Si₃N₂O)**

There is a clear indication of absorption of nitrogen into the pellet from the atmosphere indicating support for senoite formation as indicated in the XRD results. An EDAX dot map was run on a ground pellet residue from R8764 (Megy formulation, 1370 °C, 3 hrs, melted), that shows the senoite phase is a discrete phase. The dot maps clearly show several areas of high silica and nitrogen, without calcium, and clearly reduced oxygen, sitting amongst the dominant calcium silicate particles.

Thermodynamic properties for senoite were calculated by Fegley (27), and were used to calculate the temperature at which it would form in the KPA pellet. This analysis suggests that Si₃N₂O will form at 1310 °C, which is about fifty degrees hotter than the calculated temperature for the fluorapatite reaction to proceeded. This is consistent with the KPA lab pilot observation that the fluorapatite reduction reactions go to completion before the senoite formation begins. Other reactions discussed later in this section were also calculated and also shown in figure 10.
The "major" problem with the senoite is that it forms on the outside surface of the pellet which is in contact with nitrogen from the atmosphere. The phosphate reduction occurs first, and then the senoite formation occurs, eventually depleting carbon and forming what looks like an egg shell around the pellet. The reaction is:

5 \[ 2 \text{SiO}_2 + \text{N}_2 + 3 \text{C} \rightarrow \text{Si}_2\text{N}_2\text{O} + 3 \text{CO}^\uparrow \]

After the carbon in the shell is depleted, any carbon touching the surface of the pellet is used as a reductant and results in the pellet sticking on that carbon. As we ran the KPA lab pilot runs hotter and longer, sticking of the pellet to the bottom of the crucible became such a problem that we put a carbon powder bed in the crucible to support the pellet. In this case the carbon powder still adhered to the pellet in the longer, higher temperature runs, but it could be easily removed from the crucible. The sticking could cause clinker formation.
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*Elements Quantitatively analyzed*
The Si₅N₂O reaction loses more weight in CO gas formation, than it gains by nitrogen absorption. The weight loss associated with this reaction "explains" most of the excess weight loss of the high temperature reactions. For example, in the four hour run at 1330 °C the sample picked up ~1.6% nitrogen. This is equal to 2.24% excess weight loss, which is about what we observe. In general the Si₅N₂O layer is somewhat stickier after the carbon is all consumed from it, and may cause some agglomeration in the kiln. Therefore, it is important to run the process so that all the free phosphorus is removed, but get it out of the kiln before all the carbon is gone. There is a reasonable gap between the two events that make this requirement not too difficult in practice to accomplish.

Figure 10 shows the thermodynamic evaluations of several potential pellet reactions. When the free energy of reaction goes negative the reaction can proceed thermodynamically. The reactions are: (1) CaF₂ + Na₂O → 2 NaF + CaO, (2) 2 CaF₂ + 3 SiO₂ → 2 CaSiO₃ + SiF₄, (3) 3 CaF₂ + 3 SiO₂ + Al₂O₃ → 3 CaSiO₃ + 2 AlF₃, (4) Ca₁₀(PO₄)₆F₂ + 9 SiO₂ + 15 C → 3 P₂ + 15 CO + 9 CaSiO₃ + CaF₂, and (5) 2 SiO₂ + N₂ + 3 C → 3 CO + Si₂N₂O.

Sulfur

It was expected that as the carbon from the petroleum coke was consumed in the reduction reaction, that the ~6% sulfur that was in the petroleum coke would evolve into the off gas making SO₂, like it does in a power plant. However, it was found that most of the sulfur stays behind in the kiln residue.

Since petroleum coke, which contains 6.5% sulfur, is only 20% of the feed mixture, and since sulfur in the ore is only about 0.465%, the sulfur in the residue is a maximum of just over 1%. To be observable by EDAX it must concentrated in discrete phases.

Sulfur is associated with only calcium, oxygen, and silica. Oldhamite, CaS, is a mineral known here-to-fore only in carbonaceous meteorites, and is stable to >2500 °C. (28). It is the most likely candidate that is stabilizing the sulfur into the pellet. In air it reacts rapidly to form CaO and H₂S from water vapor.

No odor was detected from a residue pellet ground to 80%-100 mesh, in water. When 3% HCl was added, a barely perceptible H₂S odor was detectable to smell. It appears that when encapsulated in the calcium silicate glass it is quite stable.

