Effect of Solid Fuel Mineral Composition on the Formation of Sour Pulp in Hydro-Slug Removal System of Thermal Power Plants

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Abstract

Researches have been conducted into the causes of acidity of pulp formed in the system of circulating hydraulic ash and slag removal in thermal power plants (TPP) when using coals of Ekibastuz and Karaganda coal fields of the Republic of Kazakhstan. We have carried out a comparative study of combustion of Karazhyra and Maikube coals at the two RK TPPs with BKZ-75-39FB and BKZ-160-100FB steam boilers. For ash collection, wet ash collectors with remounted Venturi tube coagulators have been installed on TPP. In them, a chemical interaction of irrigating water with flue gases occurs, which include CO_2, SO_2, SO_3 and ash particles. The ash pulp formed moves to the pipeline, mixes with the slag pulp and is further transported along a tract to the ash dump. We have defined the relationship between the composition of the products of coal combustion and the formation of acidic pulp in the scrubber. Qualitative and quantitative composition of coals and their combustion products have been determined by the methods of X-ray and X-ray fluorescence analysis. As the analysis showed, the main components of ash and slag materials are the oxides SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O. In the wet ash collectors gaseous substances present in flue gases, are dissolved and hydrolysed in irrigating water. While hydroremoving ash and slag, the compounds are dissolved in water and undergo hydrolysis. Oxides SiO_2, SO_2, TiO_2, P_2O_5 are hydrolyzed into acid, oxides CaO, MgO, K_2O and Na_2O – into base, Al_2O_3, Fe_2O_3 – into amphoteric compounds. Chemical analysis of ash and slag pulp formed after Karazhyra coal combustion has been carried out. Calculation of the acidity of ash and slag material has been performed. Karazhyra coal ash is more acidic in nature. A lower content of amphoteric oxides in Maikube coal appears to be the cause of the pulp formation, with a higher pH. With X-ray diffraction method, the nature of combinations of metal oxides in the samples of coal, slag and ash have been determined.

Keywords: solid fuel, ash content, coal mineral impurities, coagulation, Venturi tube, rotary scrubber, hydro-ash-slag-removal, sour pulp, X-ray and X-ray fluorescence analysis.

Introduction

Kazakhstan low-grade coals with sufficiently high ash content are used as solid fuel at the majority of thermal power plants [1].

Ash content of a coal is identified by the composition of mineral impurities. The clay mineral admixtures consist of aluminosilicates (including kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and (or) hydromica $[K_{<1}Al_2(Si,Al)_4O_{10}] \cdot [OH]_2 \cdot nH_2O$), silica, Ca^{2+}, Mg^{2+}, Fe^{2+} carbonates and sulfates, sulfide (FeS_2, CaS), iron oxidesin a form of marcasite or hematite, and also sodium and potassium salts. The most important components of coal combustion are the following oxides: SiO_2, Al_2O_3, FeO, Fe_2O_3, CaO, MgO.

Ekibastuz coal ash at 96-97% consists of silica and alumina [2]. Such high content of these amphoteric oxides in the ash is a cause of its high refractoriness therefore Ekibastuz coal is burned in chambered coal-fired furnaces with solid ash removal. Physico-chemical conversions of mineral part of the coal in these furnaces lead to formation of the ash mainly consisted of mullite and silica and characterized with quite high abrasiveness and electrical resistivity.

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Venturi tube-coagulator together with centrifugal demisters [3] are widely used at TPPs for cleaning flue gases from solid and unburned carbon particles. Ash particles and water droplets moving at different speeds collide and coagulate in the diffuser of Venturi tube. Small ash particles are absorbed by larger water droplets allowing them to be better captured by centrifugal scrubber.

The presence of amphoteric aluminum and iron (III) oxides in flue gases promotes coagulation process. Hydrolysis of these oxides precedes the coagulation in Ventury tube:

$$Al^{3+} + H_2O \rightarrow (AlOH)^{2+} + H^+ ;$$
$$(AlOH)^{2+} + H_2O \rightarrow (Al(OH)_2)^+ + H^+ ;$$
$$(Al(OH)_2)^+ + H_2O \rightarrow Al(OH)_3\downarrow + H^+ ;$$

$$Fe^{3+} + H_2O \rightarrow (FeOH)^{2+} + H^+;$$
$$(FeOH)^{2+} + H_2O \rightarrow (Fe(OH)_2)^+ + H^+;$$
$$(Fe(OH)_2)^+ + H_2O \rightarrow Fe(OH)_3\downarrow + H^+.$$

Direct coagulation process (an aggregation of particles) depends on the surface area of the reacting particles. It is known [4] that the alumina is an excellent adsorbent. In our case, the value of alumina in the composition of coal and flue gas is around 26%.

