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[54] BENEFICIATION AND HOT BRIQUETTING OF PHOSPHATE ORES BY REMOVING -400 MESH FINES

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[58] **Field of Search** .... 23/312 P, 223, 313, 23/293 R; 75/3, 26; 71/44

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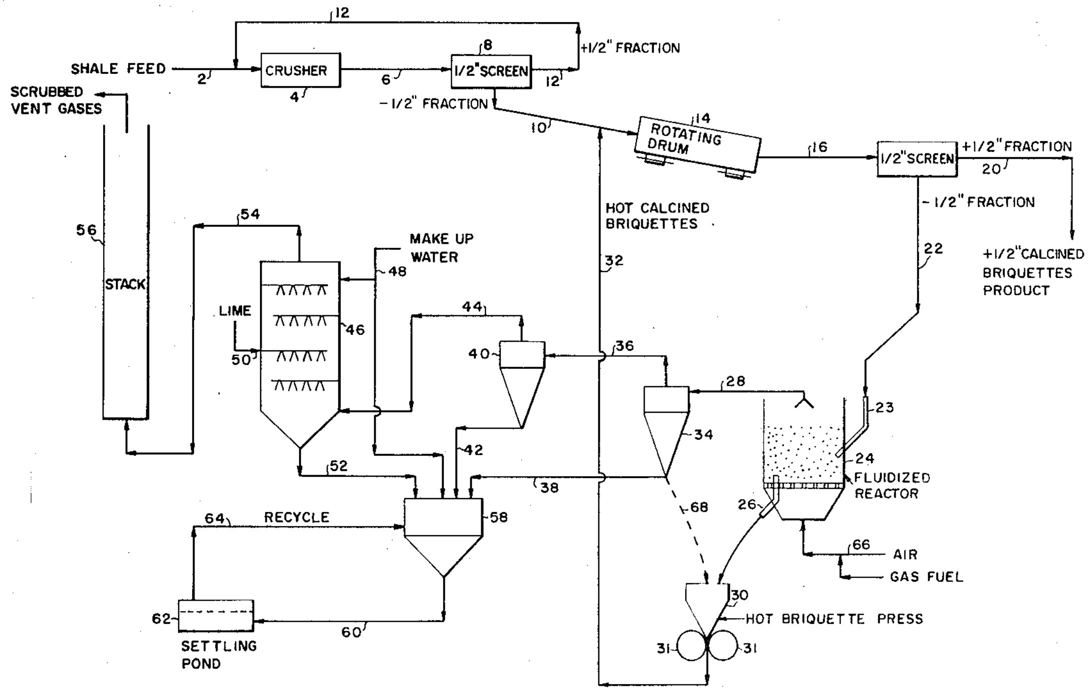
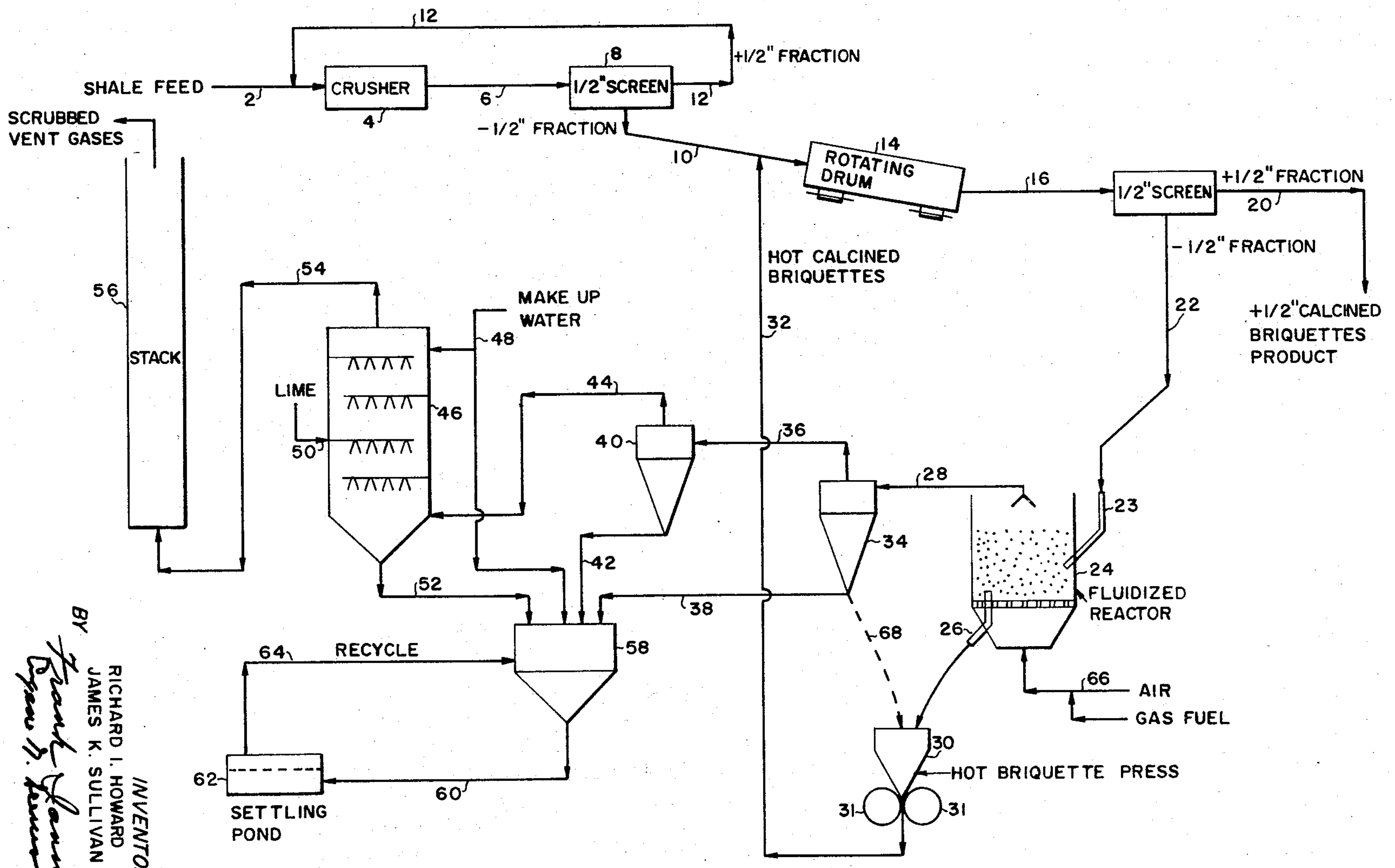
[57] ABSTRACT