Another possible candidate is SiS₂ (29), a rare chemical that normally decomposes at 1090 °C. A Japanese patent (30) claims SiS₂ can be made in high yield under conditions very similar to the KPA conditions. The encapsulation of SiS₂ in excess SiO₂, and CaO may stabilize it. No matter the exact chemical reason for the stabilization of sulfur in the residue, the finding has considerable economic value. High sulfur green coke from petroleum refineries is of almost zero value as a byproduct, because, when used as a fuel
in power plants, the cost of removing SO\textsubscript{2} from the off gas in flue gas desulphurization units adds cost, making it less attractive than low sulfur fuels. In the KPA process high sulfur green coke can be used without incurring most of the associated environmental costs. In fact high sulfur, as well as low sulfur and medium sulfur coal coke and coal, can be used.

**Fluoride**

Some of the sodium and potassium in the ore are in the fluorapatite mineral and some in the other minor minerals such as muscovite. From the thermodynamic analysis in figure 10, it is likely that any Na\textsubscript{2}O and K\textsubscript{2}O energetically convert to NaF and KF according to the reaction:

\[
\text{CaF}_2 + \text{Na}_2\text{O} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + 2 \text{NaF}
\]

The NaF and KF are somewhat volatile as shown in table 5.

<table>
<thead>
<tr>
<th>Table 5. Vapor Pressure of NaF and KF</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>NaF, temperature, °C</td>
</tr>
<tr>
<td>KF, temperature, °C</td>
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</table>

The CaF\textsubscript{2} liberated by the fluorapatite is considerably in excess of the sodium and potassium present. The excess might react with silica and/or aluminum, but the thermodynamic analysis shown in figure 10 indicates that they will not. As suggested by some of the EDAX analysis it appears the excess CaF\textsubscript{2} stays in the residue at least partially as CaF\textsubscript{2}. It is suspected some of it is in the large amount of amorphous phase present in the residue as well. At any rate, the mass balance data on the fired pellets indicates neither of these reaction mechanisms resulted in the loss of much fluoride from the pellet residue at temperatures in the operating window. During one test with significant melting, more of the fluorine was released (41% on the one test). This indicates that as long as the pellet residue stays a solid, there is limited loss of fluoride.

This observation is a considerable relief as KF and NaF, if present in large quantities in the off gas, would likely condense in the cold end of the kiln forming an “alkali ring” that would require periodic removal. Alkali buildups in cement kilns are often a problem with some raw materials that contain high alkali contents. Also any that passed out of the kiln, whether because the cold end of the kiln was purposely kept hot, or perhaps because it condenses as a dust rather than on a ring, would be absorbed in the hydrator phosphoric acid, where if it reached high enough concentration to form Na\textsubscript{2}SiF\textsubscript{6} would cause all the sledging problems common in the dihydrate process phosphoric acid product.
"At the temperature of the phosphoric acid in the off gas scrubber, data in Slack shows nearly all the H$_2$SiF$_6$ that forms would stay in the phosphoric acid product (4).

**Carbon balance on the fired pellets**

The amount of carbon put into the pellet, minus that consumed in the reactions, should equal the residual found in the residue. As shown in table 6, this balance checks pretty well, confirming the major element reactions proposed herein. At 1330 °C, the one hour test analysis shows nitrogen was lost from the feed pellet by volatilization from the coke instead of being absorbed as in the other tests. In fact, testing on the coke shows the nitrogen largely volatilized at this temperature. It appears that at the end of one hour the fluorapatite reaction still had not finished and the senoite (Si$_2$N$_2$O) reaction had not progressed very far. However, after two hours more nitrogen was absorbed from the air forming senoite than was in the feed pellet. After four hours, essentially all of the excess carbon had been consumed making senoite at 1330 °C.

