TUBE SHIELDS HAVING A THERMAL PROTECTIVE LAYER

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ABSTRACT

A tube shield, and method of manufacturing the tube shield, having a support structure with an external surface, an internal surface, and an edge, and a thermal protective layer on at least one surface of the shield support structure. The thermal protective layer is composed of a filler, one or more emissivity agent, and either an inorganic adhesive or a binder that is colloidal silica, colloidal alumina, or combinations thereof. A colorant, a surfactant, and/or a stabilizer may be incorporated into the thermal protective layer.
Fig. 4A

Fig. 4B
TUBE SHIELDS HAVING A THERMAL PROTECTIVE LAYER

BACKGROUND OF THE INVENTION

[0001] Tube shields are found in furnaces, boilers, burners, heat exchangers, incinerators, and the like, and function to protect boiler/condenser tubes used in the generation of power, steam, condensation, heat, and the like, for a variety of applications including power generation, manufacturing and production processes, such as found in the petrochemical industries. Boiler tubes carry air, water, steam or other fluid. Condenser tubes also carry fluids in the form of gasses and liquids. Boiler tubes are exposed to an extreme heat source in a combustion chamber. Condenser tubes may be used to convert gasses to liquids, such as steam to water for recycling back into a boiler, and may also be exposed to extreme temperatures. Hot air, and/or ignited fuel, is dispensed through burner tips into the combustion chamber from external fuel sources such as coal, natural gas, biomass, slag, and the like. Under these general circumstances the mixture of fuels is ejected through the burner tip and combined in the combustion chamber, possibly in the presence of ambient air. Inside the combustion chamber, the hot mixture of fuels comes in contact with the exterior surface of the tube shields, encasing the tube therein, which heats the fluid within the tube.

[0002] This is a form of heat exchange. Heat exchangers are most broadly defined as apparatuses that transfer heat from one medium to another, usually by conduction through a solid barrier. In this example of thermal communication, the heat is exchanged from the hot mixture of fuel and combustion gas in the combustion chamber to the fluids traveling through the boiler tubes. The heated fluid in the boiler tubes may then provide energy to turbines, or the like, for power, heat generation, and/or a variety of other applications. The combustion gas is frequently air, while the fuel can be coal, natural gas, wood, solid waste, medical waste, garbage, biomass, or the like.

[0003] The environment within the combustion chamber can be extremely corrosive and abrasive. The boiler tubes employed in the combustion chamber are commonly exposed to highly abrasive and corrosive environments. Exposure of the tubes to such environments often causes premature failure resulting in expensive maintenance and mounting boiler/facility downtime costs. Boiler tubes must be replaced regularly. It is also known that with boiler tubes of a refuse or solid waste incinerator-type boiler, the heat-conductive performance deteriorates when soot and slag attach to the tubes requiring cleaning, and acids generated by combustion corrode the tubes, which results in deterioration of the tubes and ultimate failure. In any case, exposed boiler tubes are subject to failure due to the hostile environment of the combustion chamber, and must be replaced frequently.

[0004] A tube shield, or its components, typically made of steel, low carbon steel, stainless steel, and/or other metals, or alloys thereof, may be attached to the surface of the boiler tubes to provide physical protection. These tube shields are typically used in an effort to reduce and delay corrosion and erosion which results in eventual failure of the boiler tubes. However, since such tube shields are readily corroded themselves with corrosive gases contained in exhaust gases, the tube shields themselves have durability of less than one year in the most hostile environments, and at worst they are corroded or eroded beyond useful life in less than three (3) months.

[0005] The tube shields cover the external surface of the boiler tubes, and are directly exposed to the extremely corrosive environment within the combustion chamber. While conventional tube shields are designed to increase the life of the boiler tubes, they are still subject to destruction due to the corrosive environment, and must be replaced regularly. Many shield type configurations have been devised to protect the tubes from hostile environments. One such configuration includes axially elongated protectors with half-circle cross sections. The shield is sized to fit over the boiler type tube to be protected. A strap may be used to hold the shields in place. U-bolts, mortar, interlocking configurations, welding, rod inserted through openings in adjacent shields, combinations thereof, and the like are also used.

[0006] It is conventional to protect boiler tubes in the path of the gas stream with tube shields. These shields may be semi-circular, elongate, and composed of stainless/steel members that are each secured to the tube by U-shaped clamps that extend around the back of the tube and are welded to the shields. It is not uncommon for tube shields to be stacked and separately clamped on a boiler tube with the objective of protecting the tube for longer periods. Conventional practice requires shutting down and opening the boiler for inspection and maintenance about every six (6) months to one and a half (1 1/2) years. Upon the first shutdown, typically several of the shields will have been so eroded that they have fallen off or need to be replaced; after the next shutdown, all of the shields on the tubes are usually removed and a new shield attached.

[0007] Coal fuel power plants use burner tips to inject hot/ignited fuel into combustion chambers, which are exposed to high temperatures and abrasion of high velocity coal particles plus slag movement. The exposed hard faced surfaces develop rough surfaces which increase eddy currents to the coal laden stream, thus reducing the velocity of flow. These eddy currents increase wear, because the stream is not moving in laminar flow, as well as affecting combustion dynamics, emissions, and chemical byproducts. Boiler tubes, and tube shields, exposed to this environment are corroded and eroded by the flow.

[0008] Also solid waste/garbage incinerators used in the generation of energy utilize boiler tubes within a combustion chamber. The high cost of energy has led society to extract usable heat from high thermal value waste streams. In some incinerator operations, a heated waste stream passes over conventional cross-flow metallic heat exchanger tubes containing clean ambient air. The ambient air is heated by the waste stream and then typically used as either facility or process heat. In other applications, such as solid waste incineration in which trash and garbage are incinerated to form gaseous products at temperatures up to 2500° F., water is passed through metallic tubes positioned within the gaseous product stream and converted to steam by the high temperatures. The steam produced by the tube assembly is then used to power a turbine-driven electrical generator, or to provide heat for commercial industrial use, such as building heat. The heated steam may then be condensed in a condenser tube for other work or to be recycled.

[0009] Tube shields for boiler tubes are known, and many configurations and designs have been developed. For example, U.S. Pat. No. 5,511,609 issued to Tyler on Apr. 30, 1996 discloses a tube shield with tongue and locking block assembly, wherein the tube shields are held in place using
straps. The Tyler invention is used for power generation and recovery boilers. The disclosed tube shields may be made of stainless steel.

[0010] U.S. Pat. No. 5,884,695 issued to Brownlee on Mar. 23, 1999 and assigned to American Magotteaux Corporation discloses boiler tube shields that interlock with each other to protect the weld of a securement strap used to secure the shields to boiler tubes in a power plant. These tube shields have semi-cylindrical tube members that terminate in first and second ends, the first end having a tongue portion and a stepped portion and the second end provided with a flanged portion and a pair of longitudinally extending bayonets. The securement strap is wound about overlapping tube, and interlocking tube shields, which are welded into place. Similarly, U.S. Pat. No. 6,065,532 also issued to Brownlee on May 23, 2000 and assigned to American Magotteaux Corporation teaches interlocking tube shields that are configured to protect the weld of a securement strap used to secure the shields to a boiler tube of a power plant. The heat shields of these Brownlee patents can be made of different materials depending upon the hostility of the environment in which they will be exposed. Different grades of stainless steel or nickel/chromium alloys may be used. The securement strap is preferably made of a stainless steel.