A beneficiated, calcined, phosphate agglomerate, useful as a phosphorus furnace feed is produced by crushing phosphate shale to substantially –½ inch, heating and calcining the crushed shale in a fluidized bed, removing a relatively phosphorus-poor fine fraction overhead from a relatively phosphorus-rich coarse fraction remaining in the fluidized bed, withdrawing a portion of the heated, coarse fraction from the fluidized bed and hot briquetting it under pressure to form strong, calcined phosphate agglomerates.

3 Claims, 1 Drawing Figure





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BENEFICIATION AND HOT BRIQUETTING OF PHOSPHATE ORES BY REMOVING -400 MESH FINES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a process for producing calcined phosphate agglomerates which are especially suitable for use as furnace feeds in the manufacture of phosphorus.

2. Description of the Prior Art

The phosphate ores obtainable in the western part of the United States are largely composed of phosphate shale containing up to about 32 percent P_2O_5 in the form of calcium phosphate. These ores also contain silica, iron oxide, organic matter, clay, small quantities of ammonium oxide and vanadium oxide and from 2 to 4 percent shale oil. One standard method for recovering the phosphorus from these ores is by reducing the phosphorus shale with carbon (coke) in an electric furnace. The phosphate ore must be fed into the electric furnace in the form of calcined lumps or calcined agglomerates in order to obtain smooth furnace operation during the conversion of the phosphate to phosphorus. To produce a suitable furnace feed, the phosphate shale is crushed in a hammer mill into particulate form to pass a 4-inch screen. The crushed shale is then further screened into fine and coarse fractions using a 14 mm. screen, and the fine fraction is agglomerated by either briquetting or pelletizing; the agglomerated fraction and previously separated coarse fraction are then calcined together in a rotary kiln. An improvement in the above process is obtained by carrying out the calcination of the agglomerated fines into briquettes, and the coarse fraction (which is normally termed "lump") into calcined lumps, on a perforated, non-agitated carrier; this generates less fines, and the non-agitated calcination forms stronger briquettes.