**Table 6.** Mass balance for carbon in lab KPA pilot tests

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</tr>
<tr>
<td>Fired wt, g</td>
<td>4.7282</td>
<td>5.2741</td>
<td>4.588</td>
<td>4.3432</td>
<td>4.3476</td>
</tr>
<tr>
<td>Total carbon in, g</td>
<td>0.5177</td>
<td>0.574</td>
<td>0.5111</td>
<td>0.464</td>
<td>0.4935</td>
</tr>
<tr>
<td>Carbon in volatiles, g</td>
<td>0.0436</td>
<td>0.0483</td>
<td>0.043</td>
<td>0.0391</td>
<td>0.0415</td>
</tr>
<tr>
<td>Carbon rx'd with CaCO$_3$, g</td>
<td>0.0192</td>
<td>0.0213</td>
<td>0.019</td>
<td>0.0172</td>
<td>0.0183</td>
</tr>
<tr>
<td>Carbon rx'd with fluorapatite</td>
<td>0.3683</td>
<td>0.4083</td>
<td>0.3635</td>
<td>0.33</td>
<td>0.351</td>
</tr>
<tr>
<td>Carbon rx's to form Si$_2$N$_2$O</td>
<td>0.0341</td>
<td>0.0066</td>
<td>0.0443</td>
<td>0.0894</td>
<td>0.0895</td>
</tr>
<tr>
<td>Calc net carbon our, g</td>
<td>0.0525</td>
<td>0.0895</td>
<td>0.0413</td>
<td>-0.0117</td>
<td>-0.0068</td>
</tr>
<tr>
<td>Analyzed net carbon out, g</td>
<td>0.0927</td>
<td>0.0949</td>
<td>0.0413</td>
<td>0.0069</td>
<td>0.0848*</td>
</tr>
</tbody>
</table>

* Suspect carbon sticking to outside of pellet gave false high carbon analysis.
Conclusions: The major high temperature side reaction is Semoite formation from excess silica and coke from the bed and nitrogen from the atmosphere. Only very limited amounts of sulfur, alkali, and fluorides escape the KPA residue.

5 Rate of Phosphorus Reduction Reaction

In the work described above, the size of the "operating window" was determined and it was demonstrated that the reduction and subsequent volatilization of phosphorus from the pellet was substantially complete in two hours at 1225 °C, when the pellet contained a well mixed mixture of the ore, silica, and green petroleum coke all sized to – 200 mesh. It was also established that provided that the silica level was at least at the "Megy" composition level (i.e. sufficient to consume all of the calcium and magnesium liberated from the fluorapatite reduction reaction), extra silica did not affect the 1225 °C lower window boundary, even up to the "Hard" composition, that contains twice as much silica as the "Megy" composition.

The next step was to determine that slow step in the reduction reaction. As part of the "Operating Window" work, it had already been determined that smaller pellets (i.e. -1/2") and larger pellets (i.e. -3/4" and four times the mass), reacted essentially at the same rate. Thus, heat transfer into the pellet does not appear to be rate limiting. It was also learned that the reaction proceeded at a temperature as low as 1150 °C at a rate that would not be useful commercially unless it could be increased by other process changes. Thus the reaction must be thermodynamically favored and must be going slowly due to some kind of slow mass transfer limitation within the pellet, over and above the slow step at about 1225 °C.

The Large Particle Tests- Four samples of the relatively high silica formulation, HL3, were made up containing first, all -200 mesh ore, silica, and green coke components, and then 60/80 mesh ore, 60/80 mesh silica, and 60/80 mesh green coke substituted, one at a time, into the other three formulations. Thermo Gravimetric Analysis, (TGA), tests were run by on each of the samples in a graphite crucible fitted with a pinhole lid in a nitrogen atmosphere as follows. Small, well mixed, but loose portions of each of the samples weighing about 200 mg were ramped rapidly (at 20 °C/min) to 1240 °C, and held for 240 minutes while the weight of the sample was monitored. The results of the four tests, superimposed in Figure 12, show that the all -200 mesh sample lost ~25% of its weight in about 2 hours, which indicates nearly complete volatilization of the phosphorus from the pellet.

The samples containing the 60/80 mesh silica reduced at almost the same rate as the all -200 mesh sample, and the 60/80 mesh ore is a little slower, indicating that their particle sizes were mildly rate limiting when the other raw materials were fine.
The sample containing the 60/80 mesh petroleum coke was very much slower in reaction, and in fact only reached on the order of 60% reduction of the phosphorus over the entire four hour of the test. Thus, the particle size of the petroleum coke is strongly involved in the rate of phosphate ore reduction.

**EDAX Analysis of Partially Reacted Pellets**

To further clarify the rate limiting step, one of the partially reacted "Megy" pellets that had been heated to 1155 °C for four hours in a lab pilot plant simulation of the KPA process that had reached about 50% phosphorus evolution was analyzed. The resulting pellet was vacuum encapsulated in epoxy and partitioned at the mid point circumferentially and given a high polish. After putting a few monolayers of Osmium on the surface of the polished sample to make the surface conductive, an EDAX analysis of the surface was conducted.

The samples containing the 60/80 mesh silica reduced at almost the same rate as the all -200 mesh sample, and the 60/80 mesh ore is a little slower, indicating that their particle sizes were mildly rate limiting when the other raw materials were fine.

