

THE INFLUENCE OF CALCITE ON THE ASH FLOW TEMPERATURE FOR SEMI-ANTHRACITE COAL FROM DONBAS DISTRICT

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This paper presents the results of research focused on the lowering of ash flow temperature at semi-anthracite coal from Donbas district by means of additive (calcite) dosing. Ash fusion temperatures were set for two coal samples (A, B) and for five various states (samples of ash without any additives, with 1%, with 3%, with 5% and with 7% of the additive) in total. The macroscopic-photographic method was used for identifying all specific temperatures. Obtained outputs prove that A type coal has a lower value of sphere temperature than B type coal in the whole scope of percentage representation of the additive. The flow temperature dropped in total from 1489 °C to 1280 °C, i.e. by 14% during the test of coal of type A with 7% of the additive; while it was near 10% for coal of type B (from 1450 °C to 1308 °C). Numerical simulations of the process showed that it is not effective to add an additive with a grain size lower than 280 µm by means of waste-vapour burners.

Keywords: coal, ash, additive, flow temperature, numerical simulation

1. INTRODUCTION

While combusting various fuels in boilers and other engineering facilities, not only pollutants (Ahn et al., 2010; Čarnogurská et al., 2012; Moroń et al., 2013), but also other indicators that characterise the quality of the combustion process are thoroughly monitored. Such an indicator is, for example, the quality (composition) of ashes during coal combustion.

Ash (Sambor and Szymanek, 2012) is a mixture of various minerals and it is usually characterised by its chemical composition. The components SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂, Na₂O, K₂O, and SO₃ are identified. The proportion of the components in ash varies (also regarding coal from the same mine) in relatively broad limits and it is determined for a given coal only experimentally.

Criteria describing ash behaviour at high temperatures are so called characteristic ash fusion temperatures (AFTs). According to the standard ASTM D1857, these are initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT) and fluid temperature (FT). The standard STN ISO 540 designates these temperatures as deformation temperature (DT),

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sphere temperature (ST), hemisphere temperature (HT) and flow temperature (FT). If there is a big temperature interval between ST and HT, ash does not flow well; it adheres to the walls of the combustion chamber and causes problems regarding boiler operation. A possible solution for reducing ash viscosity as well as decreasing the flow temperature is the use of a suitable additive and the correct position of the dosing device for additive transport into the combustion chamber.

The practical importance of knowing characteristic ash temperatures lies in the fact that they tentatively identify temperatures in a furnace that may cause failures in a combustion device, e.g. ash melting on a grate and filling the air gap between grate bars.

Many scientific papers were devoted to the development of suitable additives. The authors' attention was focused mainly on the features of melted slag and the position of out-flow from the combustion area. Relations between the composition of an ash system and an additive as well as the HT of this mixture, its viscosity and surface tension, have been studied. Some research of basicity, i.e. the proportion of CaO to SiO₂ in the mixture, the contents of Na₂O, SiO₂, CaF₂ and their influence on viscosity has also been conducted.

For example, Kong et al. (2011) dealt with problems of influence of adding various amounts of CaO on ash flow ability during coal combustion. The authors stated that the temperature of critical viscosity decreases with increasing addition of CaO and a minimum value approaches with CaO content of about 15%. Experiments on selected coal samples (Wen et al., 2010), were conducted in order to obtain information about the influence of various values of proportions of SiO₂, Al₂O₃, CaO, Fe₂O₃ and MgO on ash fusion temperatures. AFTs were determined by a standard laboratory test and, at the same time, liquid temperature was calculated using FACTSage (Thermfact/CRCT, Montreal, Canada and GTT-Technologies, Aachen, Germany). Liquid temperatures were, in all samples of coal ash, always higher than its AFTs.

Li et al. (2008) studied the influence of borax addition on ash melting on four coal types. Mullite reactivity in ash was then calculated with the density functional theory. Calculation results correspond with AFTs set in reducing atmosphere. The authors (Lolia et al., 2002) set statistical models for prediction of fusion temperatures of ashes from 17 kinds of Albanian coal. The authors examined how different forms of oxides influenced these temperatures.

