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Power Plant Ash Composition Transformations During Load Cycling

Leo Rummel, Dmitri Neshumayev*, Alar Konist

Department of Energy Technology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
Dmitri.Nesumajev@ttu.ee

Mainly due to the introduction of new renewable non-dispatchable capacities to the electric grid the load cycling of power plants is increasing. This includes condensing power plants using fossil fuels. In case of power plants working on fossil fuels, their environmental footprint is reduced by using their combustion ash in construction material production, agriculture, etc. Chemical composition of each type of ash is crucial for each specific use and the constant unpredictable variation in the ash content is a problem for power plants. We can presume that ramping up and ramping down of power plants influences this composition. The focus of this study are the effects of load cycling on power plant output ash chemical composition. The results of industrial tests on a power unit are summarized and analyzed. Bottom ash samples were taken at different loads in 3 repeated experiments. The experiments were carried out on one of the two 320 t/h boilers of a 200 MW_{el} power unit. As primary fuel the boiler uses oil shale, a low-grade solid fossil fuel with similar properties to brown coals. 6 Mt of oil shale ash is generated from 13 Mt of oil shale annually in Estonia. The utilization of this ash is still a major challenge as is the utilization of other fossil fuel ashes in other countries. The results of the study show that load cycling has a consistent impact on ash composition making it possible to anticipate certain changes. At half load the share of carbonate Carbon in the ash on the average increased twice and Sulphur components by 30 %. During ramping the according increases were 40 % and 10 %. This method of determining these trends demonstrated in the study is applicable for all solid fuel power plants. This information can then be used to produce ash by batches and by that increase its utilization.

1. Introduction

Together with the rapid increase of renewable energy production from wind turbines as well as with building of new interconnections and introduction of hour-based electricity trading, conventional power plants have been forced to increase the cycling of load. The study of power plant ash formation could help increase its utilization and therefore reduce the environmental impact. The composition of the ash does not only depend on the specific fuel, but also on the combustion technology and conditions. It has been studied that coal and oil shale ashes have different properties if they are combusted in a Circulated Fluidized Bed (CFB) boiler as compared to the Pulverized Combustion (PC) boiler studied in this article (Bityukova et al., 2010). Bityukova et al. (2010) found that oil shale PC ashes have a much higher content of free lime which is due to the different combustion temperature (CFB 850 °C, PC up to 1,400 – 1,500 °C) and smaller grain size for CFB fuel oil shale. Plamus et al (2011) demonstrated that firing oil shale with LHV 11.1 MJ/kg instead of 8.5 MJ/kg in a CFB boiler decreased the bottom ash share from 37 % to 30 % and the CO_2 emissions were decreased by 7 %. Each power plant boiler has a variety of ashes – bottom ash, cyclone ash, filter ash etc. The mineral matter in the fuel is distributed unevenly between these types. Each ash has specific properties and deriving from these properties has different possibilities for utilization. For instance, PC filter ash is used in cement production, PC cyclone ash is used in construction material production (Raado et al., 2014) and agriculture. A pilot study has also demonstrated that oil shale ash can be utilized for soil stabilization in road construction (Reinik et al., 2018). The research for further use of fossil fuel ashes in general for these purposes is ongoing – regarding the properties of activated carbon fly ash cement composites (Zheng et al., 2017), the preparation of fly ash polystyrene (Haibo, 2017), the properties of coal ash concrete (Rafieizonooz et al., 2017), fly ash and waste polysterine blocks (Zhang and Han, 2016) and the hydration of fly ash cement (Du et al., 2016). Ash could also be utilized for capturing CO_2

