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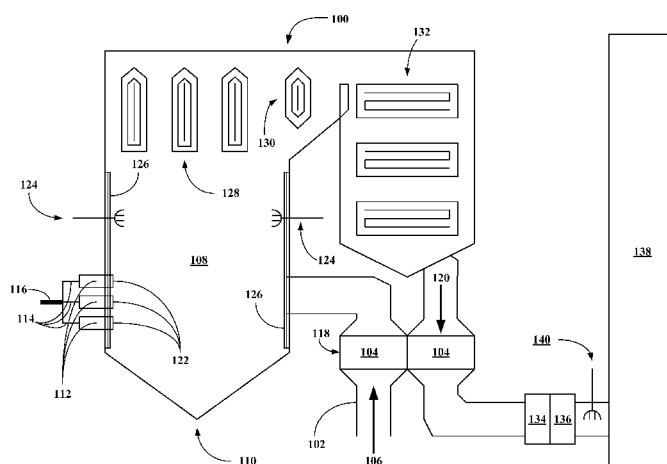
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(54) Title: A SYSTEM AND METHOD FOR DISRUPTING SLAG DEPOSITS AND THE COMPOSITIONS USED



(57) **Abstract:** Systems and methods for disrupting slag deposits formed on internal surfaces of hydrocarbon-fired combustion apparatuses (e.g., boilers), such as for easier removal thereof, and the treating compositions used therein are disclosed. In certain embodiments, the treating compositions include non-expanding and/or expanding synthetic carbon and optionally a corrosion inhibiting composition that reduces hazardous emissions. The slag deposit disrupting compositions/particulates are understood to combine or intermix with slag deposit forming materials formed during fuel combustion to co-deposit on boiler surfaces. The intermixed slag deposit disrupting compositions define an area or zone within the slag that weakens and/or reduces slag deposit integrity so that the slag deposits are more prone to flaking off, such as under their own weight, resulting in self-cleaning and/or are more easily removed using traditional cleaning or removal techniques.

A SYSTEM AND METHOD FOR DISRUPTING SLAG DEPOSITS AND THE COMPOSITIONS USED

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 62/291,063, filed February 4, 2016, the disclosure of which is hereby incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] Embodiments of the present invention generally relate to hydrocarbon-fired combustion apparatuses and, more specifically, to systems and methods for disrupting slag deposits formed on internal surfaces of hydrocarbon-fired combustion apparatuses (e.g., boilers), such as for easier removal thereof, and the treating compositions used therein.

BACKGROUND

[0003] In the generation of electricity, the often preferred fuel is natural gas. Natural gas is preferred because it contains very few, if any, contaminants. However, in the absence of relatively scarce and valuable natural gas, electric utilities are often forced to rely on less environmentally friendly fuels. These fuels may be derivatives of petroleum taken from various stages of the refining process of this increasingly expensive commodity. When price per unit of derived energy is considered, the chosen fuel is frequently coal when it is available as a viable option. Of all the fuels, coal has by far the greatest number and largest amounts of contaminants and, thus, has the greatest environmental impact when not properly and completely treated.

[0004] Contaminants often cause problems in the power generating industry. In particular, the combustion of residual petroleum or other hydrocarbon fuels, e.g., coal, in hydrocarbon-fired combustion apparatuses (e.g., boilers) produces an ash, which after fusion in the firing flames may remain sufficiently molten and adhere to the steam generating surfaces and superheater tubes, or elsewhere on fireside surfaces. Substantial amounts of the molten ash may accumulate and solidify on those surfaces, upon cooling to a certain temperature, in the form of a slag deposit. As combustion continues, this adherent encrustation of slag builds up with the consequent deleterious effects of thermally insulating, for example, the tubes through which it is desired to conduct heat of combustion, and of tending to obstruct the passage of flue gases through the firesides of the combustion apparatus, so that at times it may become practically

inoperative after relatively short periods of operation. That is, these slag deposits can interfere with the transfer of heat and the flow of combustion gases, and can reduce the effectiveness of these units, thereby increasing the need to combust additional fuel to compensate for the loss in effectiveness.

[0005] As is known in the industry, these slag deposits can be extremely difficult to remove and generally require that a boiler, for example, be placed offline, which is undesirable, so as to remove the slag. Also, various slag removal techniques can be labor intensive and, thus, costly and time-consuming. Such slag removal techniques include, for example, laser cutting, high pressure water or air nozzles or jets (including fire hoses), as well as the use of explosives, shotguns, or old-fashioned hammer and chisel techniques.

[0006] Other problems encountered with hydrocarbon-fired apparatuses, such as boilers, are the production of environmental contaminants in the exhaust of these units such as SO_x , S_xO_y , NO_x , N_xO_y , and heavy metals that are often discharged to the environment when adequate treatment is not possible.

[0007] In an effort to respond to certain of the detrimental effects of contaminants and solve various aspects of treating oil and coal in power generation, the metal elements magnesium, calcium, iron, manganese, sodium, potassium, zinc, cerium, barium, silicon, aluminum, chromium, cobalt, nickel, and copper have been tested. Many of these materials have consequently been used as active metal additives for many and varied uses, such as to control or inhibit emissions, fouling, or corrosion, in fired equipment, such as boilers, gas turbines, and diesel engines. For ease of handling, these materials are often applied as liquid formulations. For years, crude slurry formulations have reigned supreme in boiler treating. More recently, organic soluble formulations and aqueous soluble formulations including nano-sized particles have become increasingly more common. In many of these applications, the “liquid” additives are simply injected into the fuel being used at locations that are remote from the combustion equipment. In other applications, it may be necessary that the “liquid” fuel additives are sited and injected near the combustion equipment.

[0008] While various efforts have been made to combat contaminants that often cause problems in the power generating industry, there is still a need in the art for new systems and methods for disrupting slag deposits (with or without the inclusion of emission and/or corrosion inhibitors) using treating compositions, with such systems and methods reducing the frequency

or need for offline slag removal (e.g., boiler slag) and/or making slag removal easier or more desirable.

SUMMARY OF THE INVENTION

Compositions

[0009] Embodiments of the present invention provide treating compositions including an effective amount of a slag deposit disrupting composition, where the slag deposit disrupting composition disrupts by weakening and/or reducing slag deposit integrity and/or reduces slag deposit formation in hydrocarbon-fired (e.g., coal-fired) boilers (or other hydrocarbon-fired combustion apparatuses). In certain embodiments, the treating compositions also include an inhibiting amount of an emission and/or corrosion inhibiting composition that reduces hazardous emissions. The slag deposit disrupting compositions and the emission and/or corrosion inhibiting compositions include particulate materials. The slag deposit disrupting compositions/particulates are understood to combine or intermix with slag deposit forming materials formed during fuel combustion to co-deposit on boiler surfaces. The intermixed slag deposit disrupting compositions define an area or zone within the slag that weakens and/or reduces slag deposit integrity so that the slag deposits are more prone to flaking off, such as under their own weight, resulting in self-cleaning and/or are more easily removed using traditional cleaning or removal techniques. If the treating compositions include an emission and/or corrosion inhibiting composition, then the treating compositions also simultaneously reduce general deposit formation.

Apparatuses and/or Systems

[0010] Embodiments of the present invention provide hydrocarbon-fired combustion apparatuses and systems, e.g., hydrocarbon-fired (e.g., coal-fired) boilers, including a combustion unit, which can have a fuel source, a fuel conduit, a fuel delivery assembly, burners, a combustion chamber, an oxidizing agent source, an oxidizing agent conduit, an oxidizing agent delivery assembly, a treating composition source, a treating composition conduit, a treating delivery assembly, a heat transfer fluid assembly, a flue gas exhaust assembly, and a unit for converting a portion of thermal energy associated with the heat transfer fluid to a usable form of energy such as electrical energy, mechanical energy, or a combination of the two. The treating compositions are designed to disrupt slag deposit integrity by weakening and/or reducing slag deposit integrity of slag deposits that form on surfaces of the hydrocarbon-fired combustion

apparatuses and/or systems, such as hydrocarbon-fired (e.g., coal-fired) boilers. In certain embodiments, the treating compositions may also reduce hazardous emissions.

[0011] In certain embodiments, the treating delivery assembly includes at least one injector assembly, such as a high temperature injector assembly. Each injector assembly includes at least one fluid injector and an injector feed device for feeding a treating composition of the present invention into the hydrocarbon-fired combustion apparatuses/systems, such as hydrocarbon-fired (e.g., coal) boilers, particularly at one location or a plurality of locations of the boiler at a sufficient rate to disrupt by weakening and/or reducing slag deposit integrity on internal surfaces of the boiler upon which slag deposits normally form and may also reduce hazardous emissions.

[0012] In one embodiment, a system for disrupting slag deposits formed on an internal surface of a hydrocarbon-fired combustion apparatus includes a hydrocarbon-fired combustion apparatus including a combustion chamber for combusting a hydrocarbon fuel. The system further includes a hydrocarbon fuel source and a hydrocarbon fuel conduit for introducing the hydrocarbon fuel to the hydrocarbon-fired combustion apparatus. The system further includes a treating composition source and a treating composition conduit for introducing the treating composition, which includes a deposit disrupting composition, to the hydrocarbon-fired combustion apparatus, and wherein the treating composition conduit introduces an effective amount of the treating composition into the hydrocarbon-fired combustion apparatus that is sufficient to disrupt slag deposits, which form as a result of combustion of the hydrocarbon fuel, by weakening and/or reducing slag deposit integrity on an internal surface of the hydrocarbon-fired combustion apparatus where slag formation occurs.

