(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 969 124 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
01.08.2018 Bulletin 2018/31

(21) Application number: **14763928.0**

(22) Date of filing: **17.03.2014**

(51) Int Cl.:
C10L 5/04 (2006.01)
C10L 9/10 (2006.01)
C10L 10/02 (2006.01)
C10L 10/04 (2006.01)
F23J 7/00 (2006.01)

(86) International application number:
PCT/US2014/030244

(87) International publication number:
WO 2014/145473 (18.09.2014 Gazette 2014/38)

(54) REDUCING ENVIRONMENTAL POLLUTION AND FOULING WHEN BURNING COAL

REDUZIERUNG VON UMWELTVERSCHMUTZUNG UND FÄULNIS BEI DER VERBRENNUNG VON KOHLE

RÉDUCTION DE LA POLLUTION ENVIRONNEMENTALE ET DE L'ENCRASSEMENT LORS D'UNE COMBUSTION DE CHARBON

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **15.03.2013 US 201361788442 P**
14.03.2014 US 201414210909

(43) Date of publication of application:
20.01.2016 Bulletin 2016/03

(60) Divisional application:
18177527.1

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Printed by Jouve, 75001 PARIS (FR)

Description

INTRODUCTION

[0001] The invention provides compositions and methods for reducing the levels of mercury, nitrogen oxides, and/or sulfur oxides emitted into the atmosphere upon burning of mercury-containing fuels such as coal. In particular, the invention provides for addition of various halogen and other sorbent compositions into the coal burning system during combustion. Use of the sorbents reduces emission of pollutants and prevents fouling in the furnace.

[0002] Significant coal resources exist around the world capable of meeting large portions of the world's energy needs into the next two centuries. High sulfur coal is plentiful, but requires remediation steps to prevent excess sulfur from being released into the atmosphere upon combustion. In the United States, low sulfur coal exists in the form of low BTU value coal in the Powder River basin of Wyoming and Montana, in lignite deposits in the North Central region of North and South Dakota, and in lignite deposits in Texas. But even when coals contain low sulfur, they still contain non-negligible levels of elemental and oxidized mercury and/or other heavy metals.

[0003] Unfortunately, mercury is at least partially volatilized upon combustion of coal. As a result, the mercury tends not to stay with the ash, but rather becomes a component of the flue gases. If remediation is not undertaken, the mercury tends to escape from the coal burning facility into the surrounding atmosphere. Some mercury today is captured by utilities, for example in wet scrubber and SCR control systems. However, most mercury is not captured and is therefore released through the exhaust stack.

[0004] Mercury emissions into the atmosphere in the United States are approximately 50 tons per year. A significant fraction of the release comes from emissions from coal burning facilities such as electric utilities. Mercury is a known environmental hazard and leads to health problems for both humans and non-human animal species. To safeguard the health of the public and to protect the environment, the utility industry is continuing to develop, test, and implement systems to reduce the level of mercury emissions from its plants. In combustion of carbonaceous materials, it is desirable to have a process wherein mercury and other undesirable compounds are captured and retained after the combustion phase so that they are not released into the atmosphere.

[0005] Other pollutants such as nitrogen oxides (NOx) and sulfur oxides (SOx) are released upon combustion of coal. These contribute to environmental problems such as smog and acid rain. The industry is actively pursuing methods of reducing these pollutants as well.

[0006] Certain coal facility operators qualify for tax credits under §45 of the IRS code for their efforts in reducing emissions of these pollutants. Under certain circumstances, these operators have observed an undesirable fouling in their furnaces. For example, when low sulfur sub-bituminous coals are burned as fuel, deposits tend to form on boiler tube surfaces, which leads to lower heat exchange efficiency and increased costs of operation

[0007] Accordingly, operators need sorbent compositions and methods of use that will enable them to achieve desirable reduction of atmospheric pollutants without compromising on heating efficiency.

[0008] Prior art in this technical field is disclosed in documents WO 2006/099611 A1, US 2007/184394 A1, US 2006/210463 A1 and JP H11 82990 A

SUMMARY

[0009] The invention is defined by the combination of features according to claim 1. Sorbents for use especially with sub-bituminous and lignite coals are provided that contain low levels of alkali. The high levels of alkali in sorbents of the prior art can contribute to fouling of a furnace in which they are being burned. By reducing the alkalinity of the sorbents, the operator can minimize the sodium and potassium available in the gas phase for unwanted reactions that lead to formation of deposits on boiler surfaces and elsewhere.

[0010] The sorbents can be used to prepare a refined coal that can be burned to reduce emissions of one or more of mercury, nitrogen (as NOx), and sulfur (as SOx). A method of making the refined coal involves combining a sub-bituminous coal (or a lignite coal) and sorbent components. In one embodiment, the sorbents are 0.001- 1 wt % of a liquid sorbent, and 0.1 to 10% by weight of a powder sorbent, wherein the percentages are by weight based on the total weight of the refined coal. The liquid sorbent contains a bromine compound and the powder sorbent contains calcium, silica, alumina, and further comprises less than 1% Na_2O by weight and less than 1% K_2O by weight, and wherein the powder sorbent further comprises less than 0.1% by weight chlorine.

[0011] According to the invention, the powder sorbent contains cement kiln dust (CKD), which is helpful in reducing emissions of NOx, with the improvement that, when the CKD is high in alkali, some of the CKD is substituted by lower alkali materials to reach a specification of less than 2% or less than 1% total alkali. In various embodiments, the powder sorbent also meets a low chlorine specification to reduce fouling in sub-bituminous and lignite coals.

DESCRIPTION

[0012] In various embodiments, the invention provides compositions and methods for reducing emissions of mercury, nitrogen oxides (NOx), and sulfur oxides (SOx) that arise from the combustion of mercury-containing fuels such as coal. A commercially valuable embodiment is use of the invention to reduce nitrogen, sulfur and/or mercury emissions from coal burning facilities to protect the environment and comply with government regulations and treaty obligations. Improvements to powder sorbents provide superior performance by reducing fouling in coal-burning furnaces, while removal of environmental pollutants such as NOx and SOx are not deleteriously affected.

[0013] In various embodiments, the methods prevent release of mercury into the atmosphere from point sources, such as coal-burning utilities by capturing the mercury in the ash, while at the same time minimizing furnace fouling that could decrease the efficiency of the furnace. Further, the methods prevent release of mercury and other heavy metals into the environment by leaching from solid wastes such as coal ash produced by burning the mercury containing coal. In both these ways, mercury is kept out of bodies of water. Thus, prevention or reduction of mercury emissions from such facilities as coal-burning utilities leads to a variety of environmental benefits, including less air pollution, less water pollution, and less hazardous waste production, with less resulting ground contamination. For convenience but without limitation, advantageous features of the invention are illustrated as preventing air, water, and ground pollution by mercury or other heavy metals.

[0014] In one embodiment, a method of burning coal in a furnace to reduce emissions of NO_X and at least one of SOx and mercury is provided. The method involves burning a refined coal in the furnace. The refined coal in turn is an admixture of sub-bituminous coal, a bromine compound and a powder sorbent. The powder sorbent contains calcium, silica, alumina, and is further characterized by a low alkali value of less than 1% by weight Na_2O and less than 1% by weight K_2O, based on the weight of the powder sorbent, and preferably also by a low chlorine value of less than 0.5%, less than 0.3%, or less than 0.1%. In various embodiments, treat levels of the bromine compound are 0.001 to 1.0% by weight, while typical treat levels of the powder sorbent are 0.1 to 10% by weight percentages are based on the weight of the coal. In various embodiments, the powder sorbent contains CKD or a mixture of CKD with other low alkali powder described herein. The powder sorbent can also contain aluminosilicate clay such a kaolin or metakaolin.

[0015] In another embodiment, there is provided a method of generating energy through combustion of a mercury containing sub-bituminous coal in the furnace of the coal burning facility. The method involves first applying a first sorbent composition onto coal and delivering the coal with the applied first sorbent into the furnace. At the same time, a second sorbent is added into the furnace as the coal with the applied first sorbent is being delivered. The coal is then combusted in the presence of the first and second sorbents in the furnace to produce heat energy and ash. The first sorbent contains a bromine compound and the second has a composition of greater than 40% by weight CaO, greater than 10% by weight SiO_2, 2 to 10% Al_2O_3, 1 to 5% Fe_2O_3, 1 to 5% MgO, less than 1% by weight Na_2O, and less than 1% Ka_2O. In embodiments, the second sorbent has less than 0.5% chlorine

[0016] In another embodiment, a method of making a refined coal is provided. The refined coal contains sub-bituminous coal and added sorbent components. The method involves add mixing coal, a liquid sorbent (for example 0.001 to 1% by weight, based on the coal) and a powder sorbent (for example 0.1 to 10% by weight based on the coal), wherein the liquid sorbent comprises a bromine compound and powder sorbent comprises greater than 40% CaO, greater than 10% SiO_2, 2 to 10% Al_2O_3, 1 to 5% Fe_2O_3, 1 to 5% MgO, less than 1% Na_2O, and less than 1% K_2O. In various embodiments, the powder sorbent is further characterized as having less than 0.5% chlorine or less than 0.1% chlorine.

[0017] Advantageously, use of the noted powder sorbents, especially the compositions that are low in total alkali, low in chlorine, or both has been found to be effective at reducing fouling in furnaces that are burning sub-bituminous coals or lignite coal, such as those of the Powder River Basin (PRB). By using the modified sorbents described herein, furnace operators can comply with environmental regulations and qualify for certain tax benefits under the United States IRS code, and at the same time avoid undesirable fouling of the furnace and associated facilities.

[0018] Further examples of each of the limitations of the embodiments are given in the description that follows. It is to be understood that the various components and the method steps described herein can be mixed and matched to provide other embodiments not literally recited or exemplified. Examples are also given, enabling the person of skill in the art to carry out the invention and to achieve the noted environmental and operational benefits.

[0019] Various sorbent components are used in combination to treat coal ahead of combustion and/or to be added into the flame or downstream of the flame, preferably at minimum temperatures to assure complete formation of the refractory structures that result in various advantages of the methods. When the components are added to coal before combustion, the product is a refined coal, the use of which lowers environmental pollution and may qualify the utility for certain tax benefits in the United States.

[0020] The sorbent components include calcium, alumina, silica, and halogen. To reduce fouling when burning sub-bituminous or lignite coals such as those of the Powder River Basin, it has been found to be advantageous to keep K_2O of the sorbent to a maximum of 1% and to keep Na_2O of the sorbent to a maximum of 1%, wherein percentages are by weight of the powder sorbent containing calcium, alumina, silica, and other components. In embodiments, Na_2O and

K_2O are each less than 0.5% or are each less than 0.1%. In addition, in various embodiments, it has also been found advantageous to provide the powder sorbent with low chlorine, e.g. <0.5%, < 0.3%, or <0.1%.

[0021] Calcium is provided by adding to the powder sorbent a compound or composition that has a non-negligible amount of calcium. For example, many alkaline powders contain 20% or more calcium, based on CaO. Examples are limestone, lime, calcium oxide, calcium hydroxide (slaked lime), portland cement and other manufactured products or by-products of industrial processes, and calcium-containing aluminosilicate minerals. Silica and alumina content is based on SiO_2 and Al_2O_3 equivalents, even though it is appreciated that silica and alumina are often present in a more complex chemical or molecular form.

