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DEASHING OF CARBONACEOUS MATERIAL

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ABSTRACT OF THE DISCLOSURE

A process for deashing carbonaceous material by treating a mixture containing such material and an alkali metal compound with steam at a temperature above the melting point of the hydroxide of said alkali metal, washing the treated material with water to remove soluble substances therefrom, and treating the washed material with an aqueous solution of a water soluble inorganic acid capable of forming water soluble salts of said impurities.

This invention relates generally to the removal of mineral constituents and more particularly to a chemical method for reducing the amount of ash-forming impurities in solid carbonaceous material.

The efficient utilization of carbonaceous materials such as coal, char and coke is handicapped to the extent that they contain ash-forming constituents such as compounds of calcium, magnesium, aluminum, silicon, and the like. When coal and coke are employed as fuels, these impurities detract from their heating values and in addition form ashes during combustion which must be disposed of at considerable trouble and expense. When coke and similar forms of carbon are employed in metallurgical and other chemical processes as reductants and the like, such impurities detract from and interfere with the desired reducing function, contaminate the products of such processes, and form slag which is generally undesirable in more than minor amounts.

Several methods for mechanically removing some of the ash-forming constituents of coal are known. These include manual removal of slate and other such contaminants, simple washing, heavy media separation, air cleaning and the like. Such beneficiation is every effective for some coals, especially those in which the ash-forming constituents exist largely in particulate form, but is hardly effective for coals in which the ash-forming constituents exist primarily in "inherent" form. Correspondingly, similar methods are known for reducing the proportion of ash-forming constituents in coal char and coal coke to the extent that their parent or precursor coals may be beneficiated prior to charring, coking or other forms of carbonization.

Broadly, it is an object of the present invention to provide a novel and improved method for de-ashing carbonaceous material. Another object of the invention is to provide such a method which will not be subject to one or more of the above disadvantages. A further object of the invention is to provide an improved chemical method for de-ashing carbonaceous material, the term "deashing" being employed herein to mean removal of ash-forming constituents or impurities which form ash during combustion of carbonaceous material containing such constituents or impurities. Other objects and advantages will appear as the description proceeds.

In accordance with the present invention, there is provided a method for reducing the amount of ash-forming impurities in solid carbonaceous material comprising treating such material with an aqueous solution of a water soluble inorganic acid capable of forming water soluble salts of said impurities. According to a further and pre-

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ferred feature of the present invention, the solid carbonaceous material containing ash-forming impurities first treated by the method described in copending application Ser. No. 442,184, filed Mar. 23, 1965 and entitled, "Process for Desulfurization of Carbonaceous Materials With a Hydroxide of an Alkali Metal," according to which such material is treated with at least one member of the group consisting of the alkali metal hydroxides, oxides, carbides, carbonates, and hydrides at a temperature above the melting point of the hydroxide of said alkali metal, after which the treated material is washed with water to remove soluble substances therefrom and then treated with an aqueous solution of a water soluble inorganic acid capable of forming water soluble salts of said impurities.

The process of this invention may be employed for deashing any solid carbonaceous material containing ash-forming impurities such as coal of any type and quality including lignite, subbituminous, bituminous and anthracite coals, and char or coke derived from such coals or from wood and the like. To promote more intimate contact between the treating agents of the present invention and the impurities in the carbonaceous material, the latter should preferably be in particulate form with the maximum dimension of any particle being no greater than about 0.132" or of a size range no greater than is commonly described as 6 mesh U.S. Standard Sieve.

According to the invention, a water soluble inorganic acid is employed, or a mixture thereof, which forms with such impurities in the carbonaceous material salts, particularly calcium, magnesium and aluminum salts, which are soluble in water or in a solution of such acid in water, and/or the soluble acid salts of which acid likewise forms with such impurities products which are soluble in water or in a solution of such acid in water. It will accordingly be understood that reference herein to an acid capable of forming water soluble salts of such impurities is intended and does include reference to acids capable of forming salts of such impurities which are soluble in a solution of such acid in water. Although any such acid may be employed, those preferred herein are nitric (HNO_3), hydrofluoric (HF) and particularly hydrochloric (HCl) acid for reasons of economy, availability, optimal reactive and solubility properties and the like. Such acid or acids may according to the present process be employed in aqueous solution of any desired concentration, for example from about 1% to 20% or more and preferably about 3% to 15% concentration, a total amount of such solution being preferably employed containing at least about 0.3 part of such acid or acids per part by weight of such impurities.

