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International application number: PCT/US2015/052402

International filing date: 25 September 2015 (25.09.2015)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 62/085,778
Filing date: 01 December 2014 (01.12.2014)

Date of receipt at the International Bureau: 12 October 2015 (12.10.2015)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-bis)
October 11, 2015

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APPLICATION NUMBER: 62/085,778
FILING DATE: December 01, 2014
RELATED PCT APPLICATION NUMBER: PCT/US15/52402

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Under Secretary of Commerce
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Title: Improved process for phosphorous pentoxide production and purification

Inventor/s: David Blake, Joseph A. Megy, Sourabh Pachpor, Larry Handman, Theodore P. Fowler, and James A. Trainham

Abstract: A phosphorus pentoxide production method that significantly reduces dust formed in the Improved Hard Process (IHP). Scale-up of the IHP exhibited significant dust formation in the kiln used for the carbothermal reduction of phosphorous ore. The methods include processes to modify the feed agglomerates to reduce dust formation in the reduction kiln and to remove dust when formed in the process. The methods also include processes to remove ore contaminants yielding a higher quality phosphoric acid product.

Introduction: Figure 1 shows the block flow diagram disclosed in patent US 7,378,070 B2 May 27, 2008 Phosphorous Pentoxide Producing Method by Joseph A. Megy (Hereafter referred as Megy Patent). “Dust formation” in the Kiln (hereby designated as the reduction kiln) in Figure 1 was not observed at the pilot-scale as described in the Megy Patent. Dust has two major deleterious effects: 1) dust in the reduction kiln is transported to the reduction kiln freeboard and can react with the P\textsubscript{4}O\textsubscript{10} to form calcium metaphosphate resulting in a yield loss; and 2) dust can be transported to the Product Scrubber (Figure 1) where it can be rendered inoperable. It was observed at the demonstration-plant scale where the reduction kiln inside diameter was 6 feet and length of 94 feet dust formation was caused by agglomerate (balls, pellets, etc.) attrition and breakage. The agglomerates produced by the process shown in Figure 1 (shown as BALLING) were produced via a balling drum and exhibited agglomerate compressive strengths of 25 lbs or less (see Example 1).

Observing that intact agglomerates that exited the reduction kiln exhibited compression strength that far exceeded 50 lbs led to the methods and systems herein. Laboratory testing showed that hardened agglomerates exhibited low attrition and breakage in tumbling tests. Additional laboratory studies were initiated to understand the hardening phenomenon. It was discovered that hardening of the agglomerates occurred in a narrow temperature range approximately 1000 to 1100 C, which is below the carbothermal reduction temperature of phosphorous ore of 1180 C.

The process engineering described in the methods and systems herein is the practical means to achieve hardened agglomerates with compression strength above 25 lbs if heated to temperatures above 1000 C, hereby referred to as induration. Also, described in the methods and systems herein is the use of polymer additives to initially strengthen the agglomerates before they are hardened thermally.

Induration of feed agglomerates (pellets) is not a new process. In the iron industry induration has been practiced for over 50 years. Iron ore pellets have a known composition: 63-65\% Fe (~93\% Fe\textsubscript{2}O\textsubscript{3}), 3-5\% SiO\textsubscript{2}, 3-5 \% pet coke, the remaining constituents are mostly CaO and MgO. The iron ore pellets are fed to an indurating grate-kiln system or a straight grate and heated with known gas temperatures 1000-1300 C. The iron ore pellets achieve compression strength above 200 lbs. The sources of strength of the iron ore pellets is oxidation of ferrous iron oxides to ferric iron oxides which results in some bonding and bridging with re-crystallization of the iron oxides. The iron ore induration process is carried out in an oxidation environment where the pet coke is used for fuel.

It is surprising that such a heat treatment process strengthens the phosphate containing agglomerate to reduce dust in the Improved Hard Process. The chemical differences between iron ore pellets and phosphate agglomerates are striking with the agglomerates containing approximately 56\% SiO\textsubscript{2}, 20\% CaO, 11\% P\textsubscript{2}O\textsubscript{5}, 8\% pet
## Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

### Inventor(s)

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<td>P. Fowler</td>
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### Title of Invention

Improved Process for Phosphorous Pentoxide Production and Purification

### Attorney Docket Number (if applicable)

19908.009US01

### Correspondence Address

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First Name: James  
Last Name: Lake

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cove, 2% clay with 1% each of MgO, Fe₂O₃ and Al₂O₃ dry basis. The phosphorous containing agglomerate induration process is carried out under reducing conditions so that the pet cove oxidation is decreased and below the carbothermal reduction temperature of P₂O₅.