[0011] Efforts to reduce corrosion are also known. U.S. Pat. No. 7,066,242 issued to Ranville et al. on Jan. 27, 2006 disclose a sacrificial refractory tube shield assembly for use on a boiler tube in an effort to protect the underlying boiler tube from erosion by a stream of hot combustion gas containing particulates. The refractory shield assembly comprises: a semi-circular, elongate metal shield, a plurality of spaced apart anchors, whereby the refractory material is held on the shield by the anchors; and means, such as clamps, for securing the shield on a boiler tube. The refractory shield assembly is provided for the underlying boiler tube from erosion by a stream of hot combustion gas containing particulates.

[0012] U.S. Design Pat. No. D436,399 issued to Poland on Jan. 16, 2001 shows a design for a shield that appears to be one that would be applied to the outside of a burner or condenser pipe. Similarly, U.S. Design Pat. No. D437,044 issued to Poland on Jan. 30, 2001 also shows a design for a shield which appears to be one that would be applied to the outside of a burner or condenser pipe.

[0013] To prevent direct attack of the tubes by the products of combustion, while allowing the tubes to be superheated, the prior art has used refractory ceramic shields to cloak the tubes. The refractoriness of these shields provides for high thermal conductivity, integrity at high temperatures, erosion resistance and corrosion resistance. For example, U.S. Pat. No. 4,682,568 issued to Green et al. on Jul. 28, 1987 and assigned to Norton Company teaches a refractory shield for superheater tubes which are composed of a refractory material comprising a pair of elongated half shields of identical interchangeable interlocking size and shape. Each half shield has a semi-circular sidewall portion extending between and to diametrically opposite tongue and groove sidewall portions that are assembled together about the burner tube by axially inserting the tongues into the grooves. The burner shields of the Green et al. Patent are used to protect boiler super heater tubes from corrosive, erosive and abrasive action by the products of combustion during incineration of trash and garbage as fuel for the generation of energy.

[0014] The superheater tube shields, of the Green et al. Patent, are preferably nitride bonded silicon carbide refractory material made of 30% 30-90 mesh green silicon carbide, 17% 100 mesh and finer green silicon carbide, 35% 3 microns green silicon carbide, and 18% 200 and finer mesh silicon metal powder mixed with 12% water and 0.75% sodium silicate defloculant solution, and dried/fired in a mold at 1450°C. in a kiln with a nitrogen atmosphere until cured. A refractory cement disclosed in the Green et al. Patent is a mixture of 85% by weight of 10 mesh size and finer size particles of green silicon carbide and 15% of calcium alumin mixed together and with 10-15% water to form a plastic mortar. Upon firing during operation of the incinerator the mortar becomes a bonded silicon carbide layer between the tube shield and the super heater burner tubes.

[0015] U.S. Pat. No. 5,724,923 (*'923) issued to Green on Mar. 10, 1998 and assigned to Saint-Gobain/Norton Industrial Ceramics Corporation teaches a refractory tube shield design for superheater tubes, having first and second partial-tubes with C-shaped cross-sections, wherein the ends of the partial-tubes are opposably engaged and coupled with some anti-rotation means. The shields of the '923 invention may be made of material typically used as a superheater tube shield, including silicon carbide, alumina, zirconia, magnesia, chromia, and mixtures thereof. Preferably, the shields are made of nitride bonded silicon carbide whose silicon carbide component is made from mixing 30% of 30-90 mesh green silicon carbide, 17% of -100 mesh green silicon carbide, 35% of micron silicon carbide and 18% of -200 mesh silicon metal powder mixed with 12% water and 0.75 sodium silicate defloculant, and molded into shape.

[0016] U.S. Pat. No. 5,881,802 (*'802) issued to Green on Mar. 16, 1999, and also assigned to Saint-Gobain Industrial Ceramics, Inc. teaches a refractory shield design for superheater tubes to protect the superheater tube against fluid attack comprising first and second partial-tubes, each partial-tube having a C-shaped cross section, the C-shaped cross section defining first and second ends; wherein the partial-tubes comprise means for preventing radial movement of the first partial-tube relative to the second partial-tube.

[0017] The tube shields of the '802 patent may be made of any refractory material typically used as a superheater tube shield, including silicon carbide, alumina, zirconia, magnesia, chromia, and mixtures thereof. In preferred embodiments, the shields are made from a nitride bonded silicon carbide whose silicon carbide component is made from mixing 30% of 30-90 mesh green silicon carbide, 17% of -100 mesh green silicon carbide, 35% of 3 micron silicon carbide and 18% of -200 mesh silicon metal powder. This mixture is then mixed with 12% water and 0.75% sodium silicate defloculant and poured in a mold to form the desired shape. A mortar is commonly used to bond the tube shields to the superheater tubes having a silicon carbide-based mortar containing silica, alumina and aluminas.

[0018] U.S. Pat. No. 6,136,117 (*'117) issued to Shibata et al. on Oct. 24, 2000 and assigned to NGK Insulators, Ltd. and Mitsubishi Heavy Industries, Ltd. teaches a boiler tube protector and a method for attaching such protector to a boiler tube. The boiler tube protector has a cylindrical or semi-cylindrical shape around an outer peripheral face of a boiler tube with mortar, which boiler tube protectors, are a plurality of ceramic bodies closely arranged along their parting planes, wherein the parting planes include means for restraining slippage of each of the ceramic bodies along the parting planes. In order to minimize reduction in heat conductivity of that por-
tion of the boiler tube at which the boiler tube protector is attached, it is preferable to select a ceramic material having excellent heat conductivity.

[0019] Similarly, U.S. Pat. No. 6,152,087 ("087") issued to Shibata et al. on Nov. 28, 2000 and assigned to NGK Insulators, Ltd. teaches a boiler tube protector which has a plurality of ceramic bodies closely arranged along their parting planes, wherein the parting planes include a restraining portion for restraining slippage of each of the ceramic bodies. As such, ceramic material for both "117" and "087" has both corrosion resistance and heat conductivity, SiC was selected by way of example. As mortar to attach the boiler tube protector to the outer peripheral face of the boiler tube, SiC based mortar, mullite based mortar, alumina based mortar or the like may be used. A SiC based mortar was preferred. Ceramic fibers may also be used instead of a part or an entire part of the ceramic material. The ceramic fibers may be used in a mixed state with mortar, or appropriate ceramic fiber-based mortar may be used for this purpose.

