

SULFUR SELF-RETENTION IN ASH A GRAIN MODEL APPROACH

by

Vasilije MANOVIĆ, Borislav GRUBOR, and Mladen ILIĆ

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A developed overall model for sulfur self-retention in ash during coal particle combustion is presented in the paper. The total sulfur content in char, after devolatilization, is evaluated using a derived correlation. It is assumed that sulfur retention during char combustion occurs due to the reaction between SO_2 and the active part of the Ca in the form of uniformly distributed CaO grains. Parametric analysis shows that the process is limited by solid diffusion through the product layer formed on the CaO grains and that the most important coal characteristics which influence sulfur self-retention are coal rank, content of sulfur forms, molar Ca/S ratio and particle radius. The model predicts relatively well the levels of the experimentally obtained values of SSR efficiencies, as well as the influence of temperature, particle size and the surrounding conditions.

Key words: coal combustion, sulfur retention by ash, modelling

Introduction

During coal combustion the sulfur is converted into gaseous pollutants and solid compounds in ash. The process that encompasses reactions between gaseous sulfur compounds and base oxides in coal ash, due to which a part of the sulfur remains in ash, is designated as sulfur self-retention (SSR). The interest for this process was enhanced with the introduction of fluidized bed combustion (FBC) technology since the temperatures and other conditions are favourable for SSR. The numerous investigations of SSR in FBC conditions 1-6 have shown that a substantial part of sulfur may be retained in ash, decreasing the needed amount of limestone to be added. Puff *et al.* 1 reported that around 60% of sulfur is retained due to SSR, while values were near 90% with fly ash recirculation or combustion of coal rich with tailings.

SSR is influenced by various factors, which depend upon coal characteristics and combustion conditions. The most investigated coal characteristics are the molar Ca/S ratio 1-6 or $(CaO + MgO + Na_2O + K_2O)/S$ ratio 3, 7 in coal, coal particle size 4-6, content of sulfur forms in coal and coal rank 8. Combustion conditions, *i. e.* temperature, residence time of ash particles, excess air ratio, and other operating and

construction characteristics relevant for sulfur self-retention, are largely influenced by the type of combustor [8].

Apart from experimental investigations, in literature there are several models of the SSR process [4, 9] or correlations [10, 11] for estimating sulfur content in char after devolatilization and in ash after combustion, but their wider applicability has not yet been proven. In this paper an overall (comprehensive) model for SSR is presented, taking into account both devolatilization and char combustion.

Sulfur self-retention model

The processes of combustion and SSR are treated simultaneously. Various aspects of the overall model are outlined in the following sections.

Transformations of sulfur forms during devolatilization

The process of devolatilization is significantly shorter compared to char combustion and due to reducing conditions and lower temperatures the process of SSR during devolatilization is not significant. The sulfur compounds released during devolatilization are subsequently oxidized to SO_2 , outside the coal particles. The amount of sulfur that is released during devolatilization of coal (mostly in the form of H_2S and to a lesser extent with tar, or as COS and CS_2) depends largely on the coal sulfur content, forms of sulfur and to a lesser extent on other coal properties and devolatilization conditions [12]. Although the transformations of sulfur forms during devolatilization are highly complex, based on our previous investigations [13] the following simplifications may be considered:

- (1) The total amount of sulfate sulfur in coal remains in char,
- (2) One half of the pyritic sulfur (in the form of FeS) remains in char as a result of decomposition of pyrite according to the following reaction: $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$, and
- (3) The organic sulfur content in char is proportional to the organic sulfur content in coal. The proportionality coefficient can be defined as equal to $C_{\text{fix}}/(C_{\text{fix}} + VM)$, implying that the organic sulfur is evenly distributed in coal combustible matter, *i. e.* both in volatile matter and C_{fix} .

Based on the previous assumptions, the following correlation is derived for evaluating the total sulfur content in char (S_{TCh}), after devolatilization:

$$S_{\text{TCh}} = 0.5S_{\text{P}} + \frac{C_{\text{fix}}}{(C_{\text{fix}} + VM)S_{\text{O}}} S_{\text{S}} \quad (1)$$

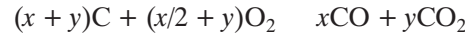
where all the values are on dry coal basis.

Char combustion

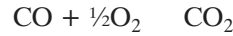
The developed model for char combustion, which belongs to the microscopic models of intrinsic reactivity and has been presented in detail [14, 15], is used as a basis for modeling the process of SSR. The model describes the dynamic behaviour of a porous char particle during combustion, *i. e.* spatial and temporal changes of all important char particle physical properties (porosity, internal specific surface area, thermal conductivity) and parameters (temperature, gas concentrations, effective diffusivity, conversion degree). The main mechanism of heat transfer inside the char particle is conduction and radiation while mass transfer is achieved by molecular diffusion, taking into account porosity and pore tortuosity.

