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Influence of Non-Uniformity of Coal and Distribution of Active Calcium on Sulfur Self-Retention by Ash—A Case Study of Lignite Kolubara

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Self-retention of SO_2 by ash of different grades of Kolubara lignite was experimentally investigated in a laboratory furnace. The peculiarity of this type of coal is that in the open pit there are distinct layers of coal and ballast matter, which complicates the formation of representative samples. Two grades of this coal (differing in ballast matter content) were investigated using 3 sieved fractions: 1−1.6 mm, 2.5−3.15 mm, and 4.76−7 mm. It was found that particle size had no significant effect on the sulfur self-retention efficiency (ηSO_2). The effect of ballast matter content on ηSO_2 was investigated by classifying two sieved fractions into classes with different density ranging from <1000 kg/m^3 to >1600 kg/m^3. It was found that most of sulfur self-retention occurs in less dense particles. For this coal only 60% of the total calcium was found to be active in relation to sulfur self-retention capability. Most of the active calcium and sulfur were found to be present in particles of lower density, which explains their dominant contribution to overall sulfur self-retention.

Introduction

The interest for the process of sulfur self-retention by ash has been enhanced with the introduction of fluidized bed combustion (FBC) technology. In FBC combustors the temperature and other conditions are more favorable for the reaction of mineral matter in coal with sulfur compounds that evolve during combustion.

Sulfur self-retention is influenced by various factors which depend on coal characteristics and combustion conditions. The most investigated coal characteristics are the Ca/S molar ratio in coal[1−9] or the (CaO + MgO + Na_2O + K_2O)/S molar ratio in coal,[7−11] coal particle size,[3,5,6] the content of sulfur forms in coal, and coal rank.[8,9] Combustion conditions, i.e., combustion temperature, residence time of ash particles, air excess ratio, and other operating and construction characteristics relevant for sulfur self-retention are largely influenced by the type of combustor.[8,9]

A reliable correlation between Ca/S molar ratio of coal and sulfur self-retention has not yet been established (even under similar combustion conditions), which may be explained as a consequence of the different degree of dispersion and reactivity of calcium, as well as the contribution of other base oxides (MgO, K_2O, Na_2O) to sulfur retention.[7−9,12] Sheng et al.[8,9] considered that the very active Ca is bound within the coal matrix as exchangeable ions, and concluded that the activity of Ca increases as the rank of coal decreases. The same authors reported that, under FBC conditions, other base oxides are significantly less reactive than CaO. On the other hand, Raask[10] and Gray[11] take the total base/sulfur molar ratio into consideration in their investigations of sulfur self-retention. Conn et al.[12] investigated the reactivity of various Ca forms in low-rank coals and state that the calcium present in clays and silicates cannot react with SO_2 at FBC conditions.

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Table 1. Ultimate and Proximate Analysis of Kolubara Coal

	ultimate analysis					proximate analysis				
grade	C (%)	H (%)	N (%)	S (%)	O (%)	moisture (%)	ash (%)	V. M. (%)	C_{fix} (%)	LHV (kJ/g)
B	31.85	4.49	1.02	0.29	18.74	32.86	43.44	34.23	22.33	13.57
D	22.86	3.29	0.57	0.45	12.74	32.89	59.79	26.85	13.35	6.82

Table 2. Chemical Analysis of Kolubara Coal Ash

grade	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	SO_3 (%)
B	52.49	32.13	6.15	4.20	1.08	0.23	1.22	1.17	0.031	0.95
D	56.61	29.29	6.00	2.10	0.91	0.35	1.47	1.08	0.028	1.15