[0020] Examples of tube shields that may be used with heat exchangers, either boilers or condensers, are shown in U.S. Pat. Nos. 5,154,648 and 5,474,123 issued to Buckshaw on Oct. 13, 1992 and Dec. 12, 1995 respectively which show tube shields designed to encase individual tubes. U.S. Pat. No. 5,094,292 also issued to Buckshaw on Mar. 10, 1992 shows a tube shield designed to shield multiple tubes at the same time which is composed of a shield with a J-shaped profile that hangs like a sheet from a top tube,

**SUMMARY OF THE INVENTION**

[0021] The present invention is drawn to an improved heat exchanger, and in particular, to improved heat exchangers which use tube shields to protect tubes within the heat exchangers. Alternative embodiments of the present invention are drawn to tube shields used in boilers and in condensers. Embodiments of the present invention are further drawn to improved combustion chambers, typically found in utility, power, heat, steam and hot water generation, and other furnaces, for example, and improved components thereof. Embodiments of the present invention contain tube shields having thermal protective layers on at least one exposed surface thereof. The tube shields are disposed over tubes that carry water, steam or other fluid to perform some work. The tube shields used to protect boiler tubes are directly or indirectly exposed to hot, and/or ignited combustible fluids, including pulverized coal, to heat the fluid contained within the boiler tubes. These applications included energy generation from coal, waste, biomass, black liquor, pulp, paper furnaces, and the like. Alternatively, cooler fluids may be circulated through the tubes to generate a cooler temperature along the outer surface of the tubes in which condensation forms on the tube shields disposed to protect the outside surface of the tubes, or the tubes may deliver hot fluids, including steam, through a cooler environment to condense the fluids within the tubes. The present invention is described in terms of heat shields used in boiler tubes disposed within combustion chambers, but is seen to encompass all forms of tube shields consistent with the present disclosure whether used in boilers, condensers, other heat exchangers, and the like.

[0022] A thermal protective layer on at least one exposed metallic/alloy surface of a burner tube shield according to an embodiment of the present invention may contain from about 5% to about 40% of an inorganic adhesive, from about 45% to about 92% of a filler, and from about 1% to about 20% of one or more emissivity agents. An alternative thermal protective layer on at least one exposed ceramic surface of a burner tube shield according to another embodiment of the present invention may contain from about 5% to about 60% of colloidal silica, colloidal alumina, or combinations thereof, from about 23% to about 79% of a filler, and from about 1% to about 20% of one or more emissivity agents. A thermal protective layer of the present invention may further contain from about 1% to about 5% of a stabilizer. A surfactant or colorant may also be present therein.

[0023] An aspect of the present invention is to extend the effective repair and replacement cycles of the heat exchangers and combustion chambers, especially tubes and tube shields. The overall cost of the utility is reduced by the concomitant reduction in maintenance costs.

[0024] The present invention extends the effective lifespan of conventional tube shields and tubes. Furthermore, it reduces down time and repair costs.

[0025] An aspect of the present invention is to reduce the overall costs of operating heat exchangers or combustion chambers. Cost savings are found in the materials for replacing the damaged tubes and tube shields, in the reduction of employee work load needed to replace the tubes and tube shields, and in reduced facility downtime and economic loss.

[0026] These and other aspects of the present invention will become readily apparent upon further review of the following drawings and specification.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0027] The novel features of the described embodiments are specifically set forth in the appended claims; however, embodiments relating to the structure and process of making the present invention, may best be understood with reference to the following description and accompanying drawings.

[0028] FIG. 1 shows a schematic perspective view of a tangentially fired combustion chamber containing tube shield encased boiler tubes, according to an embodiment of the present invention.

[0029] FIG. 2A shows a straight tube with two opposing straight tube shields disposed about the tube, according to an embodiment of the present invention.

[0030] FIG. 213 shows a U-shaped part of a tube with opposing fitted inner and outer tube shields thereon, according to an embodiment of the present invention.

[0031] FIG. 3 shows a diagrammatical perspective view of a burner tip extending from a plenum which might be used with an embodiment of the present invention.

[0032] FIG. 4A is a cutaway view of a tube shield with a thermal protective layer disposed on the exterior surface thereof according to an embodiment of the present invention.

[0033] FIG. 4B is a cutaway view of an outer fitted tube shield designed to go around a U-turn in the tubes wherein the thermal protective layer is disposed on both the exterior and interior surfaces, and along the edges of the shield according to an embodiment of the present invention.

[0034] FIG. 5A is a cross sectional side view of a tube shield having a thermal protective layer disposed on the exterior surface thereof, according to an embodiment of the present invention,

[0035] FIG. 5B is a cross sectional side view of a tube shield having a thermal protective layer disposed on the exterior and interior surfaces thereof, according to an embodiment of the present invention.
FIG. 5C is a cross sectional side view of a tube shield having a thermal protective layer disposed on the entire external surface thereof, including the edges, according to an embodiment of the present invention.

FIG. 6A is a cross sectional side view of an alternative embodiment of a tube shield according to the present invention in which the thermal protective layer is disposed on the external and internal surfaces of the tube shield.

FIG. 6B is a cross sectional side view of yet another alternative embodiment of a tube shield according to the present invention in which the thermal protective layer is disposed on the external surface of the tube shield.

FIG. 7 is a schematic perspective view of a combustion chamber containing burner tube shield encased burner tubes, according to an exemplary alternative embodiment of the present invention.

Similar reference characters denote corresponding features consistently throughout the attached drawings.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is described herein in light of a tangentially fired coal-burning furnace utilizing half shell tube shields 12, graphically represented in FIGS. 1, 1A, 2B, 4A, 4B, 5A, 5B, 5C, and 7 by example only, and is not limited to such a furnace and tube shield 12 designs, or applications. In a tangentially fired furnace, burner tips 16, shown in FIG. 3, may be located at each corner of a combustion chamber 10 having a square-shaped floor/ceiling. The axis of each burner tip 16 may be offset with respect to a central axis of the combustion chamber 10 and extend generally tangent to an imaginary cylinder, which defines a combustion zone 20, as shown in FIG. 1, where a fireball is generated during operation of the burner tips 16. Burner tips 16 are also customarily referred to simply as “burners”. Tangentially fired furnaces are used to heat many utility boilers, especially for the generation of energy from fossil fuel sources such as coal, propane, oil, petroleum, natural gas, peat, wood, wood chips, solid waste, other biomass, and the like, and combinations thereof. Alternative fuel sources include, but are not limited to, waste incineration and biofuels.

In the tangentially fired furnace of the present example, the tube shields 12 and 14, which are disposed on the boiler tubes 22 and 24 as shown in FIGS. 2A and 2B, are depicted at the top of the combustion chamber 10 in FIG. 1. The burner tips 16 are shown extending tangentially into the combustion chamber 10. In this example, the burner tips 16 are disposed in parallel groups with one set on top of a second set, as shown in FIG. 1. The combustion chamber 10 is shown diagrammatically shorter in the vertical relative to the horizontal than in actual use, as is well known in the art. The combustible fluids flow 18 into the chamber 10, and the heat in the combustion zone 20 rises to bathe the tube shield 12 and 14 and their encased boiler tubes 22 and 24 with heat. The fluid within the boiler tubes 22 and 24 flows through the combustion chamber 10 and is heated before flowing out of the combustion chamber 10. The inlet and outlet of the boiler tubes 22 and 24 are not shown but are well understood in the art. The entire assembly of boiler tubes 22 and 24, and their tube shields 12, 14 and 15, within the combustion chamber 10 may collectively be referred to as a boiler tube rack.

FIGS. 2A and 2B are schematic depictions of tubes 22 and 24 with tube shields 12, 14 and 15 having an high emissivity protective layer 32 depicted thereon. The tubes 22 and 24 each have a straight part 22 and a U-part 24 permitting tight packing of the tube shield 12, 14 or 15 encased tubes 22 and 24. The straight tube shields 12 fit over the straight part 22 of the tubes as shown in FIG. 2A. The U-part 24 is encased by the fitted tube shields 14 and 15 where the outside part of the U-part 24 is encased by the first fitted tube shield 14 and the inside part of the U-part 24 is encased by the second fitted tube shield 15. Although, the entire burner tube rack may be encased by these three burner tube shields 12, 14 and 15, the present invention is not limited to the precise configuration of burner shields depicted in the figures.

