Nov. 26, 1968 T. KOMAC ET AL 3,413,385

PROCESS FOR REPAIRING REFRACTORY WALLS

Filed Oct. 13, 1965 3 Sheets-Sheet 1

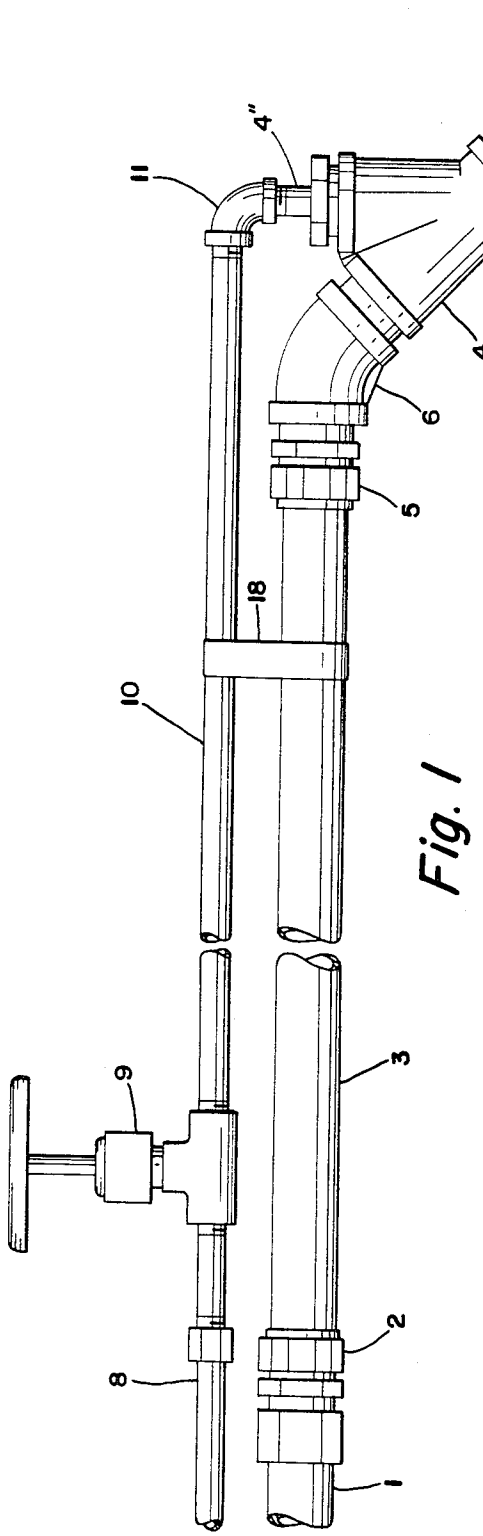


Fig. 1

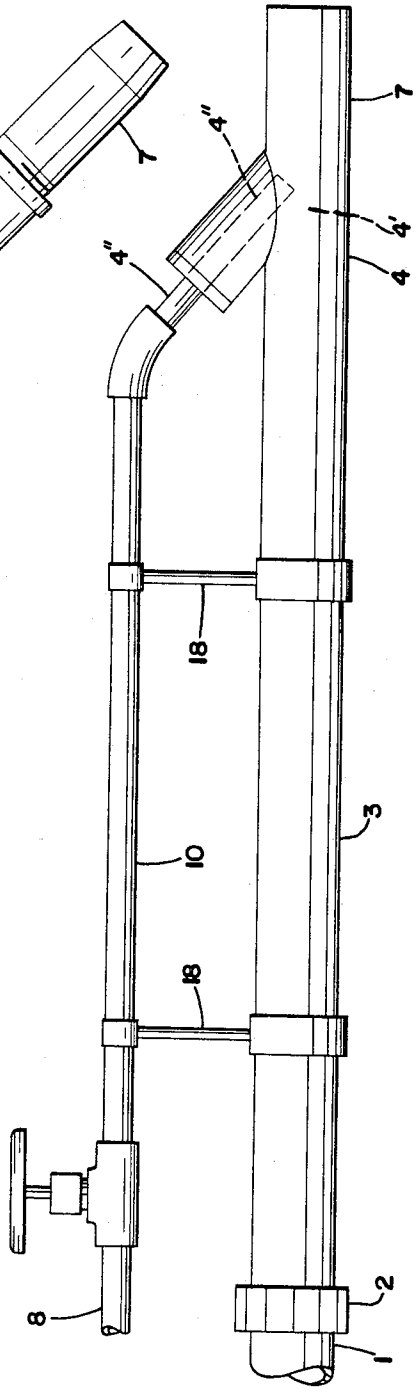


Fig. 3

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Filed Oct. 13, 1965 3 Sheets-Sheet 2