It is assumed that the main reactions of combustion are:

Reaction 1:



Reaction 2:



Reaction 1 is a heterogeneous reaction of oxidation of solid carbon that takes place both on the surface of the pores and on the surface of the char particle and its rate is:

$$\mathcal{R}_1 = \frac{dc_C}{d\tau} = A_1 \chi_{O_2} \exp \left(-\frac{E_1}{R_g T} \right) S_{por} \quad (2)$$

The values of the activation energy and the pre-exponential factor are $E_1 = 179.4$ kJ/mol and $A_1 = 254.16$ mol/m²s [16]. The primary molar CO/CO₂ ratio (Reaction 1) is defined by [17]:

$$\gamma = \frac{x}{y} = \frac{CO}{CO_2} = 2512 \exp \left(-\frac{51880}{R_g T} \right) \quad (3)$$

Reaction 2 is a homogenous reaction of oxidation of CO that takes place inside the pores and its rate is defined as:

$$\mathcal{R}_2 = \frac{dc_{CO}}{d\tau} = A_2 c_{CO} c_{O_2}^{0.5} c_{H_2O}^{0.5} \exp \left(-\frac{E_2}{R_g T} \right) \varepsilon \quad (4)$$

The activation energy for this reaction is $E_2 = 55.695$ kJ/mol [18]. The pre-exponential factor A_2 is a model parameter and is fitted for various chars, according to own experimental data [15].

At any time τ , the local and overall carbon conversion degree are calculated using the following expressions:

$$x_C = \frac{1}{c_{C,0}} \int_0^\tau \mathcal{R}_1 d\tau \quad \text{and} \quad X_C = \frac{\int_0^{R_{Ch}} x_C(r) r^2 dr}{R_{Ch}^3} \quad (5)$$

It is assumed that the local porosity increases proportionally with the local conversion degree of carbon:

$$\varepsilon = \varepsilon_0 + x_C(1 - Ash - \varepsilon_0) \quad (6)$$

The change of the specific internal surface area during combustion is taken into account using the following relation [19]:

$$S_{por} = S_{por,0} (1 - x_C) \sqrt{1 - \psi \ln(1 - x_C)} \quad (7)$$

SO₂ formation during char combustion

It is assumed that the only product of combustion of sulfur compounds in char is SO₂. Contrary to the oxidation process of sulfur released during devolatilization, oxidation of sulfur during char combustion takes place inside the char particle. The rate of SO₂ formation is assumed to be proportional to the rate of carbon conversion:

$$\mathcal{R}_f = \frac{dc_{SO_2}}{d\tau} = \mathcal{R}_1 \frac{S_{CCh}}{C_{fix}} \frac{M_C}{M_S} \quad (8)$$

Reaction between SO₂ and CaO grains in char

It is assumed that the active part of CaO in coal, formed as a result of CaCO₃ decomposition and combustion of Ca-containing organic compounds, is the only base oxide that contributes to sulfur retention. Calcium present in clays and silicates cannot react with SO₂ at FBC conditions [8, 20] since in this temperature range these Ca-containing compounds cannot decompose to CaO. The procedure for evaluation of the active part of CaO, as well as a more detailed discussion about Ca forms present in coal, its distribution and activity is presented earlier [20].

The reaction of SO₂ with CaO (sulfation) is first order with respect to SO₂ and zero order with respect to O₂ [21]. The sulfation reaction has been mostly investigated in the case of SO₂ retention by CaCO₃ as a sorbent [22]. This process is mostly used in FBC combustors, which enable sulfation to take place in the optimum temperature range (800-900 °C).

There are numerous expressions for sulfation kinetics in literature, ranging from empirical ones [23] up to expressions of the Arrhenius type [24]. Values of the kinetic parameters (pre-exponential factor and activation energy) differ significantly,

depending on the kind of physical model that is used. The basic difference between various models of sulfation is whether formation of a solid product layer of CaSO_4 , as well as diffusion through this layer [25], is taken into account. In that case the sulfation rate is diffusion limited [26].

In the existing models [4, 9] of SSR the sulfation rate is taken into account in a simplified manner. Yeh *et al.* [4] take the char pore surface area as a measure of the available surface of CaO for sulfation reaction, while Chen and Kojima [9] take into account the concentration of CaO in the coal briquette. In both cases, these simplifications are somewhat corrected by assuming that the sulfation rate decreases proportionally with the conversion degree of CaO.

In this paper a novel approach has been applied for modeling SSR, closely related to the grain model [27] used for SO_2 retention by limestone addition. It is assumed that after devolatilization all of the active Ca is present in the form of CaO grains of the same initial radius ($R_{G,0}$), which are uniformly distributed throughout the char volume. An unreacted shrinking core model is adopted for the following reaction between the CaO grains and SO_2 :



A partially sulfated CaO grain is shown in Fig. 1. It consists of the unreacted shrinking core, of radius r_c , surrounded by a product layer. As the process of sulfation progresses, the size of the grains increases ($R_G > R_{G,0}$) due to the larger molar volume of CaSO_4 . The sulfation rate and the rate constant are defined by the following expressions:

$$\mathcal{R}_s = \frac{\partial c_{\text{SO}_2}}{\partial \tau} = k_s S_{\text{CaO}} c_{\text{CaO}} c_{\text{SO}_2} \quad (10)$$

