Calcium based sorbent calcination and sintering reaction models overview

Ivan Tomanovic, Srdjan Belosevic, Aleksandar Milicevic, Nenad Crnomarkovic

University of Belgrade, Vinča Institute of Nuclear Sciences, Belgrade, Serbia

Abstract

Several models considering the pulverized sorbent reactions with pollutant gases were developed over the past years. In this paper, we present a detailed overview of available models for direct furnace injection of pulverized calcium sorbent suitable for potential application in CFD codes, with respect to implementation difficulty and computational resources demand. Depending on the model, variations in result accuracy, data output, and computational power required may occur. Some authors separate the model of calcination reaction, combined with the sintering model, and afterwards model the sulfation. Other authors assume the calcination to be instantaneous, and focus the modelling efforts toward the sulfation reaction, adding the sintering effects as a parameter in the efficiency coefficient. Simple models quantify the reaction effects, while more complex models attempt to describe and explain internal particle reactions through different approaches to modelling of the particle internal structure.

Keywords: *sorbent, calcium, calcination, sintering, sulfation, model*

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1. INTRODUCTION

It is well known that production of electric energy by coal combustion is a significant contributor to the release of pollutant gases in the atmosphere, among which sulfur oxides are present. Significant efforts are invested in the investigation and reduction of gaseous products emission in order to reduce the negative environmental impact of coal combustion. Sulfur oxides in furnace gases originate from combustible sulfur compounds contained in the coal. Considering the reduction of sulfur oxides, several different technologies are available today. Processes in such technologies usually involve the use of some kind of sorbent with the goal to capture sulfur oxides in the furnace or in flue gases. The most common and most abundant sorbent in nature is calcium in forms of calcium carbonate and calcium hydroxide. It can be used in reactors involving gas scrubbing technologies, or it can be directly injected in the boiler at different locations, depending on the implemented de-SO_x technology. One of the technologies involving sorbent injection directly into the boiler furnace is the so called furnace sorbent injection (FSI) process. Due to complexity and number of simultaneous ongoing processes, it is possibly the most difficult technology from the aspect of in-furnace process organization to apply to real-world utility boilers. To better understand the process many authors have undertaken a significant amount of experimental and theoretical work in order to broaden the knowledge on the sorbent behavior under furnace injection conditions. This resulted in several different modelling approaches to the problem. Some authors put focus mainly on quantifying the sorbent effects, without deeper understanding of the processes and transformation that occur inside the sorbent particles, while the others attempt to gain a better comprehension of the particle itself by modeling its structure, as well as to determine the influence of the particle on fluid by the modeling internal changes in the particle.

Motivation for this paper lies in the necessity to create an overview of models that can be implemented and used with numerical tools for analysis of fluid motion and reactions in simulated real-world facilities, with focus on models that can be used to describe the furnace sorbent injection processes. In order to gain better insight into the existing models and current research progress, we attempt to give a detailed review of available literature. Fundamental and most commonly used models from the literature that focus on modelling of calcium-based sorbent reactions with sulfur oxides are presented. The necessity to predict and model sorbent reactions is not new, however, prior to the recent increase in processor computational speeds and available memory the models and their applications were significantly

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Correspondence: Ivan D. Tomanović, University of Belgrade, Vinča Institute of Nuclear Sciences
e-mail: ivan.tomanovic@vin.bg.ac.rs

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limited. Today models varying both in complexity and performances are available, but many are rarely used in conjunction with computational fluid dynamics (CFD) simulations to predict processes at full-scale plants. Given the nature of observed reactions and their importance for the process as well as the dependency on local fluid conditions, it is of great importance to properly link the particle reaction models with models of other processes in a boiler furnace. This approach provides a good insight and allows prediction and efficiency estimation of different processes simultaneously under various boiler operating conditions.

Figure 1 shows the possibilities for sorbent injection in flue gas desulphurization technologies, with a focus on sorbent injection in the boiler furnace. Depending on the local conditions, especially the temperature field, the sorbent can be injected through one or more burner tiers. The internal particle surface corresponds to the specific surface area of the powder, and coefficients used in equations for particle surface development or sintering in models are determined by authors based on the experimental data for the case-study sorbents [1] or obtained above the burner tiers [1–6]. This application of the sorbent is commonly called FSI. Other technologies consider sorbent injection in the duct further down the gas canal (ESI, DSI), [6,7] where local temperatures are lower.

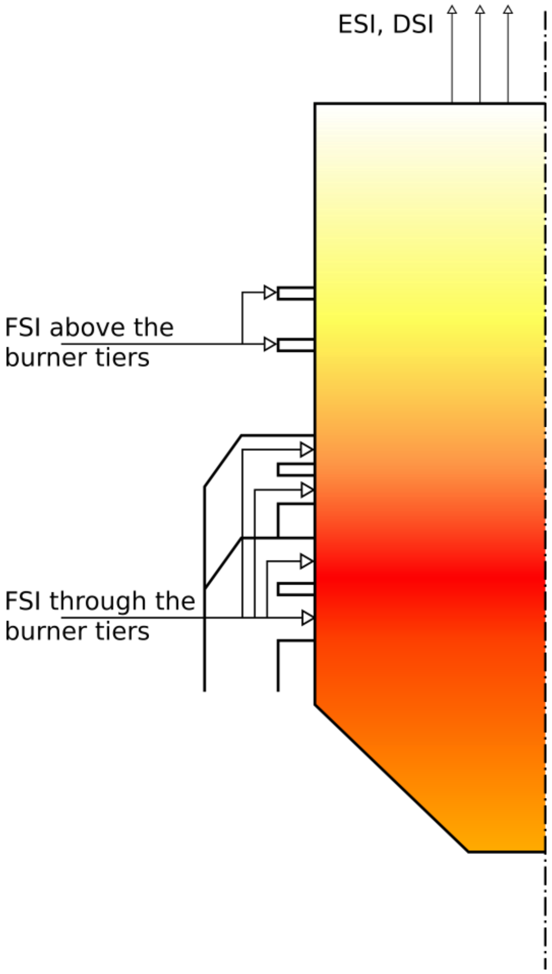

Figure 1. Schematic display of possible implementations of direct furnace sorbent injection in an utility boiler