The effect of sulfur forms and coal rank on sulfur self-retention has not yet been extensively investigated to a greater extent. Nevertheless, investigations of coal behavior during pyrolysis reveal the different behavior of various sulfur compounds.[14] Pyrite, during devolatilization, decomposes according to the reaction: $FeS_2 \rightarrow FeS + S$. FeS remains in char as a major final product of pyrite decomposition, at temperatures up to 1000 °C, independent of coal rank and devolatilization conditions.[15,16] Results of the investigation of distribution of organic sulfur depending on coal rank show that the content of sulfide functional groups decreases while the content of thiophenes increases with coal rank.[16–18] In other words, it may be said that coals of similar rank have a similar distribution of functional groups that contain sulfur. This is explained by the fact that, during carbonification, stable thiophenes are formed from less stable organic sulfur compounds (thiols and sulfides).[19]

It has been noticed that there is no increase in sulfate sulfur content during devolatilization,[16] i.e., there is practically no sulfur retention. To a certain extent H_2S, which is formed during devolatilization, reacts with carbonates and oxides forming sulfides[20,21] that later, during char combustion, oxidize and thus remain in the ash. Chen and Kojima,[13] for example, take this into account in their sulfur self-retention model.

As may be seen from the previous discussion, the influence of coal rank on sulfur self-retention is quite complex and opinions differ since low-rank coals contain more highly reactive calcium while high-rank coals have more stable sulfur compounds.

During previous investigations[5,6] the obtained sulfur self-retention efficiencies of coal Kolubara were lower than 30%, although the Ca/S molar ratio was greater than 3. In the case of many other coals, for such and even lower values of Ca/S, significantly higher sulfur self-retention efficiencies have been reported in the literature.[1–9] To determine the reasons for such unexpected and unusual behavior of Kolubara coal, certain parameters were investigated whose influence has not been investigated up to now or has been investigated only to a limited extent. The results of the investigations of the influence of nonuniformity of coal and distribution of active calcium on sulfur self-retention are presented in this paper.

Experimental Section

The sulfur self-retention of two grades of Kolubara coal, labeled as B and D, were investigated. Kolubara lignite, the most abundant coal in Yugoslavia, is open pit mined and two representative samples were obtained from two different locations. Taking into account the known variability of the Kolubara coal, five tons of raw coal was taken from two different pit locations and appropriate samples were formed for these investigations. The proximate and ultimate analyses of the samples are given in Table 1 and the chemical composition of their ashes in Table 2. As can be seen, these samples differ significantly in their ash content (although both samples have a high ash content), CaO content, and Ca/S molar ratio.

For further investigations sieve classes of 1–1.6 mm, 2.5–3.15 mm, and 4.76–7 mm of both B and D coal samples were formed. Each sample was combusted in a laboratory oven, which was preheated to 750 °C. This temperature was chosen taking the following into consideration. Due to the combustion of the coal samples, the oven temperature significantly increases (by 30–50 °C). Also, the temperature difference between the coal particles and their surrounding is higher in the oven due to the lower heat transfer rates compared to fluidized bed conditions. Thus, it was presumed that the coal particle temperatures in the oven and in FBC conditions are comparable as this coal is combusted in FBC at 800–850 °C because of the experienced agglomeration problems at higher temperatures.

Sulfur forms in the coal and sulfur in the resulting ashes were determined according to Yugoslav standards. The total sulfur in the coal was determined using the Eschka analytical procedure. Sulfate sulfur was extracted with hot diluted HCl solution and measured gravimetrically. Pyritic sulfur was determined indirectly by determining the content of pyritic Fe, utilizing the fact that pyrite is nonsoluble in diluted hot HCl solution, but is soluble in diluted hot HNO_3 solution. Organic sulfur is obtained as the difference between the total and the inorganic sulfur. The sulfur content in ash was determined by the oxidation of all sulfur compounds to sulfates in hot HCl solution, and then measuring them gravimetrically.