The paper (Li et al., 2009) analyses changes of mineral composition in slag at various temperatures before and after the addition of iron oxide and its influence on ash FT of coal from a mine in Wan-bei. Seggiani (1999) worked out correlation relations for expression of AFTs for 260 samples of coal ash and 35 samples of biomass ash. Derived relations also enable the prediction of effects of the influence of minerals (e.g. CaO) used for modification of slag behaviour.

The paper (Wang et al., 2011) presents results from combustion of high-sulphur coal with an additive (CaO) in various proportions. If a higher amount of CaO than 30% is used, a product of cement type with fixed sulphur can be obtained from the ash. The authors (Wen et al., 2009) measured AFTs of 21 typical Chinese coal ash samples and 60 synthetic ash samples in Ar and H₂ atmospheres. The comparison of measured AFTs with the values calculated with FactSage program showed good compliance, the standard deviation was lower than 30 K. Because iron oxides in coal ash samples fused under a H₂ atmosphere are reduced to metallic iron, the AFTs in a H₂ atmosphere are always higher than those with an Ar atmosphere.

The paper (Wall et al., 1998) deals with measuring shrinkage and electric conductivity during heating of samples of laboratory ash and ash from the combustion process in thermal power plants. Preliminary data evaluation from nine power plants shows that measurement of shrinkage can provide an alternative approach to characterising slag creation. The relation between individual hemisphere temperatures and flow temperatures and their display in the ternary diagrams, was examined by Huggins et al. (1981).

Thompson and Argent (1999) used thermodynamic prediction programs for real ash modelling from coal combustion with known mineralogy. They evaluated trends that were the results of local non-uniformity of mineralogical coal analysis. The authors found out that it was necessary to perform experimental research of ash composition for obtaining a realistic model and to take into account the creation of complicated minerals including more than two oxides.

Lloyd et al. (1993) determined AFTs for 70 kinds of ash from mixtures of North-American coals in an oxidising atmosphere in accordance with method D 1857 under the standard ASTM, and these temperatures were compared with respective ash fusing temperatures obtained under reducing conditions. From the chemical composition of the ash a regression equation for estimating AFTs was derived. The following text deals with the influence of calcite dosing on ash fusion from Donbas district. No data about additive influence on ash features relating to these particular semi-anthracite coals has been detected or published yet.

2. TEMPERATURE CHARACTERISTICS OF SELECTED ADDITIVES

Coal from Donbas, Kuzbas and Rostov districts forms the fuel basis in power plant Vojany (EVO) in Slovakia. It is a black, energetic, semi-anthracite coal with a lower heating value of $25 \text{ GJ}\cdot\text{t}^{-1}$. These coals have a flow temperature of ash higher than $1350 \text{ }^\circ\text{C}$; it, therefore, exceeds the value set for liquid-slag fireboxes. These coals do not achieve the required slag viscosity needed for out-flow from the combustion chamber. Slag is collected in a plastic state on the bottom of the chamber. This slag state results often in reducing boiler capacity or its total putting out of operation.

Viscosity decrease of the given coal can be achieved with a suitable additive. Oxides of alkaline types enter into reaction with minerals in slag, which results in the breakup of fused silicate chains and, therefore, in a decrease of slag viscosity. Lower viscosity enables to keep a combustion regime in the liquid-slag firebox with a temperature below $1350 \text{ }^\circ\text{C}$.

The efficiency of influence of different additives (melts) dosing on decreasing ash temperatures was examined with regard to coal analysed in the paper. Coal is burnt in a single-drum boiler with natural circulation, with pulverised coal combustion and liquid-slag firebox in the power plant EVO. Outgoing slag in liquid-slag fireboxes should have a dynamic viscosity of about 10 to 15 Pa·s. Slag hemisphere temperature regarding used coal is in the limits of 1100 to $1600 \text{ }^\circ\text{C}$, therefore, it is necessary to keep temperature under $1800 \text{ }^\circ\text{C}$ in the bottom part of the melting area of the boiler.