2. ABOUT SORBENT PARTICLE REACTION MODELS

The mathematical fundament of several different sorbent particle reaction models is presented in this paper. The models can be roughly split into two groups. The first group consists of semi-empirical models which focus on modeling the particle chemical kinetics, by means of semi-empirical equations, based on data obtained in experimental studies, mostly based on authors' perception and interpretation of the results. Models representing this group are Borgwardt's models [8,9] used to describe reactions of large sorbent particles and the Makarytchev model [1]. In the second group of models are models, which focus on the internal structure of the particle and analyze structural changes, such as the internal gas concentration profiles and other properties that have an influence on particle reactivity. Different authors have modeled the solid structure in the particle or focused on the structure of the pores [10,11]. Some use models to quantify and average the properties inside the particle as a whole [9,12], while the others try to model different particle layers determining reactant concentrations and reaction rates for each layer, thus effectively describing the influence of particle structure on reactivity [13–16]. All of these models have modelling of the internal solid particle structure and gaseous reactant penetrationin common, and use of the obtained data to determine the particle reaction rates. Models describing the internal particle structure can be found in papers [10,14,15,17-20]. Another group of models is presented by network models [10], which focus on the pore structure instead of the solid, but these are significantly less frequently found in literature on FSI and reactions modeling involving sulfur oxides. The basic assumption in network models is that the particle configuration is made of cylindrical solid structures, while the void is presented by pores, opposite to pore models where the pores assume a cylindrical shape, while the surrounding space is filled with the solid.

All models consider a two-step reaction – calcination combined with sintering, as the first reaction phase, and sulfation of the particle as the second. The sulfation directly depends on the extent of calcination. All three processes are described as parallel in most of the models, with rates governed by local conditions. Depending on the chosen sorbent ($CaCO_3$ [9,14,15,17,21–23], or $Ca(OH)_2$ [13,15]) the endothermic calcination reaction is modeled as:

$$\begin{aligned} &CaCO_3 \rightarrow CaO + CO_2 \\ &Ca(OH)_2 \rightarrow CaO + H_2O \end{aligned} \tag{1}$$

The calcination occurs rapidly at high temperatures, so that the internal reactive surface in particles develops quickly accompanied with the significant increase in CaO particle porosity. The particle exposure to high temperatures also increases sintering rates [8,14], which become significant when the gas temperature rises above a certain level (usually over 1100°C [24]). Due to intensive sintering, particles lose their internal reactive surface, leading to decreased reactivity with sulfur oxides contained in the surrounding gas. These changes in the internal particle surface are the key parameter in the sulfation reaction so that the sintering process must be monitored in order to maintain the particle reactivity as high as possible.

Sulfation reaction (absorption) is modeled according to the equation [9,13–15,17,22,23]:

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \tag{2}$$

In this exothermic reaction, CaO particles react with SO_2 and oxygen from the surrounding gas so that $CaSO_4$ is formed as the reaction product. Thus, sulfur oxides are removed from the gas and some oxygen is consumed during the reaction. In order for sulfation reaction to take place, the particles must be surrounded with a sufficient amount of oxygen besides sulfur oxides.

3. PARTICLE CALCINATION MODELS

A significant amount of information on different calcination and sintering models can be found in the paper [25], with details on the models formulated by several authors.

Borgwardt [8] determined the calcination rate under conditions usually found in fluidized bed furnaces with temperatures ranging from 516 °C to 1000 °C and proposed a correlation between the reaction rate and temperature in the form of Arrhenius equation:

$$R_c = R_{c,0} e^{-\frac{E_a}{RT}} \tag{3}$$

In the experimental studies of Dennis and Hayhurst [25,26] the temperature influence on the calcination reaction rate was found to be negligible in the temperature range from 800°C to 975°C authors, implying that the associated activation energy E_a is close to zero in the observed range [25]. The calcination rate was determined with respect to changes in the total pressure P, partial pressure P_i of CO_2 in the mixture and the equilibrium pressure P_{eq}, by the equation [25]:

$$R_c = k_c(P_{eq} - P_i - cP) \tag{4}$$

Silcox *et al.* [19] also related the calcination rate with the CO_2 partial pressure at the particle surface and the equilibrium pressure P_{eq} (5), but without the influence of the total pressure, as in the eq. (4):

$$R_c = k_D(P_{eq} - P_i) \tag{5}$$

Dependences of the rate coefficient k_D(k_D=1,22 $e^{-4026/T}$[25]) and the equilibrium pressure P_{eq} on temperature are given in the form of Arrhenius equations. Hu and Scaroni [27], introduced a correction of the calcination rate coefficient, which depends on the difference between the partial and the equilibrium pressure:

$$\begin{cases} (P_{\mathrm{eq}} - P_{\mathrm{i}}) \,\middle|\, P_{\mathrm{eq}} 10^{-2} < P_{\mathrm{i}} < P_{\mathrm{eq}'} \\ 1 \,\middle|\, P_{\mathrm{i}} \leq P_{\mathrm{eq}} 10^{-2} \end{cases} \tag{6}$$

The correction (6) corresponds to the research of Barker [28], as the CO_2 concentration was found to negligibly influence the calcination rate if the partial pressure of CO_2 is several orders of magnitude smaller than the equilibrium pressure.

A slightly different approach to calcination rate modeling was used in another study [29], which introduced a model in the exponential form:

$$R_{\mathrm{c}} = k_{\mathrm{c}} e^{-\mathrm{coef} - \frac{P_{\mathrm{i}}}{P_{\mathrm{eq}}}} \tag{7}$$

Most of the mentioned models and terms in the reaction rates were analyzed and compared in the paper [30].