An initial study of the phosphorous containing agglomerate hardening chemistry was investigated via x-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). Examination of agglomerate samples after heat treatment at 500°C, 800°C, 950°C, 1025°C and 1100°C yielded the following observations:

1. Dolomite in the 500°C sample was identified, but was not present in samples above 800°C.
2. Bridging is mostly between silica particles and amorphous glue (described in 3 below) not sticking to carbon or fluoroapatite particles.
3. Bridging material is Calcium (Magnesium) Silicate amorphous material with a surprisingly large amount of contained phosphate.
4. Some Calcite particles were found in the 500C sample, but it appears most Calcite is inside the fluoroapatite particles. The fluoroapatite particles develop porosity at 1000°C where you would expect the Calcite to decompose.
5. The hardening chemistry uses approximately 1000°C to form the strengthening bridges. Note this is just above the known Calcite decomposition temperature.
6. The bridges clearly wet the silica over long boundaries around the particles.

**Figure 1.** Megy Patent Process Flowsheet

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**Detailed Description**

Laboratory and demonstration plant (12 k-ton scale) observation, data and innovation resulted in new process technology that overcomes a major deficiency, that of dust formation in the ported kiln as described in the Megy patent and shown in Figure 1. The methods and systems herein provide specific process improvements that significantly reduce and remove dust. The methods and systems herein add process steps and equipment modifications, and provide other process improvements to the process described in the Megy patent (see Figures 2-8 for alternative flowsheets):
a) In the Megy Patent, the agglomerates described include: composition, volatile content and size. The process description in the Megy Patent does not specifically describe the “Balling” step shown in the flow diagram Figure 1. Note that in the methods and systems herein a balling drum or a balling disc can be used to form agglomerates.

b) The initial demonstration plant (first large scale, 12 k-ton plant, reduction to practice of Megy patent) uses only a “Balling Drum” to coalesce the feed ingredients (phosphate ore, silica, petroleum coke) into feed agglomerates. These agglomerates exhibit compressive strength of 25 lb, or less usually between 10-20 lb. It is observed that such agglomerates have insufficient compressive strength to be processed in the ported-reduction kiln without attrition and/or loosing integrity and producing significant dust inside the kiln. The dust reduces yield through back reaction in the kiln freeboard and significantly affects operability in downstream equipment.

c) The methods and systems herein may significantly reduce (by over 90%) the dust formation in the ported kiln by introducing additional process steps that harden the agglomerates to well over 25 lb, compressive strength. Under certain process conditions the compressive strength can exceed 100 lb.

d) The methods and systems herein may also increase heat recovery enabling increased heat integration.

e) The methods and systems herein may also increase the concentration of $P_2O_5$ leaving the ported kiln from approximately 8% to over 14% that will reduce the size of the acid plant helping to offset the additional capital investment introduced by the additional processing steps.

f) The methods and systems herein describe various processes to heat treat the agglomerates (induration) and/or the introduction of a polymer binder/coating before heat treatment or in the absence of separate heat treatment step not described in the Megy patent.

g) The methods and systems herein may add standpipes to the ports on the reducing kiln that extend above the bed height. The standpipes decrease or eliminate the capture of agglomerates and dust that are dumped from the ports at the kiln apex which leads to more dust formation and dispersion of dust in the kiln freeboard.

h) The methods and systems herein also may include intermediate storage of the agglomerates after induration that will increase plant availability (actual operating hours/planned and unplanned operating hours).

i) The methods and systems herein may provide for the removal of dust that does form during the induration process and in the ported kiln.

j) The methods and systems herein may provide for the removal of ore contaminants such as Arsenic, Cadmium, Lead and Mercury.

k) This method and systems herein may provide for the cogeneration of electricity.

The present methods and systems may provide various processes to harden the feedstock agglomerates above 25 lb, compression strength before they are feed to the ported kiln, and remove any dust formed during the induration process and in the ported kiln, thereby reducing the dust to acceptable levels, which does not reduce yield or operation of the product scrubber.
It was observed in the laboratory and at demonstration plant-scale tests that agglomerates could be indurated (hardened above 25 lb./compression strength if heated to temperatures above 1000 C). The induration process may be done under conditions that harden the agglomerates and decreases or eliminates carbon burnout (reducing conditions) and phosphorous ore carbothermal reduction (below the 1180 C reaction temperature). In addition, the agglomerates leaving the induration process may be cooled indirectly so they maintain their strength unless the indurated agglomerates are fed directly to the ported kiln. Figures 2-8 show various processes for accomplishing this induration process.