3. DETERMINATION OF ASH FUSION TEMPERATURES

AFTs of this sample of energetic coal were identified in such a way that, firstly, the so called “blank test” was performed. 10% of one of nine examined additives was always present in a homogenous mixture of ash and an additive. They were calcite, dolomite, magnesite, soda ash, kaolin, blast-furnace slag, converter slag, MgO-fly ash and fluorite. The prepared mixture was annealed in a slit furnace at 750°C for eight hours. Subsequently, samples were examined in terms of their melting characteristics in the Marsh furnace. Only five kinds of additives were selected for research of additive influence on AFTs on the basis of this test. They were calcite, soda ash, converter slag, MgO-fly ash and fluorite. Converter slag contained [wt%]: 46.7 CaO, 17.1 SiO₂, 5.9 MgO, 1.2 Al₂O₃, 23.1 FeO, 4.8 MnO, 0.8 P₂O₅. Temperature characteristics, i.e. ST, HT and FT, were identified in mixture samples with the mentioned additives in the Marsh furnace. Results are listed in Table 1.

Table 1. AFTs with 10% of selected additives

Additive	ST [°C]	HT [°C]	FT [°C]
MgO – fly ash	1210	1240	1280
calcite	1180	1200	1230
converter slag	–	1140	1210
fluorite	1005	1125	1140
soda ash	1100	1130	1185

Table 1 shows, that MgO-fly ash is the least effective agent of fusion (it has the highest FT), it was, therefore, excluded from further observations. The same energetic coal was subsequently monitored in combination with the respective additive in various percentage representations. Table 2 lists the results for 5%, 2.5% and 2% of the given additive. As the monitored parameter was FT temperature, the other two temperature figures (ST and HT) were not evaluated during all the measurements.

Table 2. AFTs with various percentage representations of selected additives

Additive	5% of additive			2.5% of additive			2.0% of additive		
	ST [°C]	HT [°C]	FT [°C]	ST [°C]	HT [°C]	FT [°C]	ST [°C]	HT [°C]	FT [°C]
calcite	-	1215	1240	1190	1230	1260	1220	1265	1280
converter slag	-	-	1210	-	1200	1240	1220	1245	1275
fluorite	-	1175	1210	-	1220	1260	1210	1225	1240
soda ash	-	-	1205	-	1200	1240	1210	1230	1255

After these experiments, a detailed examination of AFTs was performed. Two samples of semi-anthracite coal were selected, hereinafter designated as coal A and coal B. The analysis of both samples, sufficient for the needs of power plant Vojany, is listed in Table 3.

Table 3. Parameters of coal A and B samples

Parameter	dimension	as received basis (r)		dry basis (d)		dry ash free basis (daf)	
		A	B	A	B	A	B
free moisture	[%]	10.35	8.03	-	-	-	-
inherent moisture	[%]	0.87	0.71	-	-	-	-
total water	[%]	11.22	8.74	-	-	-	-
ash	[%]	14.05	16.33	15.82	17.89	-	-
dry ashes free basis	[%]	74.73	74.93	84.18	82.11	100.00	100.00
higher heating value	[MJ·kg ⁻¹]	25.79	26.29	29.05	28.81	34.52	35.08
lower heating value	[MJ·kg ⁻¹]	25.19	25.67	28.37	28.13	33.71	34.26
volatile matter	[%]	10.42	9.04	11.74	9.91	13.95	12.07
non-volatile matter	[%]	64.31	65.89	72.44	72.20	86.05	87.93
carbon	[%]	68.13	68.71	76.73	75.30	91.16	91.70
sulphur	[%]	0.46	0.63	0.52	0.69	0.61	0.83
nitrogen	[%]	1.68	1.66	1.89	1.82	2.25	2.21