Methods for Using the Treating Compositions

[0013] Embodiments of the present invention also provide methods for disrupting slag deposits including injecting a fuel into a hydrocarbon-fired combustion apparatus, such as a hydrocarbon-fired (e.g., coal-fired) boiler, where the fuel includes an effective amount of a treating composition of the present invention sufficient to disrupt by weakening and/or reducing slag deposit integrity on internal surfaces of the boiler upon which slag deposits normally form. In certain embodiments, the treating compositions also reduce hazardous emissions.

[0014] Embodiments of the present invention also provide methods for disrupting boiler slag deposits by weakening and/or reducing slag deposit integrity including injecting a treating

composition of the present invention in a location or a plurality of locations of a hydrocarbon-fired combustion apparatus, such as a hydrocarbon-fired (e.g., coal-fired) boiler, at a rate sufficient to weaken, disrupt, and/or reduce deposits on surfaces of the apparatuses upon which deposits normally form. In certain embodiments, the treating compositions also include an emission and/or corrosion inhibiting composition sufficient to reduce hazardous emissions.

[0015] In one embodiment, the method for disrupting slag deposits formed on an internal surface of a hydrocarbon-fired combustion apparatus includes introducing an effective amount of a treating composition including a deposit disrupting composition into a hydrocarbon-fired combustion apparatus, wherein the effective amount is sufficient to disrupt slag deposits during combustion of a hydrocarbon fuel by weakening and/or reducing slag deposit integrity on the internal surface of the hydrocarbon-fired combustion apparatus where slag formation occurs. In another embodiment, the method for disrupting slag deposits formed on an internal surface of a hydrocarbon-fired boiler includes introducing an effective amount of a treating composition including an expandable and/or non-expandable synthetic carbon into a hydrocarbon-fired boiler, wherein the effective amount is sufficient to disrupt slag deposits during combustion of a hydrocarbon fuel by weakening and/or reducing slag deposit integrity on the internal surface of the hydrocarbon-fired boiler where slag formation occurs.

Methods for Making Treating Compositions

[0016] Embodiments of the present invention also provide methods for making treating compositions including providing a treating composition comprising a deposit disrupting material/agent. In other embodiments, the methods include combining a plurality of deposit disrupting materials/agents to form a heterogeneous, substantially heterogeneous, homogeneous, or substantially homogeneous treating composition. The methods may also include mixing the plurality of deposit disrupting materials/agents for a time and at a temperature and a pressure sufficient to form a substantially homogeneous or homogeneous treating composition. In other embodiments, the treating compositions are prepared by combining at least one deposit disrupting material/agent and at least one emission and/or corrosion inhibitor to form a heterogeneous, substantially heterogeneous, homogeneous, or substantially homogeneous treating composition. In other embodiments, the methods include mixing the at least one deposit disrupting material/agent and the at least one emission and/or corrosion inhibitor for a time and at a temperature sufficient to form a substantially homogeneous or homogeneous treating

composition. In other embodiments, the methods may also include dispersing a treating composition in a suitable carrier to form a treating slurry composition.

Methods for Making Treated Fuels

[0017] Embodiments of the present invention provide methods for making a treated fuel including dispersing an effective amount of a treating composition of the present invention into a fuel to form the treated fuel.

BRIEF DESCRIPTION OF THE DRAWING

[0018] The invention can be better understood with reference to the following detailed description together with the appended illustrative drawing in which like elements are numbered the same:

[0019] The Figure depicts a hydrocarbon-fired (e.g., coal-fired) boiler.

DEFINITIONS USED IN THE INVENTION

[0020] The term “substantially” means that the property is within 95% of its desired value. In other embodiments, “substantially” means that the property is within 97.5% of its desired value. In other embodiments, “substantially” means that the property is within 99% of its desired value. In other embodiments, “substantially” means that the property is within 99.9% of its desired value. For example, the term “substantially complete” as it relates to a coating, means that the coating is at least 95% complete. In other embodiments, the term “substantially complete” as it relates to a coating, means that the coating is at least 97.5% complete. In other embodiments, the term “substantially complete” as it relates to a coating, means that the coating is at least 99% complete. In other embodiments, the term “substantially complete” as it relates to a coating, means that the coating is at least 99.9% complete.

[0021] The term “substantially” means that a value is within about $\pm 5\%$ of the indicated value. In certain embodiments, the value is within about $\pm 2.5\%$ of the indicated value. In certain embodiments, the value is within about $\pm 1\%$ of the indicated value. In certain embodiments, the value is within about $\pm 0.5\%$ of the indicated value. In certain embodiments, the value is within about $\pm 0.1\%$ of the indicated value. In certain embodiments, the value is within about $\pm 0.01\%$ of the indicated value.

[0022] The term “about” means that the value is within $\pm 10\%$ of the indicated value. In certain embodiments, the value is within $\pm 5\%$ of the indicated value. In certain embodiments, the value is within $\pm 2.5\%$ of the indicated value. In certain embodiments, the value is within

$\pm 1\%$ of the indicated value. In certain embodiments, the value is within $\pm 0.5\%$ of the indicated value. The term “about” means that the property is within $\pm 10\%$ of the indicated value. In certain embodiments, the property is within $\pm 5\%$ of the indicated value. In certain embodiments, the property is within $\pm 2.5\%$ of the indicated value. In certain embodiments, the property is within $\pm 1\%$ of the indicated value. In certain embodiments, the property is within $\pm 0.5\%$ of the indicated value.

[0023] The term “high flash point liquid additive” means a liquid additive having a flash point that is at least about 65°C so that it is less hazardous around combustion equipment than liquid additives previously available. Liquid additives having a flash point of at least about 70°C are designed to be safer to use in coal-burning plants. In certain embodiments, liquid additives having a flash point of at least about 70°C will be referred to as a high flash point liquid additive. It is important to maintain high flash points to avoid or minimize the danger from fires. Flash point is directly related to vapor pressure of the product. The higher the flash point, the lower the vapor pressure of the material. Thus, even after a spill or leak, higher flash point products would not produce high concentrations of vapor that could travel over distances to spark or flame that could ignite them.

[0024] The term “FP” means flash point.

[0025] The term “high temperature expandable material” means a material that undergoes a rapid increase in volume after being subjected to an expansion temperature, but does not decompose at a combustion temperature of the boilers or other combustion systems to which the treating composition is added.

[0026] The term “mixture” means that two or more components have been mixed together to form a mixture before use.

[0027] The term “combination” means that two or more components are used separately and the final composition includes a combination of materials made from single components.

DETAILED DESCRIPTION OF THE INVENTION

[0028] Systems and methods are disclosed for disrupting slag deposits formed on internal surfaces of hydrocarbon-fired (e.g., coal-fired) boilers (or other hydrocarbon-fired combustion systems), such as for easier removal thereof. Also disclosed are the treating compositions for fuels used in these hydrocarbon-fired (e.g., coal-fired) boilers where the fuels tend to cause slag deposits on internal surfaces of the boilers and other hydrocarbon-fired (e.g. coal-fired)

combustion systems, especially transfer fluid conduit surfaces. Such treating compositions include a disrupting amount of a deposit disrupting composition and may also optionally include an inhibiting amount of an emission and/or corrosion inhibiting composition. The slag deposit disrupting compositions are believed to combine or intermix with slag deposit forming materials formed during fuel combustion to co-deposit on boiler surfaces, which results in weakening and/or reducing slag deposit integrity so that the slag is or can be more easily removed.

[0029] In certain embodiments, the treating compositions are injected into the fuel prior to the fuel being injected into the hydrocarbon-fired boiler (or other hydrocarbon-fired combustion system), while in other embodiments, the boiler includes at least one high temperature injector for injecting the additive compositions into a zone or zones of the boiler (or other combustion system). The treating compositions are either present in the fuel in a sufficient amount or are injected at a sufficient rate to disrupt boiler slag deposits by combining or intermixing with slag deposit forming materials formed during fuel combustion to co-deposit on boiler surfaces, thereby weakening and/or reducing slag deposit integrity. If the treating composition includes an emission and/or corrosion inhibiting composition, then the inhibiting composition can be present in an amount sufficient to reduce emissions or are injected at a sufficient rate to reduce emissions. The benefits disclosed herein can be noted not only in pulverized coal-fired boilers, but also in oil-fired boilers or boilers using other fuels such as, for example, wood chips, bagasse, waste oils, biofuels, and others.