Various applications and designs such as whole or 360 degree cover tube shields, shown diagrammatically in cross section in FIGS. 6A and 6B, as examples, are also known in the art, and the present invention encompasses these variations of tube shields 12 as well. A further example of an alternative embodiment of a tube shield is shown in U.S. Pat. No. 5,582,212, the contents of which are incorporated herein by reference in their entirety. The thermal protective layer 32 may be disposed upon burner tube shields which have a variety of configurations including wrap-style tube shields that are in long strips which wrap around the tubes. Exemplary, alternative designs and configurations of burner tube shields are well known and include the designs depicted hereinbefore in the background of the invention among others.

FIG. 3 is a schematic diagram of a burner tip 16 which is used to eject combustible fluids into a combustion zone 20. The burner tip 16 depicted has several fluid vents 28 and a plenum 26 extending therefrom. The plenum 26 (or duct work) delivers the combustible fluids to the burner tip 16. The plenum 26 may deliver more than one combustible fluids to the burner tip 16, and the burner tip 16 may have fluid vents 28 which are in fluid communication through the plenum 26 to several separate combustible fluids which are mixed either within the burner tip 16 or just outside the burner tip 16 within the combustion chamber 10, as is well known in the industry.

Combustible fluids include the medium in which other combustible fluids flow or need to burn. For example, air is necessary for combustion and may be delivered to the combustion chamber 10 through the burner tips 16. Alternatively, water or other liquid may be used to deliver pulverized fuel to the combustion chamber 10. Furthermore, hot fluid may also be used in some embodiments where the boiler tubes 24 and tube shields 12 are bathed in hot fluids, including water and steam.

FIG. 4A depicts a generalized straight tube shield 12 having a thermal protective coating 32 disposed only on the outer surface of the support layer 30. FIG. 4B shows a first fitted tube shield 14 having the thermal protective layer 32 covering the entire surface thereof including the outer and inner surfaces of the support layer 30 and also along the edges thereof, as shown. The support layer 30 is typically comprised of metal or alloys of metals, including steel, low and high carbon steel, stainless steel, iron, aluminum, and alloys. Alternative embodiments may include tube shields having ceramic support layers 30.

FIGS. 5A through 5C show alternative embodiments of the present invention. FIG. 5A is a cross sectional side view of a half-circle tube shield 12 having a thermal protective layer 32 disposed on the exterior surface of the support layer 30 of the tube shield 12. FIG. 5B is a cross sectional side view of a tube shield 12 having a thermal protective layer 32 disposed on the exterior and interior sur-
faces of the tube shield 12. FIG. 5C is also a cross sectional side view of a tube shield 12 having a thermal protective layer 32 disposed on the entire exterior and interior surfaces, and along the edges thereof.

[0049] Alternative tube shield designs, according to an embodiment of the present invention, include thermal protective layered tube shields 17 that cover the entire circumference of the tube, shown in FIGS. 6A and 6B without the tube disposed therein. FIG. 6A is a cross sectional side view of such an alternative embodiment of a thermal protected tube shield 30 according to the present invention in which the thermal protective layer is disposed on the external and internal surfaces of the tube shield 30. FIG. 6B is a cross sectional side view of yet another alternative embodiment of a tube shield 30 according to the present invention in which the thermal protective layer 32 is disposed on the external surface of the tube shield 30.

[0050] FIG. 7 is a schematic perspective view of a combustion chamber 10 containing tube shields 12 encasing boiler tubes 24, according to an exemplary alternative embodiment of the present invention. Various combustion chambers 10 are known in the art and the present invention is not limited to combustion chambers 10 or furnace designs, and includes alternative heat exchangers.

[0051] The thermal protective layer 32 may be applied as a high emissivity thermal protective coating. Suitable coatings and methods of application are described in U.S. Pat. Nos. 7,105,047 and 6,921,431 and assigned to Wessex Incorporated, the contents of which are incorporated herein in their entirety.

[0052] A thermal protective layer 32 on at least some of the exposed metal/alloy surfaces of the tube shields 12 of the present invention may contain from about 5% to about 40% of an inorganic adhesive, from about 45% to about 92% of a filler, and from about 1% to about 20% of one or more emissivity agents. The thermal protective layer 32 may contain from about 1% to about 5% of a stabilizer. A surfactant and/or colorant may also be present.

[0053] An alternative thermal protective layer 32 on ceramic surfaces of the tube shields 12 according to an embodiment of the present invention may contain from about 5% to about 60% of colloidal silica, colloidal alumina, or combinations thereof, from about 23% to about 79% of a filler, from about 1% to about 20% of one or more emissivity agents. A thermal protective layer 32 of the present invention may also contain from about 1% to about 5% of a stabilizer. A surfactant and/or colorant may also be present.

[0054] As used herein, all percentages (%) are percent weight-to-weight, also expressed as weight/weight %, % (w/w), w/w, w/w % or simply %, unless otherwise indicated. Also, as used herein, the terms “wet admixture” refers to relative percentages of a composition of a thermal protective coating in solution and “dry admixture” refers to the relative percentages of the composition of the dry thermal protective layer. In other words, the dry thermal protective layer or a dry admixture of percentages are those present without taking water into account. Wet admixture refers to the admixture in solution (with water). “Wet weight percentage” is the weight in a wet admixture, and “dry weight percentage” is the weight in a dry admixture without regard to the wet weight percentages. The term “total solids”, as used herein, refers to the total sum of the silica/alumina and the alkali or ammonia (NH₃), plus the fraction of all solids including impurities. Weight of the solid component divided by the total mass of the entire solution, times one hundred, yields the percentage of “total solids”.

[0055] Additionally, as used herein, the term “fuel” includes pulverized solids, such as coal, natural gas, solid biofuels, other petroleum products, solid wastes, and the like, and combinations thereof, which are commonly used in the generation of power and heat. The term “fluid” includes fuel, air, water, steam, and the like, whether in gaseous or liquid state. The present invention is described herein by way of tube shields used for boiler tubes; however, the present invention encompasses any such shields, including those used in other heat exchangers such as for example condenser tubes.

[0056] Method of preparation of coating involves applying a wet admixture of the coating to the surface to be coated. Alternative methods may include spraying the wet admixture on the surface or atomizing the dry admixture and coating the surface accordingly. The dry admixture is the same as the composition of the thermal protective layer 32 once it has dried.

[0057] In a coating solution to be applied to metal/alloy support layer surfaces of tube shields according to alternative embodiments of the present invention, a wet admixture of the thermal protective coating contains from about 6% to about 40% of an inorganic adhesive, from about 23% to about 56% of a filler, from about 0.5% to about 15% of one or more emissivity agents, and from about 18% to about 50% of water. In order to extend the shelf life of the coating solution, from about 0.5% to about 2.5% of a stabilizer may be added to the wet admixture. Up to about 1.0% of a surfactant may also be added. The wet admixture coating solution may contain between about 40% and about 60% total solids.