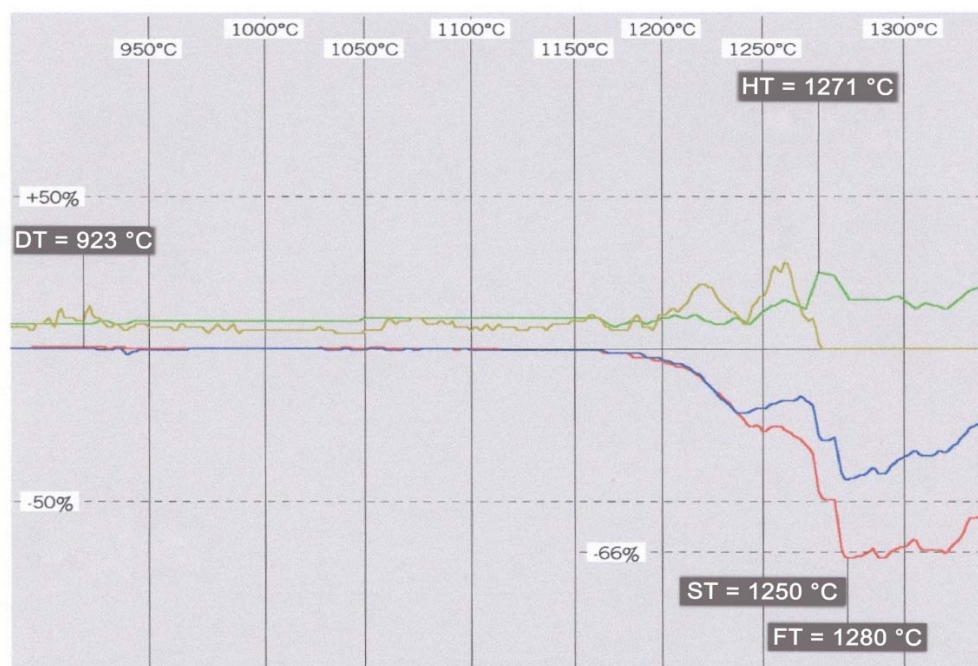
A comparison of both coal samples shows that coal A contain less ash and significantly less sulphur than coal B. On the basis of this given fact, we can expect that the same amount of additives will decrease flow temperature more with coal A than with coal B.

Calcite was, in terms of its availability and economic point of view in power plant operation, an additive for identifying AFTs in samples of coal A and coal B. Temperatures were identified in both samples for a total of five various states. The first state was a pure sample – ash sample without an additive. The second sample was a sample with 1% of an additive. The third state was characterised by 3%, the fourth state by 5% and the fifth state by 7% of an additive. Table 4 lists the measurement results of AFTs for both samples of examined coal while using calcite.

The results presented in Table 4 were obtained by the microscopic-photographic method according to STN ISO 540. Measurements were graphically recorded from the sintering process, through softening, melting to flowing with characteristic changes of appearance and shape of examined ash piece.

Table 4. Ash fusion temperatures

Coal type	calcite	ST [°C]	HT [°C]	FT [°C]
A	without additive	1294	1467	1489
	+ 1%	1281	1366	1397
	+ 3%	1274	1360	1371
	+ 5%	1264	1315	1334
	+ 7%	1250	1271	1280
B	without additive	1334	1440	1450
	+ 1%	1312	1362	1390
	+ 3%	1302	1360	1382
	+ 5%	1294	1320	1344
	+ 7%	1256	1274	1308



Comment: Grz.: 1200/30/10; St/Sp: 900/1360; Tft/Tex: 850/ 0;

Fig. 1. Courses of AFTs (coal A, proportion of calcite – 7%)

For example, Fig. 1 shows the course of characteristic temperatures for the ash of coal A with an additive of 7% of calcite and Fig. 2 shows the graphical interpretation of change of shape of the sample piece. A greater decrease of AFTs was achieved with coal A than with coal B. Therefore, only outputs obtained on the sample of coal A will be provided.

It was recommended to use calcite additive for regulation of flow temperature of problematic energetic coals from Donbas district for boiler operation in EVO on the basis of the performed tests.