Treating Compositions

[0030] Embodiments of the present invention provide treating compositions including a disrupting amount of a slag deposit disrupting composition, where the slag deposit disrupting composition disrupts by weakening and/or reducing deposit integrity and/or reduces slag deposit formation. Again, the deposit disrupting compositions are believed to combine or intermix with slag deposit forming materials formed during fuel combustion to co-deposit on internal surfaces. The intermixed slag deposit disrupting compositions define an area or zone within the slag that weakens and/or reduces slag deposit integrity so that the slag deposits are more prone to flaking off, such as under their own weight, resulting in self-cleaning and/or more easily removed using traditional cleaning or removal techniques. In certain embodiments, the treating compositions also include an inhibiting amount of an inhibiting composition that inhibits corrosion and/or reduces hazardous emissions. In other embodiments, the treating compositions include at least

one inhibitor modified deposit disrupting composition. If the treating compositions include an inhibiting composition, then the treating compositions also simultaneously reduce deposit formations that effect corrosion and/or emissions.

[0031] In certain embodiments, the inhibitor modified deposit disrupting compositions include at least one inhibitor modified expandable particulate material, at least one inhibitor modified non-expandable particulate material, at least one inhibitor modified hollow particulate material, or mixtures and combinations thereof. In other embodiments, the inhibitor modified deposit disrupting compositions include at least one inhibitor modified expandable particulate synthetic material, at least one inhibitor modified non-expandable particulate synthetic material, at least one inhibitor modified hollow particulate synthetic material, or mixtures and combinations thereof.

[0032] In certain embodiments, the deposit disrupting composition includes at least one particulate material, such as one particulate synthetic material. In other embodiments, the particulate materials include at least one expandable particulate material, including at least one expandable particulate synthetic material. In other embodiments, the particulate materials comprise at least one non-expandable particulate material, including at least one non-expandable particulate synthetic material. In other embodiments, the particulate materials comprise a mixture of at least one expandable particulate material and at least one non-expandable particulate material.

[0033] In other embodiments, the treating compositions include at least one inhibitor modified expandable particulate material, at least one unmodified non-expandable particulate material, and/or at least one corrosion inhibiting material.

[0034] In certain embodiments, the particulate materials have particle sizes ranging from about 0.01 microns or μm to about 50,000 μm , to about 25,000 μm , to about 10,000 μm , to about 5,000 μm or to about 1,000 μm . In other embodiments, the particulate materials have particle sizes ranging from about 0.1 μm to about 50,000 μm , to about 25,000 μm , to about 10,000 μm , to about 5,000 μm or to about 1,000 μm . In other embodiments, the particulate materials have particle sizes ranging from about 1 μm to about 5,000 μm to about 25,000 μm , to about 10,000 μm , to about 5,000 μm or to about 1,000 μm . In other embodiments, the particulate materials have particle sizes ranging from about 10 μm to about 5,000 μm to about 25,000 μm , to about 10,000 μm , to about 5,000 μm or to about 1,000 μm . In other embodiments, the particulate

materials have particle sizes ranging from about 100 μm to about 5,000 μm to about 25,000 μm , to about 10,000 μm , to about 5,000 μm or to about 1,000 μm . In other embodiments, the particulate materials have particle sizes ranging from about 1,000 μm to about 5,000 μm to about 25,000 μm , to about 10,000 μm , to about 5,000 μm or to about 1,000 μm . In other embodiments, the particulate materials have particle sizes ranging from about 0.01 μm to about 1,200 μm , depending upon the particular application. In certain embodiments, the particles have a size between 100 μm and about 1180 μm . In other embodiments, the particles have a size between about 10 μm and 180 μm . In other embodiments, the particles have a size between about 10 μm and 150 μm .

[0035] In certain embodiments, the expandable particulate materials comprise expandable particulate carbon based materials including expandable particulate coke, expandable particulate graphite, or mixtures and combinations thereof. In other embodiments, the expandable particulate carbon based materials include expandable synthetic particulate carbon based materials, such as expandable particulate synthetic coke, expandable particulate synthetic graphite, or mixtures and combinations thereof. In other embodiments, the expandable particulate materials comprise carbon-boron based materials, carbon-nitrogen based materials, or mixtures and combinations thereof.

[0036] In other embodiments, the non-expandable particulate materials comprise coke, graphite, carbon black, *etc.* or mixtures and combinations thereof. In other embodiments, the non-expandable particulate materials comprise synthetic carbon, such as synthetic coke and/or graphite.

[0037] In certain embodiments, the treating composition includes: a) at least one unmodified expandable coke, b) a mixture of unmodified expandable cokes, c) at least one unmodified non-expandable coke, d) a mixture of unmodified non-expandable cokes, e) at least one inhibitor modified expandable coke, f) a mixture of inhibitor modified expandable cokes, g) at least one inhibitor modified non-expandable coke, h) a mixture of inhibitor modified non-expandable cokes, i) a mixture of at least one inhibitor modified expandable coke and at least one inhibitor modified non-expandable coke, j) a mixture of at least one inhibitor modified expandable coke and at least one unmodified expandable coke, k) a mixture of at least one inhibitor modified expandable coke, at least one unmodified expandable coke, and at least one inhibitor modified non-expandable coke, l) a mixture of at least one inhibitor modified

expandable coke, at least one unmodified expandable coke, at least one inhibitor modified non-expandable coke, and at least one unmodified non-expandable coke, m) any of the above compositions may also include at least one unmodified or inhibitor modified hollow particulate agent, n) any of the above compositions also include at least one corrosion inhibiting agent, or o) mixtures and combinations of any of the above compositions.

[0038] In certain embodiments, the particulate compositions include expandable coke particles, which are synthetic. In other embodiments, the particulate compositions include expandable synthetic graphite particles. The expandable synthetic coke or graphite particles, when introduced into hydrocarbon-fired combustion systems, such as coal-fired boilers, will expand in volume instantaneously or substantially instantaneously upon heating to a given expansion temperature. In certain embodiments, the expansion temperature can be at or greater than 100°C. In another example, the temperature can be at or greater than 150°C, or at or greater than 250°. In another example, the expansion temperature can be at or greater than 300°C, or at or greater than 600°C. The particles will intermix with slag deposit forming materials formed during fuel combustion to co-deposit on internal boiler surfaces and expand to at least 150 times its initial volume to effectively define an area or zone within the slag that weakens and/or reduces slag deposit integrity. In certain embodiments, the expanded volume is at least 175 times greater than its initial volume. In other embodiments, the expanded volume is at least 200 times greater than its initial volume.

[0039] These synthetic expandable cokes and graphite are understood to be superior to expandable non-synthetic graphite and cokes. Expandable cokes do not suffer the oxidation potential of expandable graphite when used in the hot gas path. Thus, expandable cokes are capable of maintaining their mass as they move through the hot gas paths. In those embodiments including expandable cokes, the expansion allows for treatment using smaller amounts of the quantities of particulate treating compositions to achieve a desired degree of disruption of slag deposits of the combustion system surfaces or reduction of corrosion of the surfaces.

[0040] Moreover, treating compositions including inhibitor modified expandable compositions are capable of simultaneously disrupting slag deposits on surfaces and reducing or preventing corrosion of the surfaces. The simultaneous deposit disruption and inhibition occurs because, as the expandable materials expand, they release at least some of the corrosion inhibiting agents coated on, impregnated in, and/or chemically attached to the particles allowing

enhanced corrosion inhibition. In certain embodiments, the explosive expansion of the expandable materials releases some, substantially all, or all of the corrosion inhibiting agents. Additionally, as the expanded synthetic coke or graphite particles become incorporated with slag deposit forming materials on the surfaces of the boiler, any corrosion inhibiting agents remaining coated on, impregnated in, and/or chemically attached to the particles reduce or prevent surface corrosion upon combining with the materials forming boiler slag deposits. If the treating compositions include inhibitor modified non-expandable composition, then they can be designed to release some, substantially all, or all of the corrosion inhibiting agents upon impinging on system surfaces and becoming incorporated into the slag deposits forming on the boiler surfaces. In certain embodiments, the corrosion inhibiting agents include nano-particles of ultra-pure magnesium compounds. If the corrosion inhibiting agents are nano-particles of ultra-pure magnesium compounds, then when the particles impinge upon the surfaces, the inhibitors specifically target the nano-particles of ultra-pure magnesium compounds onto the surfaces onto which the slag deposits form.

[0041] In certain embodiments, the particles of expandable and/or non-expandable synthetic coke or synthetic graphite are coated with, impregnated with, and/or chemically modified by nano-particles of ultra-pure oxygenated magnesium compounds. The treating compositions combine with slag deposit forming materials to disrupt boiler slag by weakening and/or reducing deposit integrity via intermixing therewith and expanding therein. This creates slag deposits that are more prone to flaking off, such as under their own weight, resulting in self-cleaning and/or are more easily removed using traditional cleaning or removal techniques, while simultaneously reducing corrosion and/or emissions.

[0042] One advantage of treating compositions including inhibitor modified expandable particulate synthetic coke or graphite is that such compositions require smaller amounts of the compositions to achieve a desired level of simultaneous slag deposit disruption and corrosion inhibition. In embodiments using inhibitor modified expandable synthetic cokes or graphite, the amount of the composition required may be from about one tenth up to about one two hundredth compared to compositions including standard coke or graphite to achieve a desired degree of slag deposit disruption and corrosion inhibition. Not only will embodiments using inhibitor modified expandable cokes and graphite result in less of the treating compositions being required for a given degree of simultaneous slag deposit disruption and corrosion inhibition, more importantly,

fewer particles require trapping by back end environmental controls. Thus, such treating compositions not only better protect the environment, they also will provide a benefit to the user by reducing the overall costs of slag deposit cleaning and corrosion inhibition of surfaces of boilers over other methods (less material and less waste generated). The footprint of the ancillary equipment needed for cleaning would also be reduced by a reduced requirement for material helping reduce plant size, which is often at a premium since very often electrical generation sites are very near large cities – users of the electricity produced by the site.