Figure 2 shows one of the most conservative designs, where green agglomerates (agglomerates made by a balling drum or disc) are fed over a grate drier and then fed to an induration kiln, followed by a cooler, dust separator/scrubber, intermediate storage and finally to the ported reduction kiln. A benefit of such a system is the ability to harden the agglomerates, maintain their hardness and to remove dust prior to feeding the agglomerates to the reduction rotary kiln. The intermediate storage can be sized for a few hours to days. It allows de-coupling of the feed preparation section of the process from the main reaction section and final product formation. The intermediate storage container can be insulated or not. Insulating the storage of the hardened agglomerates may reduce the heat requirements in the downstream process steps. Also shown, is the use of either water-soluble polymer and Bentonite clay or natural clay. In the methods and systems herein, the clay additives may be used alone or as a mixture. It is also possible to by-pass or eliminate the indirect cooler and intermediate storage. The gas stream leaving the induration kiln in Figure 2 contains gaseous components and entrained dust. The gaseous components are a mixture of volatile organic and inorganic contaminants (for example, Cd, Pb, Hg, As) and are removed after the cyclone by a scrubber. The dust is separated by the cyclone and fed back to the feed system. The dust may also contain some of the inorganic contaminants and a small purge may be used to keep said contaminants from concentrating in the feed. Figure 2 does not show the heat integration as this will be shown in subsequent drawings.

A variation on Figure 2 is shown in Figure 3 is to add a high temperature PRE Heat Moving Grate section to the DRYER MOVING GRAVE. Part of this variation is maintaining a reducing environment in the grate section. The heat transfer gas composition may be reducing and contain little oxygen so the carbon in the agglomerate is not oxidized. The reducing environment can be achieved by recycling the off-gas leaving the PRODUCT ACID SCRUBBER back to the Aggregate Cooler where the heated gas is fed to the INDURATION KILN and then to the PRE-HEAT MOVING GRATE, then the DRYER MOVING GRATE and finally the ROTARY DRIER. The AGGREGATE COOLER is a gas-solids heat exchanger capable of utilizing reducing gas or inert gas to cool the kiln discharge solids. Heat recovery from the AGGREGATE COOLER is utilized in various locations within the plant, enabling substantial heat integration. This flowsheet has multiple locations where dust can be removed if it is formed: from the gas stream leaving the INDURATION KILN through the HIGH TEMPERATURE DUST CYCLONE, the moving grates system, after the INDIRECT WATER DELUGE COOLER, and after the PRODUCT ACID SCRUBBER. After induration a cyclone-scrubber system may separate dust from induration kiln off-gas. As with all such systems a suitable bypass may be available when the cyclone-scrubber fails. The acid plant can serve this purpose, but may use a solids removals system to trap the dust protecting it from becoming inoperable. This solids removal system may also protect the acid plant from dust that forms in the reduction kiln. Gaseous contaminants are removed via the GAS ADSORPTION COLUMN before this stream is fed to the PRE HEAT MOVING GRATE. It should be noted that some dust carry-over may occur from a single stage cyclone which can lead to plugging of the adsorption column. To reduce or minimize this issue either a second stage cyclone can be added or a filter system or both.
Figure 4 shows potentially the lowest capital design and uses a Straight Grate DRYER/Heater to indurate the agglomerates before they are fed directly to the PORTED ROTARY KILN. The grate section is a combination of a dryer and a heater. Again, the heat transfer gas composition in the grate section may be reducing and contain little oxygen to decrease carbon burnout. This is achieved by recycling the off-gas leaving the PRODUCT ACID SCRUBBER to the aggregate cooler where the heated gas provides heat to the Straight GRATE. Gaseous contaminants are removed in an adsorption column before the ROTARY DRYER. This design does not provide for intermediate indirect cooling or storage for the agglomerates.

Figure 5 is similar to Figure 4 but adds an indirect cooler and intermediate storage. It also offers similar solids removal as described above for the flowsheet described in Figure 3. Gaseous contaminants are removed in the same way as shown in Figure 4.

In Figure 6 we show how to recover heat by recycling a portion of the aggregate product back to the reducing kiln. Indurated agglomerates report to the REDUCTION ROTARY KILN from three sources: 1) Directly from the INDURATION KILN; 2) From the INDURATION KILN through an INDIRECT WATER DELUGE COOLER followed by a DOUBLE DECK SCREEN; and 3) From the INDURATED PELLET STORAGE Through the DOUBLE DECK SCREEN. Note that in this case some of aggregate product can be recycled between the INDURATED PELLET STORAGE and the DOUBLE DECK SCREEN. The choice of feed routing and ratio of recycle aggregate to indurated feed depends upon agglomerate temperature and composition to control the temperature rise in the kiln.

Figures 7 and 8 provide alternatives for temperature control in the REDUCING KILN. Figure 7 shows the introduction of a POST PRODUCT ACID SCRUBBER AFTERBURNER and Figure 8 provides a PRE PRODUCT ACID SCRUBBER COMBUSTION CHAMBER. In both cases, when used for temperature control the Reducing Kiln is operated with stoichiometric deficient oxygen for complete combustion. The reducing atmosphere within the kiln decreases carbon burnout, which contributes to temperature control, reduces dust formation, and increases phosphate conversion yield.