Milne and coworkers [21] used the modified shrinking core model to describe the calcination process, with the constant solid material density assumption. The modified model also assumes the introduction of the averaged grain size d_0 / m, which figures in the equation used to determine the calcination extent together with the calcination reaction rate:

$$X = 1 - \left(1 - \frac{k}{d_{\mathrm{o}}^{0.6}} t \right)^3 \tag{8}$$

where the reaction rate *k* itself is dependent on temperature also in a form of Arrhenius equation.

A commonly found assumption in literature is that the temperature profile in a small particle is uniform, which consequently leads to the uniform calcination process over the entire particle volume [14]. The justification for such an assumption lies in the fact that the time required for equalization of the temperature profile in the particle is several orders of magnitude smaller, as compared to other concurrent processes, which was confirmed experimentally [13]. The base equation in the calcination process used by Alvfors and Svedberg [14] is the same as the one given in the Borgwardts model for small particles [22]:

$$\frac{\mathrm{d}\left(N_{\mathrm{CaO_3}}\right)}{\mathrm{d}t} = -k_c N_{\mathrm{CaO_3}} S_{\mathrm{CaO_3}} M_{\mathrm{M,CaO_3}} \tag{9}$$

Dependence of the reaction rate coefficient in this model on temperature is described by the eq. (3). Calcination extent is determined according to the eq. (10) is derived from the eq. (9):

$$X(t) = 1 - \mathrm{e}^{-k_c S_{\mathrm{CaO_3}} M_{\mathrm{M,CaO_3}} t} \tag{10}$$

Change in the calcination extent is further used to determine development of the internal CaO surface as:

$$\sum_{\mathrm{k=1}}^{\mathrm{n}} S^{\mathrm{n,k}} \left(X_{\mathrm{c}}(t_{\mathrm{k}}) - X_{\mathrm{c}}(t_{\mathrm{k-1}}) \right) \tag{11}$$

3. 1. Particle sintering models

Modeled reactions in available literature usually use two distinct sintering models. The first, defined by German and Munir [31], used by Borgwardt [32] and Alvfors and Svedberg [14], assumes that the particle is built of spherical grains in close contact with a certain degree of overlapping. The sintering rate in this model is determined by the following equation [14]:

$$\left(\frac{S_0 - S}{S_0} \right)^{\gamma} = k_{\mathrm{s}} t \tag{12}$$

Coefficients γ and k_s are correlated to partial pressures of H_2O and CO_2, and the gas temperature. *S* and S_0 represent the current and starting internal particle surface. Eq. (12) is used to modify the calculated surface development of CaO to include sintering effects so that the internal surface is calculated as:

$$S^{\mathrm{n,k}} = S_{\mathrm{0,CaO}} \left(1 - \left(K_{\mathrm{s}} T_{\mathrm{k}} t_{\mathrm{n}} \right)^{\frac{1}{\gamma(t_{\mathrm{k}})}} \right) \tag{13}$$

Second sintering model that can be found in literature is defined by Nicholson [33]. It was applied to describe sintering of calcium particles in a model formulated by Silcox *et al.* [19], and it is based on the equation:

$$\frac{\mathrm{d}S}{\mathrm{d}t}=-k_{\mathrm{s}}\left(S-S_{\mathrm{as}}\right)^{2} \tag{14}$$

In this model the value of the coefficient k_s is a function of CO_2partial pressure and gas temperature, and the procedure used to determine k_s is highly empirical. A potential problem in the application of this model can be the necessity to know the asymptotic value S_{as}, which represents the ideal theoretical value of the particle internal surface under ideal conditions.

4. PARTICLE SULFATION MODELS

Sulfation reaction models, describing the heterogeneous chemical reaction between solid sorbent particles and sulfur oxides present in the surrounding gas, can be found in various studies in literature [9,10,13-18,22,23,34-38]. The models can be roughly categorized in three groups, based on the way the particle structure is considered [39]: unreacted core models, grain models, and pore models.

The Unreacted shrinking core model – USCM, described in detail in literature [40], is derived under the assumption that there is a clear interface between the unreacted core, consisting entirely of CaO, and a $CaSO_4$ layer covering the core. During the reaction, the particle size is assumed to remain constant, and all transformations occur in the internal structure. A similar approach to modeling can be found in studies [9,36-38,41]. In the Borgwardt formulation [9] the sorption reaction rate is related to the efficiency factor and sulfate loading of the particle, effectively including the sintering influence on the sulfation rate of the pre-calcined sorbent:

$$r=\frac{1}{W}\frac{\mathrm{d}n'}{\mathrm{d}t}=\frac{\eta}{\rho}k_{\mathrm{sulf}}c^{\mathrm{m}} \tag{15}$$

A significant change to the model was suggested by Punbusayakul *et al.* [42], who introduced a correction related to the influence of temperature at zero sulfate loading and under increased sulfate loading. Accordingly, calculation of the efficiency factor was changed yielding the equation:

$$\eta_{\mathrm{ef}}=e^{-\frac{\beta\dot{n}}{w}}e^{\left(-\frac{E_{\mathrm{a}}}{RT}\right)+\frac{E_{\mathrm{a}}}{RT_{\mathrm{ref}}}}\frac{c^{\mathrm{m}}}{c_{\mathrm{ref}}^{\mathrm{m}}}\left[-\right] \tag{16}$$

The base equation of the models is similar in form with minor variations but it disregards deeper understanding of processes in the particle in favor of the model simplicity. The focus is on the reaction that occurs on the interface between the particle and surrounding gas. Models in this group do not provide many details about the ongoing process in the particle, but rather quantify the reaction products and changes in SO_2 concentration. Most of the authors who use this semi-empirical approach focus on the sulfation model with an added correction due to particle sintering, while calcination is assumed to be instantaneous [9], or the sorbent is precalcined. Mathematical formulations describing these models are usually simple and do not require significant computational power for calculations.