One of the difficulties that has arisen in the above process is that the amount of high grade shale, that is shale containing over 28 percent P_2O_5, which is available is rapidly decreasing, and reliance for phosphate supplies has had to be limited to the so-called furnace grade shale (P_2O_5 content of from 22 to 28 percen by weight). and low-grade shale (P_2O_5 content of below 22 percent by weight). While furnace grade shale is acceptable and in use, it is desired to increase its P_2O_5 content for more efficient operation. Even more desirable is a process that can utilize the low-grade (also termed mill grade) phosphate ore which contains less than 22 percent P_2O_5. However, in the present furnaces the attempted use of feeds having phosphorus concentrations lower than 22 percent P_2O_5 makes furnace operations difficult and is uneconomical to use by conventionally known techniques.

The beneficiation of these ores has been attempted prior to the shale being treated in the conventional calcining and briquetting operations; however, the cost of the additional beneficiation step at this time does not warrant its use. As a result, large quantities of low-grade ore simply cannot be utilized, per se, in the present furnaces. Accordingly, what is desired is a process which will permit calcined phosphate agglomerates to be produced from low-grade ore without the need for special beneficiation steps. Further, such a process should also be capable of utilizing furnace-grade ores while upgrading the P_2O_5 content of the final calcined briquette. In this way, beneficiation can be effectively achieved without the cost of running separate beneficiation stages.

SUMMARY OF THE INVENTION

A process has now been found for simultaneously beneficiating and calcining a phosphate ore to produce hard, calcined, phosphate agglomerates by crushing a phosphate ore to substantially −½ inch, heating and calcining the crushed ore at a temperature of at least about 1500°F. in a fluidized bed, removing a relatively phosphorus-poor, −400 mesh fraction overhead from a relatively phosphorus-rich fraction remaining in the fluidized bed, withdrawing hot, calcined, phosphorus-rich ore from the fluidized bed and briquetting it under a sufficiently high pressure and temperature to cause plastic flow of the ore, and recovering a hard, calcined phosphate agglomerate suitable as a phosphorus furnace feed.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing there is illustrated a schematic representation of one embodiment for carrying out the present invention.

DESCRIPTION OF THE INVENTION AND THE PREFERRED EMBODIMENTS

In carrying out the present invention, the phosphate shale is initially ground or crushed by conventional means, such as an impact crusher, so that all of the shale is no larger than ½ inch in diameter. The crushing step is operated so that the maximum size of the crushed shale withdrawn is ½ inch in diameter; larger size lumps are recycled for additional crushing. In this operation large quantities of fines, that is −325 mesh sized share, are desired (e.g., 20 to 40 percent) and obtained. In many instances, grinding to a maximum size of ¼ inch is necessary to obtain a high fines content in the crushed shale, and this is a preferred procedure when possible.

The moist, crushed shale from the crusher is screened, and a −½ inch fraction is passed to a rotating drum and blended with hot calcined briquettes from a source hereinafter described. Upon being tumbled in the rotating drum, the hot (at least 1500°F.) briquettes are cooled by the moist shale, and the shale, in turn, is preheated in the rotating drum. Some portion, e.g., about 50 percent, of the moisture in the shale is evaporated during this preheating stage. The mixture of the crushed shale and the hot calcined briquettes is tumbled in the rotating drum until substantial extraction of heat from the briquette surfaces has occurred and the partially cooled briquettes can be handled on a conveyor belt surface. During this tumbling, the shale is also subject to further attrition, and more −325 mesh fines are generated in the rotating drum.