[0043] As expandable synthetic coke or graphite is heated and expands, it becomes softer. This allows the particles to occupy a greater volume, which means these particles will take up a greater volume within any slag deposit forming on the surfaces of the boiler systems thereby weakening and/or reducing slag deposit integrity. Any inhibitor remaining with the expanded coke or graphite, especially chemically attached inhibitors, will be intimately associated with the surface as slag deposits form on the surfaces.

[0044] Another property of expandable synthetic cokes and graphite including inhibitor modified expandable synthetic cokes and graphite is that they are lubricating forms of carbon. This means, where the particles become incorporated with slag deposit forming materials, the slag deposits will have greater lubricity so that the slag deposits will be more prone to flaking out or dislodging during cleaning operations or fall under their own weight resulting in self-cleaning. The thin film of carbon with or without inhibitors may also help in reducing the formation of future slag deposits on the metal surfaces as the surfaces may be slick and also may help reduce corrosion of the surface if inhibitors are also left on the surface with the carbon. The thin film of carbon with or without inhibitors will also help insulate the surfaces of the metal parts. .

[0045] The inhibitor modified expandable synthetic coke or graphite particles are coated with, impregnated with, and/or chemically modified by water soluble and/or oil soluble corrosion inhibitors to mitigate any deleterious effects of high temperature vanadium and/or sodium. In certain embodiments, the corrosion inhibitors are magnesium-based corrosion inhibitors having a high concentration (30%) of useful magnesium. Thus, the treating compositions of the present invention can simultaneously perform both slag deposit disruption and continuous protection against corrosion of boiler surfaces if corrosion inhibitors are present. In fact, the inventors believe that the rapid expansion of the inhibitor modified expandable synthetic cokes or graphite facilitate a superior distribution of the corrosion inhibitors into the boilers and facilitate a

superior distribution of the corrosion inhibitors onto surfaces on which they impinge before, during, or after expansion. Additionally, the inventors believe that inhibitor modified non-expandable synthetic particles also facilitate a superior distribution of the inhibitors onto the surface on which they impinge.

[0046] In some applications, the treating compositions of the present invention may be introduced into the boilers using a carrier, such as a solvent. In certain embodiments, the particulate compositions of the present invention may be formulated with aromatic solvents, surfactants, paraffinic solvents, or mixtures thereof. In other embodiments, the particulate compositions of the present invention may be dispersed into surfactant solutions, which may include, without limitation, fatty acids, sulfonic acids, organic carboxylic acids, polymeric materials, or mixtures thereof.

[0047] In still other applications, the particulate compositions of the present invention may be treated with suitable agents to enhance the ability for expandable particles, such as expandable synthetic coke or graphite particles, to expand or to allow easier application of the compositions for their intended role.

[0048] As described in detail herein, the treating compositions of the present invention may be introduced directly into the combustion chamber (combustor) of hydrocarbon-fired (e.g., coal-fired) boilers (or other hydrocarbon-fired (e.g., coal-fired) combustion systems), and/or into the fuel stream, for example.

[0049] In certain embodiments, the introduction of the compositions into the boiler may be repeated as needed. In certain embodiments, the introduction may be intermittent, semi-periodic, periodic, semi-continuous, or continuous.

[0050] The treating compositions of the present invention are safe and innocuous to the environment and, if spilled, are easily cleaned by sweeping, followed by soap and water washing.

Example Inhibitor Modified Deposit Disrupting Materials

[0051] In certain embodiments, the inhibitor modified particles include a magnesium compound absorbed onto expandable coke or graphite particles.

[0052] In certain embodiments, the inhibitor modified particles include high purity magnesium nanoparticles absorbed onto expandable coke or graphite particles.

[0053] In certain embodiments, the inhibitor modified particles include magnesium/boron nanoparticles absorbed onto expandable coke or graphite particles.

[0054] In certain embodiments, the inhibitor modified particles include an aluminum compound absorbed onto expandable coke or graphite particles.

[0055] In certain embodiments, the inhibitor modified particles include a boron compound absorbed onto expandable coke or graphite particles.

[0056] In certain embodiments, the inhibitor modified particles include a magnesium compound and an aluminum compound absorbed onto expandable coke or graphite particles.

[0057] In certain embodiments, the coke or graphite particles are synthetic.

Methods of Using

[0058] Embodiments of the present invention broadly relate to methods for disrupting slag deposits on hydrocarbon-fired (e.g., coal-fired) boiler surfaces (or other hydrocarbon-fired combustion apparatus surfaces) including combusting fuel used therefore in the presence of a treating composition of the present invention, where the boiler includes, for example, a combustion chamber, a heat transfer fluid assembly, a flue gas exhaust assembly, and a thermal energy conversion unit. In certain embodiments, the treating compositions simultaneously disrupt slag deposits on the internal boiler surfaces and reduce corrosion of the surfaces and emissions from the boiler. In certain embodiments, the methods include burning a fuel including an effective amount of a treating composition of the present invention. In other embodiments, the methods of the present invention include injecting an effective amount of a treating composition of the present invention at one or a plurality of locations within the combustion chamber of the boiler to affect a desired degree of slag deposit disruption. In other embodiments, the amount is sufficient to disrupt slag deposits and simultaneously to reduce surface corrosion and reduce emissions. Modified particulate agent comprising a particulate agent coated with, impregnated with, and/or chemically modified with at least one corrosion inhibiting agent and where the compositions simultaneously affect boiler slag deposits and corrosion inhibition during operation of the boiler. In other embodiments, the treating composition is either injected into the fuel on an intermittent, semi-periodic, semi-continuous, or continuous basis or into the boiler at the location(s) on an intermittent, semi-periodic, semi-continuous, or continuous basis.

[0059] Embodiments of the present invention also relate to methods for disrupting boiler slag deposits including introducing a treating composition of the present invention directly into a combustion chamber, into a fuel stream, and/or into an oxidizing agent stream of a hydrocarbon-fired combustion system, such as hydrocarbon-fired (e.g., coal-fired) boilers. In one embodiment, treating compositions having expandable synthetic coke particles and/or expandable synthetic graphite particles, are introduced into a hydrocarbon-fired (e.g., coal-fired) boiler and expand in volume instantaneously or substantially instantaneously upon heating to a given expansion temperature. In particular, the particles will mix with the slag deposit forming materials formed during fuel combustion to co-deposit on internal boiler surfaces and expand, for example, to at least 150 times initial volume. The expanded and intermixed particles define areas or zones within the slag that results in weakening and/or reducing slag deposit integrity so that the slag deposits are more prone to flaking off, such as under their own weight, resulting in self-cleaning and/or are more easily removed using traditional cleaning or removal techniques.

[0060] For any specific hydrocarbon-fired combustion apparatus, such as a coal-fired boiler, in one example, a single charge of 1-400 lbs can be to effect a single treating operation. In another example a single charge of 200 lbs can be used. It is understood that the amount as well as the specific particle size range of the treating compositions of the present invention can be selected based on field trials. The charge or charges may be held in one or more independent reservoirs and injection assemblies.

[0061] This procedure, which can be repeated sequentially, may remove on average 50% of the molten ash or slag deposits, resulting in a substantial regaining of the power lost. The actual removal may be in the 25% to 75% range, but in some instances may be as low as 10%. Higher firing temperature boilers will have ash deposits that are harder to remove than units that fire at lower temperatures. A second or third charge may be necessary. It can also be repeated as deemed necessary based on operating modes. In embodiments where the compositions include inhibitor modified particles, the particles not only disrupt slag deposits on boiler surfaces but also can reduce or prevent corrosion of the surfaces.

[0062] Lastly, another method of deploying the treating compositions of the present invention includes introducing them directly into the fuel supply system of the boiler. In embodiments including inhibitor modified particulate treating compositions, a treating ratio is three parts of inhibitor to one part of vanadium in the fuel, although the treating ratio may be

greater or smaller. The actual stoichiometric amount of inhibitor required to just react with vanadium to make compounds, which are innocuous (non-corrosive) is only about 0.7 to 1. However, additional inhibitor is generally added because, not only is the desired non-corrosive vanadate formed, but also less desirable vanadium compounds form. In the case of magnesium inhibitors, the additional magnesium forces the reaction to form the orthovanadate and offsets some of the other less desirable magnesium and vanadium products.

[0063] The corrosion inhibitors coated on, impregnated in, or chemically attached to expandable or non-expandable particles may be water soluble or oil soluble magnesium corrosion inhibitors. In one example, the magnesium corrosion inhibitors include a minimum of 30% magnesium. Such formulations would include a sufficient amount of the corrosion inhibitors coating, impregnating and/or chemically attached to the particulate materials to cause both adequate treating and adequate corrosion protection and emission suppression. With these formulations, sufficient expandable synthetic coke and/or graphite or other material would be available to maintain the boiler in a boiler slag disrupting condition.