Grain model – GM and partially sintered spheres model – PSSM both assume the particle structure to consist of small grains. The major difference between the two models is in the way they treat the internal grain distribution and structure. Both models assume that the particle consists of many smaller grains covered by the reaction product layer and forming a porous structure. PSSM introduces an additional assumption that the grains are in mutual contact with each other overlapping by a certain amount as described in various studies [10,14,17,35]. The reaction rate of individual grains in the model is controlled by a mechanism similar to that of the unreacted shrinking core model but reduced down to the grain instead of the particle itself. Thus, it depends on diffusion through the pores, diffusion through the sulfate products layer, and the reaction rate at the unreacted core surface of each individual grain. During the transformation of CaO in $CaSO_4$, grains grow in size, and thus, the particle porosity decreases while the particle size itself is not significantly affected. Equation (17) shows the reaction rate of sulfur dioxide with sorbent under quasi-stationary conditions used in PSSM [10,14,17,35]. It is solved for each grain position over the particle diameter, as it depends on the local reactant concentration in the particle.

$$r_{\mathrm{SO_2}}=\frac{c_{\mathrm{SO_2}}}{\frac{1}{k\nu S_2}+\frac{L}{D_{\mathrm{s}}S_{\mathrm{avg}}}} \tag{17}$$

This model thus considers the influence of reactant diffusion through the particle, as well as the reaction rate of the reactant on the grain surface. Simplifications can be introduced to reduce the computation times, such as averaging the concentration profile inside the particle, under the condition that particle reaction times are not significantly modified [43]. The simplifications can help.

In order to determine the reaction rate in PSSM, specific dimensionless surfaces of the product layer and unreacted grain core must be known. Dimensionless surfaces for each grain are determined by the means of the equation (18) [35], where *i* = 0,1,2 represent an index for: the starting specific dimensionless surface (which is known from calcination, and used to determine the grain dimensionless radius), the dimensionless surface of products layer, and the dimensionless surface of the unreacted grain core:

$$S_{\mathrm{i}} = \frac{3(1-\varepsilon)\left(2g_{\mathrm{i}}^{2} - n_{\mathrm{cp}} f\left(g_{\mathrm{i}},\lambda\right)\right)}{r_0\left(2 - n_{\mathrm{cp}}\left(1+\frac{1}{2}\lambda\right)(1-\lambda)^{2}\right)}[-] \tag{18}$$

Variants of the grain model were also developed by Szekely and Evans [41] and Pigford and Sliger [44] with the added gas phase mass balance in the spherical particle, as well as by Hartman and Coughlin [45] who introduced reduction of particle porosity due to changes in the sulfation reaction product layer volume.

Between the two described model groups is the Borgwardts model [22] proposed for smaller sorbent particles and applied to calcium hydroxide particles. Formulation for the sulfation reaction rate coefficient corresponds to USC models, with the expanded Arrhenius equation as a basis and added the empirical dependence on the partial pressure of sulfur oxides surrounding the grain as well as the influence of internal particle surface:

$$k_{\mathrm{d}} = 2.65{S_{\mathrm{B}}}^{2}{P_{\mathrm{SO_2}}}^{0.64}\mathrm{e}^{\left(-\frac{36600}{RT}\right)} \tag{19}$$

Influence of the internal particle surface on the sulfation rate is similar to that found in more complex and computation intensive models, thus making this model more complicated as compared to other USC models, but still simpler than GM or PSSM.

Pores model – PM belongs to the group of structural models [10,11], focusing on modeling the structure of pores in the particle. During the reaction, the pore size changes as the product layer increases. In this model, as it was the case with the previous, main reaction rate controlling mechanisms are gas diffusion through the pores, gas diffusion through the sulfation product layer and the reaction rate at the unreacted grain core surface. A significant difference in the pore model, as compared to grain models is the way it treats the particle geometry. As explained above, the grain model focuses on spherical grains inside the particle, so that sizes of the unreacted core and product layer are considered with respect to the grain, while existence and changes in the pore structure are indirectly observed. On the other hand, in the pore model, the focus is on the pore shape and structure, and changes in the internal particle structure are observed through the changes in pore geometry, and material and structure of pore walls. The solid material (internal particle structure – grains) surrounding a pore is not modeled directly. One of the first pore models assuming pores uniform in shape and neglecting structural changes in pores was proposed by Szekely and Evans [41]. Ramachandran and Smith [36] introduced individual pore changes to the model allowing for modeling of additional phenomena such as the pore clogging during the reaction. Some authors introduced modelling of pores with random intersections [10,39,46,47], while pore size distribution was considered by Christman and Edgar [48], and Kocaefe and coworkers [35]. Simons [49,50] developed a pore model with a tree-like structure of pores in the particle. To better illustrate major equations, and the way different authors model the sorbent, an overview is presented in Table 1.

Implementation and usability of described models in real life calculations should be carefully considered, as the increased model complexity can demand significant amount of computational power. Figure 2 shows the general algorithm that can be used to implement mentioned sorbent particle reaction models in a CFD code for process simulations in the utility boiler furnace. The models should be implemented in the algorithm within the Particle section, with the aim to determine particle reaction rates, efficiency factors, extent of sulfation, and other data required by the model.

Implementation of reviewed models in a numerical code can be done by two way coupling. Figure 2 provides the algorithm used to simulate sorbent particle reactions and their interactions with the rest of the simulated processes.

The initial step in coupling with CFD code would be to provide needed input data for the reaction, and accordingly to determine reaction rates, the efficiency factor (if required by the model), the extent of sulfation, and other relevant data for the implemented model. At the same time, the particle position should be updated. the next step would be to determine additional source terms, which describe influences of the particle presence and reactions on gas mixture components and the fluid flow field. After this, the particle position in the computational domain is updated. The simulation steps are repeated until the particle leaves the computation domain or the reaction reaches saturation and stopping criteria.