The blend of calcined briquettes and crushed shale is then discharged onto a conveyor to allow additional contact time for heat transfer and then passed onto a ½ inch screen. The calcined briquettes, being larger than 1/2 inch (they normally are about 1 1/8 inches square), are removed as a +1/2 inch product fraction, while the finer crushed shale falls through the screen. In addition to crushed shale, some briquette fragments also are removed in the − 1/2 inch fraction. This screened, − 1/2 inch fraction is then passed into a fluidized reactor where it is heated to calcining temperatures.

In the fluidized reactor, particles of shale are suspended in a fluidized bed which is held up by the force of a fluidizing gas passing upwardly through the vertically disposed, tube-like, fluidized reactor. In the normal procedure the upflowing, fluidizing gas is a mixture of air and burnt fuel which both fluidizes the bed and also supplies the heat required to calcine the phosphate shale. Normally, temperatures on the order of at least 1500°F. up to about 2200°F. are employed in the bed. Temperatures substantially above 2200°F. are not desirable since they cause the particles to soften and become sticky and to make fluidization difficult.

Within the fluidized bed the fluidizing gas is passed upwardly at a velocity sufficient to maintain the larger particles of the shale in the fluid bed while discharging overhead the −400 mesh fraction. The removal of these −400 mesh fines is esssential in the present process, since it has been found that the −400 fraction is substantially poorer in phosphorus values than is the +400 fraction. Accordingly, during the calcination stage in the fluidized bed the substantially phosphorus-poor ore fraction, namely the −400 mesh fraction, is simultaneously removed, allowing both beneficiation and calcination of the shale to take place simultaneously. The +400 mesh ore particles are preferably heated to approximately 1800°F. in the fluid bed to complete calcination during which organic matter and carbonates are decomposed.

The hot calcined shale, while at substantially the same temperature as the shale in the fluidized bed, is then passed into a hot briquette press and briquetted, while hot, at sufficiently high pressures so that there is plastic flow of the phosphate ore at the temperature at which the briquette is formed. this insures a dense, hard briquette whose contents are strongly adhered to one another. The resulting hot briquettes are then mixed with ground moist feed shale and passed into a rotating drum in a heat exchange relationship, as previously described. This permits the hot briquette to be cooled, and the feed shale to be preheated and partially dried prior to being fed into the fluidized reactor.

The overhead gases and −400 mesh fines from the fluidized reactor are passed into a series of cyclone separators to remove the shale fines. The overhead gases from the cyclone separators are then passed through a spray tower containing lime to remove any fluoride which is evolved during the calcining stage; the resulting scrubbed gases, free of fluorides and shale particles, are then vented to the atmosphere.

In the present process it is essential that the shale be ground or crushed sufficiently fine so that a substantial portion of −325 mesh particles are generated during the crushing operation. Thereafter, when the ground shale is passed into the fluidized reactor, beneficiation of the ore results by removal of the −400 mesh fraction overhead from the fluidized reactor during calcination of the phosphate ore. The removal of the −400 fraction beneficiates the remaining ore because this fraction contains substantially less phosphorus values than do the larger phosphate shale particles, namely, the +400 mesh fraction. The separation of the phosphate fines, which are phosphorus-poor, from the larger fraction which is substantially phosphorus-rich, is an essential feature of the instant process. This can readily be observed by typical analysis of various samples of shale ore as set forth in Table I.

TABLE I.—PHOSPHATE SHALE SAMPLE ANALYSIS

Sample	Wt. percent −325M in the shale [1]	P_2O_5 concentration in starting material	Percent		Percent of total P_2O_5 recovered in +325M fraction
			P_2O_5 in −325M	P_2O_5 in +325M	
1	31.2	26.1	12.1	32.45	85.5
2	23.0	29.2	13.6	33.86	89.3
3	37.8	20.4	8.0	27.94	85.2
4	30.4	24.4	11.6	29.99	85.5
5	29.5	24.4	11.5	29.80	86.1
6	22.0	24.4	10.8	28.24	90.3
7	10.4	24.0	13.1	25.27	94.3
8	11.8	24.0	12.4	25.55	93.9
9	27.6	26.6	10.4	32.78	89.2
10	18.8	26.0	9.8	29.75	92.9
11	13.9	26.0	12.5	28.18	93.3

[1]=Dry basis.