[0064] When treating Light Arabian crude fuels, the treating composition of the present invention may require a smaller amount of modification of the particulate materials with corrosion inhibitors or the inhibitor modified particulate materials may be “cut” with unmodified particulate materials, because these fuels normally contain lesser quantities of vanadium and consequently require less magnesium corrosion inhibitor additive for treatment. In some instances, not enough treating composition is added under normal treatment requirements. Thus a supplemental treatment may be needed to provide the desired amount of treating composition to ensure the boiler is maintained in a boiler slag disrupting state.

[0065] The advantage of using synthetic expandable and/or non-expandable coke and/or graphite materials instead of more common nutshells or even graphite is the synthetic coke and/or graphite materials will not oxidize in the flame as readily as nutshells or standard coke or graphite materials. Thus, the synthetic coke and/or graphite may persist post flame to perform its disrupting and, if modified with inhibitors, inhibiting functions. The expandable nature of the particles will lead to larger (volume) particles to impact even more surface area.

Methods for Making

[0066] Embodiments of the present invention broadly relate to methods for making the treating compositions of the present invention including step of contacting at least one disrupting

particulate material with at least one optional corrosion inhibitor under conditions to form an inhibitor modified disrupting compositions including at least one particulate treating agent coated with, impregnated with, and/or chemically modified by at least one corrosion inhibiting agent via any chemical and/or physical interaction including covalent bonding, ionic bonding, hydrogen bonding, electrostatic interactions, or any other chemical and/or physical interaction.

[0067] In certain embodiments, inhibitor modified particles are made by contacting a particulate agent and a corrosion inhibitor together in a suitable solvent for a time, temperature, and pressure to allow the corrosion inhibitor to coat, impregnate, and/or become chemically attached to the particulate agent. If the solvent is a carrier for the composition, then no further processing is needed. If the solvent is not a carrier, then the solvent may be removed by any method such as drying, distilling, evaporating, freeze drying, *etc.* In other embodiments, coupling agents may be added to facilitate chemical attachment of the corrosion inhibitors to the particulate agents. Such coupling agents may include, without limitation, bifunctional organic agents, such as diacids, anhydrides, isocyanates, or other bifunctional organic coupling agents, or mixtures and combinations thereof.

[0068] In other embodiments, inhibitor modified particles are made by spraying a corrosion inhibitor comprising nano-particles of a corrosion inhibitor in a carrier onto a fluidized particulate agent, such as expandable synthetic coke and/or graphite, so that the particulate agent becomes coated with and/or impregnated with the nano-particles.

[0069] In other embodiments, inhibitor modified particles are made by spraying a corrosion inhibitor comprising nano-particles of a corrosion inhibitor and a coupling agent in a carrier onto a fluidized particulate agent, such as expandable synthetic coke and/or graphite, so that the particulate agent becomes coated with, impregnated with and/or chemically modified by the nano-particles.

Compositional Ranges

Treating Compositions

[0070] In certain embodiments, the treating compositions include 100 wt.% of a deposit disrupting composition. In other embodiments, the treating compositions include between about 99 wt.% and about 1 wt.% of a deposit disrupting composition and between about 1 wt.% and about 99 wt.% of an inhibiting composition. In other embodiments, the treating compositions include between about 95 wt.% and about 5 wt.% of a deposit disrupting composition and

between about 5 wt.% and about 95 wt.% of an inhibiting composition. In other embodiments, the treating compositions include between about 90 wt.% and about 10 wt.% of a deposit disrupting composition and between about 10 wt.% and about 90 wt.% of an inhibiting composition. In other embodiments, the treating compositions include between about 80 wt.% and about 20 wt.% of a deposit disrupting composition and between about 20 wt.% and about 80 wt.% of an inhibiting composition. In other embodiments, the treating compositions include between about 70 wt.% and about 30 wt.% of a deposit disrupting composition and between about 30 wt.% and about 70 wt.% of an inhibiting composition. In other embodiments, the treating compositions include between about 60 wt.% and about 40 wt.% of a deposit disrupting composition and between about 40 wt.% and about 60 wt.% of an inhibiting composition. In other embodiments, the treating compositions include about 50 wt.% of a deposit disrupting composition and about 50 wt.% of an inhibiting composition.

Deposit Disrupting Compositions – Expandable and/or Non-Expandable

Materials

[0071] In certain embodiments, the disrupting composition includes 100 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials. In other embodiments, the disrupting composition includes 100 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 99 wt.% and about 1 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and between about 1 wt.% and about 99 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 95 wt.% and about 5 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and between about 5 wt.% and about 95 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 90 wt.% and about 10 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and between about 10 wt.% and about 90 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 80 wt.%

and about 20 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and between about 20 wt.% and about 80 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 70 wt.% and about 30 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and between about 30 wt.% and about 70 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 60 wt.% and about 40 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and between about 40 wt.% and about 60 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In other embodiments, the disrupting composition includes about 50 wt.% of a non-expandable particulate disrupting material or a plurality of non-expandable particulate disrupting materials and about 50 wt.% of an expandable particulate disrupting material or a plurality of expandable particulate disrupting materials. In one embodiment, the non-expandable and/or expandable particulate disrupting material may be a synthetic carbon, such as synthetic coke and/or graphite.

Deposit Disrupting Compositions Including Inhibitor Modified Materials

[0072] In certain embodiments, the disrupting composition includes 100 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials. In other embodiments, the disrupting composition includes 100 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 99 wt.% and about 1 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and between about 1 wt.% and about 99 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 95 wt.% and about 5 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and between about 5 wt.% and about 95 wt.% of an

inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 90 wt.% and about 10 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and between about 10 wt.% and about 90 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 80 wt.% and about 20 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and between about 20 wt.% and about 80 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 70 wt.% and about 30 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and between about 30 wt.% and about 70 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes between about 60 wt.% and about 40 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and between about 40 wt.% and about 60 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In other embodiments, the disrupting composition includes about 50 wt.% of an inhibitor modified non-expandable particulate disrupting material or a plurality of inhibitor modified non-expandable particulate disrupting materials and about 50 wt.% of an inhibitor modified expandable particulate disrupting material or a plurality of inhibitor modified expandable particulate disrupting materials. In one embodiment, the non-expandable and/or expandable particulate disrupting material may be a synthetic carbon, such as synthetic coke and/or graphite.

Disrupting Compositions Inhibitor Modified and Unmodified Materials

[0073] In certain embodiments, the disrupting composition includes 100 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials.

[0074] In other embodiments, the disrupting composition includes 100 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials.

[0075] In other embodiments, the disrupting composition includes between 99 wt.% and 1 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and between 1 wt.% to 99 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials. In other embodiments, the disrupting composition includes between 95 wt.% and 5 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and between 5 wt.% to 95 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials. In other embodiments, the disrupting composition includes between 90 wt.% and 10 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and between 10 wt.% to 90 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials. In other embodiments, the disrupting composition includes between 80 wt.% and 20 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and between 20 wt.% to 80 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials. In other embodiments, the disrupting composition includes between 70 wt.% and 30 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and between 30 wt.% to 70 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials. In other embodiments, the disrupting composition includes between 60 wt.% and 40 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and between 40 wt.% to 60 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials. In other embodiments, the disrupting composition includes about 50 wt.% of an inhibitor modified particulate material or a plurality of inhibitor modified particulate materials and from about 50 wt.% of an unmodified particulate material or a plurality of unmodified particulate materials.

Treating Compositions Including Inhibiting Materials

[0076] In certain embodiments, the treating compositions of the present invention are used at an effective amount, where the effective amount is an amount sufficient to disrupt slag deposits on internal surfaces of the hydrocarbon-fired boilers (or other hydrocarbon-fired combustion systems) in which the treating compositions are used. In other embodiments, the

effective amount is an amount sufficient to simultaneously disrupt boiler slag deposits on internal surfaces thereof and reduce or prevent corrosion of the surfaces and/or emissions of the boiler in which the treating compositions are used.

[0077] In certain embodiments, the effective amount of the treating composition is injected into the boiler of the present invention via the fuel, the oxidizing agent, and/or via independent injectors in an amount of at least 1 wt.% based on the fuel burned. In other embodiments, the effective amount of the treating composition used is at least 5 wt.% . In other embodiments, the effective amount used includes at least 10 wt.%. In other embodiments, the treating compositions include at least 20 wt.%. In other embodiments, the treating compositions include at least 30 wt.%.

Suitable Reagents for Use in Treating Compositions

Deposit Disrupting Materials

[0078] Suitable deposit disrupting materials include, without limitation, expandable materials, inhibitor modified expandable materials, non-expandable materials, inhibitor modified non-expandable materials, hollow materials, inhibitor modified hollow materials, or mixtures and combinations thereof. In certain embodiments, the deposit disrupting materials are non-oxidizable at the operating temperature of the boiler or other combustion apparatus during the time of treatment. Suitable deposit disrupting materials include synthetic carbons, such as coke and graphite.