[0022] According to the invention, it is advantageous for the powder sorbent to contain an effective amount of cement kiln dust (CKD), which is believed to contribute to the reduction of NOx from the coal-burning facility. Some CKD has a relatively high chlorine content, even as high as 10%. If CKD is used, depending on the source of CKD and its natural content of alkali and chlorine, the resulting powder could wind up being too high in alkali and/or chlorine for best results when burning subbituminous or lignite coals. If so, it is advantageous to blend off some of the CKD with other materials lower in sodium and potassium, preferably to achieve a specification of <1% Na_2O and <1% K_2O, or even <0.5% Na_2O and <0.5% K_2O, as well as a low chlorine spec as noted. Such low alkali materials include grind outs (cement kiln clinker that may or may not meet cement product specification and is subsequently ground for blending with CKD); kiln feed (the feed stream going into the cement kiln, including all the components for manufacturing cement, e.g. Ca, Mg, Si, Al, Fe, and so on); transition cement (cement product in silo that is emptied to make room for a specific new cement product; weathered clinker (clinker that has been impounded on site, recovered and ground before adding to the CKD); impound CKD (CKD from on-site impound or waste storage); and limestone. To the extent that any of these materials represent waste products that would otherwise go to waste or have to be landfilled, additional environmental benefits are achieved by their use in the sorbents described herein.

[0023] In various embodiments, together, the components

- reduce emissions of mercury, nitrogen oxides, and sulfur oxides;
- reduce emissions of elemental and oxidized mercury;
- increase the efficiency of the coal burning process through deslagging of boiler tubes;
- prevent the fouling of the furnace by unwanted deposits;
- increase the level of Hg, As, Pb, and/or Cl in the coal ash;
- decrease the levels of leachable heavy metals (such as Hg) in the ash, preferably to levels below the detectable limits; and
- make a highly cementitious ash product.

[0024] As used herein, all percentages are on a weight basis, unless indicated as otherwise. It should be noted that the chemical compositions of various materials described herein are expressed in terms of simple oxides calculated from elemental analysis, typically determined by x-ray fluorescence techniques. While the various simple oxides may be, and often are, present in more complex compounds in the material, the oxide analysis is a useful method for expressing the concentration of compounds of interest in the respective compositions.

[0025] In a typical coal burning facility, coal arrives in railcars. If sorbents have already been applied, it is a refined coal. It is a raw coal if sorbents have not yet been applied. In a typical illustrative embodiment, the coal is delivered onto a receiving belt, which leads the coal into a pug mill. After the pug mill, the coal is discharged to a feed belt and deposited in a coal storage area. Under the coal storage area there is typically a grate and bin area; from there a belt transports the coal to an open stockpile area, sometimes called a bunker. Stoker furnaces can be fed with coal from the bunker or from a crusher. For furnaces burning pulverized coal, the coal is delivered by belt or other means to milling equipment such as a crusher and ultimately to a pulverizer. In a storage system, coal is pulverized and conveyed by air or gas to a collector, from which the pulverized coal is transferred to a storage bin, from which the coal is fed to the furnace as needed. In a direct fired system, coal is pulverized and transported directly to the furnace. In a semi-direct system, the coal goes from the pulverizer to a cyclone collector. The coal is fed directly from the cyclone to the furnace.

[0026] During operation coal is fed into the furnace and burned in the presence of oxygen. For high btu fuels, typical flame temperatures in the combustion chamber are on the order of about 1480°C (2700°F) to about 1640°C (3000°F) or even higher, such as about 1815°C (3300°F) to about 1982°C (3600°F).

[0027] A refined coal is produced by adding sorbents to coal before combustion. The sorbents can be added by the coal producer and shipped to the furnace operator, or the refined coal can be produced in a separate facility near or on the property of the operator. In the case of refined coal, a coal containing all the sorbent components is fed to the furnace for combustion.

[0028] In various other embodiments, sorbent compositions according to the invention are added to the raw coal or into various parts of the furnace during combustion. In non-limiting fashion, sorbents are added to the coal, in the pug mill, on the receiving belt or feed belt, in the coal storage area, in the collector, in the storage bin, in the cyclone collector, in the pulverizer before or during pulverization, and/or while being transported from the pulverizer to the furnace for combustion. Conveniently, in various embodiments the sorbents are added to the coal during processes that mix the coal such as the in the pug mill or in the pulverizer. In a preferred embodiment, the sorbents are added onto the coal in the pulverizers.

[0029] Alternatively or in addition, sorbent components are added into the coal burning system by injecting them into the furnace during combustion of the fuel. In a preferred embodiment, they are injected into the fireball or close to the fireball, for example where the temperature is above about 1093°C (2000°F), above about 1260°C (2300°F), or above about 1480°C (2700°F). According to the design of the burners and the operating parameters of the furnace, effective sorbent addition takes place along with the fuel, with the primary combustion air, above the flame, with or above the overfire air, and so on. Also depending on the furnace design and operation, sorbents are injected from one or more faces of the furnace and/or from one or more corners of the furnace. Addition of sorbent compositions and sorbent components tends to be most effective when the temperature at injection is sufficiently high and/or the aerodynamics of the burners and furnace set up lead to adequate mixing of the powder sorbents with the fuel and/or combustion products. Alternatively or in addition, sorbent addition is made to the convective pathway downstream of the flame and furnace. In various embodiments, optimum injection or application points for sorbents are found by modeling the furnace and choosing parameters (rate of injection, place of injection, distance above the flame, distance from the wall, mode of powder spraying, and the like) that give the best mixing of sorbent, coal, and combustion products for the desired results.

[0030] In coal burning systems, hot combustion gases and air move by convection away from the flame through the convective pathway in a downstream direction (i.e., downstream in relation to the fireball). The convective pathway of the facility contains a number of zones characterized by the temperature of the gases and combustion products in each zone. Generally, the temperature of the combustion gas falls as it moves in a direction downstream from the fireball. From the furnace, where the coal in one example is burning at a temperature of approximately about 1480°C - 1650°C (2700°F - 3600°F), the fly ash and combustion gases move downstream in the convective pathway to zones of ever decreasing temperature. To illustrate, downstream of the fireball is a zone with temperature less than 1480°C (2700°F). Further downstream, a point is reached where the temperature has cooled to about 816°C (1500°F). Between the two points is a zone having a temperature from about 816°C (1500°F) to about 1480°C (2700°F). Further downstream, a zone of less than 1500°F is reached, and so on. Further along in the convective pathway, the gases and fly ash pass through lower temperature zones until the baghouse or electrostatic precipitator is reached, which typically has a temperature of about 149°C (300°F) before the gases are emitted up the stack.

[0031] The combustion gases contain carbon dioxide as well as various undesirable gases containing sulfur, nitrogen, and mercury. The convective pathways are also filled with a variety of ash which is swept along with the high temperature gases. To remove the ash before emission into the atmosphere, particulate removal systems are used. A variety of such removal systems, such as electrostatic precipitators and a bag house, are generally disposed in the convective pathway. In addition, chemical scrubbers can be positioned in the convective pathway. Additionally, there may be provided various instruments to monitor components of the gas such as sulfur (as SOx), nitrogen (as NOx), and mercury.

[0032] Thus, in various embodiments, the process of the present invention calls for the application of sorbents
directly into the furnace during combustion (addition "co-combustion")
directly to a fuel such as coal before combustion (addition "pre-combustion" to make a refined coal);
directly into the gaseous stream after combustion preferably in a temperature zone of greater than 500°C and preferably greater than 800°C (addition "post-combustion); or
in a combination of pre-combustion, co-combustion, and post-combustion additions.

[0033] Application of the sorbents is made "into the coal burning system" in any of pre-combustion, co-combustion, or post-combustion modes, or in any combination. When the sorbents are added into the coal burning system, the coal or other fuel is said to be combusted "in the presence" the various sorbents, sorbent compositions, or sorbent components

[0034] In a preferred embodiment downstream addition is carried out where the temperature is about 816°C (1500°F) to about (1480°C (2700°F). In some aspects, and depending upon the specifics of furnace design and the layout of the convective pathways, the cutoff point or distinction between "into the furnace", "into the fireball", and "into the convective pathways" can be rather arbitrary. At some point, the combustion gases leave what is clearly a burning chamber or furnace and enter a separate structure that is clearly a flue or convective pathway for gases downstream of the furnace. However, many furnaces are quite large and so permit addition of sorbents "into the furnace" at a considerable distance from where the fuel and air are being fed to form the fireball. For example, some furnaces have overfire air injection ports and the like specifically designed to provide additional oxygen at a location above the fireball to achieve more complete combustion and/or control of emissions such as nitrogen oxides. The overfire air ports can be 6,1m (20 feet) or higher above the fuel injection. In various embodiments, sorbent components or compositions are injected directly into the fireball along with coal being fed, at a location above the coal feed, above or below the overfire air ports, or at a higher location within the burning chamber, such as at or just under the nose of the furnace. Each of these locations is characterized by a temperature and by conditions of turbulent flow that contribute to mixing of the sorbents with the fuel and/or the combustion products (such as the fly ash). In embodiments involving applying sorbent compositions into the furnace or downstream of the furnace, application is preferably made where the temperature is above 816°C (1500°F), preferably above 1903°C (2000°F), more preferably where the temperature is above 1260°C (2300°F), and most preferably where the temperature is above 1482°C (2700°F).

[0035] In various embodiments described herein, sorbent compositions that tend to reduce or remediate the release of mercury, nitrogen, and/or sulfur from coal burning utilities also have the beneficial effect of rendering the ash produced by combustion of the fuel highly cementitious. As a result, the ash is usable in commerce as a partial or complete replacement for portland cement in various cement and concrete products.

[0036] Burning the coal with the sorbent compositions described herein results in an ash that has, in various embodiments, increased levels of the heavy metals compared to coal burned without the sorbent, but which nevertheless contains lower levels of leachable heavy metals than the ash produced without the sorbents. As a result, the ash is safe to handle and to sell into commerce, for example as a cementitious material.

[0037] To make the ash products, a carbonaceous fuel is burned to produce heat energy from combustion of the carbonaceous material. Unburned material and particulate combustion products form ash, some of which collects at the bottom of the furnace, but the majority of which is collected as fly ash from the flue by precipitators or filters, for example a bag house on a coal burning facility. The content of the bottom ash and the fly ash depends on the chemical composition of the coal and on the amount and composition of sorbent components added into the coal burning facility during combustion.