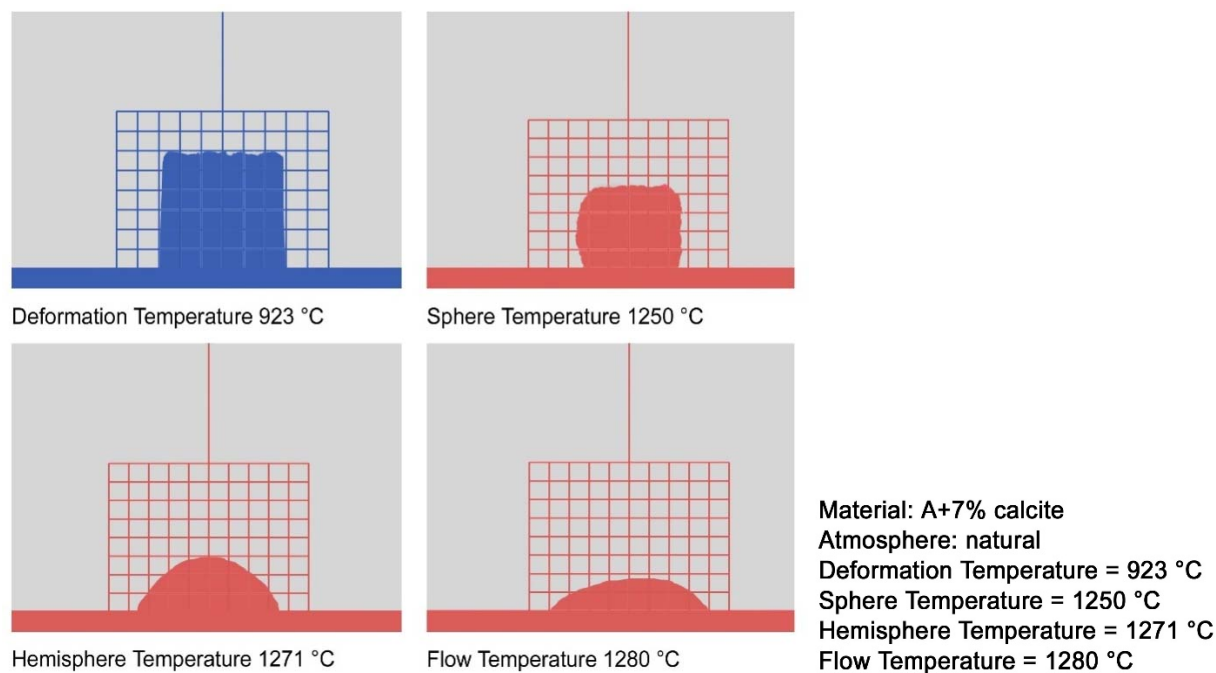


Fig. 2. Sample shapes at AFTs (coal A, 7% calcite)

The compositions of minerals in slag from coal of type A at 7% calcite dose are listed in Table 5.

Table 5. Composition of ash from coal with 7% of an additive

oxide	dimension	values without additive	values with additive
SiO ₂	[wt%]	59.23	46.3
Al ₂ O ₃	[wt%]	22.51	17.6
Fe ₂ O ₃	[wt%]	10.45	8.17
CaO	[wt%]	2.67	23.9
MgO	[wt%]	1.29	1.01
TiO ₂	[wt%]	0.86	0.673
K ₂ O	[wt%]	2.00	1.56
Na ₂ O	[wt%]	0.75	0.586
P ₂ O ₅	[wt%]	0.23	0.179
SO ₃	[wt%]	0.01	< 0.01

Ash composition was determined by an accredited testing laboratory according to the standard STN EN ISI/IEC 17025:2005 using the method of X-ray-fluorescent spectrometry. On the basis of Table 5, the dominant components of ash are three oxides: SiO₂, Al₂O₃, CaO, followed by Fe₂O₃, K₂O and MgO. Other compounds are represented by weight proportion lower than 1%.

Fig. 3 shows the course of characteristic temperatures depending on the percent of an additive for coal sample of type A. Obtained outputs provide evidence that coal of type A has in the whole range of percentage representation of used additive a lower ST than the coal of type B. Both coal samples reached the same HT (1360 °C) when 2.8% of an additive was used. The difference in FT values in both samples at 7% of additive is 28°C.