Expandable Materials

[0079] Suitable expandable materials include, without limitation, expandable synthetic graphite, expandable synthetic coke, expandable boron-nitrides, expandable silicon-carbides, dodecahedranes, Buckminsterfullerenes, other fullerenes, carbon nano-tubes (single walled or multi-walled), boron-nitride nano-tubes (single walled or multi-walled), other nano-tubes, hollow glass beads, or mixtures and combinations thereof. Exemplary synthetic coke materials are produced by Ashbury Carbons by calcining petroleum coke to above 1800°F to about 2900°F or higher. These temperatures are safely above the typical hot gas path temperatures of an operating boiler or other combustion apparatus. An example of an expanded coke material may be found in International Patent Application No. WO/2011/007228. Exemplary synthetic graphite, including expandable graphite material (e.g., intumescent flake graphite), is available from Asbury Carbons of Asbury, NJ.

[0080] In certain embodiments, the purity of the expandable synthetic coke or graphite of the present invention is generally greater than or equal to about 99%. In certain embodiments, the purity is greater than or equal to about 99.5%. In other embodiments, the purity is greater than or equal to about 99.7%. In other embodiments, the purity is greater than or equal to about 99.9%.

[0081] The expandable synthetic coke and graphite of the present invention has a greater efficacy compared to non-expandable coke and graphite, respectively. Generally, an amount of expandable synthetic coke or graphite to effect a given degree of turbine treating is at least 1/10 an amount of non-expandable (i.e., hard condensed) coke or graphite. In other embodiments, an amount of expandable synthetic coke or graphite to effect a given degree of turbine cleaning is at least 1/50 an amount of non-expandable coke or graphite. In other embodiments, an amount of expandable synthetic coke or graphite to effect a given degree of turbine cleaning is at least 1/100 an amount of non-expandable coke. In other embodiments, an amount of expandable coke to effect a given degree of turbine cleaning is at least 1/150 an amount of non-expandable coke or graphite. In other embodiments, an amount of expandable synthetic coke or graphite to effect a given degree of turbine cleaning is at least 1/200 an amount of non-expandable coke or graphite. This improved efficacy results in improved cost effectiveness and improved environmental acceptability. The improved efficacy also results in reduced storage capacity and smaller hopper sizing.

Non-Expandable Materials

[0082] Suitable non-expandable materials include, without limitation, synthetic graphite, carbon black, synthetic coke, dodecahedranes, Buckminsterfullerenes, other fullerenes, carbon nano-tubes (single walled or multi-walled), boron-nitride nano-tubes (single walled or multi-walled), other nano-tubes, boron carbides, carbon nitrides, hollow glass beads, fumed silica, zeolites, aluminosilicates, silicoaluminates, other low hardness materials, or mixtures and combinations thereof.

[0083] In other embodiments, the particulate compositions include high purity, non-expandable synthetic cokes or graphite, where high purity means that the high purity, non-expandable cokes or graphite are at least 99 wt.% carbon. In certain embodiments, the high purity, non-expandable cokes or graphite are at least 99.5 wt.% carbon.

Hollow Materials

[0084] Suitable hollow materials include, without limitation, hollow organic materials, hollow inorganic materials, or mixtures and combinations thereof. Exemplary examples of hollow organic materials include, without limitation, hollow polymer spheres, which include high temperature hollow polymer spheres, or mixtures and combinations thereof. Exemplary examples of hollow inorganic materials include, without limitation, hollow glass spheres, hollow ceramic spheres, or mixtures and combinations thereof.

Inhibitor Modified Deposit Disrupting Materials

[0085] Suitable inhibitor modified deposit disrupting materials include, without limitation, any deposit disrupting material coated with, impregnated with, and/or chemically modified by an inhibitor set forth herein.

Carriers

[0086] Suitable carriers include, without limitation, water, an aqueous solution including dispersing agents, oil, an oil solution including dispersing agents, or other similar solid particulate carriers.

[0087] Suitable carriers also include high flash point solvents. Suitable high flash point solvents for use in the present invention include, without limitation, paraffinic base oils such as Calpar 100 (FP 210°C), Calpar 325 (FP 240°C), and Calpar P950 (FP 257°C) available from Calumet Lubricants Co. of Indianapolis, Indiana, any other paraffinic base oils having a flash point of at least 200°C, and mixtures or combinations thereof.

[0088] The method of measuring flash point (FP) can be any that is commonly recognized as applicable to liquid- or solvent-containing materials. The American Society for Testing and Materials (ASTM) and other international testing standards groups have specified methods that are acceptable to a broad range of users. For example, ASTM has methods D-56 and D-92 for open cup testing and method D-93 for Pensky-Martens closed cup testing. Similarly IP34, ISO2719, and DIN 51758 are for closed cup testing. For purposes of the present invention, the relative terms “low” and “high” are the most important. A particular method or temperature cannot cover all situations. It is understood there are too many variables for each industry to completely specify either of these parameters. For example, for over the road truck transport, it is often common to use a closed cup method since it is more severe. In other applications the more forgiving open cup method is acceptable. We feel the same and

distinguish only “higher” than previously used as the only applicable term. However, we believe ASTM D-93 to be the most widely used method and therefore will recommend that method although absolute values reported are understood to be variable depending on actual flash point method utilized.

[0089] The viscosity of the high flash point liquid additive may vary. A treating composition having a magnesium content of 30 percent by weight, for example, that is diluted with low flash point solvent will have a viscosity of about 150 cSt at 38°C. Dilutions made with several of the high flash point diluents would result in viscosities of 165 cSt at 38°C with Calpar 100, 180 cSt with Calpar 325, and about 200 cSt with Calpar P950, all at 38°C and with the same magnesium content. Surprisingly, the viscosity of the additive solution having a high flash point is not greatly higher than the viscosity of presently-used solutions. This result means that flash points at least as high as 257°C can be attained with high base content liquids and reasonable values of viscosity.

Chelating Agents

[0090] Suitable chelating agents for attaching inhibitors to suitable particulate agents include, without limitation, ethylenediamine tetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-(hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), acetylacetone, aminoethylethanolamine, Aminopolycarboxylic acid, aminotris(methylenephosphonic acid) (ATMP), (1,2-bis(o-aminophenoxy)ethane- N,N,N',N'-tetraacetic acid) (BAPTA), benzene-1,3-diamidoethanethiol (BDTH2), benzotriazole, bipyridine, 2,2'-bipyridine, 4,4'-bipyridine, bis(dicyclohexylphosphino)ethane, 1,2-bis(dimethylarsino)benzene, 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diphenylphosphino)ethane, catechol, chelex 100, citric acid, corrole, crown ether, 18-crown-6, cryptand, 2.2.2-cryptand, cyclen, deferasirox, deferiprone, dexrazoxane, trans-1,2-diaminocyclohexane, 1,2-diaminopropane, dibenzoylmethane, diethylenetriamine, diglyme, 2,3-dihydroxybenzoic acid, dimercaprol, 2,3-dimercapto-1-propanesulfonic acid, dimercaptosuccinic acid, dimethylglyoxime, (2,3-o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) (DIOP), diphenylethylenediamine, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) (chelator), an amide of the acid DOTA (DOTA-TATE), diethylenetriamine penta(methylene phosphonic acid) (DTPMP), ethylenediamine-N,N'-bis(2-hydroxyphenylacetic acid) (EDDHA), ethylenediamine-N,N'-

disuccinic acid (EDDS), ethylenediamine tetra(methylene phosphonic acid) (EDTMP), ethylene glycol tetraacetic acid (EGTA), 1,2-ethanedithiol, ethylenediamine, ethylenediaminetetraacetic acid, etidronic acid, extended porphyrin, fluo-4, fura-2, gluconic acid, glyoxal-bis(mesitylimine), hexafluoroacetylacetone, homocitric acid, iminodiacetic acid, indo-1, metal acetylacetonates, metal dithiolene complex, metallacrown, nitrilotriacetic acid, pendetide, penicillamine, pentetic acid, phanephos, phenanthroline, o-phenylenediamine, phosphonate, phytochelatin, polyaspartic acid, porphin, porphyrin, 3-pyridylnicotinamide, 4-pyridylnicotinamide, sodium diethyldithiocarbamate, sodium polyaspartate, terpyridine, tetramethylethylenediamine, tetraphenylporphyrin, 1,4,7-triazacyclononane, triethylenetetramine, triphos, trisodium citrate, 1,4,7-trithiacyclononane, or mixtures and combinations thereof. Exemplary examples include, without limitation, chelating agents sold under the tradenames VERSENE[®], VERSENEX[®] and VERSENOL[®], where these tradenames are registered trademarks of Dow Chemical Company of Midland, Michigan.

Inhibitors

[0091] The inhibitors of the present invention may be included in an inhibiting composition or in inhibitor modified deposit disrupting materials. The inhibitors may be water soluble and/or oil soluble corrosion inhibitors.

[0092] The inhibitors of the present invention may contain metal. Suitable metals for the metal-containing inhibitors of the present invention include, without limitation, a first group of metals including magnesium, calcium, sodium, potassium, barium, and mixtures or combinations thereof; a second group of metals including manganese, iron, cerium, copper, zinc, and mixtures or combinations thereof; a third group of metals silicon, aluminum, chromium, cobalt, nickel, and mixtures or combinations thereof; or mixtures or combinations of any one or more of the metals from these three groups. In certain embodiments, the inhibitors may be oxygenated.