In addition, if the −325 mesh phosphorus ore fraction is analyzed, it is found that the coarser fraction within the −325 mesh fraction contains substantially more P_2O_5 than the fine fraction. For example the −325 mesh to +400 mesh fraction contains substantially more phosphorus than does the −400 mesh to the 5 micron and the particles lower than 5 micron. This is illustrated in Table II.

TABLE II.—P_2O_5 DISTRIBUTION WITHIN THE MINUS 325 MESH FRACTION OF PHOSPHATE SHALE ORES

Sample	Percent P_2O_5 in original sample	−325M+400M fraction		−400M+5μ fraction		−5μ fraction	
		Weight percent [1]	Percent P_2O_5	Weight percent [1]	Percent P_2O_5	Weight percent [1]	Percent P_2O_5
1	23.8	4.0	24.0	14.2	9.5	17.4	9.5
2	24.7	7.3	16.2	8.5	10.1	9.2	8.0
3	18.6	3.1	11.6	16.9	4.5	17.5	6.7

[1]=Weight percent of original shale.

As a result of this discovery, the present process also contemplates selectively classifying from the overhead −325 mesh fines of the fluidized reactor, those particles which are in the range of −400 mesh, and returning these to the hot briquetting process where the amount of phosphorus which these fines contain justifies it. The finer material, that is the −400 mesh, which invariably is substantially phosphorus-poor, is always removed from the fluidized reactor in order to beneficiate the remaining phosphate ore.

The invention will now be described with reference to the attached drawing. In the drawing, phosphorus shale is passed by a conveyor **2** into a crusher **4,** preferably an impact crusher, and ground to a size no larger than ½ inch. The crushed ore is then conveyed via conveyor **6** to a screen **8** having a size of no greater than ½ and preferably ¼ inch. The +½ inch fraction or oversized fraction is removed through line **12** and recycled back to the crusher **4,** while the −½ inch fraction is conveyed through conveyor **10** into rotating drum **14.** The ground shale entering drum **14** is mixed with hot calcined briquettes from line **32** having a temperature of at least about 1500°F., and they are tumbled together in the rotating drum **14.**

The tumbling of this mixed feed in drum **14** achieves two desirable results. Initially, the hot calcined briquettes are cooled by contact with the ground, moist shale while the shale is preheated and partially dried (generally 50 percent of the moisture in the shale is evaporated) prior to being introduced into the fluidized reactor. Further, the tumbling in drum **14** attrites the shale and liberates more −325 shale particles from the ground shale. The resulting mixture is passed through conveyor **16** onto a ½ inch screen **18.** The calcined briquettes, which are greater than ½ inch in diameter, are removed through line **20** as product and passed on to an electric furnace, not shown. The −½ inch fraction, which is made up of the ground shale and briquette fragments, is then passed through line **22** into the fluidized reactor feed shute **23** of fluidized reactor **24.**

The shale fines enter the fluidized reactor **24,** in which there is suspended a fluidized bed of ore particles, at a temperature of from about 1500°F. to about 2200°F. The fluidized bed is maintained in a fluidized state by passing heated air and combustible fuel up through the fluidized bed through line **66.** This air and fuel mixture, on combustion, supply the heat necessary to maintain the fluid bed at the desired temperature. The fluidizing gas is passed through the fluidized bed at a rate sufficient to remove the −325 mesh ore fractions overhead through line **28,** along with the products of combustion and other gaseous effluents which are given off during the calcining stage. The resulting, calcined ore particles which remain in the fluidized reactor **24** and which are at a temperature of at least 1500°F., are then passed from exit port **26** in fluidized reactor **24** into the hot briquette press **30** equipped with press rolls **31.** In this press **30** the hot calcined ore is briquetted under sufficient pressure to assure plastic flow of the ore during formation of the hard, adhesive briquettes. The hot calcined briquettes are then passed through line **32** into rotating drum **14,** along with the crushed −½ inch moist feed shale from line **10,** as previously described.