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from flue gases (Mohamed et al., 2017) or as a catalyst for biomass gasification (Herman et al., 2016) through leaching (Patric et al., 2017). Unexpected changes in the composition of a certain ash could result in this ash not being in accordance with the standards or for instance defects in construction materials produced from this ash, etc. In case of using oil shale ash in agriculture in Estonia a sufficient share of free CaO is the most important property and it should never fall below a certain level. The MgO in the oil shale ash used to produce light concrete building blocks in Estonia should never exceed a certain percent or cracks will start to form during the production process. The maximum level allowed is also set in an according standard (EVS 927:2015). It is important to know and consider all the variables affecting these qualities. All oil shales have a large content of ash. The Estonian oil shale used in the power plant studied has an ash content of 45 %. Currently 6 Mt of ash is generated annually, only 3 % of which is utilized, the rest being landfilled. As the ash generation is significant, it is especially important to investigate the effect that load cycling has on the properties of the PC ash. This study investigates the changes in bottom ash composition during load cycling. When combusting solid fossil fuels in PC boilers, the share of furnace ash is usually the highest and most problematic for utilization. The bottom ash share in the case of this PC boiler is 42 % (Konist et al., 2013). Full-scale experiments with ash sampling were carried out on a power unit in Estonia. Collecting and analysing data from industrial experiments from operating power plants is the best way to make conclusions regarding power plants operating on different fuels and technologies. This method has for instance been applied to compare grate and bubbling fluidized bed combustion of the same fuel (Rummel and Paist, 2016). As mineral matter does not appear or disappear in the process, it is known and has been demonstrated in earlier studies (Konist et al., 2013) that together with changes in the bottom ash the composition of other ash types changes, too. When the bottom ash, which is the focus of this study, was transformed due to load cycling, then also the compositions of other ashes like cyclone and electrostatic precipitator ash changed (Konist et al., 2013). Similar sampling could be carried through at different load levels for any solid fuel power plant. The sampling of both fuel and ash should be sufficiently extensive to consider the daily variation in fuel composition, excess air factor and other variables. Prediction algorithms can be developed which consider the share of operation time at each load level to estimate the composition of each batch of combustion ash during load cycling. The information obtained using these algorithms can be used for deciding the utilization of each batch of ash. As a result, the ash can be utilized in conformity with all standards and possible problems during utilization are avoided. No earlier studies demonstrating the link between combustion ash composition transformation and load cycling were found during the literature survey.

2. Experiment

The object of the study was one of the two 320 t/h type TP-101 boilers of a 200 MW_{el} power unit. The unit is located in Estonia and utilizes oil shale with 45 % ash content as fuel (Konist et al., 2013). The experimental series were carried out ramping the power plant unit load from 100 % maximum continuous rating (MCR) to 50 % MCR and then back to 100 % MCR. Bottom ash samples were taken during the experiments. During the experiments, the formation of gas components was measured, and the fuel consumption rate was determined at a regular interval. The PC boiler layout and the load cycling curve can be seen on Figure 1. The bottom ash samples were taken from the furnace discharge which can be seen on the left of the Figure 1.

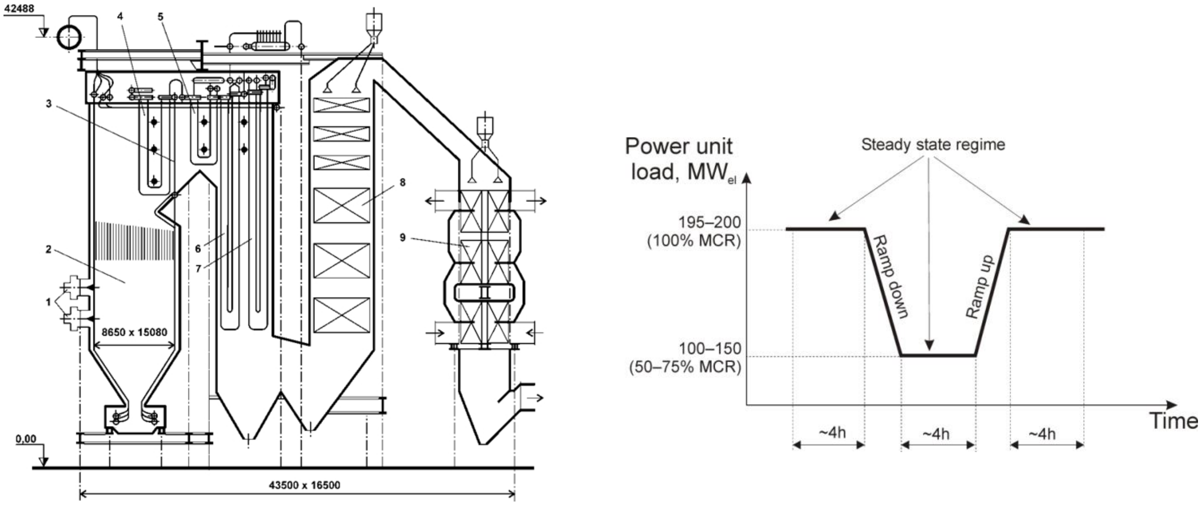

Figure 1: A schematic of the boiler (Konist et al., 2013) and the load cycling curve used in the experiments