The total Ca content in ash of coal sample B, in all three sieve classes, was determined using standard atomic absorption spectroscopy (AAS). The Ca that can be extracted by hot HCl solution is considered as active Ca, since the $CaSO_4$ formed by the reaction between CaO and SO_2 and the still-remaining CaO found in ash as such are both soluble in HCl solution. Other Ca compounds that cannot react with SO_2 at FBC conditions, such as in clays and silicates,[8,9,12] are insoluble in HCl solution. The values of active Ca obtained in this way may be somewhat overrated if ash has other Ca compounds soluble in HCl solution, but inactive for sulfur retention, such as phosphates and chlorides. The carbonate Ca was determined by measuring the CO_2, using an Orsat apparatus, while treating coal samples with HCl solution. It is assumed that all of the CO_2 originates from $CaCO_3$, while other carbonates

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Table 3. Sulfur Forms of Coal Samples and Their Ashes

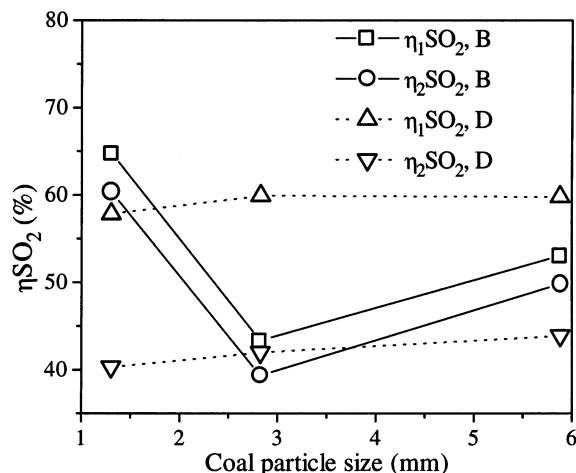| grade	sieve fraction	S_T (%)	S_S (%)	S_P (%)	S_O (%)	A (%)	S^1_A (%)	S^2_A (%)	$\eta_1 SO_2$ (%)	$\eta_2 SO_2$ (%)
B	1.0−1.6 mm	0.369	0.041	0.0	0.328	38.92	0.613	0.239	64.77	60.37
	2.5−3.15 mm	0.316	0.021	0.0	0.295	44.80	0.306	0.137	43.35	39.32
	4.76−7 mm	0.311	0.020	0.0	0.291	45.34	0.365	0.165	53.05	49.83
D	1.0−1.6 mm	0.481	0.141	0.0	0.340	59.98	0.463	0.278	57.80	40.29
	2.5−3.15 mm	0.414	0.128	0.0	0.286	63.70	0.390	0.248	59.90	41.96
	4.76−7 mm	0.445	0.126	0.0	0.319	60.48	0.439	0.266	59.78	43.89

Figure 1. Influence of particle size on sulfur self-retention for Kolubara coal grades B and D.

that do not contribute to sulfur self-retention, such as $FeCO_3$, are not present or that their content is insignificant. The part of Ca obtained as the difference between the active and carbonate Ca is considered to be present as exchangeable ions in the coal matrix and can thus be designated as organic-bound Ca.

Results and Discussion

The sulfur self-retention efficiency coefficient (ηSO_2) was calculated in two ways. One is a straightforward way, as the ratio of the sulfur retained in ash and the total sulfur in coal as usually used in the literature:

$$\eta_1 SO_2 = S^2_A / S_T \times 100 \qquad (1)$$

The other way takes into account that the sulfate sulfur in coal is practically the "inert" part of sulfur and is thus subtracted both from the sulfur retained in ash and the total sulfur in coal:

$$\eta_2 SO_2 = (S^2_A - S_S)/(S_T - S_S) \times 100 \qquad (2)$$

In this way $\eta_2 SO_2$ takes into account only the organic and pyritic sulfur that can produce gaseous SO_2, and its retention in ash, disregarding the sulfate sulfur. The first expression overestimates sulfur self-retention treating the sulfate sulfur as self-retained sulfur. On the other hand, the second expression underestimates sulfur self-retention since part of the sulfate sulfur can decompose under reducing conditions. The results of sulfur determination in the coal samples and the resulting ashes, as well as the calculated sulfur self-retention coefficients according to eqs 1 and 2, are given in Table 3.