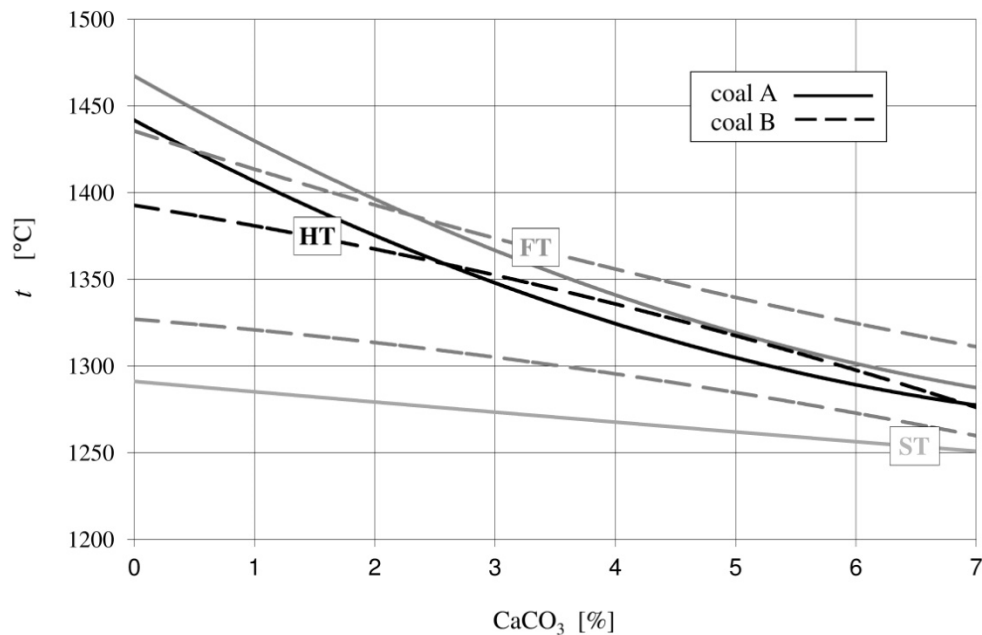


Fig. 3. Course of ST, HT and FT depending on additive percentage

Measurements showed that the differences between FT and ST values in both coals decrease with the increased proportion of calcite (within the range of 0 up to 7% of additive). For example, regarding coal of type A without additive the difference between the ST and FT values is almost 200°C, this temperature difference decreases by ca. 30°C at 7%. Similar trends are valid also for differences between HT and ST or FT and HT.

On the basis of performed experiments with the used additive, we can state that flow temperature depending on additive percent (range 0 up to 7%) can be described by relation (1) for coal of type A and by relation (2) for coal of type B. The difference in calculation of flow temperature is according to relation (1) ca. 7 °C for coal of type A as compared with the value set in the laboratory. The flow temperature for coal of type B calculated according to relation (2) differs from the value set in the laboratory by ca. 3°C

$$FT = 1.9639 \cdot (\% \text{ CaCO}_3)^2 - 39.4338 \cdot (\% \text{ CaCO}_3) + 1467.4 \quad (1)$$

$$FT = 0.7121 \cdot (\% \text{ CaCO}_3)^2 - 22.7620 \cdot (\% \text{ CaCO}_3) + 1435.7 \quad (2)$$

The experiments carried out with the coal from Donbas district confirmed that calcite as an additive supplied has a similar effect on the change of flow temperature as was known from the research results presented for other coal types, e.g. in the papers by Kong et al. (2011) and Wen et al. (2010).

AFTs values were compared also with the technique developed by Seggiani (1999). The values of individual temperatures measured for both coal types differed from calculated results transferred by means of Seggiani's correlation relations in the range from 30 up to 80°C. In doing so, all measured temperatures were lower than calculated temperatures. We may state that these regression equations are applicable for approximate determination of ATFs of ash from semi-anthracite coal from Donbas region.

4. NUMERICAL ANALYSIS OF ADDITIVE TRAJECTORY IN THE COMBUSTION CHAMBER

The aim of the numerical solution of the flow ratios in the combustion chamber was to find out whether the distribution of an additive by means of waste-vapour burners is suitable. For its correct functioning, the additive should be delivered into the bottom part of the melting area of the boiler in the highest possible amount. In order to track the trajectory of an additive delivered into the combustion chamber of a boiler by means of waste-vapour burners, type DL 2000, 6Ypl IVTKV 3510, a numerical simulation of flow ratios with a delivered additive with various grain sizes (45 μm , 90 μm , 160 μm and 280 μm) was performed.

The calculation of flow ratios in the combustion chamber was performed in Fluent program and turbulence model $k-\varepsilon$ was used. The round shape of additive particles and the interaction of particles with the walls of the combustion chamber were taken into account during this solution. After the contact of particles with the wall, the particle capturing in the melting area and particle bouncing from the wall in the cooling area were expected to happen. The density of the additive particles was $1.250 \text{ kg}\cdot\text{m}^{-3}$ and elementary composition of the fuel - see coal A in Table 3.

With regard to the size of the calculation model and the possibility of using symmetry in the boiler axis, one half of the combustion chamber was modulated. To solve the flow in the combustion chamber, the release and subsequent combustion of volatile mater were taken into account, as well as combustion of solid residue remaining. A scheme of the boiler with marked burners is presented in Fig. 4.