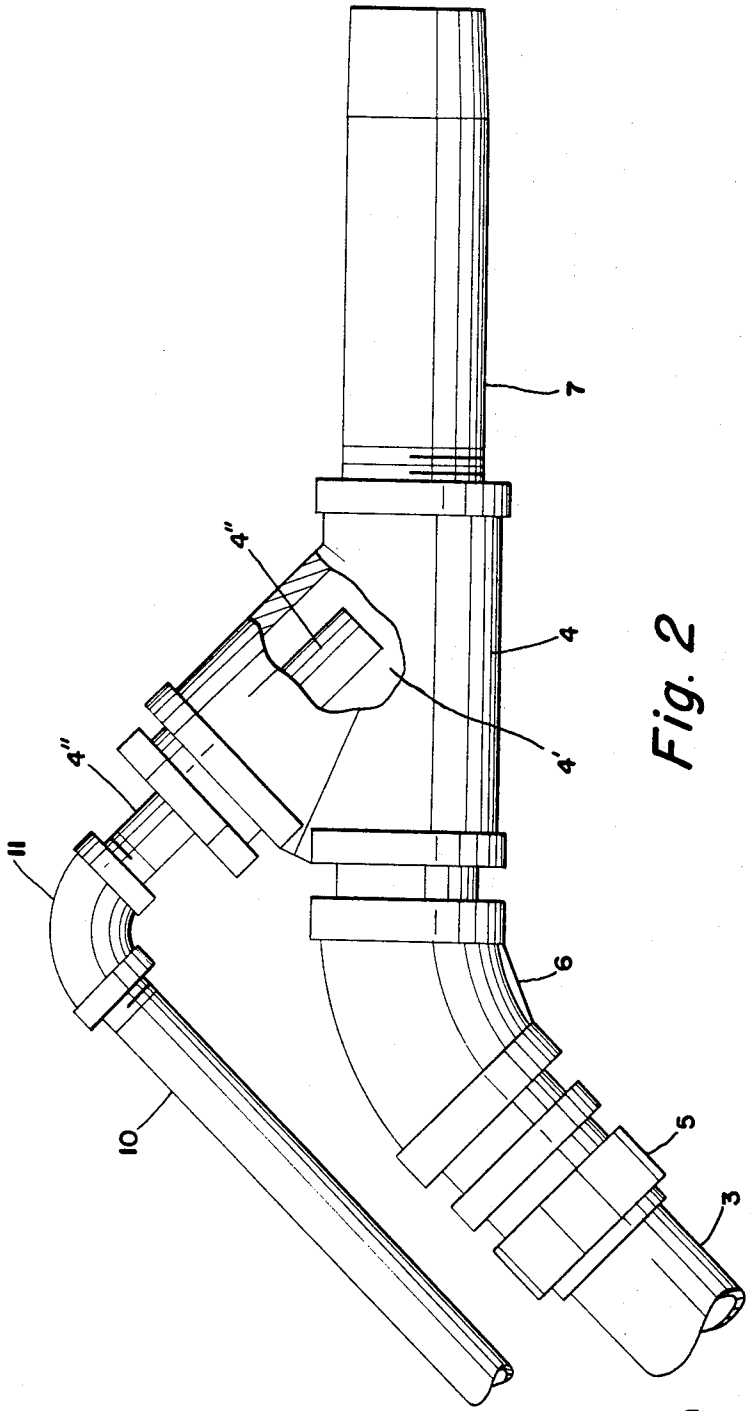


Fig. 2

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Filed Oct. 13, 1965 3 Sheets-Sheet 3

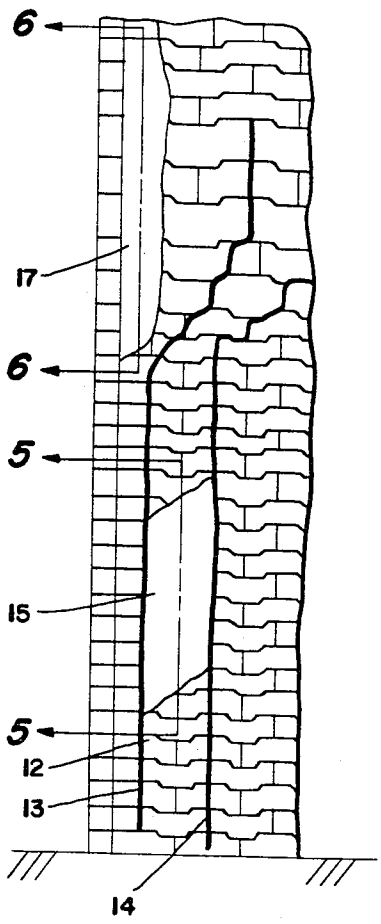


Fig. 4

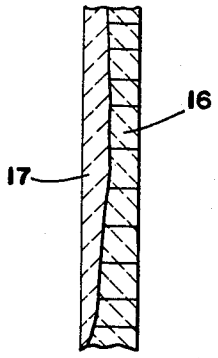


Fig. 6

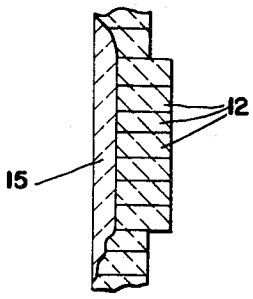


Fig. 5

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3,413,385

PROCESS FOR REPAIRING REFRACTORY WALLS

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Filed Oct. 13, 1965, Ser. No. 495,400
5 Claims. (Cl. 264—30)

ABSTRACT OF THE DISCLOSURE

The process disclosed herein comprises a method of applying to an interior refractory wall of a coke oven which is at an extremely high temperature, a mixture for repairing said interior wall comprising a dry aggregate fed through a rigid supporting pipe at least 6 feet in length into the mixing chamber of a spray gun where it makes initial contact with a mixed phosphate solution of specific composition, the initial contact of the dry aggregate with the phosphate solution being at a point in the spray gun which is in the range 9–32 inches from the area of the wall to be repaired, the specific mixed phosphate solution being one which dries particularly fast and is therefore mixed at a point close to the wall to which the mixture is to be applied.