The flow gas is tangentially introduced into the scrubber, the walls of which are irrigated with water. Coagulated particles are removed into the ash bunker. The ash and slag are pumped together or separately by slag pumps through slurry pipeline to the ash disposal [5]. The pulp is often acidic and can be the causes of equipment corrosion.

Results and Discussion

To know the causes of acidity of pulp formed in the TPP recycling ash removal system when using coals of Karazhyra and Maikuben deposits, we have carried out a comparative study of their combustion. Two RK TPPs with BKZ-75- 39FB and BKZ-160-100FB boiler plants, respectively, have been selected as the objects. Wet ash collectors with premounted Venturi tube coagulators have been installed in the system.

We have studied the physical and chemical processes occurring during the coal combustion, water irrigation in the Venturi tube and pulp transportation to the ash dump. Chemical analysis of ash and slag pulp formed after Karazhyra coal combustion has been carried out. Ash slurry in the scrubber after the Venturi tube was acidic (pH =4.49). At the outlet of the scrubber and at the beginning of pipeline, the pH of ash slurry is increased up to 5.51. This can be explained by dissolving neutral and alkaline ash components like calcium oxide and alkali metals. The solubility of these components in the scrubber is only 4.2% due to the short-time contact (1 to 10 sec) of ash particles with water. Then the ash slurry is transported through the slurry pipeline to the ash disposal, where the ash pulp is clarified and the pH is rised to 7.87.

The increase of the pH of clarified water depends on the ratio of alkali components (mainly CaO) dissolved in the water and sulfur oxides absorbed by the water from the flue gases. Thus, along with content of alkaline components, the contents of ash and sulfur in the coal play an important role in the combustion process. The higher is the ash content, the more amphoteric oxide amount is in the fuel.

Table 1 shows the results of X-ray analysis of the ash of Karazhyra and Maikuben coals.

Table 1

The results of X-ray analysis of the ash of the coal of Karazhyra and Maikuben deposits

Coal ash content	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Mn	Fe_2O_3	others	Σ
Karazhyra, %	1.15	1.20	23.52	53.22	0.36	1.60	3.36	1.23	0.08	7.21	7.05	99.98
Maikube, %	1.62	2.87	19.04	46.73	0.72	2.55	7.21	1.33	0.11	9.60	8.19	99.97

According to the results of the analysis, the basic components of coal ash are amphoteric oxides: silica, alumina and iron oxide. Typically, the ratio of various types of oxides in the ash characterizes its acidity or basicity.

Acidity (*R*) is the ratio of the total content of acidic oxides to the total content of basic and amphoteric oxides (in %):

$$R = \frac{[SiO_2]+[TiO_2]+[P_2O_5]}{[CaO]+[MgO]+[Al_2O_3]+[Fe_2O_3]} \quad ;$$

ash is acidic when $R > 1$.

Basicity (O) is the ratio of the sum of basic oxide amount to the total content of acidic and amphoteric oxides:

$$\hat{I} = \frac{[\tilde{N}\grave{a}\hat{I}]+[MgO]+[K_2O]+[Na_2O]}{[SiO_2]+[Al_2O_3]+[TiO_2]+[P_2O_5]+[Fe_2O_3]} \ ;$$

ash is basic nature when O > 1 .

For the ash of Karazhyra coal:

$$\frac{53.22+1.23+0.36}{3.36+1.20+23.52+7.21} = \frac{54.81}{35.29} = 1.55\% \ .$$

For the ash of Maikube coal:

$$R = \frac{46.73 + 1.33 + 0.72}{7.21 + 2.87 + 19.04 + 9.60} = \frac{48.78}{38.72} = 1.26\% \cdot$$

The calculations show that the acidity of ash and slag materials of the coal is equal to 1.55 and 1.26, respectively, that confirming the acidic nature of the tested coals.

To study the specificity of the interaction of water with ash and slag material we studied chemical, mineralogical and phase composition of two types of coals, their ashes and slags by X-ray fluorescence spectral analysis. The measurements were performed with RLP-21T semiconductor detector on X-ray radiometric device. The results listed in Table 2 substantially confirms the results of X-ray analysis and indicate a predominance of silica in the ash composition.