Certain grains surrounded by either silica or calcium silicate reaction product were observed. The unreacted fluorapatite is found across a reaction layer from the graphite. The ferrophos (Fe₂P) product phase was also observed.

Conclusion: Thus, the reaction rate is proportional to the surface area of the petroleum coke, and inversely proportional to the distance that the phosphorus and silica must diffuse to get to the surface of the graphite particle. The reaction rate is maximized by grinding the coke as fine as possible and distributing it as uniformly as possible in the pellet. To carry this out practically in a commercial plant dry grinding of all three raw materials together is preferred. Since the graphite and ore grind more rapidly than the silica, this strategy should give maximum intimate mixing, with a preferentially fine green petroleum coke grind. Co-ground in a batch pilot grinding test, simulating commercial dry grinding, verified concept.

**Role of Impurities in upper melting limit of window**

Most phosphate deposits in the world contain large admixtures of silica, which is expensive to remove in preparing phosphate ore feed for the dihydrate process. For the KPA process large admixtures of silica are required and floatation costs are eliminated in most cases.

Phosphate ores typically contain varying levels of organics that either must be removed by thermal or chemical oxidation prior to the dihydrate process, or they will degrade the quality of the acid produced. The KPA process requires reductant in the ore,
thus making organic impurities desirable in the ore. No organics exit the kiln, and the Occidental pilot showed a light, straw colored acid was produced from a KPA process. In addition to these economically important impurity tolerances in the KPA process, it appears there is a nominal tolerance for some of the other common components of common phosphate ores; namely MgO, Al₂O₃, Fe₂O₃, Na₂O, K₂O and CaF₂. These values remain basically with the kiln residue.

As discussed above, iron impurity in the ore is converted into ferrophos in the residue, which is present as a distinct phase, and apparently does not affect the size of the operating window. The presence of iron in the ore does reduce yield, with each 1% increase of Fe₂O₃ in the ore giving a ~1.2% loss of yield of P₂O₅ product. For this reason it is desirable to keep iron low in the raw material, but higher levels likely do not affect the operability of the process or purity of the acid produced.

Initial experimental evaluation of the effect of MgO, Al₂O₃, Na₂O and CaF₂ impurity levels on the upper temperature melting boundary have been run. The evaluation is performed by making additions of impurities into the pellet formulation, running our standard lab pilot tests, and observing whether melting in the residue from the test occurs. The chemistry of the various compositions tested is given in table 6.

### Table 6A. Compositions and observations of initial impurity study.

<table>
<thead>
<tr>
<th>Component</th>
<th>Standard HL3</th>
<th>High Al₂O₃</th>
<th>High MgO</th>
<th>High Na₂O</th>
<th>High CaF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>2.082%</td>
<td>3.703%</td>
<td>2.082%</td>
<td>2.082%</td>
<td>2.082%</td>
</tr>
<tr>
<td>MgO</td>
<td>0.282%</td>
<td>0.282%</td>
<td>0.691%</td>
<td>0.282%</td>
<td>0.282%</td>
</tr>
<tr>
<td>Na</td>
<td>0.31%</td>
<td>0.31%</td>
<td>0.31%</td>
<td>0.56%</td>
<td>0.31%</td>
</tr>
<tr>
<td>F</td>
<td>2.32%</td>
<td>2.32%</td>
<td>2.32%</td>
<td>2.32%</td>
<td>3.62%</td>
</tr>
</tbody>
</table>

**Test Results**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1310 °C - 2 hr</td>
<td>no melt</td>
</tr>
<tr>
<td>1340 °C - 2 hr</td>
<td>no melt</td>
</tr>
<tr>
<td>1350 °C - 2 hr</td>
<td>no melt</td>
</tr>
<tr>
<td>1300 °C - 2 hr</td>
<td>no melt</td>
</tr>
</tbody>
</table>

The silica used in most of the Phase I KPA pilot work contained high alumina (2.77%). Silica is available in Idaho with < 0.5% alumina. Washed matrix in Florida has sufficient silica already in the ore, and has an average alumina content of around 0.6%. Washed matrix from North Carolina also has sufficient silica already in the ore and an alumina level in the matrix of around 0.3%. It is expected the upper temperature melting boundary will improve somewhat with use of the high purity silica.