The steam parameters of the unit are 14 MPa and 540 °C. The temperature in the combustion chamber is up to 1,400 – 1,500 °C at full load. At both 100 % and 50 % MCR the power unit was operated at least 4 h at a constant load before load ramping. Ramping was done at a unit ramp rate of 2.5 MW_{el}/min (1.25 %/min) which is the allowed maximum rate for this unit. Bottom ash samples were taken at 100 % MCR 1 h before ramping, during the ramping down to 50 % MCR, 2 h into operating at 50 % MCR, 2 h later during ramping back up to 100 % MCR and 1 hour after returning to operate at 100 % MCR as shown in Figure 2. Three repeated experiments with this sequence were carried out during 3 separate days (Test A, B and C). Fuel samples were taken daily average. The composition of the fuel and ash samples was determined.

Table 1 shows the detailed chemical composition and the results of combustion lab tests of the fuel samples taken during the 3 experiments. The table shows that the share of some components in the fuel varies extensively during the 3 experiments. The maximum content of Al_2O_3, CaO and FeS_2 is relatively 17 % higher than the minimum content for each. For SiO_2 it is 13 % higher and for Fe_2O_3 it is 12 % higher. This is considered in the analysis. The variation in other components is smaller.

Table 1: Detailed chemical composition of fuel sampled during the experiments, as received and the results of combustion tests carried out in laboratory conditions

Description	Composition, as received		
	Test A	Test B	Test C
C, Carbon, wt%	18.28	21.10	19.23
H, Hydrogen, wt%	2.19	2.51	2.31
O, Oxygen, wt%	3.55	3.67	3.48
N, Nitrogen, wt%	0.03	0.02	0.01
S_o, organic Sulfur, wt%	0.37	0.30	0.28
S_p, sulfidic Sulfur, wt%	0.81	0.99	0.80
S_S, sulfate Sulfur, wt%	0.02	0.03	0.02
Cl, Chlorine, wt%	0.09	0.11	0.10
CO_2, carbonate CO_2, wt%	20.22	17.86	19.02
A_P, ash, wt%	43.48	42.73	43.55
W_{cr}, crystalline water, wt%	0.58	0.62	0.62
W^d, moisture, wt%	10.40	10.10	10.60
Total*, wt%	100.00	100.00	100.00
k_{CO_2}, the decomposition degree of carbonate minerals, -	0.97	0.97	0.97
Q_i^r, lower heating value, MJ/kg	7.41	8.84	7.84
ΔA, the difference between laboratory and corrected ash, wt%	3.15	3.14	3.16
U, carbonate CO_2 free mineral part, wt%	49.57	48.83	49.80
SiO_2, wt%	12.74	14.39	13.84
Al_2O_3, wt%	2.96	3.19	2.73
Fe_2O_3, wt%	2.18	2.45	2.21
CaO, wt%	25.35	21.65	23.95
R, organic part, wt%	27.36	30.81	28.42
K, carbonate part, wt%	48.53	42.57	45.82
T, sand-clay part, wt%	24.11	26.63	25.76
FeS_2 in the sand-clay part, wt%	7.95	6.77	7.28

* Does not include Sulphur in sulfate form.

3. Results and discussion

Figure 2 shows the ash sampling carried out at different loads and Figure 3 shows diagrams compiled based on the measurements. The diagrams also include the load ramping timeline. The samples taken are marked with points and the presumed trendlines are sketched with a dotted line. The table and the figure illustrate the effect of load cycling on the share of different chemical composites in the ash during one of the 3 experiments.