This invention relates to a method and apparatus for repairing coke oven refractory walls, particularly the end oven walls. More specifically it relates to a process for applying a refractory mixture by a technique which avoids prolonged intimate contact of the ingredients before being applied to the repair areas, and to a spray gun designed for such purpose. Still more specifically, it relates to a spraying method and spraying gun in which a particularly fast and effective solution of mixed ammonium phosphate is placed in intimate contact with the refractory aggregate for a very brief interval from the time the two components meet in the spray gun until they are impacted on the repair area.

The repair and maintenance of coke oven end walls have long presented an economic and production problem to coke oven plant operators. The No. 1 flue area of each oven normally requires patching every 4 to 6 weeks because of the relatively short life of presently available patching materials. The labor alone involved in patching the end flue zone of a 65 oven battery amounts to well over $15,000 a year. Much of this patching is necessary to maintain a gas-tight seal at the metal door frame and at the joint between the fireclay jambs and end oven wall brickwork. Although essential to maintaining good operations, the patching process is time consuming and often results in damage to the oven wall liners which under present patching methods are cooled during the patching operation. If the coke oven end walls are not patched often enough, the end oven wall brick and supporting steelwork deteriorate at an accelerating rate.

Even frequent patching by present methods merely slows down but does not stop end oven wall brick deterioration. Brick decay continues because the present patching practices include spraying the brickwork with a wet slurry of sodium silicate bonded mortars. The excessive amount of water used in this process promotes additional brick spalling through thermal shock of the wetted areas. In addition to the spray patching, the deeply spalled areas must be hand troweled with a stiff mix of the same material to maintain oven wall contour. This silicate bonded trowel mix sticks very well but tends to blister and laminate when applied in heavy layers. Therefore, large cavities must be repaired by applying relatively thin layers of material and allowing each layer to set or harden

before a succeeding layer is applied. Very often voids occur between the brick surface and the patching material due to blistering action. Carbon formation in these voids cause the patch to "grow" into the oven. In such cases, the patch must be removed to avoid difficulties in "pushing" the coke from the oven. The patch and accompanying carbon are usually difficult to dislodge and some good brick is always lost during such removal operations.

In older coke oven batteries, end flue maintenance becomes increasingly difficult. In most cases fine vertical wall cracks, originally sealed by spray patching when the battery was relatively new, widen appreciably. Generally two or more of these cracks are present in the No. 1 flue zone. Brick spalls 1" to 3" in depth are also generally present. Therefore patching time per oven is increased greatly and ovens must be taken out of operation for repair. During these extended patching periods, the exposed oven wall brick work is cooled excessively. As a result brick deterioration keeps pace with the patching program and complete end flue brick failure soon follows.

Since direct brick replacement requires cooling the oven walls involved to a point where brick masons or patchers can work effectively, the cooling and repair operation is time consuming and is expensive in loss of production. Moreover each time an oven wall is cooled to a point where brick replacement can be done effectively, additional good brick are generally permanently damaged. This means that in order to replace two bad bricks, a third good brick, in turn, is damaged and must also be replaced. This brick damage that occurs during each patching period cannot be eliminated. However, by increasing the service life of a patch, brick deterioration is decreased.

The use of gunning as a technique for applying refractory aggregates is being more widely used. In the "dry" gunning method, a dry refractory aggregate is carried in an airstream to a nozzle where it is mixed with water, and the resultant wetted mixture is blown onto the furnace wall. Castable and cement type mixes lend themselves well to this method of application. In cases where setting time is not important, a refractory aggregate and chemical bonding material may be mixed with water before it is entrained in the airstream and blown through the nozzle. This is the so-called slurry mix used in "wet" gunning. In "wet" gunning there is about twice the amount of water used as in "dry" gunning. Consequently in gunning a hot wall area there is considerably more thermal shock and resultant spalling with "wet" gunning. However, if the resultant mix is too dry, excessive rebound from the wall occurs with increased waste and cost of installation. Moreover, a dry mix very often results in poor density and segregation of the refractory aggregate on the wall. In contrast, if the mix is too wet, slumping occurs which limits the amount or thickness of material that can be applied to the wall.

At present, the bonding agents in basic gunning mixes are solium silicate, and hydraulic cements, such as the calcium aluminate type. However, none of these materials set sufficiently fast. Attempts to apply the phosphate bonding principal to aggregates containing basic magnesia have not been satisfactory in the past. Phosphoric acid reacts violently with magnesia to produce excessive heat which turns the moisture to steam and disrupts the body structure of the refractory.