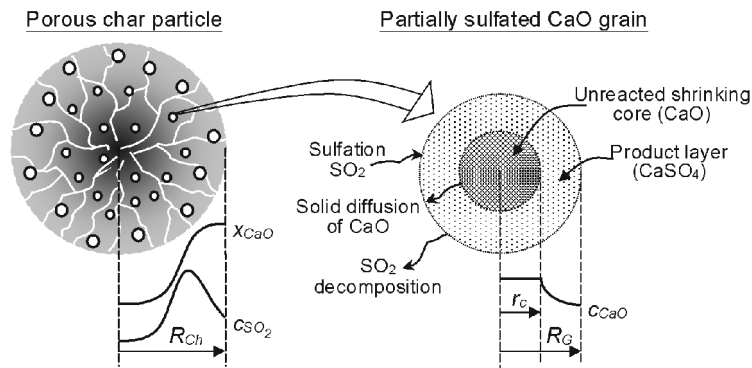


Figure 1. Schematic representation of a burning porous char particle and a partially sulfated CaO grain

$$k_s = A_s \exp \left(-\frac{E_s}{R_g T} \right) \quad (11)$$

Taking into account the content of Ca in the char particle, CaO grain dimensions and properties of the char particle, the specific surface for the sulfation reaction (m^2 of CaO grains per m^3 of char) is derived as:

$$S_{CaO} = 3Y_{CaO} \frac{\rho_{Ch,0}}{\rho_{G,0}} \frac{R_G^2}{R_{G,0}^3} \quad (12)$$

The CaO concentration (c_{CaO}) in eq. (10) is related to the surface of the CaO grains, where the sulfation reaction takes place, and it is determined using the pseudo-steady-state condition:

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{CaO}}{\partial r} \right) = 0 \quad (13)$$

with the following boundary conditions:

$$c_{CaO} \Big|_{r=r_c} = \frac{\rho_{G,0}}{M_{CaO}} \quad \text{and} \quad D_{CaO} \frac{\partial c_{CaO}}{\partial r} \Big|_{r=r_G} = k_s c_{CaO} c_{SO_2} \quad (14)$$

Solution of the partial differential eq. (13), with the boundary conditions (14), gives the CaO concentration profile in the product layer of the reacting CaO grain (Fig. 1). At the grain surface the value of the CaO concentration is:

$$c_{CaO} = \frac{\rho_{G,0}}{M_{CaO}} \frac{D_{CaO}}{D_{CaO} + R_G k_s c_{SO_2} \frac{R_G}{r_c} + 1} \quad (15)$$

The solid diffusion coefficient through the product layer is of the Arrhenius type:

$$D_{CaO} = A_D \exp \left(-\frac{E_D}{R_g T} \right) \quad (16)$$

The unreacted core radius in time is determined solving the following differential equation that takes into account the net effect of sulfation and decomposition (discussed in next section):

$$\frac{dr_c}{d\tau} = \frac{M_{CaO}}{\rho_{G,0}} \frac{R_G^2}{r_c^2} (k_d - k_s c_{CaO} c_{SO_2}) \quad (17)$$

The determined values of r_c enable calculation of the local and overall CaO conversion degree and, in turn, the value of partially sulfated CaO grain radius for each char particle segment:

$$x_{CaO} = 1 - \frac{r_c^3}{R_{G,0}^3} \quad \text{and} \quad X_{CaO} = \frac{\int_0^{R_{Ch}} x_s(r) r^2 dr}{R_{Ch}^3} \quad (18)$$

$$R_G^3 = r_c^3 + z x_{CaO} R_{G,0}^3 \quad (19)$$

where z represents the molar volume ratio of $CaSO_4$ and CaO ($z = 3.09$).

CaSO₄ decomposition

There is sufficient experimental evidence that the CaO conversion degree goes through a maximum as the temperature increases [4, 27]. This means that at higher temperatures the process of product decomposition takes place (a kind of a reverse reaction to the sulfation reaction). There are different explanations for this phenomenon in literature: thermal decomposition [21], reductive decomposition [28] (due to higher CO concentrations) or sintering [29] (which decreases the exposed surface of the CaO grains). In this model the process of decomposition is taken into account with the following expression for the decomposition rate:

$$\mathcal{R}_d = \frac{\partial c_{SO_2}}{\partial \tau} = k_d S_{CaO}, \quad \text{where} \quad k_d = A_d \exp \left(-\frac{E_d}{R_g T} \right) \quad (20)$$

Heat and mass balance and boundary conditions

Heat and mass balance, which determine the temperature and concentration profile of gaseous compounds (O_2 , CO_2 , CO , SO_2) along the char particle radius, are described by the following partial differential equations:

$$C_{p,y} \frac{\partial T}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \lambda_{eff} \frac{\partial T}{\partial r} \right) - (C_{p,j} N_j) \frac{\partial T}{\partial r} - \Delta H_1 \mathcal{R}_1 - \Delta H_2 \mathcal{R}_2 - \Delta H_3 \mathcal{R}_3 \quad (21)$$

$$\frac{\partial c_j}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{eff} \frac{\partial c_j}{\partial r} \right) + v_{1,j} \mathcal{R}_1 + v_{2,j} \mathcal{R}_2 + v_{3,j} \mathcal{R}_3 \quad (22)$$

where $j = 1-4$ ($O_2 - 1$, $CO_2 - 2$, $CO - 3$, $SO_2 - 4$), and the last terms ($\Delta H_3 \mathcal{R}_3$ and $v_{3j} \mathcal{R}_3$) represent the net effect of SO_2 formation, sulfation and $CaSO_4$ decomposition on heat and mass balance.

