

UNITED STATES PATENT OFFICE

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PROCESS OF MAKING PORTLAND CEMENT FROM COAL ASHES

No Drawing.

Application filed March 21, 1930. Serial No. 437,947.

This invention relates to the treatment of coal ashes for the recovery of an improved raw siliceous material suitable for cement or chemical manufacture.

An object of my invention is to secure from coal ashes a substantially iron-free siliceous material suitable for cement or chemical manufacture.

Another object of my invention is to obtain from coal ashes which are partially fused and exist in a very finely divided form after the burning of the coal, a siliceous material suitable for the manufacture of cement and to obtain such siliceous material by treating the coal ashes in a simple and efficient manner according to my process.

A further object of my invention is to secure such siliceous material from coal ashes by the use of an acid process which due to the by-products obtained according to my process enables me to secure this material at a very low cost from products hitherto not used for this purpose, which products have heretofore been considered waste products.

In modern power plants steam is generated by burning bituminous coal in boilers either by the use of mechanical stokers or by the burning of finely powdered coal. In this last system the coal is ground to a very fine condition and is then burned by means of special burners whereby the coal is propelled into an incandescent fire box together with air whereupon the carbon of the coal is largely burned out producing a very hot flame. The ash of the coal remains suspended in the flue gases and by virtue of its position and of the very high temperature of the flame, the ash particles become more or less globular in shape, fused or semi-fused and certain chemical and physical transformations take place which are discussed later.

The ash content of bituminous coal varies from three percent to fifteen percent of the coal weight and since the coal is very finely divided prior to burning it will be appreciated that the ash particles formed will be much finer even than the coal. Samples have been observed which show that 99% of the ash passes through a 100 mesh screen and 90% through a 300 mesh screen. It is very diffi-

cult to remove such finely divided particles from the hot flue gases but such removal has in some instances been required for when the ashes have been discharged through the stacks of the power plants they have gradually settled on the surrounding country to the detriment of vegetation, buildings and people in the neighborhood. Power plants such as are located in or near large cities sometimes separate hundreds of tons of such ash from their stack gases each twenty-four hours. A method for such separation is by means of a Cottrell electrostatic dust precipitator. The disposal of this finely divided ash has been a serious problem and a source of expense.

In the operation of the Cottrell electrostatic dust precipitator for the separation of the ash particles from the hot gas stream, the flue gases from the boilers are drawn by means of a suction fan through this device; which consists essentially of positive and negative poles where, by means of a voltage of 100,000 to 150,000 volts an electrical discharge passes through the moving gas stream and a charge or potential is thereby placed on the ash particles which causes them to be attracted to one pole and to be deposited thereupon from which they fall or are scraped to a bin underneath.

The temperature of the flame produced in burning powdered coal is upward of 2000° C., but the temperature of the flue gases falls rapidly in the boilers and flues until in the dust precipitator the temperature of the gases is only about 500° C. This high initial temperature and comparatively rapid cooling produces certain chemical and physical transformations and produces certain minerals or crystal forms in the ash particles. The effect of these chemical and physical transformations is to make the basic content of the ashes more readily soluble in suitable mineral acids, and so much of this basic content particularly the alumina content may be removed and recovered as is desirable for an economic carrying out of the process.

An initial effect of the high flame temperature is to burn out the carbon and to disrupt the mineral composition and to drive out the

combined water and another effect is to heat the ash particles to practical fusion. Now when this fused particle is cooled in the boiler and flues, more or less rapidly as the case may be, certain crystal forms or minerals are formed. It is possible that the composition produced is somewhat influenced by the electrostatic discharge in the dust precipitator although this is not definitely known. At any rate the ash produced as described has certain properties different from the original minerals and different from most naturally occurring minerals. First, the iron content of the original coal forms and separates into a magnetic oxide of iron, largely Fe_3O_4 , which may be largely separated from the ash by means of a magnetic separator and which then becomes a product of value in the art as a paint pigment or as iron ore of very high metallic iron content. Second, the ash may be treated with mineral acids such as HCl , HNO_3 , H_2SO_4 or HClO_4 or combinations of these to dissolve the base minerals such as alumina, any iron oxide that may remain after the magnetic separation, calcium or magnesium oxides, etc., leaving a residue which is essentially silica and which forms an improved raw material for cement and chemical manufacture.