Table 1 Overview of major equations governing calcination, sintering and sulfation rates in models by different authors

Ref.	Calcination	Sintering	Sulfation
[9]	Calcination rate, sorbent usually precalcined before use $R_\mathrm{C} = R_\mathrm{C,0}\mathrm{e}^{\left(-\frac{E_\mathrm{a}}{RT}\right)}$	Sintering is taken into account through the changes in efficiency coefficient η_ef	Sulfation reaction rate $r=\frac{1}{W}\frac{\mathrm{d}n'}{\mathrm{d}t}=\frac{\eta}{\rho}k_\mathrm{sulf}c^\mathrm{m}$ Efficiency coefficient correction by Punbusayakul $\eta_\mathrm{ef}=e^{-\frac{\beta\dot{n}}{w}}e^{\left(-\frac{E_\mathrm{a}}{RT}\right)+\frac{E_\mathrm{a}}{RT_\mathrm{ref}}\frac{c^\mathrm{m}}{c_\mathrm{ref}^\mathrm{m}}}\left[-\right]$
[22]	Calcination extent $X(t)=1\text{-}\mathrm{e}^{-k_c S_{\mathrm{CaO_3}} M_{\mathrm{M,CaO_3}} t}$ Calcium oxide surface development $S_\mathrm{CaO}{}^\mathrm{n}=\sum_{\mathrm{k}=1}^{\mathrm{n}} S^{\mathrm{n,k}}\left(X\left(t_\mathrm{k}\right)\text{-}X\left(t_{\mathrm{k-1}}\right)\right)$	Sintered calcium oxide surface at time step k $S^\mathrm{n,k}=S_\mathrm{0,CaO}\left(1\text{-}\left(K_\mathrm{S}T_\mathrm{k}t_\mathrm{n}\right)^{\frac{1}{\gamma t_\mathrm{k}}}\right)$	Conversion when the diffusion resistance can be neglected $1 - 3(1 - X_\mathrm{s})^{2/3} + 2(1 - X_\mathrm{S}) = k_\mathrm{d}t$ Sulfation reaction rate $k_\mathrm{d}=2.65S_\mathrm{B}{}^2P_{\mathrm{SO_2}}{}^{0.64}\mathrm{e}^{\left(-\frac{36600}{RT}\right)}$
[27]	Calcination rate: $R_\mathrm{c} = k_\mathrm{c}A_{\mathrm{CaCO_3}}$ Reaction rate coefficient $k'_\mathrm{C}=6.078\times10^7e^{-\frac{205000}{TR}}$ Reaction rate coefficient correction: $k_\mathrm{c}=k'_\mathrm{c}A$ $A=\begin{cases}(P_\mathrm{eq}-P_\mathrm{i}) \mid P_\mathrm{eq}10^{-2}<P_\mathrm{i}<P_{\mathrm{eq'}}\\ 1 \mid P_\mathrm{i}\le P_\mathrm{eq}10^{-2}\end{cases}$		
[19]	Calcination rate: $R_\mathrm{c} = k_\mathrm{D}(P_\mathrm{eq}\text{-}P_\mathrm{i})$ Reaction rate coefficient $k_\mathrm{D}=1.22e^{-\frac{4026}{T}}$	$\frac{\mathrm{d}S}{\mathrm{d}t}=\text{-}k_\mathrm{s}\left(S-S_\mathrm{as}\right)^2$ $k_\mathrm{s}=A\mathrm{e}^{-\frac{E}{RT}}\mathrm{e}^{\frac{BP^\mathrm{m}}{RT}}$	
[29]	Calcination rate: $R_\mathrm{c}=k_\mathrm{c}e^{\text{-coef}-\frac{P_\mathrm{i}}{P_\mathrm{eq}}}$		
[14,17]	Calcination extent $X(t)=1\text{-}\mathrm{e}^{-k_c S_{\mathrm{CaO_3}} M_{\mathrm{M,CaO_3}} t}$ Calcium oxide surface development $S_\mathrm{CaO}{}^\mathrm{n}=\sum_{\mathrm{k}=1}^{\mathrm{n}} S^{\mathrm{n,k}}\left(X\left(t_\mathrm{k}\right)\text{-}X\left(t_{\mathrm{k-1}}\right)\right)$	Sintered calcium oxide surface at time step k $S^\mathrm{n,k}=S_\mathrm{0,CaO}\left(1\text{-}\left(K_\mathrm{S}T_\mathrm{k}t_\mathrm{n}\right)^{\frac{1}{\gamma t_\mathrm{k}}}\right)$	Reaction rate $r_{\mathrm{SO_2}}=\frac{c_{\mathrm{SO_2}}}{\frac{1}{k\nu S_2}+\frac{L}{D_\mathrm{s}S_\mathrm{avg}}}$ Dimensionless surfaces $S_\mathrm{i}=\frac{3(1-\varepsilon)\left(2g_\mathrm{i}^2-n_\mathrm{cp}f\left(g_\mathrm{i},\lambda\right)\right)}{r_0\left(2-n_\mathrm{cp}\left(1+\frac{1}{2}\lambda\right)(1-\lambda)^2\right)}\left[-\right]$
[11]	Calcination $\frac{\mathrm{d}R_\mathrm{c}}{\mathrm{d}t}=\frac{M}{\rho}k_\mathrm{c}A$ $\begin{cases}(P_\mathrm{eq}-P_\mathrm{i}) \mid P_\mathrm{eq}10^{-2}<P_\mathrm{i}<P_{\mathrm{eq'}}\\ 1 \mid P_\mathrm{i}\le P_\mathrm{eq}10^{-2}\end{cases}$	Generation rate of new pores due to sintering and sulfation: - cylindrical pores: $\frac{\mathrm{d}\varphi_\mathrm{ij}}{\mathrm{d}t}=K_\mathrm{S}\varphi_\mathrm{i}\varphi_\mathrm{j}$ - plate-like pores $\frac{\mathrm{d}\Omega_\mathrm{ij}}{\mathrm{d}t}=K_\mathrm{S}\Omega_\mathrm{i}\Omega_\mathrm{j}$	Sulfation model for two assumed pore geometry models: - cylindrical pores $X_\mathrm{sk}=\frac{M_\mathrm{CaO}}{V_{\mathrm{CaSO_4}}}\pi\sum_\mathrm{i}\left(r_{2,\mathrm{K,i}}{}^2\text{-}r_{1,\mathrm{K,i}}{}^2\right)\varphi_\mathrm{K,i}$ - plate-like pores $X_\mathrm{sk}=\frac{M_\mathrm{CaO}}{V_{\mathrm{CaSO_4}}}\pi\sum_\mathrm{i}\left(z_{2,\mathrm{K,i}}{}^2\text{-}z_{1,\mathrm{K,i}}{}^2\right)\Omega_\mathrm{K,i}$
[15,21]	Calcination extent $X=1\text{-}\left(1-\frac{k}{d_0{}^{0.6}}\right)^3$ $\mathrm{CaCO_3}$ rate constant $k=10.303\,\mathrm{e}^{-\frac{10980}{T}}$ $\mathrm{Ca(OH)_2}$ rate constant $k=53.87\,\mathrm{e}^{-\frac{8300}{T}}$	Surface area loss $\frac{\mathrm{d}S_\mathrm{m}}{\mathrm{d}t}=\text{-}2450\left(1+50.7p_{H_2O}{}^{0.17}+10.3p_{\mathrm{CO_2}}{}^{0.67}\right)$ $e^{-\frac{29600}{T}}\pi\left(S_\mathrm{m}-5000\right)^2$	