Oxygenated Magnesium Compounds

[0093] Suitable oxygenated magnesium compounds include, without limitation, magnesium carbonate, magnesium hydroxide, magnesium sulfate, magnesium oxide, and mixtures or combinations thereof. In certain embodiments, the oxygenated magnesium compounds are magnesium oxide.

[0094] Suitable magnesium materials are sold under the trademark LMG-30E[®] or LMG-30S[®], both produced by Liquid Minerals Groups, Inc., of Houston, Texas.

Oxygenated Aluminum Compounds

[0095] Suitable oxygenated aluminum and alumina compounds include, without limitation, aluminum formate ($\text{Al}(\text{HCOO})_3$), aluminum acetate ($\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$), other aluminum carboxylates ($\text{Al}(\text{RCOO})_3$), where R is a hydrocarbyl group having between 3 and 20 carbon atoms, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), aluminum cyanide ($\text{Al}(\text{CN})_3$), aluminum nitrite ($\text{Al}(\text{NO}_2)_3$), aluminum carbonate ($\text{Al}_2(\text{CO}_3)_3$), aluminum sulfite ($\text{Al}_2(\text{SO}_3)_3$), aluminum hydroxide ($\text{Al}(\text{OH})_3$), aluminum oxide (Al_2O_3), and mixtures or combinations thereof.

Oxygenated Boron Compounds

[0096] Suitable oxygenated boron compounds include, without limitation, boric acid ($\text{B}(\text{OH})_3$), boron trioxide (B_2O_3), boron monoxide (B_2O), boron suboxide (B_6O), boron formate ($\text{B}(\text{HCOO})_3$), boron acetate ($\text{B}(\text{C}_2\text{H}_3\text{O}_2)_3$), other boron carboxylate ($\text{B}(\text{RCOO})_3$), where R is a hydrocarbyl group having between 3 and 20 carbon atoms, boron sulfate ($\text{B}_2(\text{SO}_4)_3$), boron cyanide ($\text{B}(\text{CN})_3$), boron nitrite ($\text{B}(\text{NO}_2)_3$), boron carbonate ($\text{B}_2(\text{CO}_3)_3$), boron sulfite ($\text{Al}_2(\text{SO}_3)_3$), and mixtures or combinations thereof.

Fuels

[0097] Suitable fuels for use in the present invention can include, without limitation, coal (*e.g.*, lignite, sub-bituminous, bituminous, anthracite, graphite, *etc.*), wood chips, peat, waste oils, biofuels, crude oils, contaminated fuels, fuel oils such as HFO (Heavy Fuel Oil), other heavy fuel materials, other solid or liquid fuels, and mixtures or combinations thereof, which produce slag in hydrocarbon-fired combustion apparatuses, particularly boilers.

[0098] A more friable ash or slag may be formed when contaminated fuels are burnt in various thermal installations such as: gas turbines, boilers, furnaces, diesel engines, *etc.*, for the purpose of producing heat or steam, mechanical energy, or electricity. Certain embodiments relate in particular to a method of operating a thermal installation that burns contaminated crude oil, heavy fuel oils, or coal that contain one or more of these contaminants: arsenic, barium, beryllium, boron, cadmium, chromium, thallium, selenium, molybdenum, mercury, vanadium, sulphur, and sodium.

DETAILED DESCRIPTION OF THE FIGURE

[0099] Referring to the Figure, a hydrocarbon-fired (*e.g.*, coal fired) boiler system 100 is shown to include a conduit 102 having a preheater 104 through which a combustion air stream

106 is introduced into a boiler firebox 108 of a boiler 110. The boiler 110 also includes coal burners 112 connected to coal feed conduits 114 from a coal supply conduit 116 for supplying a stream of pulverized coal for a pulverized coal supply (not shown). The coal used in the boiler system 100 can include pulverized coal. The combustion air stream 106 is pre-heated in the preheater 104 in a heat exchange process 118 with an effluent gas stream 120. At the ends 122 of each coal burner 112 in the firebox 108 would be burning coal. The arrangement of the coal burners 112 may be as shown or on opposite sides of the boiler 110. A treating composition, such as an expandable synthetic graphite material optionally mixed with an inhibitor or modified thereby, may be introduced into the firebox 108 through a spray apparatus 124 to distribute the material above the burning coal. The firebox 108 will be the location in the boiler 110 where the primary combustion occurs, where contaminants are freed from their fuel matrix, and where the action of the treating composition will begin by intermixing with contaminants, such as ash contaminants.

[00100] Combustion gases are used to boil water in water walls 126, superheaters 128, and reheaters 130 to produce steam used in the boiler plant for various functions. In the boiler system 100, the greatest amounts of slag are generally formed in the firebox 108 and beyond into the convective section (e.g., the superheater(s) 128 and/or the reheater(s) 130). Slag formation is due to condensation of vaporized and/or molten contaminants, such as ash, onto relatively cooler surfaces of the water tubes/wall 126 and other boiler components. The now combusted treating composition will help protect these areas, as well as the economizer 132 and the preheater 104, as these gases pass through those sections. In particular, the treating compositions, particularly expandable synthetic graphite particles, upon being introduced into the boiler 110 can expand in volume, for example, to at least 150 times initial volume, instantaneously or substantially instantaneously upon heating to a given expansion temperature, such as at or greater than 100°C. The intermixed expandable synthetic graphite particles in the boiler 110 deposit on surfaces along with the molten ash where slag formation occurs thereby co-depositing on those surfaces. The expanded/expanding (or non-expanding) and intermixed particles of synthetic graphite define areas or zones on and/or within the slag that results in weakening and/or reducing slag deposit integrity so that the slag deposits are more prone to flaking off, such as under their own weight, resulting in self-cleaning and/or are more easily removed using traditional cleaning or removal techniques.

[00101] An electrostatic precipitator 134 and a fabric filter 136 also can remove particulate materials and other contaminants before the exhaust gases from the effluent gas stream 120 are discharged to the atmosphere through a stack 138. In some arrangements, there may also be selective catalytic reduction (SCR) equipment 140 in the area of precipitator 134 and filter 136. Spray may be applied as a method of removing contaminants from boiler exhaust gases by spraying a reagent that interacts with the targeted contaminant to facilitate its removal.

[00102] Additionally, or alternatively, the treating composition may be introduced into or with the fuel (e.g., the coal) prior to the coal being burned by the coal burners 112. Further, the treating composition may be introduced into the combustion air stream 106.

[00103] Pulverized coal is coal that is ground to a fine powder before introduction to the firebox of a coal boiler. This is in contrast to lump, cyclone combustion, or grate firing of coal. Each of these methods has a purpose and benefits. Hard piping is not necessary for transport of the treating compositions disclosed herein, but for a permanent application hard piping may be desired to minimize risk of hoses breaking, loose fittings coming apart, and other possible risks.

[00104] All references cited herein are incorporated by reference. Although the invention has been disclosed with reference to its preferred embodiments, from reading this description those of skill in the art may appreciate changes and modification that may be made which do not depart from the scope of the invention as described above and claimed hereafter. It should be understood that the methods and the treating compositions of the present invention may be utilized in hydrocarbon-fired combustion apparatuses other than boilers, as indicated above, to disrupt slag deposits by weakening and/or reducing slag deposit integrity. Other hydrocarbon-fired combustion apparatuses include, for example, hydrocarbon-fired turbines and diesel engines.

WHAT IS CLAIMED IS:

1. A method for disrupting slag deposits formed on an internal surface of a hydrocarbon-fired combustion apparatus, the method comprising:

introducing an effective amount of a treating composition including a deposit disrupting composition into a hydrocarbon-fired combustion apparatus, wherein the effective amount is sufficient to disrupt slag deposits during combustion of a hydrocarbon fuel by weakening and/or reducing slag deposit integrity on the internal surface of the hydrocarbon-fired combustion apparatus where slag formation occurs.

2. The method of claim 1, wherein the deposit disrupting composition includes expandable and/or non-expandable synthetic carbon.

3. The method of claim 1, wherein the deposit disrupting composition includes expandable synthetic carbon.

4. The method of claim 3, wherein the synthetic carbon is an expandable synthetic coke and/or graphite material.

5. The method of claim 4, wherein the expandable synthetic coke and/or graphite material includes particles having sizes ranging between about 0.01 microns (μm) and about 1,000 microns (μm), and wherein the expandable particles are capable of expanding up to at least about 150 times their initial volume when heated above a predetermined temperature.