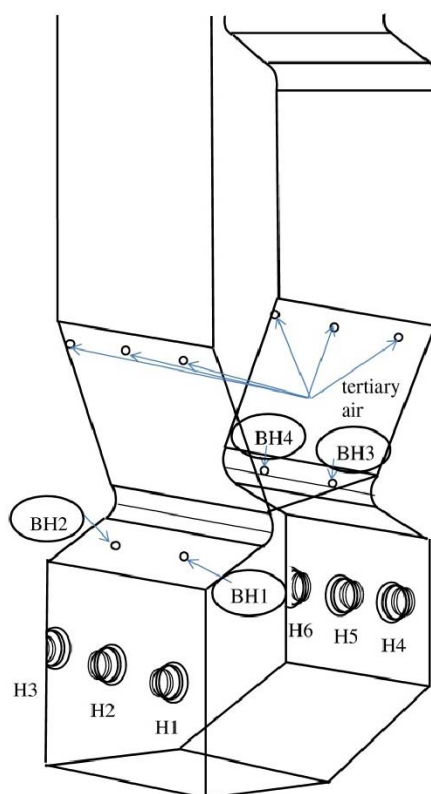


Fig. 4. Position of waste-vapour burners BH1 to BH4 (marked by circles)

Outputs gained from the solution are valid for boilers in the power plant Vojany while combusting 43200 kg of pulverised coal in an hour with particle size of 35 μm , with temperature of these particles of 240 $^{\circ}\text{C}$. The total amount of air delivered into the boiler was $327000 \text{ Nm}^3\cdot\text{h}^{-1}$, of which $64900 \text{ Nm}^3\cdot\text{h}^{-1}$, was fed by waste-vapour burners. Mean temperature of air (primary, secondary as well as tertiary) was 340 $^{\circ}\text{C}$.

Fig. 5 shows the distribution of the flow field in the combustion chamber at 7% of an additive ($3021 \text{ kg}\cdot\text{h}^{-1}$) with grain size of $280 \mu\text{m}$. As shown, the additive gets to the bottom of the combustion chamber of the boiler. The maximum speeds of the additive (on output from waste-vapour burner into combustion chamber) ranged on the level of $54.2 \text{ m}\cdot\text{s}^{-1}$. Maximum temperature in the furnace reached $1912 \text{ }^\circ\text{C}$ and mean temperature reached $1348 \text{ }^\circ\text{C}$. The temperature of flue gas behind the furnace was $991 \text{ }^\circ\text{C}$, mass rate of flow of flue gas $127.6 \text{ kg}\cdot\text{s}^{-1}$, fuel gas speed at the output from the furnace $5.6 \text{ m}\cdot\text{s}^{-1}$, oxygen level at the output from the furnace 2.6%, heat output transmitted into the walls of the furnace corresponded to the value of 129 MW.

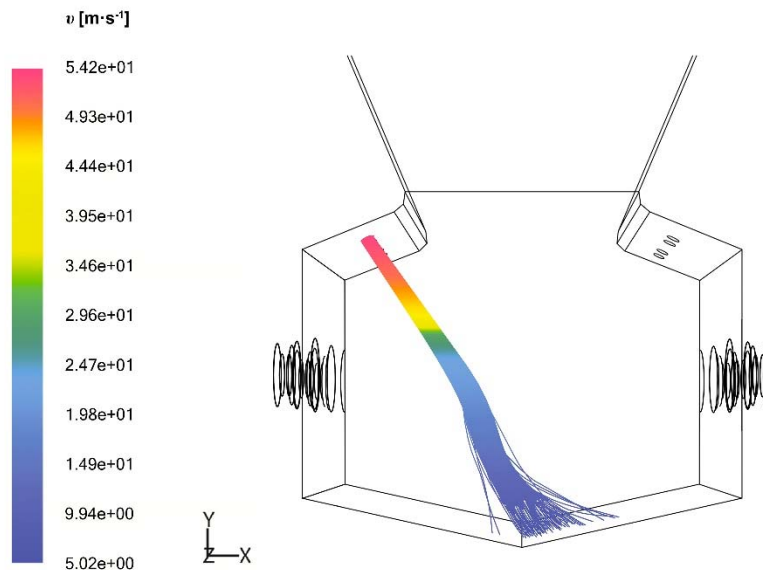


Fig. 5. Additive trajectory from burner BH1 (particle size $280 \mu\text{m}$)

A comparison of a trajectory of an additive with a particle sized $90 \mu\text{m}$ regulated by the same burner is presented in Fig. 6. The additive does not reach the bottom of the combustion chamber and this way a part of it is driven away together with the residues out of the furnace.