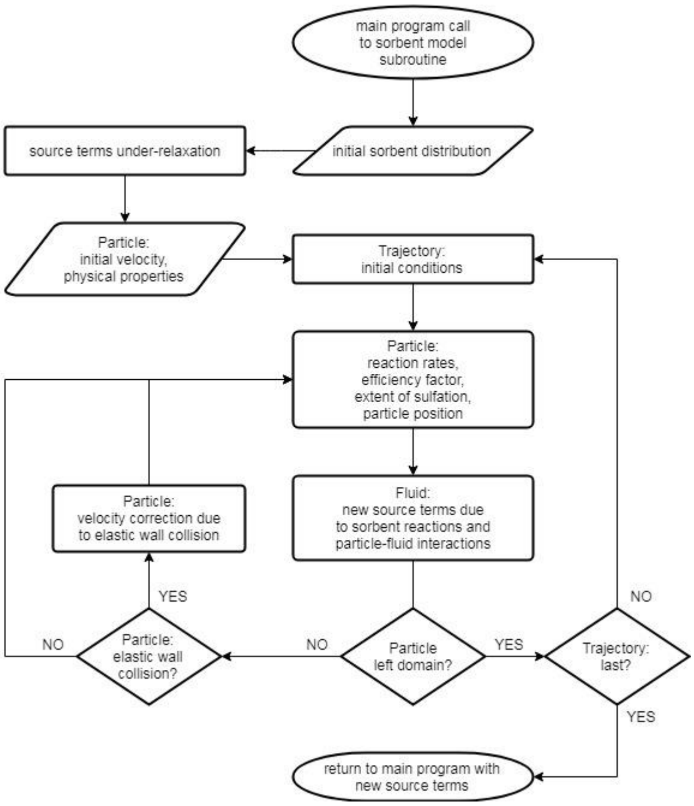

Figure 2. Sorbent particle reactions and tracking implementation algorithm in CFD code for boiler furnace simulation

5. CONCLUSION

Some of the models presented in the text can be readily implemented in CFD codes for numerical simulation of processes. The USC model and similar usually can be readily implemented to existing numerical codes without major interventions to the model structure. The computational resource requirements are usually low in these models, but the application is limited to a range of operating condition and sorbent types, and in order to utilize models the coefficients for each new type of sorbent must be experimentally determined. On the other hand, more complex and robust models, such as Grain model and PSS model cover the wider range of sorbents and temperatures and can be more readily adapted to different sorbent types [43], as they attempt to predict the sorbent behavior based on its internal structure. They usually provide better results at the cost of significantly higher computational time.

Importance of the internal particle structure and developed internal reactive surface was identified as the most influential parameter in the reaction as it significantly influences the overall sorbent reactivity. it's the Borgwardt model for smaller size particles [22] combines a complex model of particle internal structure development during calcination and sintering, with a relatively simple sulfation model in the form of extended Arrhenius equation with added influences of the internal reactive surface and sulfur dioxide partial pressure. In this model, as well as in GM and PSSM, most of the computation time is spent on determination of the changes in the particle internal reactive surface, using the equation (12), implemented in code in the form (13). Another approach to optimization of the computation time would be to use the model proposed by Silcox and coworkers [19], with the limitation that this model does not capture the initial peak in the internal surface development at lower gas temperatures.

Selection of the proper model highly depends on the complexity of the problem being solved, and computer resources at disposal. Some models can be simplified by certain modifications to accommodate shorter computation times without significant loss in computational precision.

6. NOMENCLATURE

c_{SO_2} / kmol m^{-3}	- concentration of SO_2 in the pores
c^m / g cm^{-3}	- molar concentration of SO_2in surrounding gas
c^m_{ref} / g cm^{-3}	- referent concentration of SO_2
coef	- coefficient
D_S / m^2 s^{-1}	- diffusion coefficient through the solid sulfation reaction products layer
d_0 / m	- initial particle diameter
E_a / J mol^{-1}	- activation energy