Table 2
The results of X-ray fluorescence spectral analysis of samples of slag and ash

Coal type	Al_2O_3, %	SiO_2, %	Fe, %
Maikube slag	14.5	38.1	3.32
Ash from the ash disposal (Maikube)	19.3	48.6	2.47
Karazhyra slag	18.1	40.3	6.46
Ash after the Venturi tube (Karazhyra)	25.6	53.0	4.00
Ash from the ash disposal (Karazhyra)	25.2	52.5	3.82

To determine the crystalline phases and the nature of a combination of metal oxides in coal, slag and ash, we have studied the samples by X-ray analysis [6]. Samples preliminary crushed to powder were placed in a cuvette and a binder liquid was added. The maximum grain size of ash was 0.1-0.25 mm. X-ray patterns of samples were obtained using D8ADVANCE diffractometer (Bruker AXS) with copper radiation with a monochromator on the diffracted beam. Sample shooting mode: X-ray tube voltage of 40 kV at 40 mA. Step scanning is $2\theta = 0.02^o$, time information at the point of this step is 1.0 sec. Rotation of the sample in its plane at a speed of 60 r/min was carried out during shooting. Pretreatment of the patterns was conducted with the use of F_{peak} software to determine the angular positions and intensities of the reflections. PCPDFWIN software with PDF-2 diffractometric database was used during phase analysis. XRD analysis results are given in Tables 3 and 4.

As seen from the tables, the clay materials of the coals are mainly represented by kaolinite and quartz. Only hematite in small amount (2.8%) is present in Maikube coal. Small content of several minerals like hematite, muscovite, albite, calcite and akermanite are presented in Karazhyra coal. Two X-ray amorphous phase are detected in the samples. Halo with the maximum of 24.52θ is belong to siliceous phase. Another halo in the small-angle range of X-ray diffractogram indicates an amorphous carbonaceous phase.

The presence of amorphous phase formed by the dissociation of crystalline phases and losses of crystallization water are also clearly observed in samples of ash and slag of both coals.

Table 3
The results of X-ray analysis of the mineral coal Karazhyra

Sample	Silica SiO_2, %	Mullite $3Al_2O_3$·- SiO_2, %	Kaolinite Al_2O_3·- $2SiO_2$·$2H_2O$, %	Hematite Fe_2O_3,%	Muscovite Al_2Si_3 $AlO_{10}(OH)_2$, %	Albite $Na_2O·Al_2O_3$·- $6SiO_2$, %	Calcite $CaCO_3$, %	Akermanite Ca_2SiO_4, %	Cristobalite SiO_2, %	X-Ray amorphous phase,%
Karazhyra coal	40.4	-	44.3	4.2	2.0	2.3	1.0	5.8	-	-
Slug	32.5	44.4	-	8.7	-	4.7	-	-	9.7	10.0
Ash after Venturi tube	60.2	33.5	-	6.3	-	-	-	-	-	10.0
Ash from ash disposal	55.7	37.4	-	6.9	-	-	-	-	-	10.0

An increase of quartz content was observed in the ash and slag of Karazhyra coal, and there was significant content of mullite, a new phase represented mainly by amphoteric alumina. Along with these phases, another new hematite phase is presented in the products of Karazhyra coal combustion. The slag of Maikuben coal includes such minerals as microcline (11.7%), kaolinite (8.3%) and calcite (1.7%). The increase of hematite (Fe_2O_3) content is observed in the combustion products of Karazhyra and Maikuben coal. However, its content is higher at the burning of Karazhyra coal. This indicates more intense corrosion processes in the coal slurry pipeline due to the increase of pulp acidity at the combustion of Karazhyra coal.

Table 4
The results of X-ray analysis of the mineral coal Maikuben

Sample	Silica SiO_2, %	Mullite $3Al_2O_3\cdot SiO_2$, %	Kaolinite $Al_2O_3\cdot 2SiO_2\cdot 2H_2O$, %	Hematite Fe_2O_3, %	Muscovite $Al_2Si_3AlO_{10}(OH)_2$, %	Albite $Na_2O\cdot Al_2O_3\cdot 6SiO_2$, %	Calcite $CaCO_3$, %	Akermanite Ca_2SiO_4, %	Cristobalite SiO_2, %	X-Ray amorphous phase,%
Maikube coal	49.2	-	48.0	2.8	-	-	-	-	-	-
Slug	46.9	20.2	8.3	5.3	-	4.3	1.7	11.7	1.6	10.0
Ash from ash disposal	51.7	23.3	3.1	5.7	-	-	-	6.2	-	10.0

Conclusions

1. It is found that the mineralogical composition of Maikuben and Karazhyra coals, as well as the coagulation process in the Venturi system affect formation of acidic pulp in the hydro-slug removal system. The acidic nature of the pulp is confirmed by X-ray analysis and calculations.
2. Increase of hematite content in the combustion products of both coals indicates the occurrence of corrosion process in the coal slurry pipeline.
3. Amphoteric alumina content promotes not only formation of an acidic pulp, but also leads to an increase in the content of mullite in the ash dump.

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