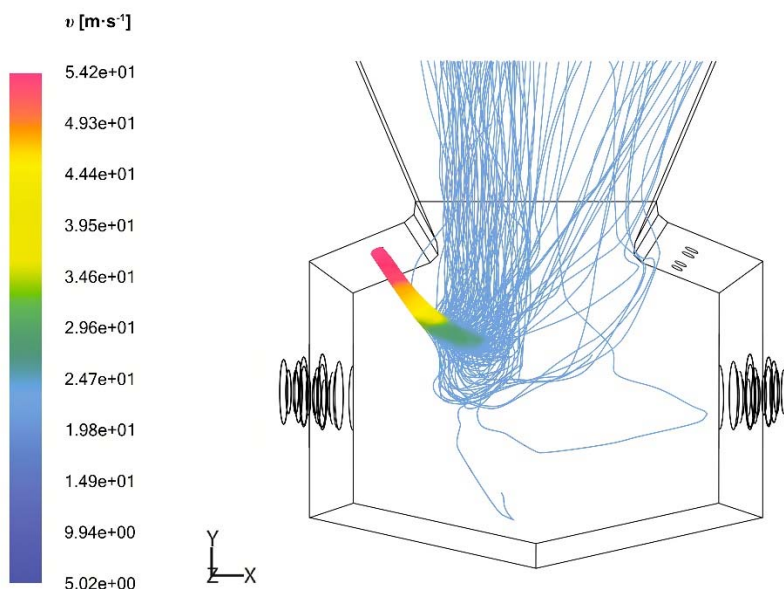


Fig. 6. Additive trajectory from burner BH1 (particle size $90 \mu\text{m}$)

Each movement of the additive in the boiler, the percentage proportion of particles captured in wet bottom furnace of the boiler and the average length of stay of particles in this space, were separately monitored for each burner during the numerical simulation of calcite dosing through waste-vapour burners. Solution results for grain size of 45 μm , 90 μm , 160 μm and 280 μm are summarised in Table 6.

Table 6. Numerical simulation results

Particle size of additive [μm]	Monitored parameters	Waste-vapour burner (BH)			
		BH1	BH2	BH3	BH4
45	retention percentage	7.6	12.5	8.7	66.7
90	retention percentage	25.7	38.6	40.5	96.9
160	retention percentage	37.5	89.1	94.7	100
280	retention percentage	100	100	100	100

The simulation showed that an increase of additive granularity means a higher percentage of particles trapped in the combustion chamber of the boiler. The difference of additive flow from waste-vapour burner No. 4 is caused by the fact that the flow from this burner gets to the bottom along the edge of the swirl which occurs in the combustion space. In the case of other waste-vapour burners, their flow gets bent, which is caused by the main flow from the coal burners.

Table 6 shows that all the additive was captured in the smelting space of the boiler at the particle size of 280 μm , while a percentage of captured particles with the grain size of 45 μm ranged for individual waste-vapour burners from 8% to 67%. In summary, only a quarter of the whole amount of the added calcite was captured in this case.

5. CONCLUSION

The positive effect of the additive on the flow temperature has been confirmed in the case of coal from Donbas district. Dosing of calcite with a proportion of 7% is sufficient for coal from Donbas because the temperature FT does not exceed 1310 $^{\circ}\text{C}$. The temperature in the furnace on the level of ca. 1350 $^{\circ}\text{C}$ ensures the smooth operation of the boiler.

The dosing place and granule size of the used additive play a significant role during additive dosing. There are more possibilities for a selection of the dosing position. Each of them has its negative as well as positive sides. Results for dosing an additive of various grain sizes through waste-vapour burners were obtained by numerical simulations. The calculation results clearly show that the greatest percentage of captured particles in the smelting space of the boiler will be reached at the additive granulate size of 280 μm . The supply of smaller granularity calcite through waste-vapour burners is not convenient since a part of the additive does not reach the bottom of the combustion space.

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