[0038] In various embodiments, mercury emissions from the coal burning facility are monitored. Emissions are monitored as elemental mercury, oxidized mercury, or both. Elemental mercury means mercury in the ground or zero oxidation state, while oxidized mercury means mercury in the +1 or +2 oxidation state. Depending on the level of mercury in the flue gas prior to emission from the plant, the amount of sorbent composition added pre-, co-, and/or post-combustion is raised, lowered, or is maintained unchanged. In general, it is desirable to remove as high a level of mercury as is practical. In embodiments, mercury removal of at least 40% up to 90% and greater can be achieved, based on the total amount of mercury in the coal. This number refers to the mercury removed from the flue gases so that mercury is not released through the stack into the atmosphere. In this aspect, the numbers correspond to the percent reductions in emissions of mercury from the facility, compared to burning the coal without sorbent. Normally, removal of mercury from the flue gases leads to increased levels of mercury in the ash. To minimize the amount of sorbent added into the coal burning process so as to reduce the overall amount of ash produced in the furnace, it is desirable in many embodiments to use the measurements of mercury emissions to adjust the sorbent composition rate of addition to one which will achieve the desired mercury reduction without adding excess material into the system.

[0039] In various embodiments of burning coal or other fuels with the added sorbent components, mercury and other heavy metals in the coal such as arsenic, antimony, lead, and others report to the bag house or electrostatic precipitator and become part of the overall ash content of the coal burning plant; alternatively or in addition, the mercury and heavy metals are found in the bottom ash. As such, emissions of mercury and other heavy metals from the facility are reduced.

[0040] In general, mercury and other heavy metals in the ash are resistant to leaching under acidic conditions, even though they tend to be present in the ash at elevated levels relative to ash produced by burning coal without the sorbent components described herein. Advantageously, heavy metals in the ash do not leach beyond regulatory levels; in fact, a decreased level of leachable heavy metal is observed in the ash on a ppm basis, even though the ash normally contains a higher absolute level of heavy metals by virtue of being produced by burning with the sorbents. Because in addition the cementitious nature of the ash is enhanced, the ash from the combustion (coal ash) is valuable for sale in commerce and use, for example, as a cementitious material to make portland cements as well as concrete products and ready mixes.

[0041] In preferred embodiments, leaching of heavy metals is monitored or analyzed periodically or continuously during combustion. The TCLP procedure of the United States Environmental Protection Agency is a commonly used method. The amount of sorbent, particularly of sorbent components with Si (SiO_2 or equivalents) and/or Al (Al_2O_3 or equivalents), is adjusted based on the analytical result to maintain the leaching in a desired range.

[0042] In one embodiment, a method is provided for burning coal to reduce the amount of mercury released into the atmosphere. The method involves applying a sorbent composition comprising a halogen compound into the system in which the coal is being combusted. The halogen compound is preferably a bromine compound; in a preferred embodiment, the sorbent is free of alkali metal compounds so as to avoid corrosion on boiler tubes or other furnace components. The coal is combusted in the furnace to produce ash and combustion gases. The combustion gases contain mercury, sulfur and other components. To accomplish a desired reduction of mercury in the combustion gases in order to limit release into the atmosphere, the mercury level in the combustion gases is preferably monitored, for example by measuring the level analytically. In preferred embodiments, the amount of the sorbent composition applied is adjusted (i.e., by increasing it, decreasing it, or in some cases deciding to leave it unchanged) depending on the value of the mercury level measured in the combustion gases. In a preferred embodiment, the sorbent is added into the system by applying it to the coal pre-combustion, then delivering the coal containing the sorbent into the furnace for combustion.

[0043] In another embodiment, sorbent components comprising a halogen (preferably bromine or iodine, and most preferably bromine) compound and at least one aluminosilicate material are applied into the coal burning system. The components are added separately or as a single sorbent composition, and are optionally added onto the coal pre-combustion, into the furnace during combustion, or into the flue gases downstream of the furnace at suitable temperatures. In a preferred embodiment, the components are added to the coal pre-combustion, and the coal containing the sorbent is then delivered into the furnace for combustion. As before, preferably mercury is monitored in the flue gases and the sorbent application rate is adjusted depending on the value of the measured mercury level. The halogen contributes to lowering the level of mercury emissions, while the aluminosilicate contributes to making mercury captured in the ash non-leaching.

[0044] In a related embodiment, a method for reducing leaching of mercury and/or of other heavy metals from ash produced from the combustion of coal or other fuel in a coal burning system or in an incinerator involves introducing sorbents containing silica and alumina into the incinerator or coal burning system during combustion, measuring leaching of mercury and/or other heavy metals from the resulting ash, and adjusting the level of silica and alumina added according to the measured leaching of heavy metals. If leaching is higher than desired, the rate of application of the sorbent can be increased to bring the leaching back down into the desired range. In a preferred embodiment, the sorbent further contains a halogen (e.g. bromine) compound to enhance capture of mercury in the ash. Advantageously, the sorbent containing silica and alumina is added in a powder composition that contains <1% Na_2O and <1% K_2O, to reduce or eliminate fouling.

[0045] In one embodiment, there is provided a method for reducing the amount of oxidized mercury in flue gases that are generated by combustion of mercury-containing carbonaceous fuel such as coal while at the same time producing a cementitious ash product. The method comprises burning the fuel in the presence of an alkaline powder sorbent wherein the powder sorbent comprises calcium, silica, and alumina. The alkaline powder is added to the coal pre-combustion, injected into the furnace during combustion, applied into the flue gases downstream of the furnace (preferably where the temperature is 816°C (1500°F) or greater, or in any combination. The powders are alkaline, characterized by a pH above 7 when combined with water, preferably above 8 and preferably above 9. Advantageously, the sorbent contains less than 1% each, less than 0.5% each, or less than 0.1% each by weight of alkalis such as Na_2O and K_2O. In various embodiments, the sorbent further contains iron and magnesium. In various embodiments, the aluminum content of the sorbent is higher than the alumina content of portland cement, preferably above about 5% or above about 7% alumina.

[0046] To monitor emissions while the fuel is burning, a level of mercury (oxidized, elemental, or both) is measured in the flue gases downstream from the furnace. The measured mercury level is compared to a target level and, if the measured level is above the targeted level, the amount of powder sorbent added relative to the amount of fuel being burned is increased. Alternatively, if the measured level is at or below the target level, the rate of sorbent addition can be decreased or maintained unchanged.

[0047] In another embodiment, the powder composition is an alkaline sorbent composition that contains an alkaline calcium component as well as significant levels of silica and alumina. In a non-limiting embodiment, the powder composition comprises 2 to 50% of an aluminosilicate material and 50 to 98% by weight of an alkaline powder comprising calcium. In a preferred embodiment, the alkaline powder comprises one or more of lime, calcium oxide, portland cement, cement kiln dust, lime kiln dust, and sugar beet lime, while the aluminosilicate material contains one or more selected from the group consisting of calcium montmorillonite, sodium montmorillonite, and kaolin. The powder sorbent comprises CKD and other material to meet a low alkali specification and/or a low chorine specification.

[0048] The powder composition is added to the coal at a rate of about 0.1 to about 10% by weight, based on the amount of coal being treated with the sorbents for a batch process, or on the rate of coal being consumed by combustion for a continuous process. In embodiments, the rate is 0.1-5%, 0.1 - 2%, 0.1-1.5%, 0.1 - 1%, from 1 to 8% by weight, 2 to 8% by weight, 4 to 8% by weight, 4 to 6% by weight, or about 6% by weight. In certain embodiments, the powder composition is injected to the fireball or furnace during combustion and/or is applied to the coal under ambient conditions, prior to its combustion. The temperature at the injection point is preferably at least about 538°C (1000°F) or higher. For some low value fuels, this corresponds to injection into or close to the fireball.

[0049] In a further embodiment, a method for reducing mercury and/or sulfur emitted into the environment during combustion of coal in a coal burning system comprises adding sorbent components comprising bromine, calcium, silica, and alumina into the coal burning system and combusting the coal in the presence of the sorbent components to produce combustion gases and fly ash. The amount of mercury in the combustion gases is measured and level of components containing bromine added into the system is adjusted depending on the measured value of mercury in the combustion gases.

[0050] In various embodiments, the four components (calcium, silica, alumina, and bromine) are added together or separately to the coal pre-combustion, to the furnace, and/or to the flue gases at suitable temperature as described herein. Sorbents containing the components preferably contain a maximum of 1% by weight Na_2O and a maximum of 1% by weight K_2O. Preferably, bromine is present at a level effective to a capture, in the ash, at least 20%, at least 40%, at least 80% or at least 90% of the mercury in the coal, and silica and alumina are present at levels effective to produce fly ash with a leaching value of less than 0.2 ppm (200 ppb) with respect to mercury, preferably less than 100 ppb Hg, less than 50 ppb, and most preferably less than 2 ppb with respect to mercury. A level of 2 ppb represents the current lower detectable limit of the TCLP test for mercury leaching.

[0051] In certain embodiments, the methods provide coal ash and/or fly ash containing mercury at a level corresponding to capture in the ash of at least 40% or of at least 90% of the mercury originally in the coal before combustion. In some embodiments, the mercury level is higher than in known fly ashes due to capture of mercury in the ash rather than release of mercury into the atmosphere. Fly ash produced by the process contains up to 200 ppm mercury or higher; in some embodiments the mercury content of the fly ash is above 250 ppm. Since the volume of ash is normally increased by use of the sorbents (in typical embodiments, the volume of ash about doubles), the increased measured levels of mercury represent significant capture in the ash of mercury that, without the sorbents, would have been released into the environment. The content in the fly ash of mercury and other heavy metals such as lead, chromium, arsenic, and cadmium is generally higher than in fly ash produced from burning coal without the added sorbents or sorbent components.

[0052] Preferably, the mercury in the coal ash is non-leaching in that it exhibits a concentration of mercury in the extract of less than 0.2 ppm when tested using the Toxicity Characteristic Leaching Procedure (TCLP), test Method 1311 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW - 846 - Third Edition, as incorporated by reference in 40 CFR §260.11. It is normally observed that fly ash from burning coal with the sorbents described herein has less leachable mercury than ash produced from burning coal without the sorbent, even though the total mercury content in ash produced from the sorbent treated coal is higher by as much as a factor of 2 or more over the level in ash produced by burning without the sorbents. To illustrate, typical ash from burning of PRB coal contains about 100-125 ppm mercury; in various embodiments, ash produced by burning PRB coal with about 6% by weight of the sorbents described herein has about 200-250 ppm mercury or more.

[0053] In another embodiment, there is provided a hydraulic cement product containing portland cement and from 0.1% to about 99% by weight, based on the total weight of the cement product, of a coal ash or fly ash described above.

[0054] In a further embodiment, there is provided a pozzolanic product comprising a pozzolan and from 0.01% to about 99% by weight, based on the total weight of the pozzolanic product of the ash described above.

[0055] There is also provided a cementitious mixture containing the hydraulic cement product.

[0056] There is further provided a concrete ready mix product containing aggregate and the hydraulic cement product.

[0057] In another embodiment, a cementitious mixture contains coal ash described herein as the sole cementitious component; in these embodiments, the ash is a total replacement for conventional cements such as portland cement. The cementitious mixtures contain cement and optionally aggregate, fillers, and/or other admixtures. The cementitious mixtures are normally combined with water and used as concrete, mortars, grout, flowable fill, stabilized base, and other applications.

[0058] The methods thus encompass burning coal with the added sorbents to produce coal ash and energy for heat or electricity generation. The ash is then recovered and used to formulate cementitious mixtures including cements, mortars, and grouts.