Table 2 shows the transformations in ash composition during load cycling for each of the 3 experiments. The 100 % MCR composition was calculated as an average of the samples taken before and after the ramping. The composition during load ramping was calculated as an average of the samples taken during both ramping down and ramping up as on average similar transformations were observed during both in the 3 experiments. For the

50 % MCR the composition is given for a single sample taken at 50 % MCR in each experiment. When possible, results from several samples were used since there is also a variation in the composition of ash due to the changes in fuel composition, excess air factor and other variables. Comparing the averages of many samples is more suitable for investigating trends as it decreases the random element.

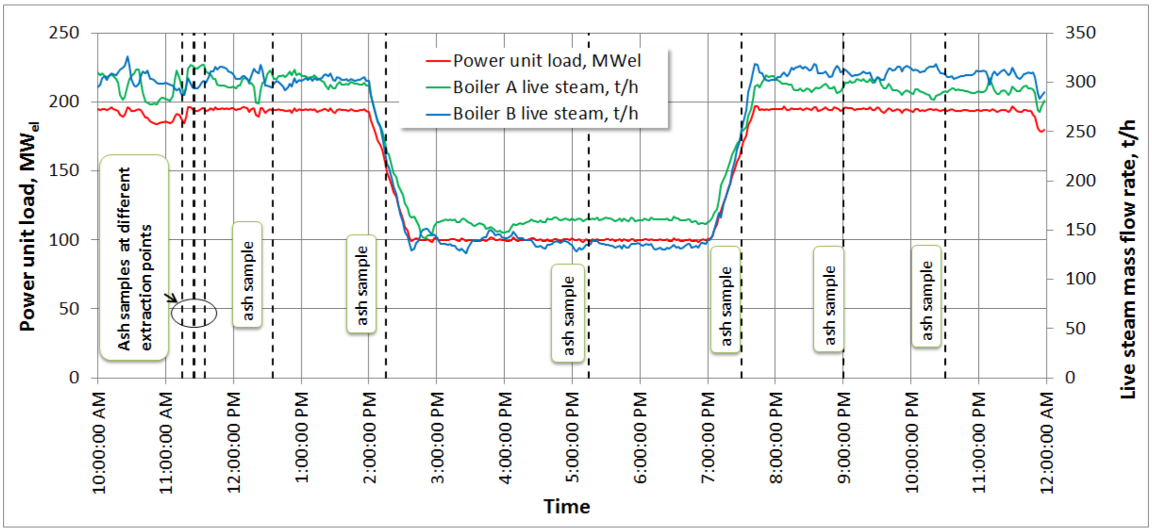

Figure 2: Sampling times of bottom ash during unit load cycling in Test A

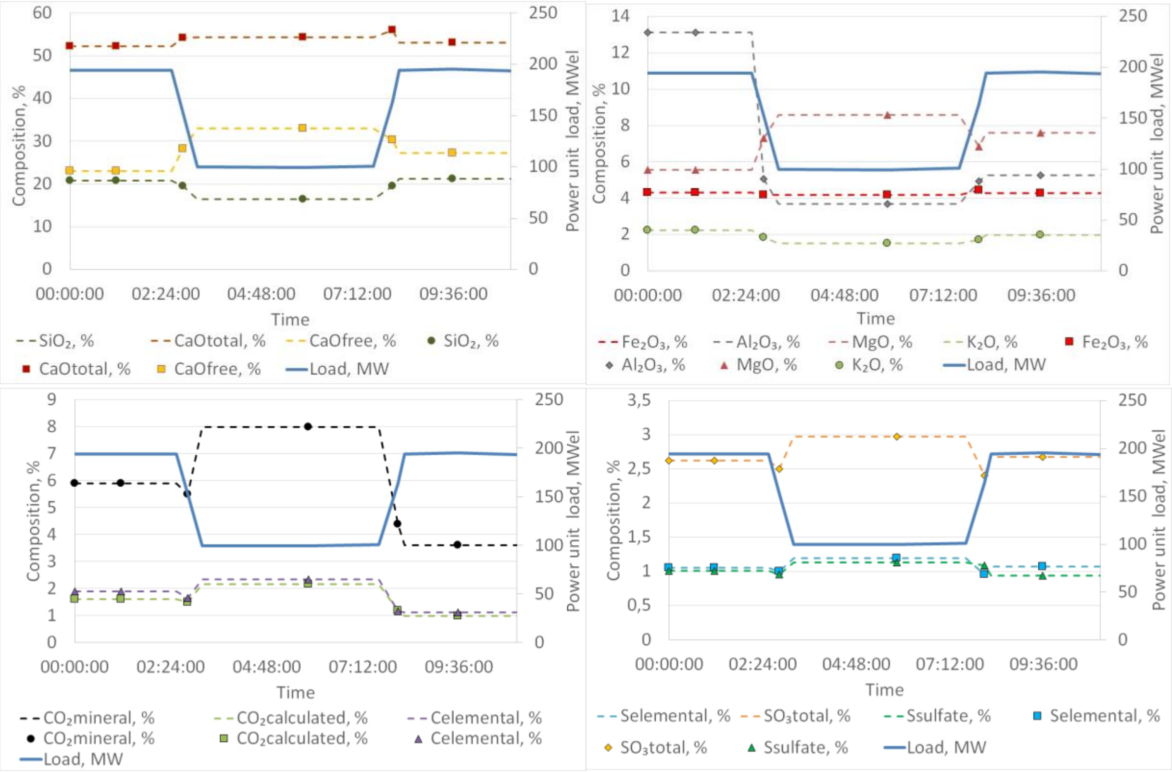

Figure 3: Transformations in bottom ash composition during unit load cycling in Test A

From Table 2 and the diagrams of Test A in Figure 3, we can see that with the reduction of the power unit load the shares of SiO_2, Al_2O_3, K_2O decrease and the shares of CaO_{total}, CaO_{free}, MgO, $CO_{2mineral}$, $CO_{2calculated}$, $C_{elemental}$, SO_{3total}, $S_{sulfate}$ all increase. The share of Fe_2O_3 mostly stays the same. During the ramping down and ramping up of the load there is a temporary decrease in the content of SO_{3total}. The transformations in bottom ash composition can be explained by the changes in combustion temperature at different loads and during