The following relations define the boundary conditions:

$$\begin{aligned} r = 0 \quad \frac{\partial c_j}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0 \\ r = R_{Ch} \quad \lambda \frac{\partial T}{\partial r} \bigg|_{r=R_{Ch}} = \alpha(T_s - T_a) - \frac{(1 - \varepsilon) \Delta H_1 \mathcal{R}_1}{S_{por}} - \sigma \varepsilon_r (T_s^4 - T_a^4), \quad \text{and} \\ D_{eff,j} \frac{\partial c_j}{\partial r} \bigg|_{r=R_{Ch}} = k_m (c_{j,s} - c_{j,a}) - \frac{v_{1,j} \mathcal{R}_1 (1 - \varepsilon)}{S_{por}} \end{aligned}$$

Supplementary expressions, used for defining thermal and physical properties of char and gaseous compounds as well as heat and mass transfer, are given in the previous paper [15].

Solution procedure

The total sulfur content in char, after devolatilization, is calculated by eq. (1). All other initial char properties, relevant to char combustion and SSR, are either evaluated from the known coal properties or experimentally determined (porosity, pore size, specific surface area, active part of Ca, *etc.*). The initial conditions (temperatures and gas concentrations) are based on the presumed values after devolatilization. The evaluation of these initial conditions is not critical, since they affect the calculations only in the first few seconds of char combustion. The values of all parameters are initially constant along the char particle radius.

For numerical purposes, the char particle is subdivided into segments (usually more than 100) of equal volume. At any time τ , parameters related to char combustion and SSR for each char particle segment are calculated using eqs. (2-8), (10-12), and (15-20), based on the current values of temperatures, gas concentrations and other necessary parameters. Then, the system of partial differential eq. (21) and (22) are solved, using the numerical method of control volumes [30]. In this way the values of temperatures and gas concentrations along the char particle radius at time $\tau + d\tau$ are obtained. The whole procedure is repeated until all of the carbon in char is consumed.

Model verification

The parametric analysis and experimental verification of the part of the model related to char combustion has been previously presented [15]. It was shown that at FBC conditions the combustion is diffusion controlled and that the agreement between model predictions and experimental results is satisfactory. For char particles of various

sizes ($R_{Ch} = 2\text{--}8\text{ mm}$), originating from coals of different rank (from lignite to semi-anthracite), and combusting in a fluidized bed reactor at different temperatures, the model was able to predict combustion time and variations of gas concentrations during combustion (measured at top of the bed) with acceptable accuracy.

The correlation for evaluating the amount of sulfur that remains in char, after devolatilization, has also been previously experimentally verified [13]. From Fig. 2 it may be seen that, regardless of the simplifying assumptions related to eq. (1), there is quite good agreement between the calculated and experimentally obtained values of S_{TCh} . This comparison was done using our own experimental data (six Yugoslav coals ranging from lignites to semi-anthracite) and data found in the literature (twenty Polish coals) with quite different properties.

Since the above-mentioned parts of the overall model were previously verified, in further text only the part dealing with SSR during char combustion will be considered in greater detail.

Assessment of model parameters

The sensitivity of the model to the variation of k_s and D_{CaO} , for different values of $R_{G,0}$, is shown in Fig. 3. The presented curves were obtained using the following set of data: $R_{ch} = 2\text{ mm}$, $Ash = 20\%$, $C_{fix} = 80\%$, $\varepsilon_0 = 50\%$, $S_{por,0} = 200\text{ m}^2/\text{cm}^3$, $S_{TCh} = S_{CCh} = 2\%$, $Ca/S = 1$, $T = 800\text{ }^\circ\text{C}$ and the surrounding gas is air ($c_{O_2} = 21\%$). It may be seen that the variation of k_s , in the range of values reported in the literature [24, 32], does not significantly influence the calculated SSR efficiency. On the other hand, the influence of D_{CaO} and $R_{G,0}$ is quite noticeable. This shows that the process of SSR is limited by solid diffusion through the product layer and that D_{CaO} and $R_{G,0}$ are important model parameters whose values should be chosen by comparing model results with experimental data. Similar conclusions were obtained for

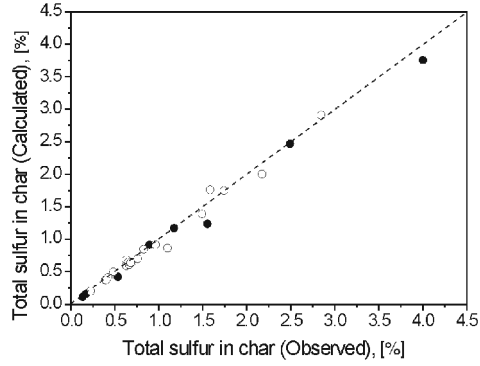


Figure 2. Experimental and calculated content of total sulfur in char (S_{TCh}) for Yugoslav (●) and Polish (○) coals [31], according to eq. (1)

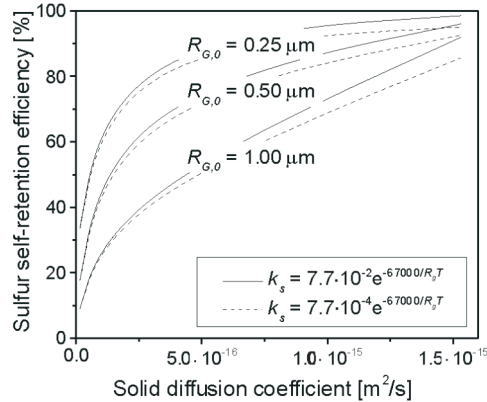


Figure 3. Sensitivity of the model to the variation of k_s and D_{CaO}

quite different sets of data. For further analysis in this work the following values of these parameters were assumed: $D_{CaO} = 10^{-10} \exp(-125000/R_gT)$, $k_s = 7.7 \cdot 10^{-3} \exp(-67000/R_gT)$ and $R_{G,0} = 0.5 \mu\text{m}$.