The overhead gases and −325 mesh fines which are removed through line **28** from the top of the fluidized bed pass into a cyclone separator or other conventional separating means **34** where the −325 +400 mesh particles are removed. If the phosphorus values of these particles are not sufficiently high, the particles are passed through line **38** into slurry tank **58.** However, if the phosphorus values of this −325 +400 mesh fraction are sufficiently high, they may be conveyed through line **68** into the hot briquette press **30,** along with the calcined shale from line **26** of fluidized reactor **24.** The overhead gases and fines from cyclone separator **34** are then passed through line **36** into cyclone separator **40** where the remaining fine particles of phosphate shale are removed through lines **42,** while the remaining gases are removed overhead through line **44** of the cyclone separator **40.** The gases in line **44** are then passed into a spray tower **46** and are scrubbed with water to remove any fine particles of phosphate ore. Additionally, any fluoride values which are evolved during the calcining stage are converted to insoluble calcium fluoride by passing lime through line **50** into the spray tower **46** in contact with the gases flowing through the spray tower **46.** The precipitated fluoride and phosphate fines are removed through line **52** and passed into slurry tank **58.** The resulting gases which are evolved from line **54** from the spray tower **46** are then passed into stack **56** where they are vented to the atmosphere.

The make up water required is added through line **48** into the scrubbing tower **46** and also into the slurry tank **58.** The slurry of phosphate fluoride and other fines is then passed through line **60** to a settling pond **62.** Water is drawn off the top of the settling pond through line **64** and recycled to the slurry tank **58** to slurry additional fines from the cyclone separators **34** and **40** and from the spray tower **46.**

In the present process, the beneficiation stage can result in increasing the P_2O_5 analysis of the ore as much as 14 percentage units, depending on the P P_2O_5 contents of the starting ore and of the P_2O_5 of the −325 mesh fraction. Moreover, while the present process obviously has its greatest advantage in beneficiating the low grade ores into higher grade phosphate ores, it should be realized that this beneficiating stage can be used to upgrade the phosphorus values of most ores, including furnace grade ores, since the −400 fines fraction is substantially poorer in phosphate values than is the coarser +400 mesh fraction.

The following example is given to illustrate the invention and is not deemed to be limiting thereof.

EXAMPLE

The equipment used in carrying out the present example was the same as illustrated in the drawing, and for clarity's sake the example will be explained with reference to the drawing. A mine run shale having a P_2O_5 content of from 20 to 24 percent (average 22 percent) was fed along with 10 percent by weight of water to an impact crusher **4** at a rate varying from 1.45 to 1.94 tons per hour. The crushed product was then conveyed by means **6** to a ½ inch screen **8,** and the −½inch fraction, which comprised about 1.31 to 1.74 tons of shale per hour and 0.145 to 0.194 ton of water per hour, were conveyed by conveyor **10** to a heat exchange and attrition drum **14.** The remaining oversize shale was recycled back to the crusher for additional grinding.

To the −½ inch ground shale in drum **14** were also added hot calcined briquettes from hot briquette press **30** through line **32** at a rate of about 1.10 tons of briquettes per hour. These were placed in the rotating drum **14,** and the briquettes and the moist shale were then tumbled in drum **14** until substantial heat exchange had taken place. The drum spill was removed through conveyor **16** to a ½ inch screen **18.** Dust and fumes which were given off from the rotating drum **14** were removed and sent to slurry tank **58** by means not shown. This dust removed from drum **14** amounted to about 0.013 to 0.019 ton of shale fines per hour and 0.073 to 0.097 ton of water per hour. The contents of the rotating drum were screened on ½ inch screen **18,** and the +½ inch fraction, which was all calcined briquette product, was removed via conveyor **20** to a phosphorus furnace. This product was removed at a rate of about 1 ton per hour and had a P_2O_5 content of from 25 to 26 percent. The −½ inch fraction which passed through screen **18** was essentially all ground shale and briquette fragments and were removed from screen **18** at a rate of 1.40 to 1.83 tons of shale per hour and 0.072–0.097 ton of water per hour and conveyed via conveyor **22** to the fluidized reactor inlet **23** of fluidized reactor **24.** In the fluidized reactor **24** air was passed upwardly through the fluidized bed through line **66** at a rate of 20.8 to 27.8 thousand standard cubic feet per minute, while, simultaneously, natural gas was injected into the fluidized bed at a rate of 1020 tO 1360 standard cubic feet per minute. The resulting fluidized bed was maintained at a temperature of about 1800°F. by means of the injected air and fuel.