Conclusion: While only this limited number of tests was run to date, it appears that the melting point on the HL3 pellets is reduced on the order of 30 °C for an increase of 1.65% Al₂O₃ or 0.4% MgO, and perhaps 60 °C for a 1.3% increase in fluoride. While these
impurity additions significantly reduce window size, with the HL3 composition, all the free phosphorous can be reduced in the pellet in two hours at 1225 °C, showing that a workable size window remains.

5 Suitable kiln refractories for the KPA process

In the Occidental program, over twenty years ago, zircon brick which is frequently used in glass manufacturing (ZrSiO₄) was recognized as being particularly suitable for the KPA process. In my discussions with technical people at Harbison Walker Refractories Company, bricks which consist of mullite grains in a continuous phase of silica have also been identified as candidates for use in the process. One of these bricks selected has seen routine use in phosphate ore nodulizing kilns for electric furnace feed. The refractories tested were TZB (zircon) and three of the silica bonded mullite type with different silica-mullite ratios, as indicated on a Al₂O₃-SiO₂ binary phase diagram, in figure 13 (31).

Figure 13 shows compositions of refractory tested, A = Kala, B = Ufala, and C = KX-99-BF which are all refractory bricks available from Harbison Walker Refractories Company. Temperature on abscissa is in °C and composition is in weight percent.

Several plugs of each type of refractory ¼" in diameter and 3/8 inch tall were cut from the face of refractory bricks. The refractory plugs were placed in the bottom of the graphite crucible that we use for the KPA lab pilot runs. A KPA feed pellet of test composition is placed on top of the refractory and a KPA lab pilot test was run as usual. To date three series of tests of the refractory/pellet interactions have been run. (Table 7).

<table>
<thead>
<tr>
<th>Test</th>
<th>Refractory........KX99BF</th>
<th>KALA</th>
<th>Ufala</th>
<th>TZB</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 Megy Pellets – 1155 °C – 4 Hrs</td>
<td>No Stick</td>
<td>No Stick</td>
<td>No Stick</td>
<td>No Stick</td>
</tr>
<tr>
<td>#2 Megy Pellets – 1280 °C – 4 Hrs</td>
<td>Not Run</td>
<td>Puddle</td>
<td>Puddle</td>
<td>Puddle</td>
</tr>
<tr>
<td>#3 HL3 Pellets – 1330 °C – 2 Hrs</td>
<td>No Stick</td>
<td>No Stick</td>
<td>No Stick</td>
<td>No Melt-Stick</td>
</tr>
</tbody>
</table>

In test #1, the refractories all showed essentially no weight or dimensional change. The color of the refractory darkened. The weight loss on the Megy pellets indicated about 50% of the phosphorus volatilized. The Megy pellets remained black, and retained a sharp edge, just like those processed in the same way without the refractory present. No sticking of the pellet to the refractory was observed.

In test #2, the Megy pellets were black with a still sharp upper edge, but with a puddle at the base of the pellet which bonded with the top of the refractory in each case. The weight loss of the combined refractory/Megy-product pellet indicated full volatilization...
of the free phosphorus, these samples were cut and polished and examined by EDAX as discussed under the heading EDAX Refractory Study below.

In test #3, HL3 pellets run at 1330 °C did not stick to the silica/mullite refractory, but did stick to the zircon. As discussed in the EDAX work, the zircon grains are very stable, but the high calcium binder used in the TZB refractory is reactive with the silica in the KPA sample leading to the sticking observation.

EDAX scans of an area that includes the refractory KPA pellet interface for the zircon refractory (TZB) and one of the mullites silica refractories are shown in figure 14.

Spot analysis of the adhering pellet mass adjacent to the zircon grains in the TZB refractory showed no zirconium had diffused into the calcium silicate pellet residue. This confirms the work at Occidental. However, a HL3 pellet stuck to the refractory at 1330 °C in test three. It is believed that the reason for this is the calcium binder in the TZB refractory. The calcium dot map for the TZB refractory shows the calcium rich area in the binder between the zircon grains has reacted with the silica in the pellet residue. The calcium in the pellet residue and the alumina in the Ufala refractory show no evidence of diffusing into each other.

Conclusion: Our preliminary tests suggest that high silica-mullite refractories may be satisfactory for the KPA process. Zircon is non-reactive, but the calcium binder contained in the TZB refractory reacts.
CLAIMS

1. A process for producing $\text{P}_2\text{O}_5$ in a direct heated rotary kiln comprising the steps of introducing kiln feed balls containing phosphate ore, silica, and a carbon source wherein the calcium oxide to silicon dioxide molar ratio is from about 0.4 to about 1.0 and the carbon to phosphorus molar ratio is in excess of 2.5 into a direct heated rotary kiln;

   heating the feed balls to a reduction temperature between about 1180 and about 1330°C to reduce the phosphate ore to produce elemental phosphorus and carbon monoxide which reports to the head space in the kiln; and

   burning the elemental phosphorus and carbon monoxide with air in the head space in a controlled manner so that the kiln feed balls are heated to the reduction temperature in a heating zone in the kiln and then maintaining the kiln feed balls at reduction temperature ±30°C for a period of about four hours to about one hour.