If the analysis of the ashes and the economic carrying out of this process to produce a siliceous hydrate is such that it is desirable to remove and recover a considerable portion of the alumina content of the ashes, this may be readily done as will be more fully explained hereinafter.

It is well known that the solubility of alumina and the basic content of clays, and similar minerals, in mineral acids, may be increased by roasting them within a very narrow range suitable for the particular clay in question. Such a range is usually less than 100°C . in order to secure the most efficient extraction of the basic content of the clay. If, however, these clays are heated to a temperature of approximately 900°C ., or above, the basic content is practically insoluble, and in some cases less than 1% can be extracted by subjecting the roasted clay to the same mineral acid treatment as will extract 70% of the basic content if the proper roasting temperature is observed.

I have found that a high extraction of the bases may be readily obtained from the ashes from powdered coal with the use of suitable mineral acids, notwithstanding the fact that such ashes have been heated to temperatures considerably more than 900°C . The reason for this may be that the ashes are partially fused and rapidly cooled or quenched, and thus the solubility of the basic content increased.

I have also found that the same condition obtains in powdered ashes derived from the grinding of clinkers from the burning of

coal. With coal ashes derived either from the burning of powdered coal or bituminous coal, which have, in the ordinary furnace practice, attained a temperature in excess of 900°C ., and thus become partially fused or sintered, extractions of 80% or more of the basic content have been obtained.

The usual range of compositions of the above described ashes and of one typical sample is given below:

SiO_2	40-50%	46.9%
Al_2O_3	25-35	29.3
$\text{Fe}_2\text{O}_3\text{—FeO}$	9-15	11.7
MgO	0.4-1.3	.9
CaO	2. -3	2.6
TiO_2	1	1.3
Carbon	5-8	6.5
Unclassified (D)		.8
		<hr/> 100.0

The composition of the ashes produced is variable due to the fact that different coals used as fuel vary as to their ash content and as to the composition of such ash, and also due to the fact that the conditions under which the coal is burned is variable, the flame temperature fluctuating.

In carrying out my process a slurry of the powdered coal ash and water is formed and this slurry can be pumped and stored in tanks and treated without serious difficulty. One convenient method of removing the magnetic iron is to pass this slurry through a magnetic separator of any suitable design and separate the magnetic oxide of iron which can readily be disposed of as a paint pigment or as iron ore of high iron content. After removal of the magnetic iron the residue is preferably treated with a suitable quantity of mineral acid, either HCl , HNO_3 , H_2SO_4 or HClO_4 or combinations of these acids, to dissolve such portion of the remaining bases from the ash that may be desired. Heat generated by the dissolving reaction is usually sufficient to maintain the solution hot, but I can heat the solution if desired.

I have found that one good method for carrying out this process is by the use of hydrochloric acid in an aqueous solution in a strength of from 5 to 20%, depending upon the physical properties and the analysis of the particular coal ashes. It is to be understood, however, that two or more of the above acids may be used simultaneously, if desired.

By adding more or less acid, and varying the time and temperature of treatment, I can control the extraction of alumina within the desired economic range. By my process I extract the amount of alumina from the ashes which the economic conditions make it desirable to extract in order to recover this alumina as a valuable by-product. That is, if it is more expensive to make a substantially complete extraction of alumina than is com-

mercially practical for the value of the alumina recovered, then only a portion of this alumina may be extracted, leaving the remaining alumina in the siliceous hydrate for the manufacture of cement.

Under favorable conditions it may be desirable to extract all of the alumina and other basic content of the ash in order to recover the alumina, leaving substantially pure siliceous hydrate for the manufacture of cement or for the manufacture of sodium silicate.

It will thus be seen that my process affords a very simple and efficient means for obtaining siliceous hydrate from coal ashes with the commercial advantages of obtaining the valuable by-products of iron oxide and such alumina as may be economically extracted, and this extraction can be controlled according to the desired results to be obtained.

It will also be seen from the analysis of coal ashes that if it be desired for economic reasons not to extract all of the alumina, the basic content left in the residue is such that the residue is desirable for cement manufacture, and a less amount of clay and lime need be added for the manufacture of Portland cement.

If, however, the desired end product be silica hydrate for the manufacture of sodium silicate then substantially all the basic content of the ash should be extracted in the manner above set forth. In case it is desired to use this residue for the manufacture of sodium silicates, the silica hydrate can be digested with caustic soda or heated to fusion with soda ash, as is well known.