Monoammonium phosphate has been proposed as a bonding agent for magnesia aggregates. However, while this compound promotes a very fast setting, it can be used in gunning mixes only where the mix is to be applied in very thin layers. This is because the fast reaction promoted by the monoammonium phosphate generates excessive amounts of heat resulting in vaporization of the

moisture in the mix at such a high rate that, if applied in any but thin layers, this moisture vapor will cause fissions or ruptures or bloating in the resulting product. Attempts to slow down the fast reaction by diluting the monoammonium phosphate results in loss of strength in the final product.

In contrast diammonium phosphate is much slower and not very satisfactory as a setting agent in gunning mixes. Even mixtures of monoammonium phosphate and diammonium phosphate set too quickly and thereby generate excessive amounts of heat that cannot be dissipated quickly enough to avoid the fisson, ruptures and bloating described above.

In the present method of patching coke ovens, a wet gunning method is used to apply a slurry using sodium silicate as the bonding agent. In the wet gunning process, the water and the variou ingredients of the patching mixture including the sodium silicate binder are premixed in a tank. Since the binder is so slow in setting the mixture, this premixing can be performed without having the mix set up or harden in the tank or in the gun in which it is applied. In preparing a slurry for wet gunning, much more water is used than in a dry gunning process where the aggregate is fed to the gun in a dry condition and the water mixed with the dry aggregate as the two are being forced through the gun.

In the wet gunning process, pressure is applied to the slurry and it is fed into a long pipe, appoximately 6–14 feet long or longer. This is extended into the interior of the coke oven to be repaired. Since this material is so slow in setting, here is little danger of having the material set in the pipe. Auxiliary air pressure is also applied in the line between the storage tank and the pipe to aid in transmitting the slurry.

Because of the time required for setting of the silicate bond, and the amount of water present, as well as other factors, it is necessary to apply the silicate material in thin layers allowing one or two minutes between the application of layers for setting and the escape of moisture. Even with such setting intervals, the silicate type of material tends to seal off the moisture so that eventually steam pockets and blisters are formed, and also carbon deposits are initiated and grow therefrom. Because of this slow setting and the resultant disadvantages, silicate bonding does not permit the restoring of contour to an oven wall, but merely permits a coating type of patch. Where deeper patches are to be applied, these must be hand-troweled with a stiffer mix of the same material.

Obviously this latter method of application requires that a worker must reach into the oven, thereby necessitating lower temperature of the oven or greater protection against heat. Also because of the number of thin layers that must be applied to build up sufficient thickness the worker must spend more time and be more exposed to heat radiation from the oven.

It is necessary consequently to shield the operator from the severe heat of the coke oven. One method of doing this is to "push" the coke from the oven and to insert a shield or bulkhead in the oven beyond the area to be repaired and thereby reduce the radiation that would otherwise strike the operator. Another method of shielding the operator is to remove some of the coke from the end of the oven to be repaired, and then spray an insulating material on the exposed coke and thereby building up a shield which will reduce the intensity of the heat being radiated towards the operator.

Even though the repair area may be just inside the door of the oven it is impossible in view of the intense heat for a workman to stand close to the oven to apply the aggregate mix, even with the heat shields and insulation described above. Attempts have been made to apply such gunning mixes by the use of a gun having a long snout or pipe extending beyond the mixing chamber of the nozzle so as to guide the gunnig mix to the area to which it is to be applied. Such a device is satisfactory for a material of very slow setting character or one which has a tremendous volume of mix passing therethrough so as to keep the inside of pipe clean from set material by the abrasive action of the refractory passing against the inside pipe wall. However, since the volume of material passing through such a device is relatively low, this abrasive action is not available in coke oven wall repair work of this type. Furthermore, in view of the intense heat being radiated from the oven, such a snout would become heated and aggravate the setting problem of a fast setting aggregate mix.

It is found that very fast satisfactory chemical bonding can be effected in basic refractory compositions suitable as gunning mixes by the use of a solution of mixed ammonium phosphates containing orthophosphate, pyrophosphate and polyphosphates, which polyphosphates include tripolyphosphate, tetrapolyphosphate and higher polyphosphates.

Particularly preferred for this purpose are aqueous solutions containing as much ammonium polyphosphate as can be dissolved. While the polyphosphate content gives a higher content of P_2O_5 in the resultant mixture, it has been found that the ammonium component is also essential since phosphorus oxide components alone, such as phosphorus pentoxide, do not give the beneficial results effected by the practice of this invention. It has been found that the ammonium phosphate mixture advantageous for the purpose of this invention has the composition of approximately 35–40% orthophosphate, 45–50% pyrophosphate, 9–11% tripolyphosphate and 2–5% higher polyphosphates. Such compositions show about 8–12% ammoniacal nitrogen and about 30–35% total P_2O_5.

In view of the very fast setting character of the above-described mixed phosphate solution, considerable difficulties have been encountered in attempting to apply such gunning mixes to the interior of hot furnaces by the type of spray gun having such a long snout. Since the phosphate solution can be in intimate contact with the refractory mix only the briefest time, the mix very often hardens in the gun.