In Figure 7, REDUCTION KILN off gas reports to the PRODUCT ACID SCRUBBER (Acid Plant), which removes the phosphorus pentoxide from the gas producing Product Acid. Liquid filtration within the acid plant removes dust that is collected along with phosphorus pentoxide within the circulating liquid. Exhaust gas from the Product Acid Scrubber reports to an AFTER BURNER, which oxidizes non-combusted carbon monoxide and hydrogen to harmless carbon dioxide and water vapor. Afterburner discharge gas passes through Heat Recovery before being exhausted to atmosphere.

Figure 8 shows the REDUCTION KILN off gas reports to a COMBUSTION CHAMBER, which oxidizes non-combusted carbon monoxide and hydrogen to harmless carbon dioxide and water vapor. COMBUSTION CHAMBER off gas reports to the PRODUCT ACID SCRUBBER (Acid Plant), which removes the phosphorus pentoxide from the gas producing Product Acid. Liquid filtration within the acid plant removes dust that is collected along with phosphorus pentoxide within the circulating liquid. Exhaust gas from the PRODUCT ACID SCRUBBER is exhausted to atmosphere.

Figure 9 is similar to Figure 2 except it shows heat integration, removal of contaminants, and cogeneration of power. The temperature of the feed agglomerates on the dryer grate will not exceed 300°C to reduce or prevent carbon oxidation. This flowsheet shows how to split the plant into two independent sections to increase operability. The contaminants are removed after induration in a dust cyclone and a scrubber.
Figure 10 depicts the grate-kiln system with heat recovery and contaminant removal. This is similar to Figure 3 and the high temperature section of the grate will need to be maintained in a reducing environment. To protect the gate components, the reducing gas may be fed downflow to the grate. The contaminant removal is accomplished via a flue gas scrubber.

Figures 2-10 show the addition of a water-soluble polymer (a water-insoluble polymer can be used but an additional mixing step is required) to the balling process step. The purpose of the polymer is to strengthen the agglomerate before it reaches a kiln (the induration and/or reduction kilns) or induration grate, thereby reducing dust formation. It can be added most conveniently in two ways: 1) the water-soluble polymer is mixed and dispersed throughout the solids mixture during the balling process; or 2) the agglomerates are coated after they are formed. The agglomerates laden with water-soluble polymer leaves the balling process and is fed to a grate dryer where the polymer reaction occurs at temperatures above 40°C strengthening the agglomerate.

A polymer can also be added to the original flowsheet described in the Megy patent. The polymer-strengthened agglomerate holds the agglomerate together long enough to reduce dust before the agglomerate is strengthened further by induration (agglomerate reaches temperatures >1000°C < 1125°C) in the front portion of the reduction kiln before the phosphorus ore reduction reaction temperature 1180°C is reached.
FIGURE 2. INDURATION AND REDUCTION ROTARY KILN with INTERMEDIATE PRODUCT STORAGE
FIGURE 4. STRAIGHT GRATE INDURATION FOLLOWED by REDUCTION KILN no INTERMEDIATE STORAGE
FIGURE 5. STRAIGHT GRATE INDURATION FOLLOWED by REDUCTION KILN WITH INTERMEDIATE STORAGE
FIGURE 6. HEAT RECOVERY using AGGREGATE PRODUCT RECYCLE
FIGURE 7. POST PRODUCT ACID SCRUBBER AFTERBURNER
FIGURE 8. PRE PRODUCT ACID SCRUBBER COMBUSTION CHAMBER
FIGURE 9. HEAT RECOVERY WITH COGENERATION PLANT
FIG 10. INTEGRATED HEAT RECOVERY AND GRATE KILN SYSTEM
Example 1 -- Laboratory Data A

Two lab sequences were run as follows:

1) Compare dry pellet strengths of Calcined Coke formulations (with High Magnesium [Mag] Pebble) at -230 mesh and -325 mesh grind at room temperature and after firing for 30 minutes at 1000C.

Raw material were lab ground Dierks tailings, Hi Mag Pebble, Calcined Pet Coke and 1% bentonite ground to -230 mesh and to -325 mesh; R=2.5, Theo C=2.0. Dierks tailings are fill material from a sand tailings disposal site in Fort Meade, Florida.

2) Compare dry pellet strengths of Calcined Coke (with High Mag Pebble) at -230 mesh and -325 mesh grind and a CaCO3 formulation at -230 mesh grind at 400, 600, 700, 800, 900 and 1100C. One percent bentonite was added to the -325 mesh sample and no bentonite was added to the -230 mesh sample. Four percent bentonite was used to develop sufficient strength in the CaCO3/sand/coke formulation.