ramping and the resulting changes in ash and flue gas formation that take place during the cycling of the unit load. Measurements show that the temperature of flue gases exiting from the furnace drops by 150 – 170 °C at 50 % MCR compared to 100 % MCR. We can conclude based on this that the temperature in the combustion zone is also lower by the same margin – around 1,300 °C instead of the usual 1,400 – 1,500 °C. Sulfur binding by free lime is more intensive at lower temperatures (Konist et. al, 2014) and this is presumably the cause for an increase in the share of sulfate Sulfur compounds in the ash.

Table 2: The transformations in bottom ash compositions for the 3 experiments

	Test A			Test B			Test C		
	100 % MCR	Ramping 100 % ↔ 50 % MCR	50 % MCR	100 % MCR	Ramping 100 % ↔ 50 % MCR	50 % MCR	100 % MCR	Ramping 100 % ↔ 50 % MCR	50 % MCR
$CO_{2mineral}$, wt%	4.76	4.95	7.98	2.73	3.16	8.08	1.68	2.76	8.12
$C_{elemental}$, wt%	1.51	1.41	2.34	0.82	0.91	2.29	0.43	0.78	2.32
$S_{elemental}$, wt%	1.06	0.98	1.19	0.91	1.02	1.49	0.87	1.03	1.06
SO_{3total}, wt%	2.65	2.45	2.98	2.28	2.54	3.73	2.16	2.58	2.65
$S_{sulfate}$, wt%	0.98	1.03	1.13	0.87	0.98	1.62	0.92	1.00	0.97
SiO_2, wt%	21.04	19.53	16.47	20.26	18.29	15.65	19.05	19.60	17.02
Fe_2O_3, wt%	4.30	4.30	4.16	4.51	4.92	3.95	4.54	4.57	3.97
Al_2O_3, wt%	9.19	5.00	3.69	4.35	3.41	3.34	4.44	4.87	3.40
CaO_{total}, wt%	52.65	55.06	54.27	53.70	58.36	49.07	59.51	56.80	56.83
CaO_{free}, wt%	25.12	29.30	32.96	27.68	33.10	25.17	32.19	31.07	33.79
MgO, wt%	6.58	7.06	8.59	9.44	6.42	12.32	6.75	6.93	4.86
K_2O, wt%	2.10	1.78	1.52	1.42	1.35	1.93	1.75	1.78	1.61
Na_2O, wt%	0.27	0.26	0.25	0.41	0.23	0.26	0.17	0.16	0.17