g_i - dimensionless radius
K_s / s^{-1} - sintering rate constant for CaO in German-Munir equation
k / m s^{-1} - reaction rate constant
k_c / mol m^{-2} s^{-1} - calcination rate constant
k_D / mol m^{-2} s^{-1} Pa^{-1} - calcination rate coefficient
k_d / m^4 g^2 $Pa^{0.64}$ - diffusion rate constant through product layer
k_S / kg m^{-2} s^{-1} - sintering rate constant
k_{sulf} / kg m^{-2} s^{-1} - sulfation rate constant
L / m - product layer thickness
$M_{M,CaCO_3}$ / kg mol^{-1} - $CaCO_3$ molar mass
N_{CaCO_3} / mol - number of $CaCO_3$ moles
n' / mol - sorbent sulphate loading
$\dot{n}$ / mol s^{-1} - number of sulfur dioxide moles given perunit of reaction time
n_{cp} - number of grains in mutual contact inside the particle
P / Pa - total pressure
P_{eq} / Pa - equilibrium pressure
P_{SO_2} / Pa - partial pressure of SO_2above the equilibrium partial pressure in flue gas
P_i / Pa - partial CO_2 pressure in gas mixture
R / J mol^{-1} K^{-1} - universal gas constant
R_c / mol m^{-2} s^{-1} - calcination rate
$R_{c,0}$ / mol m^{-2} s^{-1} - calcination rate at zero calcination
r / mol g^{-1} s^{-1} - sulfur oxides formation rate
r_{SO_2} / kmol m^{-3} s^{-1} - volumetric reaction rate of $SO_2$with sorbent
S / m^2 m^{-3} - specific internal particle surface
S_B / m^2 m^{-3} - specific internal particle surface
S_0 / m^2 m^{-3} - starting specific internal particle surface
$S_{0,\,CaO}$ / m^2 g^{-1}] -maximum specific internal surface of CaO if there was no sintering obtained under ideal conditions
S_1 / m^2 m^{-3} - specific product layer surface, given per m^3 of particle
S_2 / m^2 m^{-3} - specific internal grain surface, given per m^3 of particle
S_{avg} / m^2 m^{-3} - averaged specific surface
S_{as} / m^2 g^{-1} - asymptotic value of calcined sorbent BET surface (experimentally obtained under ideal conditions)
S_{asCaCO_3} / m^2 g^{-1} - specific internal $CaCO_3$ particle surface
S_{CaO}^n / m^2 g^{-1} - internal surface of CaO available for reaction in n^th^ time step
$S^{n,k}$ / m^2 g^{-1} - sintered internal surface that sintered in nth time step
T / K - temperature
T_{ref} / K - temperature
t / s - time
W / g - solid sorbent particle mass
w / g - initial sorbent particle mass
X - calcination extent
β / g mol^{-1}] - coefficient
γ - exponent in German-Munir equation
ε - local porosity at current time step
η - efficiency factor, defined as the ratio of true reaction rate and theoretic maximum value
η_{ef} - effective efficiency factor
λ - structural parameter
ρ / kg m^{-3} - density
v - volumetric part of CaO in the grain structure

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REFERENCES

[1] Makarytchev SV, Cen KF, Luo ZY. Staged desulphurization by direct sorbent injection in pulverized-coal boilers. *Energy*. 1994;19(9):947-956.

[2] Zhou W, Maly P, Brooks J, Nareddy S, Swanson L, Moyeda D. Design and Test Furnace Sorbent Injection for SO 2 Removal in a Tangentially Fired Boiler. *Environ Eng Sci*. 2010;27(4):337-345.

[3] Muzio LJ, Often GR. Assessment of Dry Sorbent Emission Control Technologies Part I. Fundamental Processes. *JAPCA*. 1987;37(5):642-654.

[4] Toole-O'Neil B. Furnace Sorbent Injection. *J Air Waste Manage Assoc*. 1990;40(12):1716-1718.

[5] Shi L, Liu G, Higgins BS, Benson L. Computational modeling of furnace sorbent injection for SO2 removal from coal-fired utility boilers. *Fuel Process Technol*. 2011;92(3):372-378.

[6] Carpenter AM. *Low Water FGD Technologies*. Vol December N.; 2012.

[7] Stouffer MR, Yoon H, Burke FP. An investigation of the mechanisms of flue gas desulfurization by in-duct dry sorbent injection. *Ind Eng Chem Res*. 1989;28(1):20-27.

[8] Borgwardt RH. Calcination kinetics and surface area of dispersed limestone particles. *AIChE J*. 1985;31(1):103-111.

[9] Borgwardt RH. Kinetics of the reaction of sulfur dioxide with calcined limestone. *Environ Sci Technol*. 1970;4(1):59-63.

[10] Lindner B, Simonsson D. Comparison of structural models for gas-solid reactions in porous solids undergoing structural changes. *Chem Eng Sci*. 1981;36(9):1519-1527.

[11] Adánez J, García-Labiano F, Fierro V. Modelling for the high-temperature sulphation of calcium-based sorbents with cylindrical and plate-like pore geometries. *Chem Eng Sci*. 2000;55(18):3665-3683.

[12] Borgwardt RH, Harvey RD. Properties of carbonate rocks related to sulfur dioxide reactivity. *Environ Sci Technol*. 1972;6(4):350-360.

[13] Fan L-S, Ghosh-Dastidar A, Mahuli S, Agnihotri R. High Temperature Desulfurization of Flue Gas Using Calcium-Based Sorbents. In: *Dry Scrubbing Technologies for Flue Gas Desulfurization*. Boston, MA: Springer US; 1998:421-527.

[14] Alvfors P, Svedberg G. Modelling of the simultaneous calcination, sintering and sulphation of limestone and dolomite. *Chem Eng Sci*. 1992;47(8):1903-1912.

[15] Milne CR, Silcox GD, Pershing DW, Kirchgessner DA. High-temperature, short-time sulfation of calcium-based sorbents. 1. Theoretical sulfation model. *Ind Eng Chem Res*. 1990;29(11):2192-2201.

[16] Milne CR, Silcox GD, Pershing DW, Kirchgessner DA. High-temperature, short-time sulfation of calcium-based sorbents. 2. Experimental data and theoretical model predictions. *Ind Eng Chem Res*. 1990;29(11):2201-2214.

[17] Alvfors P, Svedberg G. Modelling of the sulphation of calcined limestone and dolomite—a gas-solid reaction with structural changes in the presence of inert solids. *Chem Eng Sci*. 1988;43(5):1183-1193.

[18] Li S, Xu T, Sun P, Zhou Q, Tan H, Hui S. NOx and SOx emissions of a high sulfur self-retention coal during air-staged combustion. *Fuel*. 2008;87(6):723-731.