[0058] In a coating solution to be applied to ceramic tube shields according to additional alternative embodiments of the present invention, a wet admixture of a thermal protective coating contains from about 15% to about 60% of colloidal silica, colloidal alumina, or combinations thereof, from about 23% to about 55% of a filler, from about 0.5% to about 15% of one or more emissivity agents, from about 0.5% to about 2.5% of a stabilizer and from about 10% to about 40% water. The wet admixture coating solution contains between about 40% and about 70% total solids.

[0059] The inorganic adhesive is preferably an alkali/alkaline earth metal silicate taken from the group consisting of sodium silicate, potassium silicate, calcium silicate, and magnesium silicate. The colloidal silica is preferably a mono-dispersed distribution of colloidal silica, and therefore, has a very narrow range of particle sizes. The filler is preferably a metal oxide taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide and boron oxide. The emissivity agent is preferably taken from the group consisting of silicon hexaboride, carbon tetraboride, silicon tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chrome, and metallic oxides such as iron oxides, magnesium oxides, manganese oxides, copper chromium oxides, chromium oxides, cerium oxides, terbium oxides, and derivatives, and combinations thereof. The copper chromium oxide, as used in the present invention, is a mixture of cupric chrome and cupric oxide. The stabilizer may be taken from the group consisting of bentonite, kaolin, magnesia alumina silica clay, tabular alumina, and stabilized zirconium oxide. The stabilizer is preferably bentonite. Other bull clay stabilizers may be substituted herein as a
stabilizer. Colloidal alumina, in addition to or instead of colloidal silica, may also be included in the admixture of the present invention. When colloidal alumina and colloidal silica are mixed together one or the other requires surface modification to facilitate mixing, as is known in the art.

The corresponding coating in solution (wet admixture) for this embodiment contains from about 20.0% to about 35.0% colloidal silica, from about 25.0% to about 55.0% silicon dioxide, from about 18.0% to about 35.0% water, and from about 2.0% to about 7.5% one or more emittance agent(s), and from about 0.50% to about 2.50% bentonite powder. Preferably deionized water is used. Preferred embodiments of the wet admixture have a total solids content ranging from about 50% to about 65%.

A most preferred thermal protective coating of the present invention contains a dry admixture from about 15.0% to about 35.0% colloidal silica, from about 68.0% to about 78.0% silicon dioxide powder, about 2.00% to about 4.00% bentonite powder, and from about 4.00% to about 6.00% of an emittance agent. The emittance agent is taken from one or more of the following: zirconium boride, boron silicide, and boron carbide.

A most preferred wet admixture contains about 27.0% colloidal silica based on a colloidal silica solids content of about 40%, from about 25% to about 50% silicon dioxide powder, about 1.50% bentonite powder, and from about 2.50% to about 5.50% of an emittance agent, with the balance being water. The emittance agent is most preferably taken from the group consisting of zirconium boride, boron silicide, and boron carbide. Preferred embodiments include those where the emittance agent comprises about 2.50% zirconium boride, about 2.50% boron silicide, or from about 2.50% to about 7.50% boron carbide. The specific gravity of a most preferred wet admixture is about 1.40 to 1.50 and the total solids content is about 50% to about 60%.

An inorganic adhesive, which may be used in the present invention, includes N (trademark) type sodium silicate that is available from the PQ Corporation (of Valley Forge, Pa.). Sodium silicate, also known as waterglass, is a versatile, inorganic chemical made by combining various ratios of sand and soda ash (sodium carbonate) at high temperature. Sodium silicates (Na₂O·nSiO₂) are metal oxides of silica. All soluble silicates can be differentiated by their ratio, defined as the weight proportion of silica to alkali (SiO₂ / Na₂O). Ratio determines the physical and chemical properties of the coating. The glassy nature of silicates imparts strong and rigid physical properties to dried films or coatings. Silicates air dry to a specific moisture level, according to ambient temperature and relative humidity. Heating is necessary to take these films to complete dryness—a condition in which silicates become nearly insoluble. Reaction with other materials, such as aluminum or calcium compounds, will make the film coating completely insoluble. The N (trademark) type sodium silicate, as used in the examples below, has a weight ratio SiO₂ / Na₂O is 3.22, 8.90% Na₂O, 28.70% SiO₂, with a density (at room temperature of 20°C) of 41.00 lb/gal, 11.6 lb/gal or 1.38 g/cm³. The pH is 11.3 with a viscosity of 180 centipoises. The N type sodium silicate is in a state of a syrupy liquid.

The term “total solids” refers to the sum of the silica and the alkali. The weight ratio is a most important silicate variable. Ratio determines the product solubility, reactivity and physical properties. Ratio is either the weight or molar proportion of silica to alkali. Density is an expression of total solids and is typically determined using a hydrometer or a pycnometer.

Ludox (trademark)™ 50 colloidal silica are available from Grace Davidson (of Columbia, Md.). The particles in Ludox (trademark) colloidal silica are discrete uniform
spheres of silica which have no internal surface area or detectable crystallinity. Most are dispersed in an alkaline medium which reacts with the silica surface to produce a negative charge. Because of the negative charge, the particles repel one another resulting in stable products. Although most grades are stable between pH 8.5-11.0, some grades are stable in the neutral pH range. Ludox (trademark) colloidal silica is aqueous colloidal dispersions of very small silica particles. They are opalescent to milky white liquids. Because of their colloidal nature, particles of Ludox (trademark) colloidal silica have a large specific surface area which accounts for the novel properties and wide variety of uses. Ludox (trademark) colloidal silica is available in two primary families: monodispersed, very narrow particle size distribution of Ludox (trademark) colloidal silica and poly-dispersed, broad particle size distribution of Ludox (trademark) P. The Ludox (trademark) colloidal silica is converted to a dry solid, usually by gelation. The colloidal silica can be gelled by (1) removing water, (2) changing pH, or (3) adding a salt or water-miscible organic solvent. During drying, the hydroxyl groups on the surface of the particles condense by splitting out water to form siloxane bonds (Si—O—Si) resulting in coalescence and interbonding. Dried particles of Ludox (trademark) colloidal silica are chemically inert and heat resistant. The particles develop strong adhesive and cohesive bonds and are effective binders for all types of granular and fibrous materials, especially when use at elevated temperature is required.

[0072] Colloidal alumina is available as Nynacol (trademark) colloidal alumina available from Nynacol Nano Technologies, Inc. (Ashland, Mass.), and is available in deionized water to reduce the sodium and chlorine levels to less than 10 ppm. Nynacol may contain about 20 percent by weight of Al₂O₃, a particle size of 50 nm, positive particle charge, pH 4.0, specific gravity of 1.19, and a viscosity of 10 cPs.

[0073] The filler may be a silicon dioxide powder such as Min-U-Sil (trademark) silicon dioxide available from U.S. Silica (of Berkeley Springs, W. Va.). This silicon dioxide is fine ground silica. Chemical analysis of the Min-U-Sil (trademark) silicon dioxide indicates contents of 98.5% silicon dioxide, 0.06% iron oxide, 1.1% aluminum oxide, 0.02% titanium dioxide, 0.04% calcium oxide, 0.03% magnesium oxide, 0.03% sodium oxide, 0.03% potassium oxide and a 0.4% loss on ignition. The typical physical properties are a compacted bulk density of 41 lbs/ft³, an uncompacted bulk density of 36 lbs/ft³, a hardness of 7 Mohs, a median diameter of 1.7 microns, an oil absorption (D-1483) of 44, a pH of 6.2, 97%-5 microns, 0.005%<325 Mesh, a reflectance of 92%, a 4.2 yellowness index and a specific gravity of 2.65.