The influence of coal particle size on ηSO_2 is shown in Figure 1. Taking into account that coal samples B and D originate from the same coal and that they differ

practically only in mineral matter content, the different levels of ηSO_2 and the different effect of particle size cannot be explained except as a result of the profound nonuniformity. The nonuniformity is related foremost to the content and dispersion of mineral matter in the coal particles, even in those belonging to the same sieve classes. This coal belongs to those extreme cases where there are particles of coal with a small amount of uniformly dispersed mineral matter, particles of "mechanically" bound coal and mineral matter and particles of predominantly mineral matter.
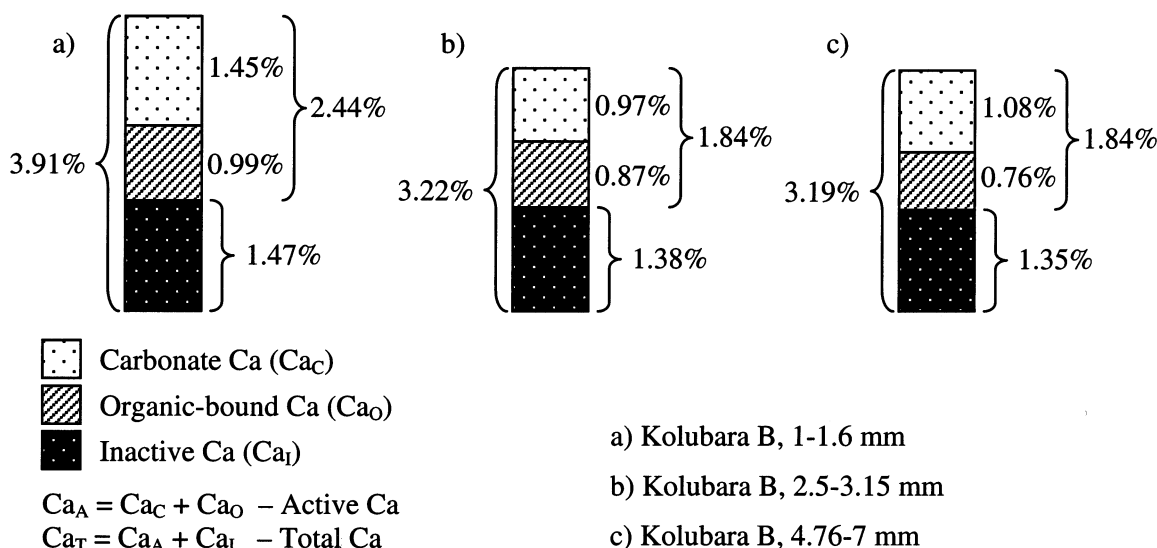
To clarify the effect of nonuniformity, the two sieve classes of coal sample B (2.5−3.15 mm and 4.76−7 mm) were separated into fractions with different density using the float−sink technique with solutions of $ZnCl_2$ of different densities. For each fraction, ηSO_2 was determined in the same way as before and the results are shown in Table 4.

It may be seen that the sulfur content is significantly lower in high-density fractions (with dominantly mineral matter) which is consistent with the fact that most of the sulfur is organic. But contrary to expectations, these fractions also have a lower content of sulfate sulfur, which may be explained by the fact that a significant portion of the sulfates in this coal probably originates from the infiltration of soluble sulfates into the coal matrix. Since these more dense fractions have a large content of mineral matter, this phenomenon is less pronounced and thus their sulfate sulfur content is smaller. Another explanation for the larger sulfate sulfur content in less dense fractions may be found in the fact that the values for sulfate sulfur can be overrated since they are determined by extraction using hot HCl solution. In this way, part of the organic compounds may be dissolved and thus part of the organic sulfur is treated as sulfate sulfur. This could also explain the negative values of $\eta_2 SO_2$ in Table 4, which would incorrectly imply that less sulfur remains in the ash than there was sulfate sulfur in the coal.