[0059] In a preferred embodiment, powder sorbent compositions described herein contain one or more alkaline powders containing calcium, along with lesser levels of one or more aluminosilicate materials. The halogen component, if desired, is added as a further component of the alkaline powder or is added separately as part of a liquid or powder composition. Advantageously, use of the sorbents leads to a reduction in emissions or releases of sulfur, nitrogen, mercury, other heavy metals such as lead and arsenic, and/or chlorine from the coal burning system.

[0060] Sorbent compositions used in various embodiments of the invention described above and herein contain components that contribute calcium, silica, and/or alumina, preferably in the form of alkaline powders. In various embodiments, the compositions also contain iron oxide, In a non-limiting example, the powder sorbent contains about 2-10% by weight Al_2O_3, greater than 40%, for example about 40-70% CaO, >10% SiO_2, about 1-5% Fe_2O_3, and <2% of total alkalis such as sodium oxide and potassium oxide, preferably less than 1%. The components comprising calcium, silica, and alumina - and other elements if present - are combined together in a single composition or are added separately or in any combination as components to the fuel burning system. In preferred embodiments, use of the sorbents leads to reductions in the amount of NOx, SOx, and/or mercury released into the atmosphere

[0061] Advantageously, the sorbent compositions contain suitable high levels of alumina and silica. It is believed that the presence of alumina and/or silica leads to several advantages seen from use of the sorbent. To illustrate, it is believed that the presence of alumina and/or silica and/or the balance of the silica/alumina with calcium, iron, and other ingredients contributes to the low acid leaching of mercury and/or other heavy metals that is observed in ash produced by combustion of coal or other fuels containing mercury in the presence of the sorbents.

[0062] As noted, the components that contribute calcium, silica, and/or alumina are preferably provided as alkaline powders. Without being limited by theory, it is believed that the alkaline nature of the sorbent components leads at least in part to the desirable properties described above. For example, it is believed the alkaline nature of the powders leads to a reduction in sulfur pitting. After neutralization, it is believed a geopolymeric ash is formed in the presence of the sorbents, coupling with silica and alumina present in the sorbent to form a ceramic like matrix that reports as a stabilized ash. The stabilized ash is characterized by very lowing leaching of mercury and other heavy metals. In some embodiments, the leaching of mercury is below detectable limits. However, for some coals, it is also observed that high alkali in the sorbent components tends to contribute to undesirable fouling. Accordingly, the present teachings describe how to overcome that disadvantage by using sorbents of lower alkalinity (as measured by content of Na_2O and K_2O) and/or lower chlorine, especially for use with sub-bituminous and lignite coals.

[0063] Sources of calcium for the sorbent compositions of the invention include, without limitation, calcium powders such as calcium carbonate, limestone, dolomite, calcium oxide, calcium hydroxide, calcium phosphate, and other calcium salts. Industrial products such as limestone, lime, slaked lime, and the like contribute major proportions of such calcium salts. As such, they are suitable components for the sorbent compositions of the invention.

[0064] Other sources of calcium include various manufactured products. Such products are commercially available, and some are sold as waste products or by-products of other industrial processes. In preferred embodiments, the products further contribute either silica, alumina, or both to the compositions of the invention. Non-limiting examples of industrial products that contain silica and/or alumina in addition to calcium include portland cement, cement kiln dust, lime kiln dust, sugar beet lime, slags (such as steel slag, stainless steel slag, and blast furnace slag), paper de-inking sludge ash, cupola arrester filter cake, and cupola furnace dust.

[0065] These and optionally other materials are combined to provide alkaline powders or mixtures of alkaline powders that contain calcium, and preferably also contain silica and alumina. Other alkaline powders containing calcium, silica, and alumina include pozzolanic materials, wood ash, rice hull ash, class C fly ash, and class F fly ash. In various embodiments, these and similar materials are suitable components of sorbent compositions, especially if the resulting composition containing them as components falls within the preferred range of 2 to 10% by weight Al_2O_3, greater than 40% by weight CaO, greater than 10% by weight SiO_2, about 1 to 5% Fe_2O_3, and less than 2% by weight total alkali. Mixtures of materials are also used. Non-limiting examples include mixtures of portland cement and lime, and mixtures containing cement kiln dust, such as cement kiln dust and lime kiln dust.

[0066] Sugar beet lime is a solid waste material resulting from the manufacture of sugar from sugar beets. It is high in calcium content, and also contains various impurities that precipitate in the liming procedure carried out on sugar beets. It is an item of commerce, and is normally sold to landscapers, farmers, and the like as a soil amendment.

[0067] Cement kiln dust (CKD) generally refers to a byproduct generated within a cement kiln or related processing equipment during portland cement manufacturing.

[0068] Generally, CKD comprises a combination of different particles generated in different areas of the kiln, pre-treatment equipment, and/or material handling systems, including for example, clinker dust, partially to fully calcined material dust, and raw material (hydrated and dehydrated) dust. The composition of the CKD varies based upon the raw materials and fuels used, the manufacturing and processing conditions, and the location of collection points for CKD within the cement manufacturing process. CKD can include dust or particulate matter collected from kiln effluent (i.e., exhaust) streams, clinker cooler effluent, pre-calciner effluent, air pollution control devices, and the like. Commercial CKD has a range of alkalinity, depending on its source. In some embodiments, it is possible to meet the low alkali spec of the powder sorbents described herein by using the low alkali CKD. If only high alkali CKD is available, it may be necessary to blend off or substitute part of the high alkali CKD product with the lower alkali material described above.

[0069] While CKD compositions will vary for different kilns, CKD usually has at least some cementitious and/or pozzolanic properties, due to the presence of the dust of clinker and calcined materials. Typical CKD compositions comprise silicon-containing compounds, such as silicates including tricalcium silicate, dicalcium silicate; aluminum-containing compounds, such as aluminates including tricalcium aluminate; and iron-containing compounds, such as ferrites including tetracalcium aluminoferrite. CKD generally comprises calcium oxide (CaO). Exemplary CKD compositions comprise about 10 to about 60% calcium oxide, optionally about 25 to about 50%, and optionally about 30 to about 45% by weight. In some embodiments, CKD comprises a concentration of free lime (available for a hydration reaction with water) of about 1 to about 10 %, optionally of about 1 to about 5%, and in some embodiments about 3 to about 5%. Further, in certain embodiments, CKD comprises compounds containing alkali metals, alkaline earth metals, and sulfur, *inter alia.*

[0070] Other exemplary sources for the alkaline powders comprising calcium, and preferably further comprising silica and alumina, include various cement-related byproducts (in addition to portland cement and CKD described above). Blended-cement products are one suitable example of such a source. These blended cement products typically contain mixes of portland cement and/or its clinker combined with slag(s) and/or pozzolan(s) (*e.g.,* fly ash, silica fume, burned shale). Pozzolans are usually silicaceous materials that are not in themselves cementitious, but which develop hydraulic cement properties when reacted with free lime (free CaO) and water. Other sources are masonry cement and/or hydraulic lime, which include mixtures of portland cement and/or its clinker with lime or limestone. Other suitable sources are aluminous cements, which are hydraulic cements manufactured by burning a mix of limestone and bauxite (a naturally occurring, heterogeneous material comprising one or more aluminum hydroxide minerals, plus various mixtures of silica, iron oxide, titania, aluminum silicates, and other impurities in minor or trace amounts). Yet another example is a pozzolan cement, which is a blended cement containing a substantial concentration of pozzolans. Usually the pozzolan cement comprises calcium oxide, but is substantially free of portland cement. Common examples of widely-employed pozzolans include natural pozzolans (such as certain volcanic ashes or tuffs, certain diatomaceous earth, burned clays and shales) and synthetic pozzolans (such as silica fume and fly ash).

[0071] Lime kiln dust (LKD) is a byproduct from the manufacturing of lime. LKD is dust or particulate matter collected from a lime kiln or associated processing equipment. Manufactured lime can be categorized as high-calcium lime or dolomitic lime, and LKD varies based upon the processes that form it. Lime is often produced by a calcination reaction conducted by heating calcitic raw material, such as calcium carbonate ($CaCO_3$), to form free lime CaO and carbon dioxide (CO_2). High-calcium lime has a high concentration of calcium oxide and typically some impurities, including aluminum-containing and iron-containing compounds. High-calcium lime is typically formed from high purity calcium carbonate (about 95% purity or greater). Typical calcium oxide content in an LKD product derived from high-calcium lime processing is greater than or equal to about 75% by weight, optionally greater than or equal to about 85% by weight, and in some cases greater than or equal to about 90% by weight. In some lime manufacturing, dolomite ($CaCO_3 \cdot MgCO_3$) is decomposed by heating to primarily generate calcium oxide (CaO) and magnesium oxide (MgO), thus forming what is known as dolomitic lime. In LKD generated by dolomitic lime processing, calcium oxide can be present at greater than or equal to about 45% by weight, optionally greater than about 50% by weight, and in certain embodiments, greater than about 55% by weight. While LKD varies based upon the type of lime processing employed, it generally has a relatively high concentration of free lime. Typical amounts of free lime in LKD are about 10 to about 50%, optionally about 20 to about 40%, depending upon the relative concentration of calcium oxide present in the lime product generated.

[0072] Slags are generally byproduct compounds generated by metal manufacturing and processing. The term "slag" encompasses a wide variety of byproduct compounds, typically comprising a large portion of the non-metallic byproducts of ferrous metal and/or steel manufacturing and processing. Generally, slags are considered to be a mixture of various metal oxides, however they often contain metal sulfides and metal atoms in an elemental form.

[0073] Various examples of slag byproducts useful for certain embodiments of the invention include ferrous slags, such as those generated in blast furnaces (also known as cupola furnaces), including, by way of example, air-cooled blast furnace slag (ACBFS), expanded or foamed blast furnace slag, pelletized blast furnace slag, granulated blast furnace slag (GBFS), and the like. Steel slags can be produced from basic oxygen steelmaking furnaces (BOS/BOF) or electric arc furnaces (EAF). Many slags are recognized for having cementitious and/or pozzolanic properties, however the extent to which slags have these properties depends upon their respective composition and the process from which they are derived, as recognized by the skilled artisan. Exemplary slags comprise calcium-containing compounds, silicon-containing compounds, aluminum-containing compounds, magnesium-containing compounds, iron-containing compounds, manganese-containing compounds and/or sulfur-containing compounds. In certain embodiments, the slag comprises calcium oxide at about 25 to about 60%, optionally about 30 to about 50%, and optionally about 30 to about 45% by weight. One example of a suitable slag generally having cementitious properties is ground granulated blast furnace slag (GGBFS).

[0074] As described above, other suitable examples include blast (cupola) furnace dust collected from air pollution control devices attached to blast furnaces, such as cupola arrester filter cake. Another suitable industrial byproduct source is paper de-inking sludge ash. As recognized by those of skill in the art, there are many different manufactured/industrial process byproducts that are feasible as a source of calcium for the alkaline powders that form the sorbent compositions of the invention. Many of these well known byproducts comprise alumina and/or silica, as well. Some, such as lime kiln dust, contain major amounts of CaO and relatively small amounts of silica and alumina. Combinations of any of the exemplary manufactured products and/or industrial byproducts are also contemplated for use as the alkaline powders of certain embodiments of the invention.