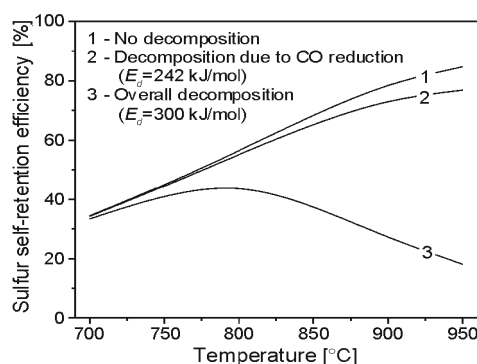


Figure 4. Sensitivity of the model to the variation of E_d

The influence of the intensity of decomposition on the temperature dependency of SSR efficiency is shown on Fig. 4. If it were assumed that there is no decomposition, the SSR efficiency would continually increase with surrounding temperature (curve 1). As previously stated, this is not in accordance with the available experimental data in literature that show that there is an optimal temperature after which the SSR efficiency decreases. If only reduction with CO is assumed, using the corresponding $E_d = 242.0 \text{ kJ/mol}$ [33], the SSR efficiency maximum would be at much higher temperatures (curve 2) than reported in literature (around 850 °C in the case of limestone). For further anal-

ysis in this work a greater value for E_d (300 kJ/mol) is assumed which leads to a temperature maximum of around 800 °C (curve 3), in compliance with the majority of data for SSR temperature dependency in literature.

Parameter sensitivity analysis

The sensitivity of the model to the variation of molar Ca/S ratio and char particle radius is shown in Fig. 5. Higher values of Ca/S lead to higher SSR efficiencies, as is well known from literature [1, 2, 4-6, 8-11]. Also, the model predicts that higher values of Ca/S shift the temperature maximum towards higher temperatures. This is a consequence of the still available CaO in the outer layers of the char particle which retain SO_2 at lower temperatures (close to the surrounding conditions) and where the effect of decomposition is thus relatively smaller. With the increase of the char particle radius the residence time of SO_2 inside the char particle increases which leads to higher SSR efficiencies. The shift of the temperature maximum is a consequence of higher temperatures inside larger char particles.

The process of SSR during char combustion may be analysed through the spatial and temporal changes of CaO conversion that are shown in Fig. 6a. Initially, only the CaO in outer layers contribute to the SSR. As combustion proceeds, the SO_2 concentration increases inside the char particle, Fig. 6b, due to which the CaO conversion gradually progresses towards the char particle centre. The final local CaO conversion differs along the char particle radius, decreasing towards the particle centre.

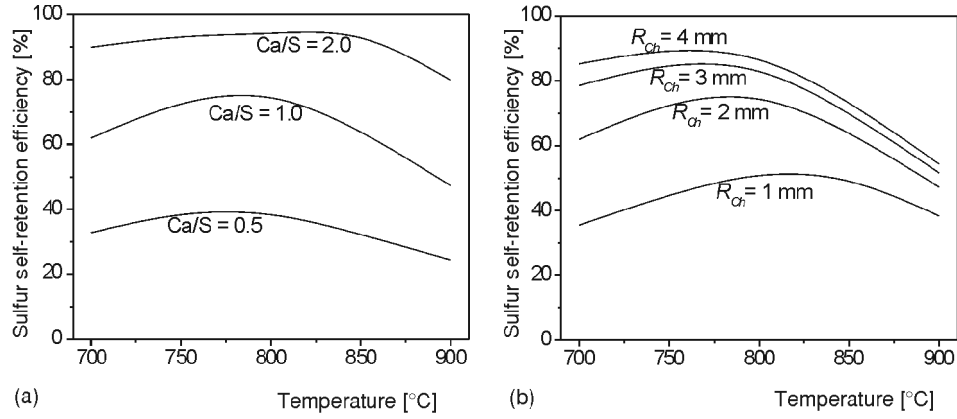


Figure 5. Influence of Ca/S (a) and R_{ch} (b) on sulf-retention (model predictions)

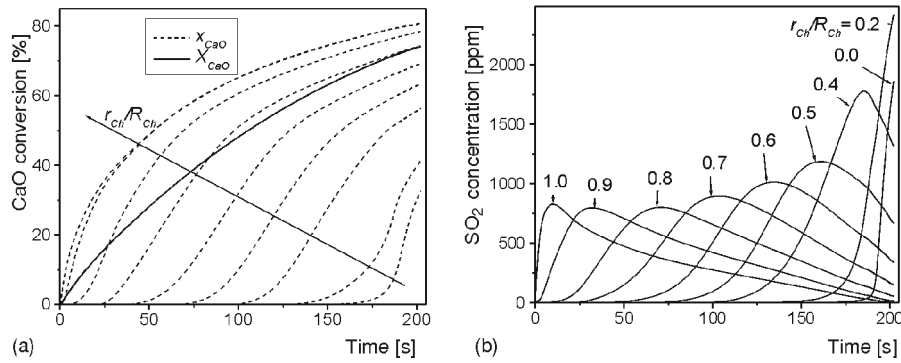


Figure 6. Model predictions of spatial and temporal changes of CaO conversion (a) and SO_2 concentration (b) inside a char particle during combustion