The ash content and values for $\eta_1 SO_2$ for various samples of coal B are shown in Figure 2. The parent coal samples are labeled "before FS" (FS: float−sink treatment). For various density fractions, the values for the ash content and $\eta_1 SO_2$ are given on the parent coal basis and labeled "after FS". The values "before FS" and cumulative "after FS" should be the same and small discrepancies are a result of experimental errors. The last values labeled as "sludge" represent the small and fine particles that broke off parent coal particles and sank to the bottom of the containers used for the float−sink technique. They were filtered and joined together as one sample. As expected, the ash content increases with increasing coal particle density and is particularly high in the "sludge" which is practically pure mineral matter grains that have fallen off coal particles during the float−sink treatment.

Table 4. Sulfur Forms and Sulfur Self-retention Efficiency of Coal Fractions of Different Densities

sieve fraction	density fraction (g/cm³)	$U_F{}^a$ (%)	S_T (%)	S_S (%)	S_P (%)	S_O (%)	A (%)	$S^1{}_A$ (%)	$S^2{}_A$ (%)	$\eta_1 SO_2$ (%)	$\eta_2 SO_2$ (%)
2.5−3.15 mm	<1.0	20.9	0.443	0.071	0.0	0.372	16.12	1.630	0.263	59.37	51.61
	1.0−1.2	9.0	0.487	0.060	0.0	0.427	11.59	2.879	0.334	68.58	64.17
	1.2−1.6	19.3	0.504	0.049	0.0	0.455	17.77	1.595	0.283	56.15	51.43
	>1.6	15.1	0.192	0.016	0.0	0.176	65.13	0.005	0.003	1.56	−7.39
	sludge	35.6	0.104	0.015	0.0	0.089	77.06	0.018	0.014	13.46	−1.12
4.76−7 mm	<1.0	16.7	0.387	0.075	0.0	0.312	8.98	2.731	0.245	63.31	54.49
	1.0−1.2	18.0	0.460	0.057	0.0	0.403	9.34	2.940	0.275	59.78	54.09
	1.2−1.6	16.4	0.545	0.060	0.0	0.485	18.54	1.545	0.286	52.48	46.60
	>1.6	16.4	0.151	0.008	0.0	0.143	72.42	0.018	0.013	8.61	3.50
	sludge	32.5	0.159	0.021	0.0	0.138	77.51	0.031	0.024	15.09	2.17

^{a} Content of density fraction in coal.
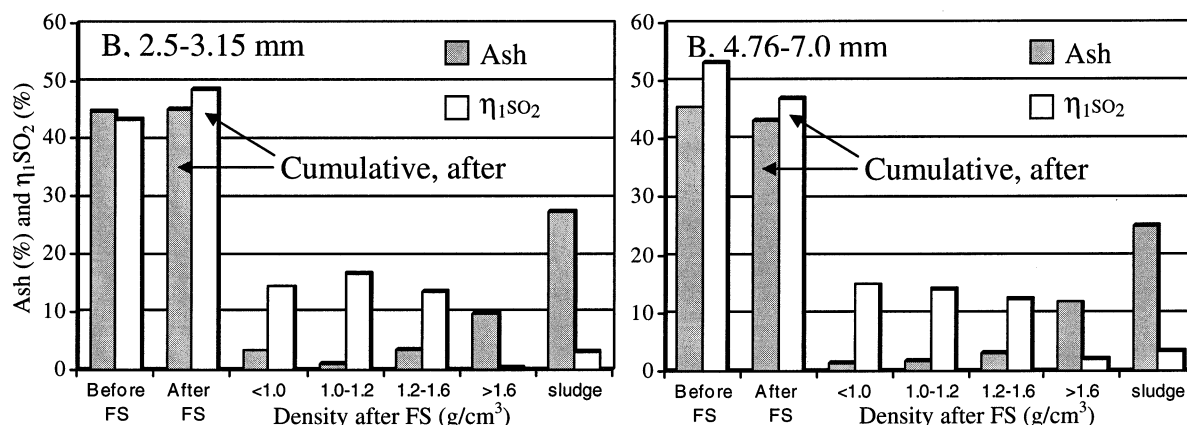
Figure 2. Contribution of various density fractions of Kolubara coal grade B to total ash content and sulfur self-retention.