The treatment of the carbonaceous material with the defined aqueous acid solution according to the process of the present invention may be carried out in any desired manner. For example, the treatment may be carried out in a continuous manner by continuously passing a stream of the acid solution through a bed of the particulate carbonaceous material in any desired direction but preferably upwardly to simultaneously agitate the material until the effluent is free of acid salts. The treated material may then be drained and dried if the presence of residual acid in the material is unobjectionable, or it may be first washed acid free (e.g., to a pH of the wash water of at least about 6.5) with water and then dried. The treatment with the acid solution may be at ambient or room temperatures although better results as regards removal of ash-forming impurities are usually achieved with a hot solution, for example at a temperature of about 50° C. up to the boiling point.

Alternatively, the treatment may be carried out batchwise, preferably with agitation, the duration of treatment or residence time being dependent on the amount and type

of impurities, the concentration of acid, temperature of treatment and the like, and readily predetermined by routine experimentation for establishing conditions for maximum removal of ash-forming impurities from the carbonaceous material. Generally, about $\frac{1}{2}$ to 3 hours are sufficient. The treated material may then be drained and dried, or first washed to remove soluble substances as described above.

According to a further feature of the invention, a relatively greater reduction in the amount of ash-forming impurities, and incidentally sulfur and sulfur-containing impurities, is generally achieved by first treating the carbonaceous material by the process described in the above-mentioned copending application, which description is accordingly incorporated herein by reference thereto.

As described in said copending application, the pretreatment to be employed herein involves contacting the carbonaceous material, preferably in similar particulate form, with a hydroxide, oxide, carbide, carbonate or hydride of an alkali metal, or a mixture thereof, preferably a hydroxide of lithium, potassium, and particularly sodium, at a temperature above the melting point of the hydroxide of the alkali metal employed, i.e., at a temperature at which such hydroxide is a liquid, or between its melting point and its decomposition or boiling temperature. The dry particulate carbonaceous material may be mixed with dry alkali metal compound, or more preferably with an aqueous solution thereof, after which the mixture is heated to the above-defined temperatures which are generally at least 500° C. and maintained thereat for the requisite amount of time while at least periodically exposing the mixture to an atmosphere containing at least 2% moisture or steam. In most instances it has been found preferable to maintain the temperature range between about 550 and 850° C. for periods between about 10 and 180 minutes.

The intermittent introduction of steam into the hot mixture, preferably in the form of a fluidized bed, meets the requirement for chemical reaction between the treating agents and the impurities in the carbonaceous material, some movement of gas through the material being desirable to sweep out the volatile sulfides and other volatile sulfur compounds released during the reaction. Native volatile matter incidentally driven out of the solid carbonaceous material may serve as part of this sweep gas, but it is preferred to supplement this sweep gas with additional steam as required.

The aforementioned pretreatment with alkali metal compound serves to improve the deashing result of the present invention even though the carbonaceous material being deashed contains little or no sulfur impurities. When such material contains sulfur impurities, an amount of alkali metal compound such as sodium hydroxide should be employed in this pretreatment about twice the weight of such impurities. The pretreatment incidentally of course reduces the amount of sulfur impurities in the said material as described and claimed in said copending application. Even when little or no sulfur impurities are present, this treatment is still advantageously carried out using about 0.1 to 10 parts of the alkali metal compound for each part by weight of total impurities (ash-forming and sulfur).

Following the pretreatment as described above, the carbonaceous material is washed with water to remove soluble substances therefrom and then treated with a water soluble inorganic acid in accordance with the fundamental details of the present invention as fully set forth hereinbefore.

In order to facilitate understanding of this invention, there are set forth below several illustrative examples of the removal of ash-forming impurities in carbonaceous material in accordance with the present invention. All parts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLE 1

A sample of Ohio bituminous coal which had been charred at 650° F. and all of which passed through a 6 mesh U.S. Standard Sieve, analyzed 11.2% ash and 4.33% sulfur. 100 grams of this sample was mixed with 300 cc. of 3.7% hydrochloric acid solution. After 30 minutes the mixture was heated to boiling and then permitted to cool and stand for two hours. This char was then washed with water and dried, following which it analyzed 10% ash and 4.42% sulfur.