The overall model predictions, taking into account both devolatilization and char combustion, are shown in Fig. 7. Two sets of data for coal characteristics are considered. One set corresponds to a lower rank coal ($C_{fix} = 30\%$, $VM = 50\%$), Fig. 5a, and the other to a higher rank coal ($C_{fix} = 60\%$, $VM = 20\%$), Fig. 5b. In both cases $Ash = 20\%$ and $S_O + S_P = 4\%$, while Ca/S and S_O/S_P ratios are varied. The most noticeable difference for these two types of coal is in the amount of sulfur that remains in char, after devolatilization (full lines). This difference increases as the S_O/S_P ratio increases, as a consequence of sulfur forms behaviour during devolatilization, taken into account by eq. (1). The molar Ca/S ratio determines the amount of sulfur in char that can be retained in ash during char combustion. From the aspect of overall SSR, the model predicts higher SSR efficiencies for higher rank coals. In the case of lower rank coals it is beneficial if the present sulfur in coal is in the form of pyritic sulfur while in the case of higher rank coals.

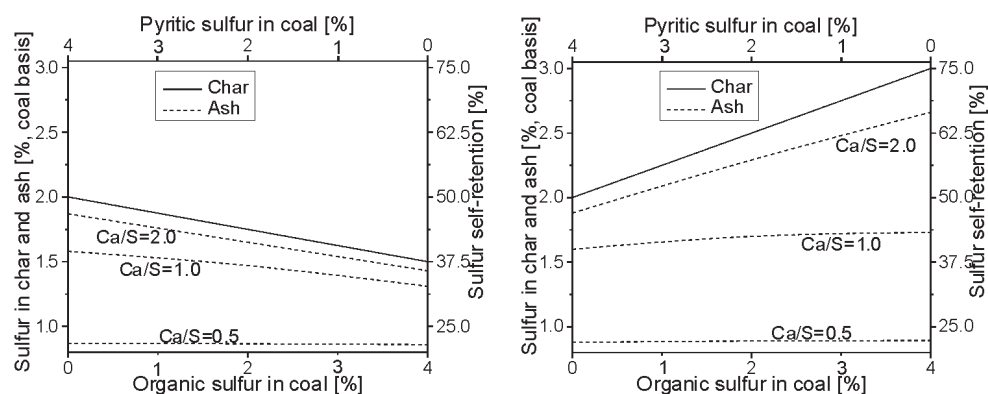


Figure 7. Overall model predictions in the case of low rank coal (a) and high rank coal (b)

Comparison with experimental results

The results of batch combustion runs were used for experimental verification of the model. Two coals were used, Kolubara and Bogovina, whose characteristics are given in Table 1 and 2. The main differences between these two coals are in their rank, sulfur content and molar Ca/S ratio (only the active part of Ca is taken into account).

Table 1. Chemical analysis of coals

Coal	Proximate analysis ^a				Ultimate analysis [*]				
	Ash [%]	VM [%]	C _{fix} [%]	LHV [kJ/g]	C [%]	H [%]	N [%]	S [%]	O [%]
Kolubara	16.34	47.69	35.97	15.14	52.69	4.62	0.62	0.82	24.89
Bogovina	19.75	39.21	41.04	15.76	54.38	4.73	0.92	4.16	16.06

* All values (apart from moisture) given on dry coal basis

Table 2. Sulfur and calcium* analysis of coals

Coal	S _s [%]	S _p [%]	S _o [%]	S _T [%]	Ca _A [%]	Ca _A /S [-]
Kolubara	0.11	0.00	0.73	0.84	0.53	0.51
Bogovina	0.22	0.09	4.31	4.62	4.64	0.80

* Active calcium content (Ca_A) determined by analytical procedure given in [20]

The batch combustion tests were carried out both in a fluidized bed (FB) reactor and in a laboratory oven. For both coals the experiments were done with three particle size fractions (4.0-7.0 mm, 7.0-10 mm and 10-13 mm) and on three surrounding temperatures (750 °C, 800 °C, and 850 °C). The SSR efficiency was determined taking into account the total sulfur content in coal and in ash, after combustion: $\eta_{SO_2} = S_{Ash}/S_T \cdot 100$. During the tests performed in the FB reactor the SO_2 concentrations at top of the bed were monitored. A more detailed description of the equipment used as well as the experimental procedure is given in [6, 20].

From Fig. 8a it can be seen that a substantial part of sulfur evolves during devolatilization and that the concentrations of SO_2 , monitored at top of the bed, are significantly higher than during char combustion. Since the evolution of SO_2 during devolatilization is taken into account in the model by the eq. (1), the comparison between experimental and model predicted SO_2 concentrations was done only during char combustion, Fig. 8b. It may be seen that the model can adequately predict the evolution of SO_2 during char combustion.