Agglomerate Preparation

The formulation for the agglomerates and preparation was as follows:

1) -230 & -325 mesh calcined petroleum coke formulation --

1 part High Mag Pebble, 1.54 parts Dierks tailings, and 0.247 parts calcined coke. Three components ground in lab mortar and pestle to pass 230 mesh screen (first sample) or 325 mesh screen (second sample). 1% bentonite added prior to mixing with 14% by weight water and making the pellets in ½” die under 300 lb; pressure. Pellets weighed and measured and then dried and weighed and measured again. Some agglomerates crushed without firing and the rest fired at selected temperatures in the lab tube furnace in a boat with the tube purged with nitrogen. Fired pellet weighed and measured and crushed.

2) CaCO3 formulation --

1 part lab pure CaCO3, 9 parts Dierks tailings, 1 part green coke, and 0.4 parts bentonite were lab ground to pass 230 mesh sieves. Mixed with 14% water and formed into ½” diameter pellets under 300 lb; pressure. The pellets were then treated as above.

Results

The results from the two sequences are reported together. The major observation is that the pellet (agglomerate) strength was not enhanced until temperature approached 1000C as shown in Figure 9.

The variation of agglomerate density with firing temperature (Figure 10) was also measured which showed that the strengthening of the agglomerate at 1000-1100C was accompanied by a significant density increase for the 230 and 325 formulations, but not the CaCO3 formulation.

Weight loss in the pellets upon firing and the change in volume of the agglomerates versus temperature is shown in Figures 11 and 12. The ore agglomerates lost considerable volume at 1000 and 1100C, but the CaCO3 agglomerates did not. All of the agglomerates had weight loss that increased with agglomerate firing temperature.
Since the CaCO3 agglomerate and the ore pellets develop strength at the same temperature, the data suggest that the reaction of CaCO3 with SiO2 occurs at about 950 °C (known to react at a reasonable rate at 930 °C) is involved in the strengthening of the pellets. The reaction involved is:

\[ \text{CaCO}_3 + (1+x) \text{SiO}_2 \rightarrow \text{CaSiO}_3-\{\text{SiO}_2\} \]

**Example 2 -- Laboratory Data B**

Table 1 provides data on agglomerate hardening as a function of time and temperature. 5 agglomerates of composition and size shown in Table 1 were placed in a crucible and heated in a Thermolyne 47900 lab furnace and held at temperatures between 1000 and 1100 °C under a nitrogen purge of 10 ft³/hr. Initial furnace temperature was set at approximately 350 °C and then ramped up to the desired temperature and held for the time listed in Table 1. The agglomerates were then removed from the crucible and air cooled before compression strength was measured.

**Table 1. Agglomerate strength as a function of temperature and time. 5 agglomerates of 5/16 in. diameter per run and composition: approximately 55.7% SiO₂, 20.4% CaO, 10.9% P₂O₅, 1.2% MgO, 7.5% pet coke, 2.1% clay with 1.1% each of Fe₂O₃ and Al₂O₃ dry basis.**

<table>
<thead>
<tr>
<th>Temperature, C</th>
<th>Time, min.</th>
<th>Ball Strength, lb₉</th>
<th>Ball Strength Average, lb₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>30</td>
<td>24 30 12 27 40</td>
<td>27</td>
</tr>
<tr>
<td>1000</td>
<td>60</td>
<td>31 23 37 50 35</td>
<td>35</td>
</tr>
<tr>
<td>1000</td>
<td>90</td>
<td>19 35 26 36 43</td>
<td>32</td>
</tr>
<tr>
<td>1025</td>
<td>30</td>
<td>48 27 31 36 31</td>
<td>35</td>
</tr>
<tr>
<td>1025</td>
<td>60</td>
<td>32 63 65 23 48</td>
<td>46</td>
</tr>
<tr>
<td>1025</td>
<td>90</td>
<td>47 45 47 45 48</td>
<td>46</td>
</tr>
<tr>
<td>1050</td>
<td>30</td>
<td>52 79 58 103 108</td>
<td>80</td>
</tr>
<tr>
<td>1050</td>
<td>60</td>
<td>82 72 55 56 71</td>
<td>67</td>
</tr>
<tr>
<td>1050</td>
<td>90</td>
<td>68 52 64 43 65</td>
<td>58</td>
</tr>
<tr>
<td>1075</td>
<td>30</td>
<td>72 118 80 87 105</td>
<td>92</td>
</tr>
<tr>
<td>1075</td>
<td>60</td>
<td>48 68 64 54 47</td>
<td>56</td>
</tr>
</tbody>
</table>

**Example 3 -- Laboratory Data C**

The effect of silica to (calcium + magnesium) mole ratio was investigated and the results are shown Figure 15. Samples of agglomerates were prepared varying the Si/(Ca + Mg) ratio from 1.5 to 3.25. Agglomerates were prepared and heated in the same equipment as Example 2 and held at 1100 °C for 75 minutes. Results show significant increase in compression strength for Si/(Ca + Mg) above 2.