2. A process for producing $\text{P}_2\text{O}_5$ in a direct heated rotary kiln comprising the steps of introducing solid feed of a rotary directed heated kiln feed balls containing phosphate ore, silica, and a carbon source wherein the calcium oxide to silicon dioxide molar ratio is from about 0.4 to about 5.0 and the carbon to phosphorus molar ratio is in excess of 2.5 where the carbon source is ground to 80% -200 mesh and the phosphate ore, silica and carbon source are co-ground to obtain intimate mixing;

   heating the feed balls to a reduction temperature between 1180 and 1330°C to reduce the phosphate ore to produce elemental phosphorus and carbon monoxide which reports to the head space in the kiln; and

   burning the elemental phosphorus and carbon monoxide with air in the head space in a controlled manner so that the kiln feed balls are maintained at the reduction temperature ±30°C for a period to reduce at least 95% of the phosphate in the kiln feed balls.

3. A process for producing $\text{P}_2\text{O}_5$ in a direct heated rotary kiln comprising the steps of introducing solid feed of a rotary directed heated kiln feed balls containing co-ground and finely ground phosphate ore, silica, and a carbon source wherein the calcium oxide to silicon dioxide molar ratio is from about 0.4 to about 1.0 and the carbon to phosphorus molar ratio is in excess of 2.5;

   heating the feed balls to a reduction temperature between 1180 and 1330°C to reduce the phosphate ore to produce elemental phosphorus and carbon monoxide which reports to the head space in the kiln; and
burning the elemental phosphorus and carbon monoxide with air in the head space in a controlled manner so that the kiln feed balls are maintained at the reduction temperature ±30°C for a period sufficient to complete the reduction by reducing at least 90% of the phosphate values in the kiln feed balls; and

5 discharging the kiln feed balls from the kiln when the reduction is complete before all the carbon source of the kiln feed balls is burned out.
Figure 1. Thermodynamic analysis of when phosphorus reduction reaction proceeds, unit solids activity.
Fig. 2
Figure 3a. TGA study of KPA onset temperature for three different silica addition levels.
Figure 4. KPA lab pilot data from 35 runs showing "operating window" between 1225 °C and 1360 °C
Fig. 5

Grinder

Agglomerator

Drier

Silica
Coke
Water
Binder

Screened Ore
Beneficiated Ore

50

52

Silica Coke

End Zone

Hot Kiln Solids Discharge

Dried Hot Feed Balls

Kiln Solids Discharge
Figure 6. Weight loss from “Megy” pellet lab pilot runs (left) and “Eutectic” pellets (right), with examples of pellets both just before and after melting was observed.
Figure 8. The Operating Window for the KPA process
Figure 10 Thermodynamic evaluations of several potential pellet reactions. When the free energy of reaction goes negative the reaction can proceed thermodynamically. The reactions are: (1) CaF$_2$ + Na$_2$O $\rightarrow$ 2 NaF + CaO, (2) 2 CaF$_2$ + 3 SiO$_2$ $\rightarrow$ 2 CaSiO$_3$ + SiF$_4$, (3) 3 CaF$_2$ + 3 SiO$_2$ + Al$_2$O$_3$ $\rightarrow$ 3 CaSiO$_3$ + 2 AlF$_3$, (4) Ca$_{10}$(PO$_4$)$_3$F$_2$ + 9 SiO$_2$ + 15 C $\rightarrow$ 3 P$_2$ + 15 CO$^\Delta$ + 9 CaSiO$_3$ + CaF$_2$, and (5) 2 SiO$_2$ + N$_2$ + 3 C $\rightarrow$ 3 CO$^\Delta$ + 3N$_2$O.
Figure 12. TGA tests showing weight loss at 1240 °C with large particle components of ore formulation.
Figure 13. Compositions of refractory tested, A = Kala, B = Ufala, and C = KX-99-BF which are all refractory bricks available from Harbison Walker Refractories Company. Temperature on abscissa is in °C and composition is in weight percent.