[0075] In various embodiments, desired treat levels of silica and/or alumina are above those provided by adding materials such as portland cement, cement kiln dust, lime kiln dust, and/or sugar beet lime. Accordingly, it is possible to supplement such materials with aluminosilicate materials, such as without limitation clays (e.g. montmorillonite, kaolins, and the like) where needed to provide preferred silica and alumina levels. In various embodiments, supplemental aluminosilicate materials make up at least about 2%, and preferably at least about 5% by weight of the various sorbent components added into the coal burning system. In general, there is no upper limit from a technical point of view as long as adequate levels of calcium are maintained. However, from a cost standpoint, it is normally desirable to limit the proportion of more expensive aluminosilicate materials. Thus, the sorbent components preferably comprise from about 2 to 50%, preferably 2 to 20%, and more preferably, about 2 to 10% by weight aluminosilicate material such as the exemplary clays. A non-limiting example of a sorbent is about 93% by weight of a blend of CKD and LKD (for example, a 50:50 blend or mixture) and about 7% by weight of an aluminosilicate clay.

[0076] In various embodiments, an alkaline powder sorbent composition contains one or more calcium-containing powders such as portland cement, cement kiln dust, lime kiln dust, various slags, and sugar beet lime, along with an aluminosilicate clay such as, without limitation, montmorillonite or kaolin. The sorbent composition preferably contains sufficient SiO_2 and Al_2O_3 to form a refractory-like mixture with calcium sulfate produced by combustion of the sulfur-containing coal in the presence of the CaO sorbent component such that the calcium sulfate is handled by the particle control system; and to form a refractory mixture with mercury and other heavy metals so that the mercury and other heavy metals are not leached from the ash under acidic conditions. In preferred embodiments, the calcium containing powder sorbent contains by weight a minimum of 10% silica and 2-10% alumina. Preferably, the alumina level is higher than that found in portland cement, that is to say higher than about 5% by weight, preferably higher than about 6% by weight, based on Al_2O_3.

[0077] In various embodiments, the sorbent components of the alkaline powder sorbent composition work together with optional added halogen (such as bromine) compound or compounds to capture chloride as well as mercury, lead, arsenic, and other heavy metals in the ash, render the heavy metals non-leaching under acidic conditions, and improve the cementitious nature of the ash produced. As a result, emissions of harmful elements are mitigated, reduced, or eliminated, and a valuable cementitious material is produced as a by-product of coal burning.

[0078] Suitable aluminosilicate materials include a wide variety of inorganic minerals and materials. For example, a number of minerals, natural materials, and synthetic materials contain silicon and aluminum associated with an oxy environment along with optional other cations such as, without limitation, Na, K, Be, Mg, Ca, Zr, V, Zn, Fe, Mn, and/or other anions, such as hydroxide, sulfate, chloride, carbonate, along with optional waters of hydration. Such natural and synthetic materials are referred to herein as aluminosilicate materials and are exemplified in a non-limiting way by the clays noted above.

[0079] In aluminosilicate materials, the silicon tends to be present as tetrahedra, while the aluminum is present as tetrahedra, octahedra, or a combination of both. Chains or networks of aluminosilicate are built up in such materials by the sharing of 1, 2, or 3 oxygen atoms between silicon and aluminum tetrahedra or octahedra. Such minerals go by a variety of names, such as silica, alumina, aluminosilicates, geopolymer, silicates, and aluminates. However presented, compounds containing aluminum and/or silicon tend to produce silica and alumina upon exposure to high temperatures of combustion in the presence of oxygen

[0080] In one embodiment, aluminosilicate materials include polymorphs of $SiO_2 \cdot Al_2O_3$. For example, silliminate contains silica octahedra and alumina evenly divided between tetrahedra and octahedra. Kyanite is based on silica tetrahedra and alumina octahedra. Andalusite is another polymorph of $SiO_2 \cdot Al_2O_3$.

[0081] In other embodiments, chain silicates contribute silicon (as silica) and/or aluminum (as alumina) to the compositions of the invention. Chain silicates include without limitation pyroxene and pyroxenoid silicates made of infinite chains of SiO_4 tetrahedra linked by sharing oxygen atoms.

[0082] Other suitable aluminosilicate materials include sheet materials such as, without limitation, micas, clays, chrysotiles (such as asbestos), talc, soapstone, pyrophillite, and kaolinite. Such materials are characterized by having layer structures wherein silica and alumina octahedra and tetrahedra share two oxygen atoms. Layered aluminosilicates include clays such as chlorites, glauconite, illite, polygorskite, pyrophillite, sauconite, vermiculite, kaolinite, calcium montmorillonite, sodium montmorillonite, and bentonite. Other examples include micas and talc.

[0083] Suitable aluminosilicate materials also include synthetic and natural zeolites, such as without limitation the analcime, sodalite, chabazite, natrolite, phillipsite, and mordenite groups. Other zeolite minerals include heulandite, brewsterite, epistilbite, stilbite, yagawaralite, laumontite, ferrierite, paulingite, and clinoptilolite. The zeolites are minerals or synthetic materials characterized by an aluminosilicate tetrahedral framework, ion exchangeable "large cations" (such as Na, K, Ca, Ba, and Sr) and loosely held water molecules.

[0084] In other embodiments, framework or 3D silicates, aluminates, and aluminosilicates are used. Framework aluminosilicates are characterized by a structure where SiO_4 tetrahedra, AlO_4 tetrahedra, and/or AlO_6 octahedra are linked in three dimensions. Non-limiting examples of framework silicates containing both silica and alumina include feldspars such as albite, anorthite, andesine, bytownite, labradorite, microcline, sanidine, and orthoclase.

[0085] In one aspect, the sorbent powder compositions are characterized in that they contain a major amount of calcium, preferably greater than 20% or greater than 40% by weight based on calcium oxide, and that furthermore they contain levels of silica, and/or alumina higher than that found in commercial products such as portland cement. In preferred embodiments, the sorbent compositions comprise greater than 5% by weight alumina, preferably greater than 6% by weight alumina, preferably greater than 7% by weight alumina, and preferably greater than about 8% by weight alumina.

[0086] Coal or other fuel is treated with sorbent components at rates effective to control the amount of nitrogen, sulfur and/or mercury released into the atmosphere upon combustion. In various embodiments, total treatment levels of the sorbent components ranges from about 0.1% to about 20% by weight, based on the weight of the coal being treated or on the rate of the coal being consumed by combustion, when the sorbent is a powder sorbent containing calcium, silica, and alumina. When the sorbent components are combined into a single composition, the component treat levels correspond to sorbent treat levels. In this way a single sorbent composition can be provided and metered or otherwise measured for addition into the coal burning system. In general, it is desirable to use a minimum amount of sorbent so as not to overload the system with excess ash, while still providing enough to have a desired effect on sulfur and/or mercury emissions. Accordingly, in various embodiments, the treatment level of sorbent ranges from about 0.1% to about 10% by weight, in some embodiments from about 1 or 2% by weight to about 10% by weight. For many coals, an addition rate of 6% by weight of powder sorbent has been found to be acceptable.

[0087] Sorbent compositions comprising a halogen compound contain one or more organic or inorganic compounds that contain a halogen. Halogens include chlorine, bromine, and iodine. Preferred halogens are bromine and iodine. The halogen compounds are sources of the halogens, especially of bromine and iodine. For bromine, sources of the halogen include various inorganic salts of bromine including bromides, bromates, and hypobromites. In various embodiments, organic bromine compounds are less preferred because of their cost or availability. However, organic sources of bromine containing a suitably high level of bromine are considered within the scope of the invention. Non-limiting examples of organic bromine compounds include methylene bromide, ethyl bromide, bromoform, and carbon tetrabromide. Non-limiting inorganic sources of iodine include hypoiodites, iodates, and iodides, with iodides being preferred. Organic iodine compounds can also be used.

[0088] When the halogen compound is an inorganic substituent, it is preferably a bromine or iodine containing salt of an alkaline earth element. Exemplary alkaline earth elements include beryllium, magnesium, and calcium. Of halogen compounds, particularly preferred are bromides and iodides of alkaline earth metals such as calcium. Alkali metal bromine and iodine compounds such as bromides and iodides are effective in reducing mercury emissions. But in some embodiments, they are less preferred as they tend to cause corrosion on the boiler tubes and other steel surfaces and/or contribute to tube degradation and/or firebrick degradation. In various embodiments, it has been found desirable to avoid potassium salts of the halogens, in order to avoid problems in the furnace.

[0089] In various embodiments, it has been found that the use of alkaline earth salts such as calcium tends to avoid such problems with sodium and/or potassium. Thus in various embodiments, the sorbents added into the coal burning system contain essentially no alkali metal-containing bromine or iodine compounds, or more specifically essentially no sodium-containing or potassium-containing bromine or iodine compounds.

[0090] In various embodiments, sorbent compositions containing halogen are provided in the form of a liquid or of a solid composition. In various embodiments, the halogen-containing composition is applied to the coal before combustion, is added to the furnace during combustion, and/or is applied into flue gases downstream of the furnace. When the halogen composition is a solid, it can further contain the calcium, silica, and alumina components described herein as the powder sorbent. Alternatively, a solid halogen composition is applied onto the coal and/or elsewhere into the combustion system separately from the sorbent components comprising calcium, silica, and alumina. When it is a liquid composition it is generally applied separately.

[0091] In various embodiments, liquid mercury sorbent comprises a solution containing 5 to 60% by weight of a soluble bromine or iodine containing salt. Non-limiting examples of preferred bromine and iodine salts include calcium bromide and calcium iodide. In various embodiments, liquid sorbents contain 5-60% by weight of calcium bromide and/or calcium iodide. For efficiency of addition to the coal prior to combustion, in various embodiments it is preferred to add mercury sorbents having as high level of bromine or iodine compound as is feasible. In a non-limiting embodiment, the liquid sorbent contains 50% or more by weight of the halogen compound, such as calcium bromide or calcium iodide.

[0092] In various embodiments, the sorbent compositions containing a halogen compound further contain a nitrate compound, a nitrite compound, or a combination of nitrate and nitrite compounds. Preferred nitrate and nitrite compounds include those of magnesium and calcium, preferably calcium.