**Example 4 -- Laboratory Data D**

The use of a polymer resin, 43-ACRYLIC/IND POWDER, CODE WC66-6707M, Supplier: PPG industries, to strengthen the agglomerates before indurating is shown in Table 2. Seventeen agglomerate samples were prepared with polymer and 12 without by thoroughly mixing the ingredients (shown below) compacted in a hydraulic press to 300 lb₉, dried at 100 °C for 12 minutes than compression tested. A known composition was
prepared for a baseline comparison that contained no clay and no polymer. The average compression strength between the agglomerates with polymer and the known composition was 64.8 lb, versus 15.2 lb, respectively.

Table 2. Comparison of agglomerates with and without a polymer additive

Agglomerate Known Composition: 57.1% SiO₂, 20.4% CaO, 11.2% P₂O₅, 88.2% pet coke with approximately 1% each of MgO, Fe₂O₃, and Al₂O₃ dry basis

Agglomerate Composition with polymer added: 51.5% SiO₂, 18.4% CaO, 10.1% P₂O₅, 7.4% pet coke, 10% polymer with approximately 0.9% each of MgO, Fe₂O₃, and Al₂O₃ dry basis

<table>
<thead>
<tr>
<th>Agglomerate Known Composition</th>
<th>Compression Strength, lb₀</th>
<th>Average, lb₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.9 15.0 17.8 19.5 15.3</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>12.7 13.8 14.5 14.1 13.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.8 15.7</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Agglomerate with Polymer Composition</th>
<th>Compression Strength, lb₀</th>
<th>Average, lb₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70.6 50.1 55.8 73.1 74.2</td>
<td>64.8</td>
</tr>
</tbody>
</table>

Example 5 -- Demonstration Plant Data A

The kiln was operated at 982°C as measured by the hottest spot on the kiln brick with an approximate residence time of one hour.

- Dried green balls were fed with typical quality. ~20+ lb₀ compression strength and 50% +3/8’’ sizing
- Samples were taken directly off of the kiln discharge and allowed to air cool within a sample pan
- After cooled, the compression strength averaged 84 lb₀.
- These balls were tumbled and the dust generated was less than 0.2%.

The test was repeated but at a slightly higher temperature of ~1038°C

- Similar to above feed conditions and sampling.
- The compression strength averaged 105 lb₀.
- After tumble dust was still below 0.2% on average
- These balls had the appearance of a dark grey interior with a very thin outer lighter grey shell.
- Because the balls were exposed to oxygen, some carbon may have burned out which could reduce yields. These balls were tested in the lab for yield and 85% was achieved.
Example 6 -- Demonstration Plant Data

Figure 13 and 14 show the effects of induration on the agglomerate (ball/pellet) compression strength and dust formation versus non-indurated balls, respectively. The results generated were from two different plant tests, run under nominally the same operation conditions: kiln temperature at hot spot 1038 C, feed rate 5-6 tons/hour, solids residence time 45-60 minutes, off-gas oxygen concentration 6-8%. Figure 13 shows the compression strength of indurated agglomerate is increased by over a factor of 5 versus non-indurated agglomerate. Figure 14 shows that the propensity to dust is reduced by an order of magnitude by indurating agglomerates. Sampling the feed balls to the kiln and balls that exit the kiln after induration and then run in a tumble tester generated the data in Figure 14.

Example 7

Table 3 shows the change in contaminant metals concentration in the feed agglomerates before and after induration for 30 and 60 minutes. The feed agglomerates were prepared in a balling disk and then dried at approximately 100 C. The agglomerates were then placed in a crucible and heated in a furnace with a nitrogen sweep for 30 minutes and 60 minutes. The concentration of Arsenic was reduced by a factor of 3, Cadmium was reduced from 1.47 mg/kg to undetectable, Lead was reduced from 4.25 mg/kg by a factor of 7.8 after 30 minutes and to undetectable limits after 60 minutes, and Mercury to undetectable limits after 60 minutes. All other components were not affected by the induration process.

Table 3. Selected element concentration in feed agglomerates and concentration in the agglomerate after induration at 1000 C for 30 and 60 minutes.

I – The reported value is between the laboratory method detection limit and the laboratory practical quantitation limit.