[0074] Emittance agents are available from several sources. Emissivity is the relative power of a surface to emit heat by radiation, and the ratio of the radiant energy emitted by a surface to the radiant energy emitted by a blackbody at the same temperature. Emissance is the energy radiated by the surface of a body per unit area.

[0075] The boron carbide (B₃C), also known as carbon tetraboride, which may be used as an emissivity agent in the present invention, is available from Electro Abrasives (of Buffalo, N.Y.). Boron Carbide is one of the hardest man made materials available. Above 1300° C., it is even harder than diamond and cubic boron nitride. It has a four point flexural strength of 50,000 to 70,000 psi and a compressive strength of 414,000 psi, depending on density. Boron Carbide also has a low thermal conductivity (29 to 67 W/mK) and has electrical resistivity ranging from 0.1 to 10 ohm-cm. Typical chemical analysis indicates 77.5% boron, 21.5% carbon, iron 0.2% and total Boron plus Carbon is 98%. The hardness is 2800 Knoop and 9.6 Mohs, the melting point is 4262° F. (2350° C.), the oxidation temperature is 952° F. (500° C.), and the specific gravity is 2.52 g/cc.

[0076] Green silicon Carbide (SiC), an optional emissivity agent, is also available from Electro Abrasives. Green Silicon Carbide is an extremely hard (Knoop 2600 or Mohs 9.4) man made mineral that possesses high thermal conductivity (100 W/m-K). It also has high strength at elevated temperatures (at 1110° C., Green SiC is 7.5 times stronger than Al₂O₃. Green SiC has a Modulus of Elasticity of 410 GPa, with no decrease in strength up to 1600° C., and it does not melt at normal pressures but instead dissociates at 2815.5° C. Green silicon carbide is a batch composition made from silica sand and coke, and is extremely pure. The physical properties are as follows for green silicon carbide: the hardness is 2600 Knoop and 9.4 Mohs, the melting point is 4712° F. (2600° C.), and the specific gravity is 3.2 g/cc. The typical chemical analysis is 99.5% SiC, 0.2% SiO₂, 0.03% total Si, 0.04% total Fe, and 0.1% total C. Commercial silicon carbide and molybdenum disilicide may need to be cleaned, as well known in the art, to eliminate flammable gas generated during production.

[0077] Boron silicide (B₃Si) is available from Cerac (of Milwaukee, Wis.). The boron silicide, also known as silicon hexaboride, available from Cerac has a ~200 mesh (about 2 microns average) and a typical purity of about 98%. Zirconium boride (ZrB₂) (Item# Z-1031) is also available from Cerac with a typical average of 10 microns or less (~325 mesh), and a typical purity of about 99.5%. Iron oxide available from Hoover Color (of Hiwassee, Va.) is a synthetic black iron oxide (Fe₃O₄) which has an iron oxide content of 60%, a specific gravity of 4.8 gm/cc, a tap density (also known as bulk density) of 1.3 gm/cc, oil absorption of 15 lbs/100 lbs, a 325 mesh residue of 0.005, and a pH ranging from 7 to 10.

[0078] The admixture may include bentonite powder, tabular alumina, or magnesium alumina silicate clay. The bentonite powder permits the coating to be prepared and used at a later date. Otherwise, the coating must be applied to the support layer as soon as mixed. The examples provided for the present invention include Polargel bentonite powder available from Mineral and Pigment Solutions, Inc. (of South Plainfield, N.J.). Bentonite is generally used for the purpose of suspending, emulsifying and binding agents, and as Theological modifiers. The typical chemical analysis is 59.00% to 61.00% of silicon dioxide (SiO₂), 20.00% to 22.00% of aluminum oxide (Al₂O₃), 2.00% to 3.00% calcium oxide (CaO), 3.50% to 4.30% magnesium oxide (MgO), 0.60% to 0.70% ferric oxide (Fe₂O₃), 3.50% to 4.00% sodium oxide (Na₂O), 0.02% to 0.03% potassium oxide (K₂O), and 0.10% to 0.20% titanium dioxide and a maximum of 8.0% moisture. The pH value ranges from 9.5 to 10.5. Typical physical properties are 83.0 to 87.0 dry brightness, 2.50 to 2.60 specific gravity, 20.82 pounds/solid gallon, 0.0480 gallons for one pound bulk, 24 ml minimum swelling power, maximum 2 ml gel formation, and 100.00% thru 200 mesh. Tabular alumina and magnesium alumina silicate clay are also available from Mineral and Pigment Solutions, Inc.

[0079] Colorants, which may be added to the present invention, include but are not limited to inorganic pigments. Suitable inorganic pigments, such as yellow iron oxide, chromium oxide green, red iron oxide, black iron oxide, titanium
dioxide, are available from Hoover Color Corporation. Additional suitable inorganic pigments, such as copper chromite black spinel, chromium green-black hematite, nickel antimony yellow rutile, manganese antimony titanium buff rutile, and cobalt chrome blue-green spinel, are available from The Shepherd Color Company (of Cincinnati, Ohio).

A surfactant may be added to the wet admixture prior to applying the thermal protective layer to the tube shield or plenum. The surfactant was Surlynol (trademark) available from Air Products and Chemicals, Inc. (of Allentown, Pa.). The Surlynol (trademark) has a chemical structure of ethoxylated 2,4,7,9-tetramethyl 5 decyn-4,7-diol. Other surfactants may be used, such as STANDAPOl (trademark) T, INCI which has a chemical structure of triethanolamine lauryl sulfate, liquid mild primary surfactant available from Cognis-Care Chemicals (of Cincinnati, Ohio). The amount of surfactant present by weight in the wet admixture is from about 0.05% to about 0.2%.

The thermal protective layer on the tube shields. The surface may be a metallic substrate such as iron, aluminum, alloys, steel, cast iron, stainless steel, and the like, or it may be a ceramic surface. Ceramic and metal/ alloy surfaces of tube shields and exposed surfaces within the chamber are well known in the art. The coating is typically applied wet, and either allowed to air dry, heat dry, or dry upon facility start up.

The coating is typically applied directly to the support structure 30. The preparation of the tube shield support structure 30 involves surface preparation, preparation of thermal protective coating, and application of the thermal protective coating to the surface of the support layer 30 of the tube shield. First, preparation of the surface occurs. The surface is prepared first by grit blasting and then cleaning the surface. Grit blasting is desirable to remove oxidation and other contaminants. Grit media should be chosen depending on metal type, and may include aluminum oxide, glass beads, black beauty, and the like.

Gun pressure will vary depending on the cut type, condition of the metal and profile desired; very old metal requires 60-80 psi; while newer metal may only require 40-60 psi. Oil free air should be used. The surface then cleaned after the grit blasting, the surface should be thoroughly cleaned to remove all loose particles with air blasts. Acetone can also be used on a clean cloth to wipe the surface clean. Acetone should be used under proper ventilation and exercising all necessary precautions. A cleaning compound may be used on certain stainless steel surfaces in lieu of grit blasting.