[0093] To further illustrate, one embodiment involves the addition of liquid mercury sorbent directly to raw or crushed coal prior to combustion. For example, mercury sorbent is added to the coal in the coal feeders. Addition of liquid mercury sorbent ranges from 0.01 to 5%. In various embodiments, treatment is at less than 5%, less than 4%, less than 3%, or less than 2%, less than 1%, less than 0.5%, and less than 0.2% where all percentages are based on the amount of coal being treated or on the rate of coal consumption by combustion. Higher treatment levels are possible, but tend to waste material, as no further benefit is achieved. Preferred treatment levels are from 0.025 to 2.5% by weight on a wet basis. The amount of solid bromide or iodide salt added by way of the liquid sorbent is of course reduced by its weight fraction in the sorbent. In an illustrative embodiment, addition of bromide or iodide compound is at a low level such as from 0.01 % to 1% by weight based on the solid. When a 50% by weight solution is used, the sorbent is then added at a rate of 0.02% to 2% to achieve the low levels of addition. For example, in a preferred embodiment, the coal is treated by a liquid sorbent at a rate of 0.02 to 1%, preferably 0.02 to 0.5 % calculated assuming the calcium bromide is about 50% by weight of the sorbent. In a typical embodiment, approximately 1%, 0.5%, or 0.25% of liquid sorbent containing 50% calcium bromide is added onto the coal prior to combustion, the percentage being based on the weight of the coal. In a preferred embodiment, initial treatment is started at low levels (such as 0.01% to 0.1%) and is incrementally increased until a desired (low) level of mercury emissions is achieved, based on monitoring of emissions. Similar treatment levels of halogen are used when the halogen is added as a solid or in multi-component compositions with other components such as calcium, silica, alumina, iron oxide, and so on.

[0094] When used, liquid sorbent is sprayed, dripped, or otherwise delivered onto the coal or elsewhere into the coal burning system. In various embodiments, addition is made to the coal or other fuel at ambient conditions prior to entry of the fuel/sorbent composition into the furnace. For example, sorbent is added onto powdered coal prior to its injection into the furnace. Alternatively or in addition, liquid sorbent is added into the furnace during combustion and/or into the flue gases downstream of the furnace. Addition of the halogen containing mercury sorbent composition is often accompanied by a drop in the mercury levels measured in the flue gases within a minute or a few minutes; in various embodiments, the reduction of mercury is in addition to a reduction achieved by use of an alkaline powder sorbent based on calcium, silica, and alumina.

[0095] In another embodiment, involves the addition of a halogen component (illustratively a calcium bromide solution) directly to the furnace during combustion. In another embodiment, the invention provides for an addition of a calcium bromide solution such as discussed above, into the gaseous stream downstream of the furnace in a zone characterized by a temperature in the range of 1482°C (2700°F) to 816°C (1500°F), preferably 1204°C (2200°F) to 816°C (1500°F). In various embodiments, treat levels of bromine compounds, such as calcium bromide are divided between co-, pre- and post-combustion addition in any proportion.

[0096] In one embodiment, various sorbent components are added onto coal prior to its combustion to make a so-called refined coal. The coal onto which the sorbents are applied is preferably particulate coal, and is optionally pulverized or powdered according to conventional procedures. In a non-limiting example, the coal is pulverized so that 75% by weight of the particles passes through a 75μm (200 mesh) screen (a 200 mesh screen has hole diameters of 75 μm). In various embodiments, the sorbent components are added onto the coal as a solid or as a combination of a liquid and a solid. Generally, solid sorbent compositions are in the form of a powder. If a sorbent is added as a liquid (illustratively as a solution of one or more bromine or iodine salts in water), in one embodiment the coal remains wet when fed into the burner. In various embodiments, a sorbent composition is added onto the coal continuously at the coal burning facility by spraying or mixing onto the coal while it is on a conveyor, screw extruder, or other feeding apparatus. In addition or alternatively, a sorbent composition is separately mixed with the coal at the coal burning facility or at the coal producer. In a preferred embodiment, the sorbent composition is added as a liquid or a powder to the coal as it is being fed into the burner. For example, in a preferred commercial embodiment, the sorbent is applied into the pulverizers that pulverize the coal prior to injection. If desired, the rate of addition of the sorbent composition is varied to achieve a desired level of mercury emissions. In one embodiment, the level of mercury in the flue gases is monitored and the level of sorbent addition adjusted up or down as required to maintain the desired mercury level.

[0097] In preferred embodiments, nitrogen, mercury, and sulfur are monitored using industry standard methods such as those published by the American Society for Testing and Materials (ASTM) or international standards published by the International Standards Organization (ISO). An apparatus comprising an analytical instrument is preferably disposed in the convective pathway downstream of the addition points of the mercury and sulfur sorbents. In a preferred embodiment, a mercury monitor is disposed on the clean side of the particulate control system. Alternatively or in addition, the flue gases are sampled at appropriate locations in the convective pathway without the need to install an instrument or monitoring device. In various embodiments, a measured level of mercury or sulfur is used to provide feedback signals to pumps, solenoids, sprayers, and other devices that are actuated or controlled to adjust the rate of addition of a sorbent composition into the coal burning system. Alternatively or in addition, the rate of sorbent addition can be adjusted by a human operator based on the observed levels of mercury and/or sulfur.

[0098] In various embodiments, the ash produced by burning coal in the presence of the sorbents described herein is cementitious in that it sets and develops strength when combined with water. The ash tends to be self-setting due its relatively high level of calcium. The ash serves alone or in combination with portland cement as a hydraulic cement suitable for formulation into a variety of cementitious mixtures such as mortars, concretes, and grouts.

[0099] The cementitious nature of ash produced as described herein is demonstrated for example by consideration of the strength activity index of the ash, or more exactly, of a cementitious mixture containing the ash. As described in ASTM C311-05, measurement of the strength activity index is made by comparing the cure behavior and property development of a 100% portland cement concrete and a test concrete wherein 20% of the portland cement is replaced with an equal weight of a test cement. In the standard test, strength is compared at 7 days and at 28 days. A "pass" is considered to be when the strength of the test concrete is 75% of the strength of the portland cement concrete or greater. In various embodiments, ashes of the invention exhibit of strength activity of 100% to 150% in the ASTM test, indicating a strong "pass". Similar high values are observed when tests are run on test mixtures with other than an 80:20 blend of portland cement to ash. In various embodiments, a strength activity index of 100% to 150% is achieved with blends of 85:15 to 50:50, where the first number of the ratio is portland cement and the second number of the ratio is ash prepared according to the invention. In particular embodiments, the strength development of an all-ash test cementitious mixture (i.e., one where ash represents 100% of the cement in the test mixture) is greater than 50% that of the all-portland cement control, and is preferably greater than 75%, and more preferably 100% or more, for example 100 - 150%. Such results demonstrate the highly cementitious nature of ash produced by burning coal or other fuel in the presence of the sorbent components described herein.

[0100] Because the ash resulting from combustion of coal contains mercury in a non-leaching form, it is available to be sold into commerce. Non-limiting uses of spent or waste fly ash or bottom ash include as a component in a cement product such as portland cement. In various embodiments, cement products contain from about 0.1% up to about 99% by weight of the coal ash produced by burning compositions according to the invention. In one aspect, the non-leaching property of the mercury and other heavy metals in the coal ash makes it suitable for all known industrial uses of coal ash.

[0101] Coal ash especially the fly ash collected by the particle control systems (bag house, electrostatic precipitators, etc.) is used in portland cement concrete (PCC) as a partial or complete replacement for portland cement. In various embodiments, the ash is used as a mineral admixture or as a component of blended cement. As an admixture, the ash can be total or partial replacement for portland cement and can be added directly into ready mix concrete at the batch plant. Alternatively, or in addition, the ash is inter-ground with cement clinker or blended with portland cement to produce blended cements.

[0102] Class F and Class C fly ashes are defined for example in U.S. Standard ASTM C 618. The ASTM Standard serves as a specification for fly ash when it is used in partial substitution for portland cement. It is to be noted that coal ash produced by the methods described herein tends to be higher in calcium and lower in silica and alumina than called for in the specifications for Class F and Class C fly ash in ASTM C 618. Typical values for the fly ash of the invention is >50% by weight CaO, and <25% $SiO_2/Al_2O_3/Fe_2O_3$. In various embodiments, the ash is from 51 to 80 % by weight CaO and from about 2 to about 25% of total silica, alumina, and iron oxide. It is observed that fly ash according to the invention is highly cementitious, allowing for substitutions or cutting of the portland cement used in such cementitious materials and cementitious materials by 50% or more. In various applications, the coal ash resulting from burning coal with sorbents described herein is sufficiently cementitious to be a complete (100%) replacement for portland cement in such compositions.

[0103] To further illustrate, the American Concrete Institute (ACI) recommends that Class F fly ash replace from 15 to 25% of portland cement and Class C fly ash replace from 20 to 35%. It has been found that coal ash produced according to the methods described herein is sufficiently cementitious to replace up to 50% of the portland cement, while maintaining 28 day strength development equivalent to that developed in a product using 100% portland cement. That is, although in various embodiments the ash does not qualify by chemical composition as Class C or Class F ash according to ASTM C 618, it nevertheless is useful for formulating high strength concrete products.

[0104] Coal ash can also be used as a component in the production of flowable fill, which is also called controlled low strength material or CLSM. CLSM is used as a self leveling, self compacting back fill material in place of compacted earth or other fill. The ash described herein is used in various embodiments as a 100% replacement for portland cement in such CLSM materials. Such compositions are formulated with water, cement, and aggregate to provide a desired flowability and development of ultimate strength. For example, the ultimate strength of flowable fill should not exceed 1035 kPa (150 pounds per square inch) if removability of the set material is required. If formulated to achieve higher ultimate strength, jack hammers may be required for removal. However, when it is desired to formulate flowable fill mixes to be used in higher load bearing applications, mixtures containing a greater range of compressive strength upon cure can be designed.

[0105] Coal ash produced according to the methods described herein is also usable as a component of stabilized base and sub base mixtures. Since the 1950's numerous variations of the basic lime/fly ash/aggregate formulations have been used as stabilized base mixtures. An example of the use of stabilized base is used as a stabilized road base. To illustrate, gravel roads can be recycled in place of using ash according to the composition. An existing road surface is pulverized and re-deposited in its original location. Ash such as produced by the methods described herein is spread over the pulverized road material and mixed in. Following compaction, a seal coat surface is placed on the roadway. Ash is useful in such applications because it contains no heavy metals that leach above regulatory requirements. Rather, the ash produced by methods of the invention contains less leachable mercury and less leachable other heavy metals (such as arsenic and lead) than does coal ash produced by burning coal without the sorbents described herein.

[0106] Thus, there are provided various methods of eliminating the need to landfill coal ash or fly ash resulting from combustion of coal that contains high levels of mercury. Instead of a costly disposal, the material can be sold or otherwise used as a raw material.

[0107] In a preferred embodiment, use of the sorbents results in a cementitious ash that can replace portland cement in whole or in part in a variety of applications. Because of the re-use of the cementitious product, at least some portland cement manufacture is avoided, saving the energy required to make the cement, and avoiding the release of significant amounts of carbon dioxide which would have arisen from the cement manufacture. Other savings in carbon dioxide emissions result from the reduced need for lime or calcium carbonate in desulfurization scrubbers. There is provided, in various embodiments, methods for saving energy and reducing green house emissions such as carbon dioxide. Further detail of various embodiments are given below.

EXAMPLES

Example 1

[0108] The following are the required specifications for powder sorbent and halide sorbent for use in production of Refined Coal using sub-bituminous coal.