In accordance with the present invention, it has been found that repairs can be made to the interior walls of coke ovens by a process in which the mixture of phosphate solution and aggregate is made to travel only a very short distance after being mixed in the nozzle of the spray gun and before it is impacted on the repair area. The spray gun of this invention comprises a considerable length of rigid pipe supporting the nozzle of the spray gun, through which pipe the aggregate travels before it enters the mixing chamber where the mixed phosphate solution is introduced for intimate contact with the aggregate. The length of the snout or extension from the nozzle mixing chamber is in the range of 2–12 inches and the distance from the point of the initial contact of solution and dry aggregate is approximately 3–14 inches from the exit end of the snout. The distance between the end of the snout and the surface to be repaired is advantageously 6–18 inches. Consequently the overall distance from the point of the said initial contact or mixing is 9–32 inches, preferably 12–25 inches.

In feeding the solution into the mixing chamber the stream of solution can be fed in at an angle of 15–90°, advantageously 30–60°, with the linear axis of the mixing chamber.

The rigid supporting pipe through which the dry aggregate is fed is at least 6 feet long and as long as 14 feet or even longer depending on the distance the repair area is from the inlet to the coke oven.

In operating the gunning equipment of this invention, the primary air supply into which the dry refractory mix is fed for introduction into the mixing chamber of the nozzle is preferably about 80 p.s.i. although it can be varied considerably depending on various other operating conditions, but is advantageously in the range of 50–

100 p.s.i. The dry aggregate can be fed from a hopper into such an airstream, and an air pressure of 10–30 p.s.i. is desirably maintained above the material in the hopper. The phosphate solution is advantageously fed to the mixing chamber under a pressure of about 30–60 p.s.i.

The method and apparatus of this invention permit the very fast setting mixture described above to be mixed and applied almost instantaneously to wall areas at a considerable distance into the coke oven from the point at which the spray gun is introduced, without having to shut down and lower the temperature of the coke oven. In addition to the fast setting character of the mixture described herein, the mixture has other desirable properties such as water vaporization rate that avoids bubble formation in the setting mix, and very good physical properties in the ultimate refractory layer as more fully described hereinafter.

In the drawings, FIG. 1 is a side elevational view of the spray gun assembly of this invention.

FIG. 2 is a side elevational cross-sectional view of the nozzle and mixing chamber portion of the spray gun shown in FIG. 1.

FIG. 3 is a side elevational view of another modification of the spray gun of this invention.

FIG. 4 is a front view of a coke oven end wall on which a section has been patched by the process and apparatus of this invention.

FIG. 5 is a cross-sectional side view of the patched section of the end wall of FIG. 4 showing displacement of loose bricks into the flu so that the refractory layer applied by gunning returned the wall to its original contour.

FIG. 6 shows a cross-sectional side view of another section of the coke oven end wall of FIG. 4 in which a section of the wall in which the brickwork has been spalled has been repaired to the original end wall contour by gunning according to this invention.

In FIG. 1 flexible hosing **1** is attached by coupling **2** onto rigid pipe **3** which in turn is connected to nozzle **4** by coupling **5** and pipe elbow **6**. Snout or pipe nipple **7** determines the distance through which the refractory and the mixed phosphate solution must travel in intimate contact before being applied to the area to be repaired. The mixed phosphate solution is fed through flexible hose **8** at a rate controlled by valve **9** into pipe **10** through elbow **11** and into the nozzle **4** having in its interior, mixing chamber **4'** as shown in the cross-sectional view of FIG. 2.

FIG. 3 shows a modification in which the spray gun comprises one long straight pipe having sections corresponding to the unitary sections shown in FIG. 1. The nozzle inlet **4''** for the liquid stream is at the same angle with the axis of the snout **7** and mixing chamber **4'** as in FIG. 1. In this case also, the two feed pipes **3** and **10** are likewise parallel. In this case, snout **7** is merely an extension of pipe **3** which has an intermediate section **4** comprising the nozzle and the mixing chamber **4''**. In both the designs of FIGURES 1 and 3, brackets **18** are used to support or brace the pipe **10** by the indicated connection with larger pipe **3**.

In FIGS. 4 and 5, the bricks **12** between cracks **13** and **14** are shown pushed backward into the flue section. Patched section **15** is shown as bringing the wall back to its original contour.

FIG. 6 shows how a depressed wall section caused by spalling of the brickwork **16** has been filled in by patched section **17** by the practice of this invention to restore the original wall contour.

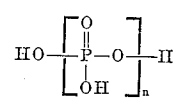
By the practice of this invention it has been found possible to build up considerable thickness of refractory layer without any intermediate setting or drying period since the setting agent acts so quickly that successive sweeps of the spraying gun back and forth over the area permits sufficient time for the setting agent to work in setting the thickness applied each time the gun sweeps first in one direction and then in the other. By the time the gun has swept back over the same area, the aggregate mix is sufficiently hard to receive the next application or layer of the refractory mix. In this way patch thicknesses of up to 6 inches or even higher can be easily built up in one application. In many gunning mixes, such as those using silicates, the application of any considerable thickness without intermediate drying or setting results in the trapping of moisture which eventually causes bubble formation or spalling or rupture of the repair layer.