6. The method of claim 1, wherein the hydrocarbon fuel is coal.

7. The method of claim 1, wherein the hydrocarbon-fired combustion apparatus is a hydrocarbon-fired boiler.

8. The method of claim 7, wherein the hydrocarbon-fired boiler is a coal-fired boiler.

9. The method of claim 1, wherein the treating composition further includes a corrosion inhibitor.
10. The method of claim 9, wherein the inhibitor comprises one or more metal compounds, wherein the metal compounds are selected from the group consisting of a first group of metals including magnesium, calcium, sodium, potassium, barium, and mixtures or combinations thereof, a second group of metals including manganese, iron, cerium, copper, zinc, and mixtures or combinations thereof, a third group of metals silicon, aluminum, chromium, cobalt, nickel, and mixtures or combinations thereof, and mixtures or combinations of any one or more of the metals from these three groups.
11. The method of claim 10, wherein the metal compounds comprise oxygenated metal compounds selected from the group consisting of oxygenated magnesium, oxygenated aluminum or alumina compounds, oxygenated boron compounds and mixtures or combinations thereof.
12. The method of claim 1, wherein the deposit disrupting composition is an inhibitor modified deposit disrupting composition.
13. The method of claim 1, wherein introducing an effective amount of a treating composition includes introducing an effective amount of a treating composition during combustion of the hydrocarbon fuel.
14. The method of claim 1, wherein introducing an effective amount of a treating composition includes introducing the effective amount into a hydrocarbon fuel prior to the fuel entering into the hydrocarbon-fired combustion apparatus.
15. The method of claim 1, wherein introducing an effective amount of a treating composition includes introducing the effective amount into one location or a plurality of locations of the hydrocarbon-fired combustion apparatus.

16. A method for disrupting slag deposits formed on an internal surface of a hydrocarbon-fired boiler, the method comprising:

introducing an effective amount of a treating composition including an expandable and/or non-expandable synthetic carbon into a hydrocarbon-fired boiler, wherein the effective amount is sufficient to disrupt slag deposits during combustion of a hydrocarbon fuel by weakening and/or reducing slag deposit integrity on the internal surface of the hydrocarbon-fired boiler where slag formation occurs.

17. The method of claim 16, wherein the expandable and/or non-expandable synthetic carbon is an expandable synthetic coke and/or graphite material.

18. The method of claim 17, wherein the expandable and/or non-expandable synthetic carbon is an expandable synthetic graphite material.

19. The method of claim 18, wherein the expandable graphite material includes particles having sizes ranging between about 0.01 microns (μm) and about 1,000 microns (μm), and wherein the expandable particles are capable of expanding up to at least about 150 times their initial volume when heated above a predetermined temperature.

20. The method of claim 16, wherein the hydrocarbon-fired boiler is a coal-fired boiler and the hydrocarbon fuel is coal.

21. The method of claim 16, wherein the treating composition further includes a corrosion inhibitor.

22. A system for disrupting slag deposits formed on an internal surface of a hydrocarbon-fired combustion apparatus, the system comprising:

a hydrocarbon-fired combustion apparatus including a combustion chamber for combusting a hydrocarbon fuel;

a hydrocarbon fuel source and a hydrocarbon fuel conduit for introducing the hydrocarbon fuel to the hydrocarbon-fired combustion apparatus; and

a treating composition source and a treating composition conduit for introducing the treating composition, which includes a deposit disrupting composition, to the hydrocarbon-fired combustion apparatus,

wherein the treating composition conduit introduces an effective amount of the treating composition into the hydrocarbon-fired combustion apparatus that is sufficient to disrupt slag deposits, which form as a result of combustion of the hydrocarbon fuel, by weakening and/or reducing slag deposit integrity on an internal surface of the hydrocarbon-fired combustion apparatus where slag formation occurs.

23. The system of claim 22, wherein the hydrocarbon-fired combustion apparatus is a hydrocarbon-fired boiler.

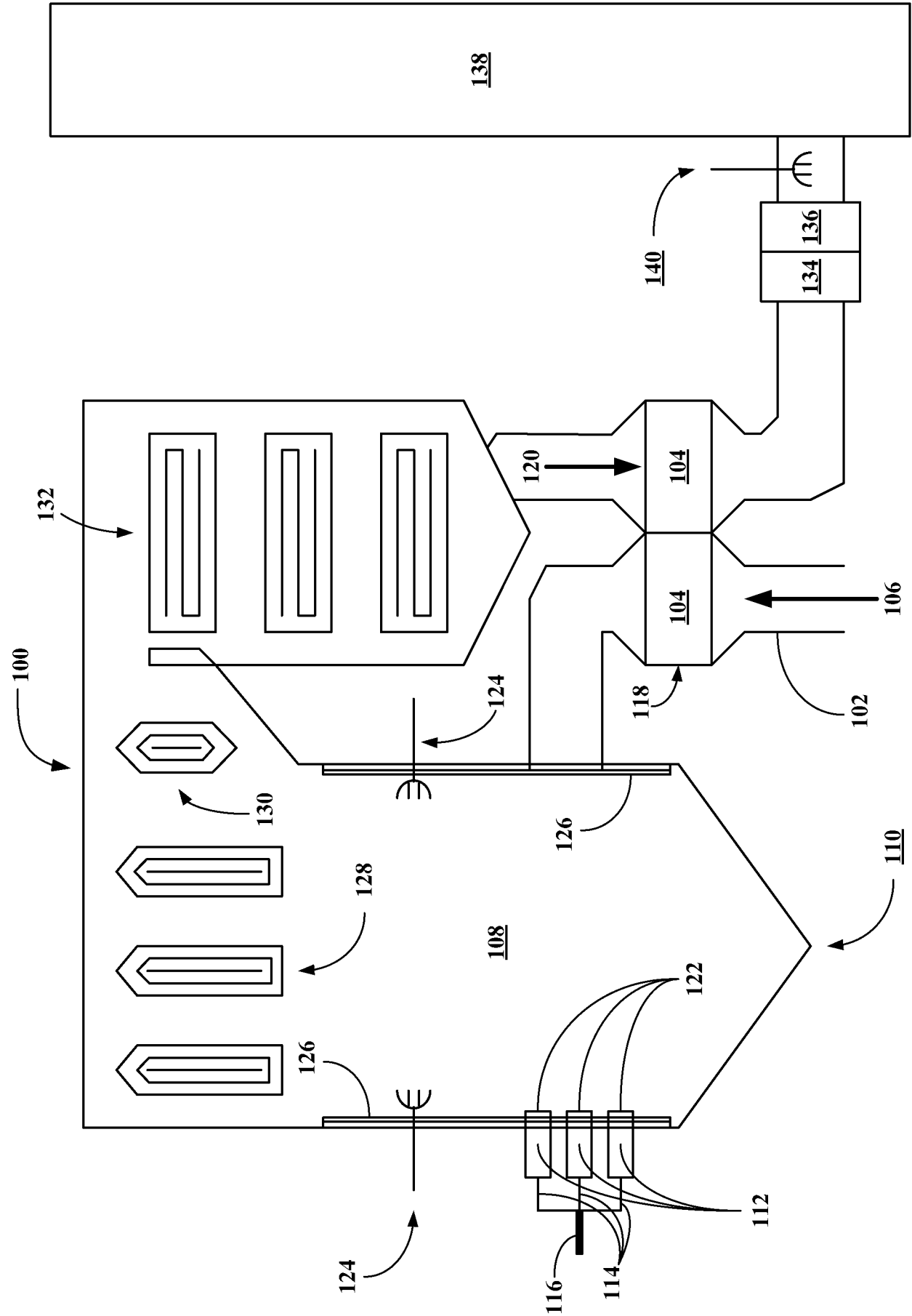
24. The system of claim 23, wherein the hydrocarbon-fired boiler is a coal-fired boiler and the hydrocarbon fuel is coal.

25. The system of claim 22, wherein the deposit disrupting composition includes expandable and/or non-expandable synthetic carbon.

26. The system of claim 25, wherein the expandable and/or non-expandable synthetic carbon is an expandable synthetic carbon.

27. The system of claim 26, wherein the synthetic carbon is an expandable synthetic coke and/or graphite material.

28. The system of claim 22, wherein the treating composition further includes a corrosion inhibitor.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US17/16439

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C04B 5/00, 5/06; C10L 9/00, 9/02, 9/06, 9/10, 9/12; C22B 7/04 (2017.01)

CPC - C04B 5/06, 5/065; C10L 9/02, 9/06, 9/10, 9/12; C22B 7/04; Y02W 30/543

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0312206 A1 (DORNER R. W. et al.) December 13, 2012; paragraphs [0019], [0022], [0039], [0041]; claims 1, 3, 4, 8, 11, 18	1, 6-9, 12-15
X	US 2008/0223270 A1 (ARADI A. A. et al.) September 18, 2008; abstract; paragraphs [0018], [0019], [0060]	1, 6-10, 15
—		11, 28
Y		
X	US 2007/0119351 A1 (WIDMER N. C. et al.) May 31, 2007; figure 1; paragraphs [0021], [0022], [0034]	1, 6-8, 15, 22-24
—		28
Y		
Y	JPH 11172320 A (TATE M.) June 29, 1999; see machine translation	11
A	US 5,611,838 A (FRITZ E. et al.) March 18, 1997; entire document	1-28
A	US 5,397,643 A (VON BONIN W. et al.) March 14, 1995; entire document	1-28
A	US 2,670,284 A (ZVANUT C. M. et al.) February 23, 1954; entire document	1-28
A	US 5,740,745 A (SMYRNIOTIS C. R. et al.) April 21, 1998; entire document	1-28
A	US 5,891,214 A (INNES J. et al.) April 6, 1999; entire document	1-28

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

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