Powder Sorbent:

Constituent	Content (Mass %)	Constituent	Content Mass (%)
Calcium Oxide (CaO)	>40%	Potassium Oxide (K_2O)	<1%
Silicon Oxide (SiO_c)	>10%	Sodium Oxide (Na_2O)$_1$	<1%
Aluminum Oxide (Al_2O_3)	2 - 10%	Sulfur Oxide (SO_3)	<7%[1]
Iron Oxide (Fe_2O_3)	1 - 5%	Chloride (Cl)	<0.5%
Magnesium Oxide (MgO)	1 - 5%	Mercury (Hg)	<0.1 µg/g[2]
Size Distribution	>80% passing 75µm (200 mesh)	Size distribution shall be determined by fine wire screen analysis	

[1] In addition to the hard limit of 7% SO_3, the ratio between CaO and SO_3 should not fall below 6:1 and preferably should remain greater than 8:1. This ensures sufficient CaO to absorb the added sulfur.

[2] As practical matter, the Hg content of the powder sorbent should be maintained less than or equal to that of the coal being treated.

Acceptable test methods for Oxide Analysis are:

ASTM D3682	Standard Test Methods for Major and Minor Elements in Combustion Residues from Coal Utilization Processess
ASTM C114	Standard Test Methods for Chemical Analysis of Hydraulic Cement

Acceptable test methods for Mercury content:

ASTM D6414	Standard Test Method For Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption
ASTM D6722	Standard Test Method for Total Mercury In Coal and Coal Combustion Residues by Direct Combustion Analysis
EPA 7473	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technque)

Halide Sorbent

Constituent	Content (Mass %)	Determination Method
Calcium Bromide ($CaBr_2$)	52 - 54	Process blending control and specific gravity measurement
Water (H_2O)	46 - 48	Process Blending control and specific gravity measurement

Example 2

[0109] A series of tests were performed in the Energy & Environmental Research Center's (EERC's) combustion test facility (CTF) to determine the effect of sorbents on the emissions of NO_x and Hg during combustion of a Powder River Basin (PRB) sub-bituminous coal. Testing was conducted to support efforts to confirm that the process employed produces "refined coal," as is defined in Section 45 of the Internal Revenue Code. Section 45(c)(7)(A) defines refined coal to include a fuel which 1) is a solid fuel produced from coal, 2) is sold by the taxpayer with the reasonable expectation that it will be used for the purposes of producing steam, and 3) is certified by the taxpayer as resulting (when used in the production of steam) in a "qualified emission reduction."

[0110] Section 45(c)(7)(B) defines the term "qualified emission reduction" to mean a reduction of at least 20% of the emissions of NO_x and at least 40% of the emissions of either SO_2 or Hg released when the refined coal is burned as compared to the emissions released when the feedstock coal is burned.

Description of Facilities and Procedures

[0111] The CTF is used extensively to investigate SO_x and NO_x emissions and the transformation of toxic trace metals (Hg, As, and Pb) during the combustion of coal and other fuels or waste materials. The CTF is capable of producing gas and particulate samples that are representative of those produced in industrial-and full-scale pulverized coal (pc)-fired boilers. The test facility has several pollution control devices that may be used to reduce emissions, including an electrostatic precipitator (ESP) or fabric-filter baghouse for particulate control, a selective catalytic reduction (SCR) column for NO_x control, and a wet scrubber for control of sulfur emissions. The CTF was designed to replicate almost all types and configurations of full-scale pc-fired boilers used by U.S.-based utilities to generate electricity from steam. For example, the CTF can fire pc at a rate between 161 and 220 kW (550,000 and 750,000 Btu/hr), depending upon desired operating conditions. Although the CTF is adjusted to simulate conditions of full-scale pc-fired boilers, because of the numerous variables that can impact combustion effects in a commercial boiler, it is not possible to exactly replicate what will be observed in regular commercial operations. The firing rate is typically a function of the coal rank, with low-rank coals fired at the low end of the range and higher-rank coals fired at the mid- to upper level of the indicated range. Because the CTF furnace is refractory-lined, the firing rate is set based on the furnace exit gas temperature (FEGT) desired to simulate a specific boiler that would be used at a coal-fired power plant. For sub-bituminous coals, a firing rate between 161 and about 176 kW (550,000 and 600,000 BTU/hr) will typically produce a FEGT between 1149°C and 1204°C (2100° and 2200° F), which is typical of many coal-fired power plants that burn sub-bituminous coals such as the coal tested here.

[0112] Combustion air in the CTF is provided by a forced-draft fan in this balanced-draft system. The induced-draft fan at the back of the system is used to maintain a slight vacuum in the combustion zone and exhaust the combustion flue gases to a stack. Combustion air is typically preheated using an electric air heater and is split between primary, secondary, and overfire air (OFA).

[0113] Combustion gas analysis is provided by continuous emission monitors (CEMs) at two locations: the furnace exit, which is used to monitor and maintain a specified excess air level for all test periods, and the outlet of the particulate control device, which is used to access any air inleakage that may have occurred so that emissions of interest sampled at the back end of the system can be corrected for the dilution caused by the inleakage. For this test series, flue gas analyses were obtained from the duct at the outlet of the ESP. Each CEM rack contains five modules for determination of O_2, CO_2, CO, SO_2, and NO_x. With the exception of SO_2, each of the modules was manufactured by Ametek. Each of the analyzers uses a flue gas conditioner to remove moisture from the gas stream prior to analysis. All data reported here are on a dry gas basis. All gas analyses are continuously monitored and recorded by the CTF's data acquisition system. National Instruments provided both the hardware and software (LabView) used to collect all data presented here.

[0114] The CEM analyzers are individually calibrated prior to every test conducted on the CTF. Nitrogen is used as the zero gas, while several span gases are used to calibrate each instrument over the range used during testing. Typically, O_2 is measured over a 0% to 10% range, CO_2 is measured over a 0% to 20% range, CO is measured over a 0 to 500 ppm range, and NO_x is measure over a 0 to 1000 ppm range. SO_2 measurements are made over various ranges, depending upon the sulfur content of the coal being tested. During this test series, the SO_2 measurement instrument was calibrated over a range from 0 to 1000 ppm, which is appropriate for the sulfur content of the subbituminous PRB coal tested here.

[0115] Flue gas mercury (Hg) measurements were obtained separately by a continuous Hg monitor (CMM) manufactured by Tekran® Instruments Corporation. The system draws a gas sample from the flue gas ducting at the exit of the particulate control device. Moisture is removed from gas stream prior to analysis. The flue gas conditioning system uses a 10% NaOH solution to remove CO_2 and SO_2 to prevent interference with the ability of the analyzer to accurately measure the flue gas Hg concentration. Since all Hg analyzers can only measure elemental mercury, Hg^0, the total mercury, $Hg_{(T)}$, concentration is obtained by reducing the oxidized mercury, Hg^{2+}, portion with a 10% NaOH solution containing stannous chloride. The Tekran instrument traps Hg^0 from the conditioned sample onto a cartridge containing an ultrapure gold adsorbent. The amalgamated Hg is then thermally desorbed and detected using cold-vapor atomic fluorescence spectrometry. A dual-cartridge design enables alternate sampling and desorption, resulting in continuous measurement of the sample stream. Similar to the CEM calibration described above, the CMM is also zeroed and spanned prior to testing and checked at the completion of testing. No drift was noted during the tests conducted and reported here.

The CTF configuration utilized during these tests included only an ESP for particulate control, with both Hg and NO_x measurements obtained from the duct at the outlet of the ESP. At the completion of the feedstock and refined coal test periods, fuel and fly ash samples were collected and submitted for analysis. The samples collected during testing are described within the following discussion.

Fuel Preparation and Analysis

[0116] The sub-bituminous coal tested was a sample obtained from a coal pile. The coal is a PRB sub-bituminous coal with a gross calorific value approximately in the range from 19.8 to about 23.3 kJ/g (8500 to 10,000 Btu/lb), depending on moisture content, which is sourced from several mines located in Wyoming.

[0117] The as-received coal was inspected for surface moisture upon receipt and floor-dried as necessary. The air-dried sample was crushed to 6,4mm (1/4-inch) top size and fed to a hammer mill pulverizer, creating a size distribution of approximately 70% passing 75 μm (200 mesh) for use during testing, typical of the coal processing achieved at most coal-fired power plants. This size distribution is typical of that achieved by the pulverizers at most full-scale utility boilers. The refined coal sample used during this test series was produced by the EERC and is considered comparable to the refined coal produced at the Section 45 facilities. The sorbents used to prepare the refined coal were applied to the pulverized fuel as described below. This differs from full-scale application, where the sorbents are applied to the coal as it is reclaimed from stockpiles in the coal yard, mixed, crushed, and then sent to the pulverizers. The primary reason for application of the sorbents to the pc for utilization in the pilot-scale tests is the potential loss of material to the dust collection system utilized during pulverization of fuel samples. All pilot-scale fuel samples are remotely crushed and pulverized prior to utilization. By preparing the refined fuel from the pc sample, the potential loss of the sorbents to the dust collection system is avoided and results in the best simulation of what occurs at full scale.

[0118] The pulverized fuel was split into two parts: a feedstock sample and a second coal sample that is processed into refined coal. The refined coal was prepared by laying out a weighed quantity (about 227kg (500 lb)) on the floor of the coal preparation facility. Weighed quantities of halide sorbent and powder sorbent were carefully applied to the coal, which was periodically mixed while the sorbents were applied. The powder solvent was distributed by hand, making several passes over the extent of the coal pile, with mixing of the fuel after each pass. The halide sorbent was placed in a small pressurized metal spray canister such that the spray canister muzzle produced a mist that was applied to the exposed surface of the pile. Treatment required several passes to completely distribute the sorbent. After each pass, a rake was used to turn the pile over, exposing new surface for the next treatment pass. In each case, several small portions of the sorbents were distributed over the coal pile, followed by mixing until the specified treatment rate was achieved 0.008 wt% halide sorbent and 0.25 wt% powder sorbent.

[0119] Each of the samples (feedstock coal and refined coal) was transferred to storage hoppers for use in the pilot-scale testing described below. These storage hoppers sit directly above the coal feed hopper during testing. A rotary valve is used to transfer the coal and refined coal samples, respectively, from the storage hoppers to the feed hopper. The storage hoppers and feed hopper are cleaned with a dilute acid solution after each test to remove any trace of the treated fuel.

Fuel analysis

[0120] During each test period, a coal sample is conveyed from the storage hopper through a small tube that penetrates the sidewall of the feeder at a 70° angle, with the open end situated immediately below the rotary valve between the storage hopper and the feed hopper. This rube intercepts a small portion of the fuel each time the feed hopper fills. In this manner, a true as-fired sample of the fuel is obtained. The coal sample falls by gravity into a sample bag attached to the end of the sample tube. A new bag is attached to the sample tube prior to each new test period, separating the fuel samples representing the feedstock and refined coal test periods.

[0121] The as-fired coal is continuously sampled to determine the emission baseline from combusting the feedstock coal and the emissions from similarly combusting the refined coal. The feedstock coal and refined coal were submitted separately for determination of proximate and ultimate analyses, heating value, inorganic elemental oxide analysis (by x-ray fluorescence), and chlorine and mercury contents. Results from those analyses are provided in Table 1. Fuel samples undergo several handling steps that tend to allow evaporation of some portion of the as-received moisture content. The greatest reduction occurs during pulverization of the fuel. The hammer mill pulverizer creates an induced draft that tends to dry the newly exposed surfaces of the fine coal particle resulting from the pulverization. The extent of the drying that occurs is primarily a function of ambient atmospheric conditions (temperature and relative humidity) at the time of fuel preparation. As a result, the composition of the as-fired analyses so that comparisons between the feedstock coal and the refined coal can be readily made.