After the grit blast, the surface should be thoroughly cleaned to remove all loose particles with clean oil and water free air blasts. Avoid contaminating surface with fingerprints. Acetone can be used (under proper ventilation and exercising all necessary precautions when working with acetone) on a clean cloth to wipe the surface clean. A cleaning compound may be used on certain stainless steel in lieu of grit blasting. Durum available from Blue Wave Ultrasomics (of Davenport, Iowa), a powdered alkaline cleaner, may be used in cleaning metal surface instead of, or in addition to, acetone.

When using the wet admixture containing a stabilizer, solids may settle during shipment or storage. Prior to use all previously mixed coating must be thoroughly re-mixed to ensure all settled solids and clumps are completely re-dispersed. When not using a stabilizer, the coating may not be stored for any period of time. In any case, the coating should be used immediately after mixing to minimize settling.

Mixing instructions for one and five gallon containers. High speed/high shear saw tooth dispersion blade 5" diameter for one gallon containers and 7" diameter for five gallon containers may be attached to a hand drill of sufficient power with a minimum load speed of 2000 rpm shear. Dispersion blades can be purchased from numerous suppliers. Mix at high speed to ensure complete re-dispersion for a minimum of 30 minutes.

The product should be applied directly after cleaning a metal surface so minimal surface oxidation occurs. The product should be applied in a properly ventilated and well lit area, or protective equipment should be used appropriate to the environment, for example within the combustion chamber 10. The mixed product should not be filtered or diluted.

A high volume low pressure (HVLP) spray gun should be used with 20-40 psi of clean, oil and water free air. Proper filters for removal of oil and water are required. Alternatively, an airless spray gun may be used. Other types of spray equipment may be suitable. The applicator should practice spraying on scrap metal prior to spraying the actual part to ensure proper coverage density. An airless sprayer system is preferable for applications on ceramic surfaces such as the refractory materials. Suitable airless spray systems are available from Graco (of Minneapolis, Minn.). Suitable HVLP spray systems, which are desirable for metal/ alloy process tubes, are available from G.H. Reed Inc. (of Hanover, Pa.). A high speed agitator may be desirable. Suitable spray gun tips may be selected to provide the proper thickness without undue experimentation.

Controlling the coverage density may be critical to coating performance. Dry coating thickness should be from about two (2) mils (about 50 microns (i)) to about ten (10) mils (about 255 μ), depending upon type, size and condition of substrate. One (1) mil equals 25.4 μ. Proper thickness may vary. If possible, rotate the part 90 degrees at least once to maintain even coverage. Allow 1 to 4 hours of dry time before the part is handled, depending upon humidity and temperature.

The tube shields 12, 14, 15, and 17 at the very least have a thermal protective layer 32 on the external surface thereof, but may also have the thermal protective layer 32 disposed on the entire surface, or on both the external and internal surfaces. The core surfaces of the tube shields 12, 14, 15, and 17 are not in direct contact or adjacent to the enclosed tubes. The internal surface of the tube shields 12, 14, 15, and 17 is the part that comes in direct contact with the boiler or condenser tubes. The edge of the tube shields are the part of the tube shields 12, 14 and 15 which mate with or contact adjacent tube shields 12, 14 and 15. Any braces, such as straps and the like, used with tube shields may also have a thermal protective layer disposed thereon. Further embodiments of the tube shields include shields which substantially cover the burner tube by wrapping around the burner tube, and others have a flexible construction forming a sleeve fitting over and covering most of the surface of the tube shield for 360 degrees, as shown in cross section in FIGS. 6A and 6B. The present invention is seen to include all types of tube shields having a protective layer on at least one surface thereof.

Prior to application of a thermal protective coating to the prepared surface, the thermal protective coating should
be thoroughly remixed to ensure all settled solids and clumps are completely redispersed. Also, the remixed thermal protective coating should be used promptly after remixing to minimize settling. To mix, a high speed/high shear dispersion blade should be attached to a hand drill of sufficient power with a minimum speed of 2300 rpm. Dispersion blades can be purchased from numerous suppliers. The thermal protective coating is prepared by mixing at high speed while moving the blade up and down inside the coating's container to ensure complete redispersion for a minimum of 10 minutes. Alternative equivalent mixing procedures may be used.

It is desirable to apply the thermal protective coating to the surface directly after cleaning the surface so minimal surface oxidation occurs. The prepared surface should be at, or near, room temperature (60°F to 80°F) and humidity should be below 50%, if possible.

Spray equipment which may be used include a high volume low pressure (HPLV) spray gun, which should be used with 20-40 psi of clean, oil free air. Other types of spray equipment may be suitable, as well, including airless spray equipment. Controlling the coverage density is desirable to enhance coating performance. If possible, the support layer 30, or the spray equipment, should be rotated 90 degrees at least once to maintain even coverage. Never reapply after the coat has completely dried. Allow 2 to 4 hours of dry time before the shield 12, 14, 15, or 17 is handled depending upon humidity and temperature.

Example 1 contains N grade Sodium Silicate 15.0% dry weight and 20.0% wet weight based on sodium silicate solids content of 37.45%, Min-U-Sil SiO₂ powder 70.0% dry weight and 39.5% wet weight, B₃C 5.00% dry weight and 2.50% wet weight, PolarGel bentonite powder 100.0% dry weight and 0.50% wet weight, and 37.5% water, based on sodium silicate solids content of 37.45%. The pH of example 1 is 11.2±1.0, the specific gravity is 1.45±0.05, and the total solids content is 50±3.0%. Example 1 may be prepared by placing the liquid ingredients in a clean, relatively dry mixing container. While mixing, the remaining ingredients are added slowly to the mixture to prevent the powders from clumping and sticking to the side of the mixing container. The mixture is then mixed at high power for at least 20 minutes depending on the configuration of the mixer. The mixing was carried out in a high shear mixer with a 2.5 inch Cowles Hi-Shear Impeller blade at 0.5 horsepower motor generating 7500 rpm without load.

Example 2 contains N grade Sodium Silicate 15.0% dry weight and 20.0% wet weight based on sodium silicate solids content of 37.45%, min-U-Sil SiO₂ powder 69.0% dry weight and 34.5% wet weight, B₃C 15.0% dry weight and 7.5% wet weight, PolarGel bentonite powder 100.0% dry weight and 0.500% wet weight, and 37.5% water, based on sodium silicate solids content of 37.45%. The pH of example 2 is 11.2±1.0, the specific gravity is 1.45±0.05, and the total solids content is 50±3.0%. Example 2 is prepared in the same fashion as example 1. This embodiment is a preferred embodiment for sintering applications. Example 2 may be prepared in the same manner as Example 1.

A tube shield was coated with the composition of example 1 and observed under real-life field circumstances. Coated and sintered tube shields were placed in the superheater of a CE, VU40, coal fired, tangential burners (no tills), 65 MWe/mer unit. Coating still shedding slag and protecting tubes after fifteen (15) months of service.

It is to be understood that the present invention is not limited to the embodiments described above, but encompasses any and all embodiments within the scope of the following claims.