If the temperature of the brick in the coke oven wall is reduced below 1200° F., inversion or shrinking occurs in the brick, resulting in cracks, etc. Therefore, it is most important to maintain a temperature of at least 1200° F. preferably at least 1400° F.

With the "dry" gunning mixes used in this invention there is only 10–15% water, as compared to 25–30% in the "wet" gunning or silicate type. Therefore, with the gunning mix used in this invention, there is not the thermal shock and resultant spalling as is encountered with silicate wet gunning mixes. As a result repairs made by the gunning process of this invention last 6–9 months, whereas repairs are required about every 6 weeks with silicate bonding. Moreover, the repairs made possible by this invention make it unnecessary to replace brick as would otherwise be necessary. This would require shutting down ovens, with resultant loss of production. Furthermore, the patches produced by this invention have much improved resistance to permeability as compared with silicate patches.

In the refractory compositions of this invention, the magnesia content advantageously ranges from 1 to 30%, preferably 5–15%, by weight of the aggregate portion and in the developed composition the phosphate content (calculated as P_2O_5 content) can range from 0.5 to 6%. While the phosphate content is introduced as ammonium phosphates, the resulting ultimate product has lost substantially all of the ammonium content since ammonia is given off during the various drying and/or firing operations.

The ammonium phosphate solution useful in the practice of this invention can be prepared by the reaction of polyphosphoric acid with concentrated ammonium hydroxide. The polyphosphoric acid is 115 percent phosphoric acid and has a P_2O_5 content of approximately 83.2%. This is distributed as 5% orthophosphoric acid, 16% pyrophosphoric acid, 17% triphosphoric acid, 16% as tetraphosphoric acid and 46% higher polymer acid. The polyphosphoric acid can be represented by the formula



When n equals 1, this formula represents orthophosphoric acid. When n equals 2, the formula represents pyrophosphoric acid. When n equals 3, it represents triphosphoric acid. When n equals 4 is represents tetraphosphoric acid, and when n is higher than 4, it represents the higher polymer acids.

When the ammonium hydroxide is reacted with this polyphosphoric acid, some of the hydroxy groups of this formula are converted to $—ONH_4$ radicals. Since the water present in the ammonium hydroxide solution converts some of the polymeric acid to the ortho and pyro forms, the ratios of these forms in the ammonium phosphate product become higher than in the initial acid form. For most of the purposes of this invention it is desirable to have as high as possible the concentration of ammonium polyphosphates. The various ammonium phosphates can be represented by substituting the ammonium radical (NH_4) for the H of one or more of the hydroxy groups shown in the formula.

For example, if approximately 41 parts of the polyphosphoric acid (115% H_3PO_4) is reacted with approxi-

mately 73 parts of 35% ammonium hydroxide, the resultant ammonium phosphate solution has a P_2O_5 content of approximately 34%, an ammoniacal nitrogen content of approximately 10%, and a water content of approximately 50%. Some of the water has been used to break down the polymer structure and give higher proportions of the orthophosphoric acid and pyrophosphoric structures than were present originally. The concentrations are approximately those cited above as suitable for the practice of this invention.

The indicated ratios of the various components of the above-indicated solution are in equilibrium at the concentration described. It is very often desirable for gunning application that additional water be present to give a more suitable consistency. For many gunning operations the addition of as much an equal volume of water is satisfactory. However, where the mix is being applied to a very hot wall and the vaporization loss is very rapid as much as two volumes of water per volume of ammonium phosphate solution can be added.

This extra water is added advantageously shortly before the mix is to be applied so as to minimize the shift in the equilibrium ratio of the phosphate components. Generally, the dilution can be made at the beginning of the day for the solution to be used during that day, although diluted solution standing for approximately 24 hours can be used satisfactorily.

For purpose of simplification, the amount of ammonium phosphate solution desirable for the purpose of this invention is generally indicated as 4–25 parts of solution per 100 parts of aggregate, or in some cases 5–25 parts of solution. This is based on a P_2O_5 content of approximately 34.2% in the ammonium phosphate solution. Where the P_2O_5 content varies from the 34.2 value, the amount of solution is adjusted to give the equivalent P_2O_5 content. This range can also be stated as being equivalent to about 1.35–8.55 parts by weight of P_2O_5 content per 100 parts of aggregate.

Particularly suitable ammonium phosphate for the purpose of the invention is a commercial product known as sequestered phosphatic solution, which is used primarily as an agriculture fertilizer. Such solutions contain orthophosphate, pyrophosphate and polyphosphates. A typical analysis shows 10.2% ammoniacal nitrogen, and 34.2% total P_2O_5. The P_2O_5 distribution is approximately 38% as othophosphate, 48% as pyrophosphate, 10% as tripolyphosphate, 3% as tetrapolyphosphate and 1% as higher polyphosphates.

This commercial material has approximately 4% of impurities, which do not adversely affect its use in the practice of this invention. These impurities comprise approximately 1.7% sulfuric acid, 0.6% iron, 0.5% aluminum and 0.05% fluorine. This commercial product also contains roughly about 50% water.