$$Ca_A = Ca_C + Ca_O \quad - \text{Active Ca}$$
$$Ca_T = Ca_A + Ca_I \quad - \text{Total Ca}$$

a) Kolubara B, 1-1.6 mm

b) Kolubara B, 2.5-3.15 mm

c) Kolubara B, 4.76-7 mm

Figure 3. Distribution of the various forms of Ca in Kolubara coal grade B ash.

Sulfur self-retention occurs practically only in particles with densities less than 1.6 g/cm³ (predominantly with coal, i.e., combustible, matter). Also, most of the sulfur is concentrated in these particles. During these investigations another interesting phenomenon was noticed. The ash particles originating from lower density coal particles were much more prone to attrition and mechanical degradation even during careful handling. The implication of this is that these particles represent the greatest fraction of the total fly ash during fluidized bed combustion. This, in turn, may explain the fact that fly ash is richer in retained sulfur than bottom bed ash.[7]

The results of the determination of Ca forms are shown in Figure 3 (%Ca forms given on ash basis). The highest content of total and active Ca is found in the sieve class 1−1.6 mm, which could explain the highest ηSO_2 values for this sieve class (Table 3). The ratio of total vs active Ca is around 0.6. The other 40% of Ca cannot react with SO_2 and this shows that not all the Ca should be taken into account for sulfur retention considerations and modeling. The carbonate Ca represents around 1/3 of the total Ca. Around 1/4 of the Ca is bound as exchangeable ions in the coal matrix and thus the CaO formed from it should be highly reactive since it is well dispersed, comparable to the molecular level.

Although not shown in this paper, the CO_2 content was also measured in all density fractions of coal B. It was found that high-density particles do not contain CO_2, implying that their Ca content is very low, which explains their low values of ηSO_2.

The application of the obtained data on sulfur self-retention to FBC conditions is not straightforward. On one hand, reducing conditions in certain parts of the combustor may significantly decrease sulfur self-retention. On the other hand, the ash particles in the combustor, after retaining part of their own sulfur, may still retain sulfur emitted from other coal particles that are still combusting.

Conclusions

On the basis of the presented investigations of the two grades of Kolubara coal, coals with significant nonuniformity should be closely investigated in regard to sulfur self-retention. In the case of Kolubara coal, the nonuniformity is related foremost to the content and dispersion of mineral matter in the coal particles. Investigations of fractions with different densities revealed that there are, on one hand, particles rich in combustibles, with high sulfur content and low ash content, but with well-dispersed ash rich with active Ca. In these particles most of the SO_2 is formed, but also most of the sulfur self-retention takes place. On the other hand, there are particles containing mostly mineral matter, with low sulfur content, but also with practically no potential for sulfur self-retention since they contain practically no active Ca.

In Kolubara coal only around 60% of Ca is active and can participate in sulfur self-retention. More than half of this Ca originates from carbonates, while the remaining part of active Ca is mostly present as exchangeable ions in the coal matrix. These investigations also show that it is not always correct to take into account the total Ca/S molar ratio as a parameter for sulfur self-retention data analysis or modeling.

Glossary

A	ash content in coal, %
S^1_A	sulfur content in ash (on ash basis), %
S^2_A	sulfur content in ash (on coal basis, $S^2_A = S^1_A \cdot A/100$), %
S_O	organic sulfur content in coal, %
S_P	pyritic sulfur content in coal, %
S_S	sulfate sulfur content in coal, %
S_T	total sulfur content in coal, %
$\eta_1 SO_2$	sulfur self-retention efficiency coefficient, defined by eq 1, %
$\eta_2 SO_2$	sulfur self-retention efficiency coefficient, defined by eq 2, %

EF0200119