[0122] The feedstock coal (Test AF-CTS-1461) was determined to have an as-fired heating value of 22.4 kJ/g (9621 Btu/lb) at a moisture content of 20.03 wt%. Moisture-free heating value and ash content were determined to be 28.0 kJ/g (12,031 Btu/lb) and 4.91 wt%, respectively. The feedstock coal sulfur content was determined to be 0.37 wt% on a moisture-free basis (0.267 kg/GJ (0.624 lb SO_2/MMBtu)). The powder sorbent and liquid halide sorbent have no heating value, and the liquid halide sorbent introduces additional moisture into the refined coal because of the water content of the liquid, so a reduction in the heating value (kJ/g (Btu/lb)) of the refined coal is generally expected in comparison to the kJ/g (Btu/lb) of the feedstock coal. Ash analysis of the inorganics contained in each fuel indicate that the refined coal is enriched in CaO and SO_3, while depleted in SiO_2, Al_2O_3, and Fe_2O_3 relative to the feedstock coal. Mercury content was determined to be 0.0570 μg/g (2.55 g/GJ (5.924 lkb/TBtu), dry basis) and 0.0556 μg/g (2.54 g/GJ (5.908 lb/TBtu), dry basis) in the feedstock and refined coal samples, respectively. The chlorine content of the feedstock and refined coal samples was determined to be 19.4 and 30.0 µg/g, respectively.

[0123] Dry sieve analyses completed on feedstock and refined coal samples collected during each test are presented in Example 2 Table. Results for the feedback coal indicate 84.3 wt% passes 75 µm (200 mesh) and 69.2 wt% passes 44 µm (325 mesh), while 87.1 wt% passes 75 µm (200 mesh) and 73.1 wt% passes 44 µm (325 mesh) for the refined coal sample.

Example 2

[0124] The feedstock coal is PRB coal. The refined coal is feedstock PRB coal plus 0.008% by weight halide sorbent and 0.25% powder sorbent. The powder sorbent is 15% CKD and 85% grindouts. The halide sorbent is from Example 1. NOx and Hg emissions were measured for the feedstock and refined coals.

Example 2a -

[0125]

			NO_x Results		
	O_2, %	NO_x, ppm	NOx, ppm Corrected to 2.5% O_2	NO_x, g/GJ (lb/MMB tu)	NO_x, Reduction %
Feedstock Coal	2.71	151	152	84,8 (0.197)	NA*
Refined Coal	2.75	116	117	66,3 (0.154)	21.83
			Hg Results		
	O_2, %	CO_2, %	$Hg_{(T)}$, µg/dNm^3 corrected to 2.5% O_2	Hg, g/GJ (lb/TBtu)	Hg Reduction %
Feedstock Coal	2.71	15.97	2.052	0,599 (1.392)	NA
Refined Coal	2.75	16.08	0.826	0,248 (0.576)	58.62
* not applicable					

[0126] Mercury concentration was 0.558 µg/g in the ash of the feedstock coal and 0.833 µg/g in the ash of the refined coal

Example 3 - mid-American sub-bituminous coal

[0127] The feedstock coal is PRB coal. The refined coal is feedstock PRB coal plus 0.005% by weight halide sorbent and 0.25% powder sorbent. The powder sorbent is 15% CKD and 85% grindouts. The halide sorbent is from Example 1. NOx and Hg emissions were measured for the feedstock and refined coals.

[0128] The morning hours were used to establish baseline emissions from combustion of feedstock coal fired at an average rate of 27.4 kg/hr (60.28lb/hr) to achieve a FEGT of approximately 1171°C (2139°F). Excess oxygen was controlled to 3.05% (about 16.98% excess air) at the furnace exit, with OFA utilized at 15.13%simulating the NOx controls used at the generating station.

[0129] The refined coal was fired at a rate of 58.91 lb/hr, achieving a FEGT of 1171°C (2139°F) at 3.1% excess oxygen(about 17.33% excess air) at the furnace exit, with OFA maintained at 15.18%. Resultant emission reduction are given in the following table.

			NO_x Results		
	O_2, %	NO_x, ppm	NOx, ppm Corrected to 2.5% O_2	NO_x, (g/GJ) (lb/MMB tu)	NO_x, Reduction %
Feedstock Coal	3.86	243	256	141 (0.327)	NA*
Refined Coal	3.84	191	200	108 (0.252)	22.94
			Hg Results		
	O_2, %	CO_2, %	$Hg_{(T)}$, µg/dNm^3 corrected to 2.5% O_2	Hg, (g/GJ) (lb/TBtu)	Hg Reduction %
Feedstock Coal	3.86	17.07	2.877	0,869 (2.018)	NA

(continued)

			Hg Results		
	O_2, %	CO_2, %	$Hg_{(T)}$, μg/dNm^3 corrected to 2.5% O_2	Hg, (g/GJ) (lb/TBtu)	Hg Reduction %
Refined Coal	3.84	18.22	1.618	0,482 (1.119)	44.55
* not applicable					

Claims

1. A method of burning coal in a furnace to reduce emissions of nitrogen oxides and at least one of sulfur oxides and mercury, the method comprising burning a refined coal in the furnace, wherein the refined coal comprises an admixture of sub-bituminous coal or lignite coal, bromine compound, and a powder sorbent, and
wherein the powder sorbent comprises calcium, silica, alumina, and further comprises less than 1% by weight Na_2O and less than 1% by K_2O, based on the weight of the powder sorbent, wherein the powder sorbent comprises cement kiln dust (CKD).

2. Method according to claim 1, wherein the powder sorbent comprises less than 0.5% Na_2O and less than 0.5 % K_2O.

3. Method according to claim 1, wherein the coal is Powder River Basin coal.

4. Method according to claim 1, wherein the refined coal comprises 0.001 to 1.0 % by weight bromine compound and 0.1 to 10% by weight powder sorbent, or wherein the refined coal comprises 0.002 to 1.0% by weight of the bromine compound and 0.1 to 2.0% by weight of the powder sorbent.

5. Method according to claim 1, wherein the powder sorbent comprises said cement kiln dust (CKD) and one or more of grind outs, kiln feed, transition cement, weathered clinker and impound CKD.

6. Method according to claim 1, wherein the powder sorbent comprises aluminosilicate clay.

7. Method according to claim 1, wherein the powder sorbent contains kaolin.

8. Method according to claim 1, wherein the powder sorbent contains less than 0.1% chlorine.

9. Method according to claim 5, wherein the powder sorbent contains less than 0.1% chlorine.

Patentansprüche

1. Ein Verfahren zur Kohleverbrennung in einem Ofen, um Emissionen von Stickoxiden und wenigstens einem der Schwefeloxide und Quecksilber zu reduzieren, das Verfahren umfassend Verbrennen einer raffinierten Kohle in dem Ofen, wobei die raffinierte Kohle eine Beimischung von subbituminöser Kohle oder Braunkohle, bromhaltiger Verbindung, und einem Pulversorptionsmittel umfasst, und
wobei das Pulversorptionsmittel Kalzium, Silizium, Aluminium umfasst und ferner weniger als 1 Gewichtsprozent Na_2O und weniger als 1 % K_2O umfasst, basierend auf dem Gewicht des Pulversorptionsmittel, wobei das Pulversorptionsmittel Zementofenstaub (CKD) umfasst.

2. Verfahren gemäß Anspruch 1, wobei das Pulversorptionsmittel weniger als 0,5 % NA_2O und weniger als 0,5 % K_2O umfasst.

3. Verfahren gemäß Anspruch 1, wobei die Kohle Powder River Basin Kohle ist.

4. Verfahren gemäß Anspruch 1, wobei die raffinierte Kohle 0,001 bis 1,0 Gewichtsprozent bromhaltiger Verbindung und 0,1 bis 10 Gewichtsprozent Pulversorptionsmittel umfasst, oder wobei die raffinierte Kohle 0,002 bis 1,0 Gewichtsprozent von der bromhaltigen Verbindung und 0,1 bis 2,0 Gewichtsprozent von dem Pulversorptionsmittel umfasst.

5. Verfahren gemäß Anspruch 1, wobei das Pulversorptionsmittel den Zementofenstaub (CKD) und ein oder mehr der Grindouts, Ofenspeisung, Übergangszement, gealterte Schlacke und aufgestauter CKD umfasst.

6. Verfahren gemäß Anspruch 1, wobei das Pulversorptionsmittel Aluminiumsilikattonerde umfasst.

7. Verfahren gemäß Anspruch 1, wobei das Pulversorptionsmittel Kaolin enthält.

8. Verfahren gemäß Anspruch 1, wobei das Pulversorptionsmittel weniger als 0,1% Chlor enthält.

9. Verfahren gemäß Anspruch 5, wobei das Pulversorptionsmittel weniger als 0,1% Chlor enthält.

Revendications

1. Procédé de combustion de charbon dans un four pour réduire les émissions d'oxydes d'azote et d'au moins l'un parmi les oxydes de soufre et le mercure, le procédé comprenant la combustion d'un charbon raffiné dans le four, dans lequel le charbon raffiné comprend un mélange d'un charbon subbitumineux ou d'un charbon de lignite, d'un composé bromé, et d'un sorbant pulvérulent, et
dans lequel le sorbant pulvérulent comprend du calcium, une silice, une alumine, et comprend en outre moins de 1 % en poids de Na_2O et moins de 1 % de K_2O, sur la base du poids du sorbant pulvérulent, dans lequel le sorbant pulvérulent comprend une poussière de four à ciment (CKD).

2. Procédé selon la revendication 1, dans lequel le sorbant pulvérulent comprend moins de 0,5 % de Na_2O et moins de 0,5 % de K_2O.

3. Procédé selon la revendication 1, dans lequel le charbon est du charbon du bassin de la rivière Powder.

4. Procédé selon la revendication 1, dans lequel le charbon raffiné comprend 0,001 à 1,0% en poids d'un composé bromé et 0,1 à 10% en poids d'un sorbant pulvérulent, ou dans lequel le charbon raffiné comprend 0,002 à 1,0 % en poids du composé bromé et 0,1 à 2,0 % en poids du sorbant pulvérulent.

5. Procédé selon la revendication 1, dans lequel le sorbant pulvérulent comprend ladite poussière de four à ciment (CKD) et un ou plusieurs parmi des scories broyées, une alimentation pour four, un ciment de transition, des scories altérées et une CKD mise en réserve.

6. Procédé selon la revendication 1, dans lequel le sorbant pulvérulent comprend une argile d'aluminosilicate.

7. Procédé selon la revendication 1, dans lequel le sorbant pulvérulent contient un kaolin.

8. Procédé selon la revendication 1, dans lequel le sorbant pulvérulent contient moins de 0,1 % de chlore.

9. Procédé selon la revendication 5, dans lequel le sorbant pulvérulent contient moins de 0,1 % de chlore.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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