What is claimed is:

1. A tube shield for protecting an external surface of a tube having a tube wall, comprising:
   a. a support structure having an internal surface and an external surface,
   b. said internal surface formed to encompass the tube and be disposed adjacent the tube wall; and
   c. a thermal protective layer disposed on at least one surface of said shield support structure, wherein said thermal protective layer has
      a. from about 5% to about 40% of an inorganic adhesive, from about 45% to about 92% of a filler, and from about 1% to about 20% of one or more emissivity agents; or
      b. from about 5% to about 60% of colloidal silica, colloidal alumina, or combinations thereof; from about 23% to about 79% of a filler; and from about 1% to about 20% of one or more emissivity agents.
2. The tube shield of claim 1, wherein:
   a. said support structure is an elongated half-circle shell configured to mate with a second tube shield to receive the tube therebetween; and
   b. said support structure further comprises an edge surface running along a periphery of said internal and external surfaces and extending therebetween.
3. The tube shield of claim 1, wherein:
   a. said thermal protective layer is disposed on said external surface of said support structure; disposed on said internal surface of said support structure; disposed on said external surface and on said internal surface; or disposed substantially on all surfaces of said support structure.
4. The tube shield of claim 1, wherein:
   a. said support structure comprises a metallic substrate or a ceramic substrate.
5. The tube shield of claim 4, wherein:
   a. said metallic substrate is taken from the group consisting of steel, low carbon steel, stainless steel, cast iron, iron, aluminum, and alloys, and combinations thereof.
6. The tube shield of claim 1, wherein:
   a. said thermal protective layer further comprises from about 1.0% to about 5.0% of a stabilizer; from about 1.0% to about 5.0% of a stabilizer taken from the group consisting of bentonite, kaolin, magnesium alumina silica clay, tabular alumina, and stabilized zirconium oxide; and up to about 1.0% of a surfactant; or a colorant; or combinations thereof.
7. The tube shield of claim 1, wherein:
   a. said adhesive is taken from the group consisting of an alkali/alkaline earth metal silicate taken from the group consisting of sodium silicate, potassium silicate, calcium silicate, and magnesium silicate; and said filler is taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, and boron oxide; and said one or more emissivity agents are taken from the group consisting of silicon hexaboride, boron carbide, silicon...
tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides;
said emissivity agents are a metal oxide taken from the group consisting of iron oxide, magnesium oxide, manganese oxide, chromium oxide, and derivatives thereof; or combinations thereof.

8. The tube shield of claim 1, wherein:
said thermal protective layer contains
a. from about 5% to about 40% of an inorganic adhesive, the inorganic adhesive is taken from the group consisting of an alkalai/alkaline earth metal silicate taken from the group consisting of sodium silicate, potassium silicate, calcium silicate, and magnesium silicate; from about 45% to about 92% of a filler, the filler taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, and boron oxide; and from about 1% to about 20% of one or more emissivity agents taken from the group consisting of silicon hexaboride, boron carbide, silicon tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides;
b. from about 5% to about 60% of colloidal silica, colloidal alumina, or combinations thereof; from about 23% to about 79% of a filler taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, and boron oxide; and from about 1% to about 20% of one or more emissivity agents taken from the group consisting of silicon hexaboride, boron carbide, silicon tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides;
c. from about 5% to about 40% of an inorganic adhesive, the inorganic adhesive taken from the group consisting of an alkalai/alkaline earth metal silicate taken from the group consisting of sodium silicate, potassium silicate, calcium silicate, and magnesium silicate; from about 45% to about 92% of a filler, the filler taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, and boron oxide; and from about 1% to about 20% of one or more emissivity agents taken from the group consisting of silicon hexaboride, boron carbide, silicon tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides; and from about 8% to about 5% of a stabilizer taken from the group consisting of bentonite, kaolin, magnesium alumina silica clay, tabular alumina, and stabilized zirconium oxide; or
d. from about 5% to about 60% of colloidal silica, colloidal alumina, or combinations thereof; from about 23% to about 79% of a filler taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, and boron oxide; and from about 1% to about 20% of one or more emissivity agents taken from the group consisting of silicon hexaboride, boron carbide, silicon tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides; and from about 1% to about 5.0% of a stabilizer taken from the group consisting of bentonite, kaolin, magnesium alumina silica clay, tabular alumina, and stabilized zirconium oxide.

9. The tube shield of claim 1, further comprising:
(a) a brace disposed to secure said tube shield in place, said brace having a support structure with the thermal protective layer disposed thereon.

10. The tube shield of claim 1, wherein:
said support structure formed into an elongated half-circle shell is bent to form an inner or an outer elbow to accommodate a turn in the tube and coupled with a second tube shield bent to form an opposing inner or outer elbow to encapsulate the turn in the tube.

11. The tube shield of claim 1, having
from about 2% to about 20% of a first emissivity agent taken from the group consisting of boron carbide, silicon carbide powder, silicon tetraboride, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides; and from about 0.5% to about 3.5% of a second emissivity agent taken from the group consisting of silicon hexaboride.

12. A method of manufacturing a tube shield having a thermal protective layer, comprising:
providing a support structure having an exposed surface, wherein the exposed surface is on interior surface, or on an exterior surface, or on combinations thereof;
mixing a thermal protective coating containing
a. from about 6% to about 40% of an inorganic adhesive, from about 23% to about 56% of a filler, from about 0.5% to about 15% of one or more emissivity agents, and from about 18% to about 50% water, or
b. from about 15% to about 60% of colloidal silica, colloidal alumina, or combinations thereof; from about 23% to about 55% of a filler, from about 0.5% to about 15% of one or more emissivity agents, and from about 10% to 50% water; and
applying the mixed thermal protective coating to the exposed surface using a spray gun to form a thermal protective layer from about 2 mils (5 microns) to about 10 mils (254 microns) thick.

13. The method of claim 12, further comprising:
the thermal protective layer further comprises
from about 0.5 percent to about 2.4 percent of a stabilizer; or
up to about 1.0% of a surfactant;
from about 0.5 percent to about 2.4 percent of a stabilizer taken from the group consisting of bentonite, kaolin, magnesium alumina silica clay, tabular alumina, and stabilized zirconium oxide; or
a colorant; or
combinations thereof.

14. The method of claim 12, wherein:
the inorganic adhesive is taken from the group consisting of an alkalai/alkaline earth metal silicate taken from the group consisting of sodium silicate, potassium silicate, calcium silicate, and magnesium silicate; the filler is taken from the group consisting of silicon dioxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, and boron oxide; the one or more emissivity agents are taken from the group consisting of silicon hexaboride, boron carbide, silicon tetraboride, silicon carbide, molybdenum disilicide, tungsten disilicide, zirconium diboride, cupric chromite, and metallic oxides;
the emissivity agents are a metal oxide taken from the group consisting of iron oxide, magnesium oxide, manganese oxide, chromium oxide, and derivatives thereof; or combinations thereof.

15. The method of claim 12, wherein:
the spray gun is taken from the group consisting of an high volume low pressure spray gun or an airless spray gun.

16. The method of claim 12, further comprising:
agitating the solution of thermal protective coating prior to applying.

17. The method of claim 12, further comprising:
rotating the direction of spray to facilitate an even thickness.

18. The method of claim 12, further comprising:
allowing the thermal protective layer to air dry from about two to about four hours.

19. The method of claim 12, wherein:
the support structure comprises a metallic substrate or a ceramic substrate.

20. The method of claim 12, further comprising:
preparing the exposed surface first by cleaning, grit blasting, or combinations thereof.