From Table 2, we can see that the shares of $CO_{2mineral}$, $C_{elemental}$, SO_{3total}, $S_{sulfate}$, SiO_2 in the bottom ash are higher in all the experiments both during the ramping process and at 50 % MCR part-load compared to 100 % MCR. The shares of Fe_2O_3, Al_2O_3 and CaO_{total} at 50 % MCR are lower in all the experiments. During ramping down of the load, the shares of Fe_2O_3 and CaO_{total} are lower on the average. Al_2O_3 level during load ramping does not change on the average. The share of MgO on the average is higher, however there are 2 measurements which show a decrease in the share, one at 50 % MCR in Test B and one during ramping in Test C. In case of K_2O and Na_2O the measurements show inconsistent changes in the shares towards both directions which refer to the fact that there is no consistent correlation between load cycling and the changes in their share in the bottom ash. CaO_{free} generally increased during load cycling, a decrease was observed in Test C during ramping and Test B at 50 % MCR. The decrease in CaO_{free} is negative for utilization of ash in agriculture for liming of acidic soils and generally also as a cement additive and the increase in MgO is negative for utilization of ash in aerated concrete tile production as it increases the formation of cracks during the production process. The obtained results can be explained by the changes in combustion temperature that occur during load ramping and at part load. The reason for the measured 150 – 170 °C drop in the flue gases exiting the furnace is that the excess air factors at 50 % MCR are increased to 1.7 – 1.9 compared to the 1.5 – 1.6 at 100 % MCR according to set procedures. Additional air decreases the temperature in the combustion zone and additional Oxygen increases reactions where binding of SO_2 with CaO takes place. As a result, $CaSO_4$ is formed and this can be seen from the increase in the share of SO_{3total}. This is also supported by combustion gas composition measurements which confirm the decrease in SO_2 from 2000–2500 mg/Nm^3 (at 6 % O_2) at 100 % MCR to 1000 mg/Nm^3 (at 6 % O_2) 50 % MCR.

The CaO is formed during the decomposition of $CaCO_3$ and $CaMg(CO_3)_2$. In addition to SO_2 also SiO_2, Fe_2O_3 and Al_2O_3 are bound by CaO. The increase in free CaO_{free} and the decrease in Fe_2O_3, Al_2O_3 in 50 % MCR and a means that the binding of Fe_2O_3, Al_2O_3 with CaO forming $CaO{\cdot}Fe_2O_3$ and $CaO{\cdot}Al_2O_3$ in the bottom ash decreases. Therefore, they leave the furnace with the fly ash. The decrease in the share of CaO_{total} means that also more CaO leaves with fly ash. Earlier studies show that the proportion of CaO decreases both in PF and CFB boilers along the boiler gas pass, from the average of 49 % in bottom ash to 30 % in the last fields of electrostatic precipitators (Bityukova et al., 2010).

The changes in excess air factor and combustion temperature cause ash components to be redistributed among different ash fractions along the flue gas path and some elements to be bound in the ash instead of leaving with flue gases. The results show that there is a direct link between both unit load ramping and operation at part loads and ash properties. Similar experiments can be carried out in any solid fuel power plant. Together with continuous monitoring of fuel properties and combustion gas temperature power plant operators can predict the ash composition and produce it in patches depending on the properties needed for each application.

4. Conclusions

In this study ash samples from a power plant unit PC boiler were collected at nominal load, during load ramping between 100 % MCR and 50 % MCR and at 50 % MCR part-load in 3 experiments. 4 samples at full load, 2 samples during load ramping and 1 samples at 50 % MCR were taken during each experiment. Fuel samples of the oil shale used were taken daily. The chemical composition of the fuel and ash samples was determined. The most important result of this study is the demonstration of a direct correlation between unit operation at part load and the resulting transformation in the composition of ashes in the experiments. In all the experiments the share of Carbon and Sulfur components in the ash increased during both load ramping and at part load, accordingly 40 % and 10 % during ramping and twice and 30 % at 50 % MCR. The reason for the increase in the share of sulfate Sulfur in the ash is the 150 – 170 °C decrease in combustion temperature caused by a higher excess air factor at part load which increases SO_2 binding by free CaO content into $CaSO_4$. As a result, also the share of total Sulfur is increased. This is consistent with the rest of the results. The decrease in the share of Fe_2O_3, Al_2O_3 and CaO_{total} and an increase in MgO content at part load were observed in most of the experiments. The consistency in the results shows that the transformations in the composition during load cycling cannot be attributed only to other variables like the changes in fuel composition, etc.

