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### COKE-OVEN PATCHING MATERIAL

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16 Claims

### ABSTRACT OF THE DISCLOSURE

A refractory composition for patching coke oven walls comprises siliceous aggregate, plastic clay, a chemical binder and a source of manganese oxide.

### BACKGROUND OF THE INVENTION

Refractory walls of by-product coke ovens, which are constructed of silica brick, have expected useful lives of from 15 to 30 years. The alternate heating and cooling of such oven walls often results in the formation of cracks in the walls after only a few years of service. Since the ends of the oven are subject to a higher and more frequent fluctuation in temperatures, cracks are particularly common near oven ends. Such cracks can cause gas short circuiting between the ovens and combustion chambers, which results in hot spots in the wall, smoke emission to the combustion system, and accelerated wall wear. Commonly, cracks in coke oven walls have been patched, or a portion of the walls near the end of the oven has been replaced to eliminate the cracks. Cooling ovens to a sufficiently low temperature to permit rebuilding a portion of the oven is quite costly and very time consuming and, thus, uneconomical. Patching of coke oven walls has been done by pneumatic gunning on hot walls, or on cold walls by cold patching which requires shutting down the oven or blanking off selected ovens and trowelling a patching mix into the cracks.

Patching of coke oven walls is not normally successful because heretofore there has been no suitable patching material. Materials used to patch ovens prior to the present invention have generally included a siliceous base (quartzite sand, used silica brick, etc.) with clay additions to provide workability and binding agent such as sodium silicates or phosphates to promote adhesion to the surrounding walls. No such patching material has ever given satisfactory permanent bonding with used silica brick. As a result, the patching material has been effective for no more than a few months.

### OBJECTS OF THE INVENTION

It is the principal object of our invention to provide a patching material for coke ovens, having a long lasting bond with used silica brick.

It is also an object of our invention to provide a patching material for coke oven walls which can be applied to either hot or cold silica brick walls.

We have found that certain siliceous compositions containing small amounts of a source of manganese oxide adhere to used silica brick walls at a temperature in a range of 1500 to 2800° F. in both oxidizing and reducing atmospheres. Compositions without manganese oxide are not strongly adherent over the entire range of temperatures.

Our patching material consists essentially of 50 to 93% siliceous aggregate, 3 to 15% plastic clay, 2 to 12% chemical binder and 1 to 25% of a suitable source of manganese oxide. The total manganese oxide content of the patching material as MnO should be from about 0.5% to about 15%.

The preferred range of our patching material is from 72 to 84% siliceous aggregate, from 8 to 12% plastic

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clay, from 5 to 8% chemical binder and from 3 to 12% manganese oxide source.

Our siliceous aggregate is preferably quartzite or other ground silica brick, but may also be some other siliceous material such as sands or clays. The siliceous aggregate is sized minus 3 mesh and preferably minus 10 mesh to allow penetration of the material into the cracks being patched. From about 5 to 25% of the siliceous aggregate should be sized minus 100 mesh. All screen sizes are Tyler Standard.

10 The plastic clay is a fire clay product sized minus 14 mesh and preferably minus 100 mesh. The pyrometric cone equivalent (PCE) (ASTM) of this clay should be from 26 to 33.

15 Our chemical binder is preferably sodium silicate, but may be some other chemical binder, such as chromic acid, boric acid, sodium sulfate, magnesium sulfate, sodium phosphate or a suitable organic binder such as lignin sulfates or dextrose. The binder may be added in either solid or liquid form.

20 Our manganese oxide source is preferably a manganese ore containing more than 50% manganese (as MnO). Other sources of manganese oxide may be used such as ferro-manganese flue dusts or chemically pure manganese oxides. The manganese oxide source should be sized minus 48 mesh and preferably minus 100 mesh.

25 The material is mixed in dry form and may be premixed with sufficient water to obtain the desired workability prior to shipment to the patching location, or may be shipped in dry form and mixed with water at the site. 30 About 10 to 20% water must be added to obtain a workable mixture when the mix is to be trowelled. Higher amounts of water may be used when pumping or gunning with nutrients.