Various types of aggregate can be used. A typical satisfactory composition is made by using 95–99 parts of graded firebrick aggregate and fireclay, 1–5 parts of lightly calcined or dead-burned magnesia and 5–25 parts of the sequestered phosphatic solution. In such compositions, the rate of setting is controlled by the degree of calcination and the fineness of the magnesia.

Since both magnesia and the phosphatic solution are fluxes for the fireclay aggregate, they are desirably kept to a minimum while still using sufficient to give the necessary strength and refractoriness desired. In some cases the sequestered phosphatic solution is diluted, particularly in applications where it is desirable to use high proportions of liquid material for imparting proper temper or consistency to the resultant mix.

Although magnesia is preferred, it is possible to substitute calcine dolomite, which has a substantial magnesia content, for the magnesia or for a part of the magnesia. Sometimes the calcined dolomite reacts to give off excessive heat which, unless controlled, causes undesirable steam formation. However, this can be controlled by having present in the mixture sufficient relatively inert aggregate, such as the silica or firebrick, for dissipation or absorption of the heat.

When the magnesia is used with silica, the ranges are advantageously in the order of 1–30, preferably 5–15 percent magnesia and 70–99, preferably 85–95 percent of silica. In such cases 6–12 parts of sequestered phosphatic solution per 100 parts of aggregate is desirable. Where extremely high temperatures are not being used, firebrick can be substituted for part or all of the silica depending upon the particular temperature.

Moreover, where references are made above to preferred proportions of magnesia, etc., it has been pointed out above that the advantages of this invention can be had with any aggregate mixture in which there is at least one percent of magnesia, either as such or as a component, such as in calcined dolomite.

With regard to the particle size of the aggregate, it has been found particularly suitable for gunning operations to have a particle size distribution of the aggregate of 60% in the range of 6 to +28 mesh (Tyler) and 40% of fines −100 mesh.

In the present invention, the magnesia in the aggregate is reacted with the ammonium ortho, pyro and polyphosphates to produce chemical bonding.

The phosphate bonding can be accomplished with either lightly calcined or dead-burned magnesia, but for refractory use, the aggregate is preferably dead-burned. As is well known in the industry, dead-burning is effected by calcining above about 2700° F. and light burning or light calcining is effected at about 1800–2000° F. Dead-burned magnesia is often referred to as periclase.

Various methods of practicing the invention are illustrated by the following examples. These examples are intended merely to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced. The parts and percentages recited therein and all through the specification, unless specifically provided otherwise, are by weight.

Example I

A number of coke oven walls having spalled sections and wide deep cracks similar to those shown in FIGS. 4 and 5 were patched using the spray gun of FIGS. 2 and 3 and an aggregate mix of 60% fireclay grog (from reclaimed or reject bricks) having a particle size that passed a 6 mesh screen and is retained on a 28 mesh screen (Tyler), 20% fireclay grog having a particle size that will pass through a 100 mesh screen, and 20% of first quality fireclay. The mixed phosphate solution is the commerical SPS (sequestered phosphate solution) described above, diluted with an equal volume of water. The air supply line was operated at a pressure of about 80 p.s.i., the aggregate hopper had a pressure of about 25 p.s.i. at the top of the hopper feeding the aggregate into the air line. The liquid tank supplying the phosphate solution was operated at a pressure of 50 p.s.i. The aggregate and the phosphate solution were mixed in the gun and applied to the cracks and spalled areas of the oven walls, thicknesses as high as three inches being applied. The aggregate-solution mix coming from the nozzle has a composition of 10–15% solution and 85–90% aggregate. The time of application was no more than had previously been used to spray-patch the areas with silicate bonding material. Repairs of the type illustrated in FIGS. 4, 5, and 6 were made. In these same regions conventional hand trowel patching had been previously attempted with little success, which was time consuming and gave short patch life of approximately 4–6 weeks. After repairs were made according to the above description using the technique of this invention, little change was noted in the body of the patches 6 months after being installed. In the coke side of the wall where there is considerable coke abrasion, the patch life has averaged 6 to 9 months.

Example II

The procedure of Example I is repeated with similar results substituting in place of the fireclay an equal amount of siliceous clay (having about 75% silica as compared to about 40% silica in the fireclay).

Example III

A comparative test of the permeability of patches made by the procedure of Example I and patches made from a sodium silicate patching material now in commercial use was made as follows. Samples of the phosphate type of patch which had been applied according to the procedure of Example I on a coke-over wall at about 1400° F. were removed after about three months application and use. On a wall in this same coke oven still maintained at about 1400° F., a patch was applied of a sodium silicate commercial material in present use being sold under the trademark "Super-Chief" Airset Mortar. This was applied by trowelling the material on the hot wall. The patch was taken off after twenty-four hours for this test. Since it is known that permeability of a patch increases on aging, the comparison in this case because of the greater aging of the phosphate patch is heavily in favor of the newer sodium silicate patch. Cube-shaped specimens having dimensions of 2 x 2 x 2 inches were cut from the respective phosphate and silicate samples. Four specimens of each type were tested according to this procedure and the results averaged for each type of patch:

A rubber specimen-sealing gasket is made to fit tightly around the 2 x 2 x 2 inch test specimen. This gasket has an opening through its center which is 2 inches in length and a cross-section of $1\frac{15}{16}$ inches square. This smaller dimension in the cross-section of the opening provides a tight fit against the contacting surfaces of the 2 x 2 x 2 cubical specimens.