U – The compound was analyzed for but not detected. The value shown is the laboratory method detection unit.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Units</th>
<th>Feed Agglomerates</th>
<th>30 minute Induration</th>
<th>60 minute Induration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>mg/kg</td>
<td>9.29</td>
<td>3.15</td>
<td>2.88</td>
</tr>
<tr>
<td>Barium</td>
<td>mg/kg</td>
<td>30</td>
<td>36.7</td>
<td>48.7</td>
</tr>
<tr>
<td>Cadmium</td>
<td>mg/kg</td>
<td>1.47</td>
<td>0.07 U</td>
<td>0.07 U</td>
</tr>
<tr>
<td>Chromium</td>
<td>mg/kg</td>
<td>24.1</td>
<td>22</td>
<td>22.9</td>
</tr>
<tr>
<td>Lead</td>
<td>mg/kg</td>
<td>4.25</td>
<td>0.54</td>
<td>0.16 U</td>
</tr>
<tr>
<td>Selenium</td>
<td>mg/kg</td>
<td>0.80 U</td>
<td>0.80 U</td>
<td>0.80 U</td>
</tr>
<tr>
<td>Silver</td>
<td>mg/kg</td>
<td>0.06 U</td>
<td>0.06 U</td>
<td>0.06 U</td>
</tr>
<tr>
<td>Mercury</td>
<td>mg/kg</td>
<td>0.023 l</td>
<td>0.022 l</td>
<td>0.011 l</td>
</tr>
<tr>
<td>Aluminum</td>
<td>mg/kg</td>
<td>6,330</td>
<td>2,910</td>
<td>3,370</td>
</tr>
<tr>
<td>Calcium</td>
<td>%</td>
<td>14.4</td>
<td>16.5</td>
<td>16.7</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/kg</td>
<td>8,700</td>
<td>11,700</td>
<td>11,800</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/kg</td>
<td>6,620</td>
<td>7,740</td>
<td>8,010</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>%</td>
<td>5.68</td>
<td>6.99</td>
<td>6.77</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mg/kg</td>
<td>3,000</td>
<td>3,800</td>
<td>4,120</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/kg</td>
<td>61.9</td>
<td>257</td>
<td>397</td>
</tr>
<tr>
<td>Fluoride</td>
<td>%</td>
<td>3.14</td>
<td>2.9</td>
<td>3.06</td>
</tr>
<tr>
<td>Silica</td>
<td>%</td>
<td>46.1</td>
<td>59.5</td>
<td>60.1</td>
</tr>
</tbody>
</table>
Features

The features described include:

1. A phosphorous pentoxide producing method comprising:

   Forming feed agglomerate prior to entering a rotary kiln (that produces $P_2O_{10}$ gas, see Figures 2-10) that exhibits compression strength above 25 lb, such as crush strength above 50 lb, including compression strength above 100 lb. The agglomerate may be produced via a balling drum or disc and then heated in a reducing or inert atmosphere that hardens the agglomerate to the desired compression strength. The agglomerate may be heated to temperature above 950 C, but less than 1180 C, such as at temperatures of 1000 -1125 C. The agglomerate may be held at these high temperatures for a minimum of 25 minutes. The agglomerate may contain phosphate ore particles, carbonaceous material particles, clay particles, sufficient silica particles for the agglomerate to exhibit a calcium-to-silica mole ratio less than one, and silica-to-(calcium + magnesium) ratio greater than 2.

2. The method of feature 1 where the heating of the agglomerates is accomplished by a rotary kiln (a separate induration kiln, see Figures 2,3,6,7,8 ).

3. The method of feature 1 where the heating of the agglomerates is accomplished by a grate heater (grate only induration, see Figures 4 and 5). The agglomerates are then fed to the reducing kiln where $P_2O_{10}$ gas is produced.

4. The method of feature 1 where the heating of the agglomerate is accomplished by a grate-heater-kiln system (see Figures 3, 6, 7, 8).

5. The method of feature 2 comprising maintaining a bed of agglomerates having a length, maintaining the bed at or above 950 C but less than 1180 C along the entire bed length.

6. The method of feature 3 comprising maintaining a bed of agglomerates having a length, maintaining the bed at or above 950 C but less than 1180 C along the entire bed length.

7. The method of feature 4 comprising maintaining a bed of agglomerates having a length, are pre-heated on the grate to temperatures at or near 950 C, then maintaining the bed in the kiln at or above 950 C but less than 1180 C along the entire bed length.

8. The method in feature 7 where the product acid scrubber off-gas is used to heat the bed of agglomerates on the grate-heater.

9. The method in feature 1 where a cooler is used between the induration process (straight grate, kiln, grate kiln) and the reducing kiln.

10. The method in feature 1 where most of the dust formed during the induration process is removed: on the grate, after the cooler and product scrubber.