In the fluidized reactor **24** the −325 mesh solid shale particles were removed overhead at a rate of 0.29 to 0.73 ton of shale fines per hour, along with 0.072 to 0.097 ton of water vapor per hour, as well as decomposition gases. These were conveyed overhead from fluidized reactor **24** via conduit **28** to a first cyclone separator **34.** Gases and −400 mesh shale fraction were removed via line **36** to a second cyclone separator **40,** whi'e the −325 mesh to +400 mesh fraction was removed via line **38** and sent to slurry tank **58.** On occasion where the P_2O_5 content of the fines fraction from cyclone separator **34** was sufficiently high grade, a portion of the fines was returned via line **68** to the hot briquette press **30.** The −325 +400 mesh fraction removed from the first cyclone **34** separator was removed at a rate of 0.05 to 0.07 ton of shale fines per hour. The waste gases and − 400 mesh particles which were conveyed to the second cyclone separator **40** through line **36** were then separated into substantially waste gases and into remaining shale fines. The remaining shale fines weighing 0.18 to 0.58 ton of shale per hour were sent via line **42** to the slurry tank **58.** The overhead gases were sent through line **44** to a spray tower **46** where they were scrubbed with water to remove any remaining fine shale particles. Further, the gases were treated with excess lime, introduced through line **50** into tower **46,** to convert all fluoride gases which were evolved during the calcining reaction to insoluble calcium fluorides. The slurry from the base of the spray tower **46** was then conveyed through line **52** to slurry tank **58.** The resulting scrubbed gases were then vented through line **54** and stack **56** at a rate of 0.06 to 0.8 ton of gases per hour.

The calcined +325 mesh solids in the fluidized reactor **24** were removed through exit port **26** and conveyed to the hot briquette press **30** at a rate of about 1.1 tons per hour and there hot briquetted between rollers **30** and **31** at a temperature of about 1700°F. The briquette press was equipped with a feed screw to create the additional pressures necessary for the hot briquetting operation. The temperature and pressure within the briquette press were sufficient to cause plastic flow of the shale during the briquetting operation. Make up water was added through line **48** into spray tower **46** and into slurry tank **58** at a rate sufficient to flow about 0.145 to 0.194 ton of water per hour to the settling pond **62** which was sufficient to remove 0.24 to 0.67 ton of shale fines per hour from the slurry tank **58.** Recycle water from the settling pond **62** was removed and recycled through line **64** back to the slurry tank as was required.

As a result of the above example, mine run shale having an average of 22 percent P_2O_5 (analysis 20–24 percent P_2O_5) was beneficiated into a product containing 25–26 percent P_2O_5) was beneficiated into a product containing 25–26 percent P_2O_5, and the product was in the form of hard, calcined agglomerates which are eminently suitable for feed in a phosphorus furnace.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclousre otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A process for simultaneously beneficiating and calcining a phosphate ore to produce hard calcined phosphate agglomerates which comprises crushing a phosphate ore to substantially −½ inch, heating and calcining the crushed ore at a temperature of at least about 1500°F. in a fluidized bed, removing, without recycle a relatively phosphorus-poor, −400 mesh fraction overhead from a relatively phosphorus-rich fraction remaining in the fluidized bed, withdrawing hot, calcined, phosphorus-rich ore from said fluidized bed and briquetting said phosphorus-rich ore under sufficiently high pressures and temperatures to cause plastic flow of the ore, and recovering a calcined phosphate agglomerate suitable as a phosphorus furnace feed.

2. Process of claim **1** wherein the fluidized bed is maintained at a temperature of from about 1500°F. to about 2200°F.

3. Process of claim **1** wherein substantially all of the phosphate ore is crushed to −¼ inch in diameter.

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