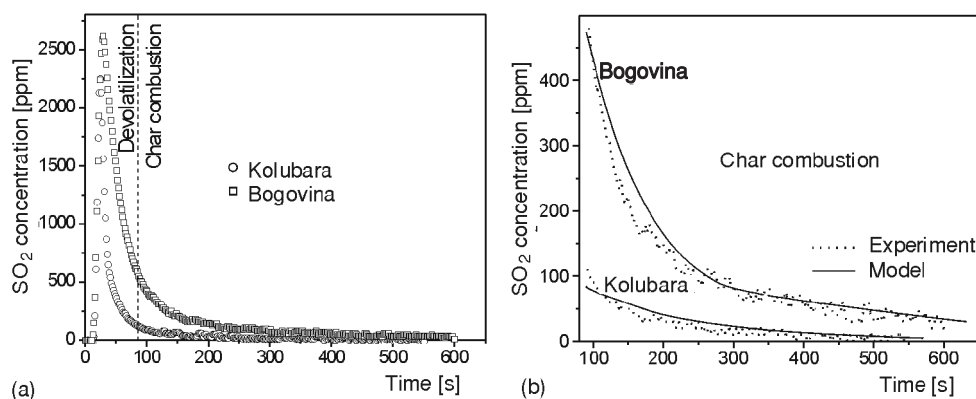


Figure 8. SO_2 concentration at top of the bed during batch combustion of coal,
 $T_{bed} = 750\text{ °C}$, $R_{ch} = 2\text{-}3.5\text{ mm}$

(a) experimental values during the whole process of combustion,
 (b) experimental values and model predictions during char combustion

Model predictions for overall SSR efficiency were compared with the obtained experimental data in Fig. 9. It may be seen that the model relatively well predicts the levels of the SSR efficiencies, as well as the influence of temperature and particle size. In fluidized bed conditions the maximum values of SSR were obtained at around 800 °C while in the laboratory oven the SSR decreases with temperature. The same dependencies are predicted by the model and they can be explained due to different levels of temperatures inside the char particles during combustion. For the same surrounding temperature, the temperatures inside the char particles are higher when

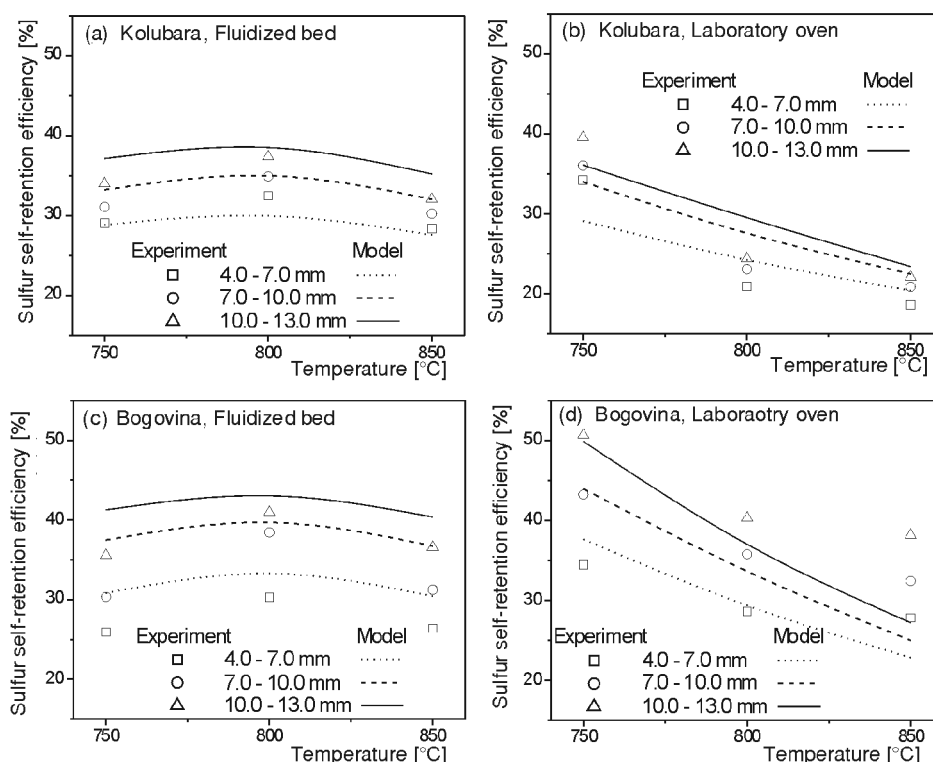


Figure 9. Experimental values and model predictions of overall sulfur self-retention efficiency for batch combustion of coals Kolubara and Bogovina in FB reactor and laboratory oven

combusting in the laboratory oven due to the lower heat transfer between the particles and the ambient. The increase of SSR levels with the increase of particle size is noticed in all cases and may be explained as a consequence of longer SO_2 diffusion paths in larger particles. The existence of the SSR temperature maximum in the case of FBC conditions and the beneficial effect of particle size are also reported by other authors [4].

Although the model predicts relatively well the levels of SSR and the influence of temperature and particle size, differences between model predictions and experimentally obtained data are in some cases significant, especially in the case of combustion in the laboratory oven. Apart from the significant non-uniformity of the investigated coals [20], the possible reasons for these differences can also be found in the simplifications adopted in the model, especially concerning the CaSO_4 decomposition. In the model this phenomena is taken into account by the reaction rate that depends only on temperature, disregarding the effect of the reducing conditions and/or sintering phenomena.

Conclusion

The developed overall model considers the process of sulfur self-retention both during devolatilization and char combustion. Transformations of sulfur forms during devolatilization are treated in a simplified way, *i. e.* a derived correlation is used to evaluate the total sulfur content in char, after devolatilization. The model used for char combustion (as a basis for modeling sulfur self-retention) belongs to the microscopic intrinsic models that describe the dynamic behaviour of a porous char particle during combustion. A novel approach has been applied for modeling SSR during char combustion, closely related to the grain model used for SO₂ retention by limestone as a sorbent. It is assumed that SSR is a result of the reaction between SO₂ and CaO in the form of uniformly distributed grains in char.