11. The method in feature 1 where the agglomerates can be stored after the Indirect Cooler.

12. The method in feature 11 where the agglomerates can be stored between 100 C to 1000 C in an insulated tank under a reducing or inert atmosphere.
13. The method in feature 11 where the agglomerates can be stored at ambient conditions.

14. A phosphorous pentoxide producing method comprising:

Forming feed agglomerate that exhibits compression strength above 25 lb., such as above 50 lb., including above 100 lb. that is produced via the use of a polymer additive that hardens the agglomerate to a compression strength above 25 lb., before it is heated to temperature above 950 C, but less than 1180 C, such as at temperatures of 1000 -1100 C for a minimum of 25 minutes enabling the agglomerate to achieve the final desired compression strength. The agglomerate may be produced via a balling drum or disc using a polymer and then heated on a grate dryer at temperatures between 40 to 150 C. This hardens the agglomerate to initial compression strength above 25 lb. The agglomerate contains: phosphate ore particles, carbonaceous material particles, sufficient silica particles for the agglomerate to exhibit a calcium-to-silica mole ratio less than one, a polymer, and clay particles.

15. The method of feature 14 where the heating of the agglomerates is accomplished by a rotary kiln (a separate induration kiln, see Figures 2,3,6,7,8).

16. The method of feature 14 where the heating of the balls is accomplished by a grate heater (grate only induration, see Figures 4 and 5). The agglomerates are then fed to the reducing kiln where P₄O₁₀ gas is produced.

17. The method of feature 14 where the heating of the balls is accomplished by a grate-heater-kiln system (see Figures 3,6,7,8).

18. The method of feature 12 comprising maintaining a bed of agglomerates having a length, maintaining the bed at or above 950 C but less than 1180 C along the entire bed length.

19. The method of feature 13 comprising maintaining a bed of agglomerates having a length, maintaining the bed at or above 950 C but less than 1180 C along the entire bed length.

20. The method of feature 14 comprising maintaining a bed of agglomerates having a length, are pre-heated on the grate to temperatures at or near 950 C, then maintaining the bed in the kiln at or above 950 C but less than 1180 C along the entire bed length.

21. The method in feature 16 where the product acid scrubber off-gas is used to heat the bed of agglomerates on the grate-heater.

22. The method in features 10-17 where the polymer is one of the following types: acrylic, silicones, cross-linkable, polyimides, epoxy

23. Standpipes are added to the ports on the reducing kiln and are of sufficient height to extend above the bed of agglomerates.

24. The standpipes in feature 23 are made of a castable ceramic in a cone shape (large diameter attached to the kiln castable ceramic wall) with a hollow cylindrical core to enable air to pass into the kiln freeboard.

25. The method in feature 14 where most of the dust formed during the induration process is removed: on the grate, after the cooler and product scrubber.
26. The method in features 1 and 14 where most of the dust formed during the induration process is removed by a cyclone and returned upstream to the rotary dryer.

27. The method in feature 26 where a fraction of the recycle dust to the rotary dryer is purged.

28. The method in features 1 and 14 where trace impurities in the gas stream leaving the dust cyclone are removed in a packed column before returning to the process.

29. The method in feature 28 where the packed column packing can be made of one or more type of adsorbent, or multiple packed columns in series are used containing different adsorbents in each column.

30. The method in feature 29 where the packing in the column(s) is any of the following: carbon or metal oxides of Al, Fe, Cu, Zn, Ce and Ca.

31. The method in features 1 and 14 that electricity can be cogenerated in the process by recovering heat from the aggregate cooler.

32. The method in features 1 and 14 where dust and trace impurities generated during induration are removed via a dust cyclone and scrubber.

33. The method in features 1 and 14 depicted in Figures 3-10 where heat is generated in one or more of these sources: induration kiln, the moving grate heater, and the reduction kiln and can be recovered from either the aggregate cooler, and/or the grate cooler.

34.
Figure 9. Strength of three types of pellets over a range of temperatures for 30 minutes each show significant strengthening at 1000-1100 C. CaCO$_3$ pellets were run to elucidate strengthening mechanism.
Figure 10. Density increases at 1000-1100°C when pellet strength increases. Density of CaCO3 does not increase at 1100°C.

Figure 11. The ore pellets lost weight with increasing temperature of firing.

Figure 12. The ore pellets lost volume at 1000 and 1100°C, but the CaCO3 did not, consistent with the density changes.
FIGURE 13. COMPRESSION STRENGTH VERSUS RUN TIME

FIGURE 14. PERCENT DUST GENERATED AFTER TUMBLE TEST VERSUS RUN TIME (HOURS)
FIGURE 15. COMPRESSION VERSUS SILICA RATIO (SILICA/(CA + MG))