The outer surface of the gasket resembles two truncated cones having their two bases superimposed and joined and the narrowing or tapering portions of the cones extending to the top and bottom of the gasket so that the largest circular cross-section of the gasket is at the mid-point of the height of the gasket with the outer wall tapering therefrom to the top and bottom of the gasket. This taper measures about 10 degrees. A tapered stainless steel gasket-holder is used to contain the gasket after a test sample has been inserted in the opening described above. This gasket holder is made of two identical sections, one to fit the top and one to fit the bottom of the gasket with an interior opening having dimensions and taper corresponding to the outside of the gasket and having an opening in both the top and bottom of the gasket holder to permit gas flow to the top and bottom of the specimen inserted in the gasket. The two halves of the gasket holder are held under hydraulic pressure so as to provide gas-type seal between the gasket holder and the gasket on one hand, and between the specimen and the interior of the gasket on the other hand. The gasket-holder, gasket and specimen are positioned in a system adapted to provide nitrogen gas under desired pressure to one of the exposed surfaces of the specimen, and the other exposed surface is in communication with flowmeters adapted to measure the flow of gas passing through the specimen. The system is also equipped with a manometer adapted to measure the differential pressure between the two exposed surfaces of the specimen. A drier bottle filled with a desiccant and a strainer are provided to remove any water or dirt from the nitrogen before it enters the flowmeters.

Before being inserted in the gasket for test, the specimens are dried for 16 hours at 220–230° F. and cooled to room temperature. After drying, all surfaces of the test specimen are blown free of dust with clean dry air. The rate of the nitrogen flow through the specimen is measured for a variety of differential pressures for each specimen and the permeability at room temperature is calculated in centidarcys using one of the formulas below depending upon whether a mercury or a water manometer is used. Since nitrogen was used as the permeating media in these tests, the permeability as calculated by these formulas is increased by 5% to allow for difference between nitrogen and air used in such tests.

(1)

$$\frac{(0.451)\ (\text{Flow, cc./min.})}{(\text{Differential pressure, cm. mercury})\left(1+\frac{\text{Differential pressure, cm. mercury}}{152}\right)}$$

or

(2)

$$\frac{(6.13)\ (\text{Flow, cc./min.})}{\text{Differential pressure, cm. water}}$$

The specimens from the phosphate patch produced according to Example I were tested at differential pressures of 1, 2 and 4.1 inches of mercury. Since the silicate patch specimens proved to be much more porous with resultant greater flow of nitrogen therethrough, the differential pressure was measured with the water manometer and the differential pressures were 1.7, 3.5 and 6.9 inches of water. From the above procedure and the calculations in the formulas, the phosphate patch specimens were found to have an average permeability of 3.82×10^{-3} darcys; whereas the sodium silicate specimens were found to have an average permeability of 46.22×10^{-3} darcys. These tests show that in spite of the more favorable shorter aging period of the silicate patch, the phosphate patch of this invention has much greater resistance to permeability than the prior art sodium silicate type of patch in present commercial use.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. The process of repairing an interior refractory wall of a coke oven while the brick of said coke oven wall is at a temperature of at least 1200° F. comprising the steps of

(1) inserting a spray gun into the interior of said coke oven;

(2) feeding a dry aggregate containing at least one percent by weight of magnesia therein through a rigid supporting pipe at least 6 feet in length into the mixing chamber of said spray gun by means of an air stream at a pressure of 50–100 p.s.i.;

(3) separately feeding into said mixing chamber a mixed phosphate aqueous solution under a pressure of 30–60 p.s.i., the point of initial contact of said dry aggregate with said solution being in the range of about 9–32 inches from the area of said wall to be repaired, and

(4) directing the flow of resultant aggregate-solution mix against said wall area; said mixed phosphate solution consisting essentially of ammonium phosphates in weight proportions of 35–40% orthophosphate, 45–50% pyrophosphate, 8–12% tripolyphosphate and 2–5% higher polyphosphates, the ammonium phosphate content being equivalent to about 10% by weight ammoniacal nitrogen and about 34% by weight P_2O_5, said solution containing 100–300 parts by weight of water per 100 parts of said phosphates.

2. A process of claim 1 in which said phosphate content is distributed on a weight basis of approximately 38% as orthophosphate, 48% as pyrophosphate, 10% as tripolyphosphate, 3% as tetrapolyphosphate and 1% as higher polyphosphates.

3. A process of claim 2 in which said aggregate comprises 5–15 percent by weight of magnesia and 85–95 percent by weight of fireclay aggregate.

4. A process of claim 2 in which said aggregate comprises 5–15 percent by weight of magnesia and 85–95 percent by weight of silica aggregate.

5. A process of claim 2 in which said air stream feeding said aggregate is maintained at a pressure of approximately 60 p.s.i.

References Cited

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