Parametric analysis shows that the process is limited by solid diffusion through the product layer formed on the CaO grains. The most important coal characteristics which influence sulfur self-retention are coal rank, content of sulfur forms, molar Ca/S ratio and particle radius. The model predicts relatively well the levels of the experimentally obtained values of SSR efficiencies in a FB reactor and a laboratory oven, as well as the influence of temperature, particle size and the surrounding conditions.

The comparison with the experimentally obtained values in a FB reactor and a laboratory oven has shown that the model can adequately predict the kinetics of the process, the levels of the obtained values of SSR efficiencies, as well as the influence of temperature, particle size and the surrounding conditions. The greater differences, in some cases, between model predictions and experimentally obtained data are attributed to the significant non-uniformity of the investigated coals, but also may be the result of the simplifications adopted in the model, especially concerning the CaSO₄ decomposition.

Nomenclature

A_D	– pre-exponential factor for solid diffusion of CaO through CaSO ₄ , [m ² /s]
A_i	– pre-exponential factor for i – chemical reaction, 1 st – [mol/m ² s], 2 nd – [mol/m ³ s]
A_s, A_d	– pre-exponential factor for sulfation and decomposition reaction, [m ⁴ /mol s], [mol/m ² s]
Ash	– ash content in coal, [% on dry coal basis]
C_{fix}	– fixed carbon content in coal, [% on dry coal basis]
c_j	– concentration of j -component or element (a – ambient, s – char particle surface), [mol/m ³]
$C_{p,j}$	– specific heat capacity of j -component, [J/mol·K]
$C_{p,v}$	– specific heat capacity of porous char particle, [J/m ³ K]
D_{CaO}	– solid diffusion coefficient of CaO through CaSO ₄ , [m ² /s]
D^{eff}	– effective gas diffusion coefficient, [m ² /s]
E_D	– activation energy for solid diffusion of CaO through CaSO ₄ , [J/mol]
E_i	– activation energy of i -chemical reaction, [J/mol]
E_s, E_d	– activation energy of sulfation and decomposition reaction, [J/mol]
k_m	– mass transfer coefficient between char particle and its surrounding, [m/s]

k_s, k_d	– reaction rate constant for sulfation and decomposition, [$\text{m}^4/\text{mol s}$], [$\text{mol}/\text{m}^2\text{s}$]
M_j	– molar mass of j -component or element, [kg/mol]
N_j	– molar flux of j -component, [$\text{mol}/\text{m}^2\text{s}$]
r, R	– current radius and particle radius, [m]
r_c	– unreacted core radius of CaO grain, [m]
R_g	– universal gas constant, [$\text{J}/\text{mol}\cdot\text{K}$]
\mathcal{R}	– reaction rate, [$\text{mol}/\text{m}^3\text{s}$]
S^{Ash}	– sulfur content in ash, [% on dry coal basis]
S_{CaO}	– specific surface for the sulfation reaction, [m^2 of Ca grains/ m^3 of char]
S_{CCh}	– combustible sulfur content in char ($S_{\text{CCh}} = S_{\text{TCh}} - S_s$), [% on dry coal basis]
S_{TCh}	– total sulfur content in char, [% on dry coal basis]
S_o	– organic sulfur content in coal, [% on dry coal basis]
S_p	– pyritic sulfur content in coal, [% on dry coal basis]
S_s^{por}	– specific surface area of porous char particle, [m^2/m^3]
S_s	– sulfate sulfur content in coal, [% on dry coal basis]
S_t	– total sulfur content in coal, [% on dry coal basis]
T	– temperature (a – ambient, s – char particle surface), [K]
VM	– volatile matter in coal, [% on dry coal basis]
x_c	– local carbon conversion degree
X_c	– overall carbon conversion degree
x_{CaO}	– local CaO conversion degree
X_{CaO}	– overall CaO conversion degree
x_p, X_j	– local and total conversion degree of j -component, [-]
Y_{CaO}	– mass fraction of CaO in char, [-]

Greek letters

α	– convective heat transfer coefficient between char particle and ambient, [$\text{W}/\text{m}^2\text{K}$]
γ	– primary molar CO/CO ₂ ratio
ε	– char particle porosity, [-]
ε_r	– emissivity, [-]
λ_{eff}	– effective heat conductivity of porous char particle, [W/mK]
$\nu_{i,j}$	– stoichiometric coefficients for i -reaction and j -component, [-]
ρ	– density, [kg/m^3]
σ	– Stefan-Boltzman constant, [$\text{W}/\text{m}^2\text{K}^4$]
τ	– time, [s]
χ_{O_2}	– molar fraction of O ₂ , [-]
ψ	– model parameter for the specific internal surface area evolution, [-]

Subscripts

0	– initial value
Ch	– related to char particle
d	– related to decomposition of CaSO ₄
f	– related to formation of SO ₂ due to combustion
G	– related to CaO grain
s	– related to sulfation

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Authors' addresses:

V. Manović
Mining and Geology Faculty of Belgrade University,
Džušina 7, 11000 Belgrade, Yugoslavia

B. Grubor, M. Ilić
VINČA Institute of Nuclear Sciences,
P. O. Box 522, 11001 Belgrade, Yugoslavia

Corresponding author (B. Grubor):
E-mail: grub@rt270.vin.bg.ac.yu

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