35 Our patching material may be applied by trowelling or plastering over a cracked area on either a cold or hot wall, by pumping or injecting the material into cracks in a cold or hot wall, or by pneumatic gunning or other suitable application technique.

40 Three specific examples of composition of our patching material are shown in Table 1.

TABLE 1

Component and mesh size	Trowelling mix		
	A	B	C
Quartzite:			
—4	40	0	0
—10	61	36	0
—100	15	0	0
Siliceous clay, —10	0	0	80
Plastic clay, —100	10	10	10
Sodium silicate	6	6	6
Manganese ore (68% MnO), —100	8	8	4
Water added	13-14	0	0

Tests showed excellent bonding of all mixes to used silica brick from a 15-year old coke oven at temperatures of from 1500 to 2800° F. in both oxidizing and reducing atmospheres. Tests using the same mixtures without manganese oxide showed no bonding under the same conditions. Little or no bonding was obtained from experimental mixtures containing a variety of other additives such as iron oxide, titania, magnesia, iron and steel slags, chromic oxide, sodium phosphate, fluorspar, alumina, volatilized silica, chrome ore, sodium-lime-silica glasses, etc.

65 Mixes A, B and C (Table 1) were applied on both cold and hot coke oven walls. In all cases, the bonding of the patching material to the used silica brick walls was superior to that obtained from any other patching material that had been heretofore employed.

70 Although the exact bonding mechanism between the silica brick and patching material which is promoted by the presence of manganese oxide is not completely understood, petrographic examination seems to indicate that

the excellent bonding results from the formation of a liquid which is subsequently absorbed into the silica brick.

From the foregoing, it is readily apparent that we have invented a coke oven patching material having good adherence with used silica brick walls when applied either to hot or cold walls by trowelling, plastering, pumping or gunning.

We claim:

1. A refractory composition for patching coke oven walls comprising:
  - a. from about 50 to about 93% siliceous aggregate, all of which is sized to -3 mesh;
  - b. about 3 to about 15% plastic clay;
  - c. about 2 to about 12% chemical binder selected from the group consisting of sodium silicate, chromic acid, boric acid, sodium sulfate, magnesium sulfate, sodium phosphate and organic binders; and
  - d. from about 1 to about 25% of a source of manganese oxide, whereby the total manganese content of the composition as MnO is from about 0.5% to about 15%.
2. A composition according to claim 1, wherein said siliceous aggregate is selected from the group consisting of quartzite, ground silica brick, silica sands and silica clays.
3. A composition according to claim 1, wherein said siliceous aggregate is -4 mesh.
4. A composition according to claim 3, wherein from 5 to 25% of said composition is -100 mesh siliceous aggregate.
5. A composition according to claim 1, wherein the plastic clay has a pyrometric cone equivalent of from 26 to 33.
6. A composition according to claim 1, wherein said plastic clay is -14 mesh.
7. A composition according to claim 1, wherein said plastic clay is -100 mesh.

8. A composition according to claim 1, wherein said chemical binder is sodium silicate.

9. A composition according to claim 1, wherein said manganese oxide source is selected from the group consisting of manganese ores, ferro-manganese and chemically pure manganese oxides.

10. A composition according to claim 9, wherein said source of manganese oxide is a manganese ore containing more than 50% manganese as MnO.

11. A composition according to claim 1, wherein said source of manganese oxide is -48 mesh.

12. A composition according to claim 1, wherein said source of manganese oxide is less than 100 mesh.

13. A composition according to claim 1, wherein said siliceous aggregate is present in the amount of from 72 to 84%.

14. A composition according to claim 1, wherein said plastic clay is present in an amount from about 8 to about 12%.

15. A composition according to claim 1, wherein said chemical binder is present in an amount from about 5 to about 8%.

16. A composition according to claim 1, wherein said manganese oxide source is present in an amount from about 3 to about 12%.

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