Another sample of the same char was first desulfurized by treatment according to the method described in said copending patent application. 1000 grams of char were mixed with a solution of 100 grams sodium hydroxide in 100 cc. water. The mixture was then alternately fluidized with steam and let rest for 5 minute periods over a total time of approximately 1 hour at a temperature ranging from 550° C. to 750° C. The mixture was then cooled and washed with water, after which the char analyzed 16.67% ash and 1.3% sulfur. 100 grams of this desulfurized char was mixed with 300 cc. of 3% hydrochloric acid (aqueous) solution and treated in the same manner as the sample described in the foregoing paragraph. After washing and drying it analyzed 6.5% ash and 1.13% sulfur.

EXAMPLE 2

A sample of Ohio bituminous coal which had been charred at 800° F. and all of which passed through a 6 mesh U.S. Standard Sieve, analyzed 11.1% ash and 4.22% sulfur. A 650 gram sample of this char was desulfurized in accordance with the method described in said copending patent application by mixing it with 65 grams sodium hydroxide mixed in 65 cc. water. The mixture was then alternately fluidized with steam and let rest for approximately 5 minute periods over a total time of about 1 hour at a temperature ranging from 550° C. to 750° C. This mixture was then cooled and washed with water, following which it analyzed 17.5% ash and 0.94% sulfur.

210 grams of this desulfurized char was mixed with 600 cc. of 3.7% hydrochloric acid solution, brought to boiling temperature and cooled. Thirty minutes after mixing, the char was washed with water and dried, after which it analyzed 7.2% ash and 0.87% sulfur.

Another sample of the same desulfurized char was similarly treated except that a 6.2% hydrochloric acid solution was employed. After washing and drying it analyzed 6.7% ash and 0.74% sulfur.

EXAMPLE 3

A sample of Alleghany County Pennsylvania bituminous coal crushed to pass through a 16 mesh U.S. Standard Sieve, analyzed 10.3% ash, 24.6% volatile and 2.04% sulfur. This coal was desulfurized according to the method specified in said copending patent application. A 1500 gram sample of this coal was mixed with a solution of 150 grams sodium hydroxide in 150 cc. water. The mixture was then alternately fluidized with steam and let rest for approximately 5 minute periods over a total time of about 2 hours at a temperature of 750° C., after which it was cooled and washed with water. Following this treatment it analyzed 13.5% ash, 5.5% volatile and 0.91% sulfur.

250 grams of this desulfurized coal were mixed with 500 cc. of 4.4% hydrochloric acid solution. This mixture was brought to boiling temperature, cooled and then washed with water. After drying, it analyzed 8.3% ash and 0.89% sulfur.

EXAMPLE 4

After charring at 980° F., a sample of Texas lignite analyzed 23.1% ash and 2.25% sulfur and passed through a 16 mesh U.S. Standard Sieve. This char was partially desulfurized according to the method specified in said copending patent application by mixing a 1000 gram sample of it with 100 grams sodium hydroxide dissolved in 100 cc. water. This mixture was alternately fluidized with

steam and let rest for approximately 5 minute periods over a total time of about 90 minutes at 750° C. It was then cooled and washed with water, after which it analyzed 30.3% ash and 1.64% sulfur.

A 214 gram sample of this desulfurized char was mixed with 600 cc. of 4.6% hydrochloric acid solution. The mixture was heated to 90° C. and cooled. After washing with water and drying, this char analyzed 18.9% ash.

EXAMPLE 5

A sample of metallurgical coke made from Virginia coal in a beehive type coking oven was crushed to pass through a 16 mesh U.S. Standard Sieve, after which it analyzed 4.25% ash and 0.73% sulfur.

A 100 gram portion of this sample was mixed with 250 cc. of 5% hydrochloric acid solution, the mixture was heated to 90° C. and permitted to cool. One hour after mixing, this coke was washed with water and dried, following which it analyzed 3.82% ash and 0.76% sulfur.