References

Bityukova L., Mõtlep R., Kirsimäe K., 2010, Composition of oil shale ashes from pulverized firing and circulating fluidized bed boiler in Narva thermal power plants, Estonia, Oil Shale, 27(4), 339-353.

Estonian Centre for Standardisation, 2015, EVS 927:2015: Burnt shale for building materials. Specification, performance and conformity, Tallin, Estonia.

Du J., Shen X., Feng G., Zhu W., Xu C., 2016, Hydration mechanism of fly ash cement and grouting simulation experiment, Chemical Engineering Transactions 51, 565-570, DOI: 10.3303/CET1651095.

Haibo L., 2017, Experimental study on preparation of fly ash polystyrene new insulation building material, Chemical Engineering Transactions, 59, 295-300, DOI: 10.3303/CET1759050.

Herman A.P., Yusup S., Shahbaz M., 2016, Utilization of bottom ash as catalyst in biomass steam gasification for hydrogen and syngas production, Chemical Engineering Transactions, 52, 1249-1254, DOI: 10.3303/CET1652209.

Konist A., Loo L., Valtsev A., Maaten B., Siirde A., Neshumayev D., Pihu T., 2014, Calculation of Estonian oil shale combustion products in regular and oxy-fuel mode in a CFB boiler. Oil Shale, 31(3) 211−224.

Konist A., Pihu T., Neshumayev D., Siirde A., 2013, Oil shale pulverized firing: boiler efficiency, ash balance and flue gas composition, Oil Shale, 30 (1), 6-18, DOI: 10.3176/oil.2013.1.02.

Mohamed M., Yusup S., Bustam M.A., Azmi N., 2017, Effect of coal bottom ash and binder addition into CaO-based sorbent on CO_2 capture performance, Chemical Engineering Transactions, 56, 325-330, DOI: 10.3303/CET1756055.

Patrick D.O., Yusup S., Osman N. B., Zabiri H., Shahbaz M., 2017, Performance of water-leached coal bottom ash as catalyst in thermogravimetric analyser (TGA) biomass gasification, Chemical Engineering Transactions, 61, 1681-1686, DOI: 10.3303/CET1761278.

Plamus K., Ots A., Pihu T., Neshumayev D., 2011, Firing Estonian oil shale in CFB boilers – ash balance and behaviour of carbonate minerals, Oil Shale, 28(1), 58-67, DOI: 10.3176/oil.2011.1.07.

Raado L.-M., Hain T., Liisma E., Kuusik R., 2014, Composition and properties of oil shale ash concrete, Oil Shale, 31(2), 147-160, DOI: 10.3176/oil.2014.2.05.

Reinik J., Irha N., Koroljova A., Meriste T., 2018, Use of oil shale ash in road construction: results of follow-up environmental monitoring, Environmental Monitoring and Assessment, 190(59), DOI: 10.1007/s10661-017-6421-5.

Rafieizonooz M., Salim M.R., Hussin M.W., Mirza J., Yunus S. M., Khankhaje E., 2017, Workability, compressive strength and leachability of coal ash concrete, Chemical Engineering Transactions 56, 439-444, DOI: 10.3303/CET1756074

Rummel L., Paist A., 2016, Case study comparison of bubbling fluidised bed and grate-fired biomass combined head and power plants, Chemical Engineering Transactions 52,1147-1152, DOI: 10.3303/CET1652192.

Zhang X., Han Y., 2016, Thermal insulation properties of fly ash and waste polystyrene mixed block building materials, Chemical Engineering Transactions, 55, 253-258, DOI: 10.3303/CET1655043.

Zheng C., Liu Z., Xu J., Li X., Yao Y., 2017, Compressive strength and microstructure of activated carbon – fly ash cement composites, Chemical Engineering Transactions, 59, 475-480, DOI: 10.3303/CET1759080.