Furthermore, it is to be understood that the particular compounds disclosed, and the procedure set forth, are presented for purposes of explanation and illustration and that various equivalents can be used and modifications of said procedure can be made without departing from my invention as defined in the appended claims.

What I claim is:

1. The process of producing siliceous material, mainly composed of silica hydrate, from coal ashes which have been subjected to a sufficiently high temperature so that upon cooling at least some magnetic oxide of iron will be formed, which consists in magnetically extracting the magnetic iron from the ashes and treating the ashes with mineral acid to dissolve the basic content, and separating the siliceous material from the acid solution whereby a silica hydrate suitable for the manufacture of cement is produced.

2. The process of treating ashes from powdered coal which have been subjected to a sufficiently high temperature so that upon cooling at least some magnetic oxide of iron will be formed, which consists in subjecting the ashes to the action of a magnetic separator to extract the iron oxide, treating the

ashes with a mineral acid to dissolve the basic content, separating the solution from the residue whereby a suitable raw siliceous material for the manufacture of cement is produced.

3. The process of treating partially sintered, finely divided ashes from burning powdered coal, which consists in subjecting the ashes to the action of a magnetic separator to extract the iron oxide, treating the ashes with a solution of hydrochloric acid under suitable conditions to extract the desired basic content, and separating the siliceous residue with the remaining basic content from the solution whereby a suitable raw material for the manufacture of Portland cement is produced.

4. The process of treating partially sintered, finely divided ashes from burning powdered coal, which consists in treating the ashes with a solution of hydrochloric acid under suitable conditions to extract the desired basic content, and separating the siliceous residue with the remaining basic content from the solution whereby a suitable raw material for the manufacture of Portland cement is produced.

5. The process of manufacturing a siliceous material suitable for the manufacture of Portland cement, which consists in magnetically extracting the magnetic iron content of the partially fused ashes produced by the burning of powdered coal, treating the ashes with an aqueous solution of hydrochloric acid to dissolve all the basic content, and separating the siliceous residue from the acid solution.

6. The process of treating coal ashes to obtain a silicious material mainly composed of silica hydrate, which comprises burning the coal at a sufficiently high temperature to partially fuse the ashes, whereby the bases are made more soluble, subjecting the ashes to the action of a magnetic separator to extract the magnetic iron content of the ashes, treating the ashes with a mineral acid to dissolve the basic content, and separating the siliceous material from the solution.

7. The process of treating coal ashes to obtain a silicious material composed of silica hydrate and a comparatively large percentage of the basic content of the ashes as a by-product, which comprises burning the coal at a temperature of at least 900° C. to partially fuse the ashes and to render the basic content of the ashes more readily soluble in mineral acids, treating the ashes with a mineral acid to dissolve the basic content, and separating the silicious material from the solution.

8. The process of treating coal ashes to obtain a silicious material and a comparatively large percentage of the basic content of the ashes as a by-product, which comprises burning powdered coal at a temperature sub-

stantially above 900° C., thereby obtaining ashes in a substantially fused state, cooling the ashes rapidly and treating them with an acid to dissolve the basic content, and finally separating the siliceous material from the solution.

9. The process of treating coal ashes in which some iron is present to obtain a siliceous material, magnetic oxide of iron and basic material, which comprises burning coal at a temperature of at least 900° C. to partially fuse the ashes, thereby oxidizing the iron into a magnetic form and effecting a change in the basic ingredients of the ashes so as to render them more soluble in mineral acids, subjecting the ashes to the action of a magnetic separator to remove the magnetic iron oxide, treating the ashes to dissolve the basic content, and separating the siliceous material from the solution.

10. The process of treating coal ashes in which some iron is present to obtain a siliceous material, magnetic oxide of iron and basic material, which comprises burning powdered coal at a temperature substantially above 900° C., thereby obtaining ashes in a substantially fused state, cooling the ashes rapidly, subjecting them to a magnetic separator to remove the magnetic oxide, treating the ashes to dissolve the basic content, and separating the siliceous material from the solution.

11. The process of treating coal ashes in which some iron is present to obtain siliceous material, iron oxide and basic material having a high aluminum content, which comprises burning powdered coal at a temperature of substantially above 900° C., thereby obtaining ashes in a substantially fused state, cooling the ashes rapidly, extracting the magnetic iron oxide which is formed, treating the powdered ashes with a mineral acid to dissolve the basic content, and separating the siliceous material from the solution.

In testimony whereof I affix my signature.

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