Another portion of the same metallurgical coke sample was partially desulfurized according to the method specified in said copending patent application, by mixing 1500 grams with 75 grams sodium hydroxide in solution in 100 cc. water. This mixture was fluidized with steam and let rest for 5 minute intervals over a period of 30 minutes at a temperature of 815° C., after which it was cooled and washed with water. Following this treatment, it analyzed 4.5% ash and 0.63% sulfur.

200 grams of this desulfurized coke, while still wet with adsorbed wash water, were mixed with 500 cc. of 5% hydrochloric acid solution. The mixture was heated to 90° C. and permitted to cool. One hour after mixing, it was washed with water and dried, following which it analyzed 2.2% ash and 0.58% sulfur.

EXAMPLE 6

A sample of Adirondack hardwood charcoal, crushed to pass through a 16 mesh U.S. Standard Sieve, analyzed 2.86% ash and 0.3% potassium (0.36% basis K₂O). Potassium in an alkali metal that is a naturally occurring ash-forming constituent of wood and of charcoal.

A 200 gram portion of this sample was mixed with 400 cc. of a 15% hydrochloric acid solution, the mixture was heated to 90° C. and then permitted to cool to room temperature. One hour after mixing, this charcoal was washed with water and dried, after which it analyzed 1.21% ash, a reduction of 58%.

We claim:

1. A method of reducing the amount of sulfur and ash-forming impurities in solid carbonaceous material comprising treating a dry intimate particulate mixture containing such material and about 0.1 to 10 parts, per part by weight of said impurities in said material, of at least one member of the group consisting of the alkali metal hydroxides, oxides, carbides, carbonates, and hydrides in the form of a fluidized bed with steam at a temperature of about 500–850° C. and above the melting point of the hydroxide of said metal, washing the treated material with water to remove soluble substances therefrom, and then treating the washed material with an aqueous solution of a water soluble inorganic acid capable of forming water soluble salts of said impurities.

2. A method as defined in claim 1 wherein said member is NaOH and said acid is HCl.

3. A method of reducing the amount of sulfur and

ash-forming impurities in solid carbonaceous material comprising treating a dry intimate particulate mixture containing such material and about 0.1 to 10 parts, per part by weight of said impurities in said material, of at least one member of the group consisting of alkali metal hydroxides, oxides, carbides, carbonates, and hydrides in the form of a fluidized bed with steam at a temperature of about 500–850° C. and above the melting point of the hydroxide of said alkali metal, washing the treated material with water to remove soluble substances therefrom, treating the washed material with a hot aqueous solution containing at least about 0.3 part, per part by weight of said impurities, of a water soluble inorganic acid capable of forming water soluble salts of said impurities, and then washing the material with water until the wash water has a pH of at least about 6.5.

4. A method as defined in claim 3 wherein said member is NaOH and said acid is HCl.

5. A method of reducing the amount of sulfur and ash-forming impurities in solid carbonaceous material comprising treating a dry intimate particulate mixture containing such material and about 0.1 to 10 parts, per part by weight of said impurities in said material, of an alkali metal hydroxide in a form of fluidized bed with steam at a temperature of about 500–850° C. and at which said hydroxide is a liquid, washing the treated material with water to remove soluble substances therefrom, and then treating the washed material with an aqueous solution of a water soluble inorganic acid capable of forming water soluble salts of said impurities.

6. A method as defined in claim 5 wherein said alkali metal is sodium and said acid is HCl.

7. A method of reducing the amount of sulfur and ash-forming impurities in solid carbonaceous material comprising treating a dry intimate particulate mixture containing such material and about 0.1 to 10 parts, per part by weight of said impurities in said material, of an alkali metal hydroxide in a form of fluidized bed with steam at a temperature of about 500–850° C. and at which said hydroxide is a liquid, washing the treated material with water to remove soluble substances therefrom, treating the washed material with a hot aqueous solution containing at least about 0.3 part, per part by weight of said impurities, of a water soluble inorganic acid capable of forming water soluble salts of said impurities, and then washing the material with water until the wash water has a pH of at least about 6.5.

8. A method as defined in claim 7 wherein said alkali metal is sodium and said acid is HCl.

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