[19] Silcox GD, Kramlich JC, Pershing DW. A mathematical model for the flash calcination of dispersed calcium carbonate and calcium hydroxide particles. *Ind Eng Chem Res*. 1989;28(2):155-160.

[20] Damle AS. Modeling a Furnace Sorbent Slurry Injection Process. *Air Waste*. 1994;44(1):21-30.

[21] Milne CR, Silcox GD, Pershing DW, Kirchgessner DA. Calcination and sintering models for application to high-temperature, short-time sulfation of calcium-based sorbents. *Ind Eng Chem Res*. 1990;29(2):139-149.

[22] Borgwardt RH. Calcium Oxide Sintering in Atmospheres Containing Water and Carbon Dioxide. *Ind Eng Chem Res*. 1989;28(4):493-500.

[23] Mahuli SK, Agnihotr R, Jadhav R, Chauk S, Fan L-S. Combined calcination, sintering and sulfation model for CaCO3-SO2 reaction. *AIChE J*. 1999;45(2):367-382.

[24] Cheng J, Zhou J, Liu J, et al. Sulfur removal at high temperature during coal combustion in furnaces: a review. *Prog Energy Combust Sci*. 2003;29(5):381-405.

[25] Stanmore BR, Gilot P. Review—calcination and carbonation of limestone during thermal cycling for CO2 sequestration. *Fuel Process Technol*. 2005;86(16):1707-1743.

[26] Dennis JS, Hayhurst AN. Mechanism of the sulphation of calcined limestone particles in combustion gases. *Chem Eng Sci*. 1990;45(5):1175-1187.

[27] Hu N, Scaroni AW. Calcination of pulverized limestone particles under furnace injection conditions. *Fuel*. 1996;75(2):177-186.

[28] Baker EH. 87. The calcium oxide–carbon dioxide system in the pressure range 1—300 atmospheres. *J Chem Soc*. 1962;0(0):464-470.

[29] Khinast J, Krammer GF, Brunner C, Staudinger G. Decomposition of limestone: The influence of CO2 and particle size on the reaction rate. *Chem Eng Sci*. 1996;51(4):623-634.

[30] García-Labiano F, Abad A, de Diego LF, Gayán P, Adánez J. Calcination of calcium-based sorbents at pressure in a broad range of CO2 concentrations. *Chem Eng Sci*. 2002;57(13):2381-2393.

[31] German RM, Munir ZA. Surface Area Reduction During Isothermal Sintering. *J Am Ceram Soc*. 1976;59(9-10):379-383.

[32] Borgwardt R. H. Sintering of nascent calcium oxide. *Chem Eng Sci*. 1989;44(1):53-60.

[33] Nicholson D. Variation of surface area during the thermal decomposition of solids. *Trans Faraday Soc*. 1965;61:990.

[34] Borgwardt RH, Bruce KR, Blake J. An investigation of product-layer diffusivity for calcium oxide sulfation. *Ind Eng Chem Res*. 1987;26(10):1993-1998.

[35] Kocaefe D, Karman D, Steward FR. Interpretation of the sulfation rate of CaO, MgO, and ZnO with SO2 and SO3. *AIChE J*. 1987;33(11):1835-1843.

[36] Ramachandran PA, Smith JM. A single-pore model for gas-solid noncatalytic reactions. *AIChE J*. 1977;23(3):353-361.

[37] Ramachandran PA, Smith JM. Effect of sintering and porosity changes on rates of gas—solid reactions. *Chem Eng J*. 1977;14(2):137-146.

[38] Ramachandran PA, Doraiswamy LK. Modeling of noncatalytic gas-solid reactions. *AIChE J*. 1982;28(6):881-900.

[39] Wang W, Bjerle I. Modeling of high-temperature desulfurization by Ca-based sorbents. *Chem Eng Sci*. 1998;53(11):1973-1989.

[40] Levenspiel O. *Chemical Reaction Engineering*. 3rd ed. New York: Wiley; 1998.

[41] Szekely J, Evans JW. A structural model for gas—solid reactions with a moving boundary. *Chem Eng Sci*. 1970;25(6):1091-1107.

[42] Punbusayakul N, Charoensuk J, Fungtammasan B. Modified sulfation model for simulation of pulverized coal combustion. *Energy Convers Manag*. 2006;47(3):253-272.

[43] Tomanovic I, Belosevic S, Milicevic A, Tucakovic D. Modeling of calcium-based sorbent reactions with sulfur dioxide. *J Serbian Chem Soc*. 2015;80(4):549-562.

[44] Pigford RL, Sliger G. Rate of Diffusion-Controlled Reaction Between a Gas and a Porous Solid Sphere - Reaction of SO_2 with $CaCO_3$. *Ind Eng Chem Process Des Dev*. 1973;12(1):85-91.

[45] Hartman M, Coughlin RW. Reaction of sulfur dioxide with limestone and the grain model. *AIChE J*. 1976;22(3):490-498.

[46] Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: I. Isothermal, kinetic control. *AIChE J*. 1980;26(3):379-386.

[47] Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: II. Diffusion and transport effects. *AIChE J*. 1981;27(2):247-254.

[48] Christman PG, Edgar TF. Distributed pore-size model for sulfation of limestone. *AIChE J*. 1983;29(3):388-395.

[49] Simons GA, Garman AR. Small pore closure and the deactivation of the limestone sulfation reaction. *AIChE J*. 1986;32(9):1491-1499.

[50] Simons GA, Garman AR, Boni AA. The kinetic rate of SO2 sorption by CaO. *AIChE J*. 1987;33(2):211-217.

SAŽETAK

Pregled modela reakcija kalcinacije i sulfatizacije sorbenta na bazi kalcijuma

Ivan Tomanović, Srđan Belošević, Aleksandar Milićević, Nenad Crnomarković

Univerzitet u Beogradu, Institut za nuklearne nauke Vinča, Beograd, Srbija

(Stručni rad)

Više modela koji razmatraju reakcije sprašenog sorbenta sa štetnim gasovima je razvijeno u prethodnom periodu. U ovom radu je predstavljen detaljan pregled dostupnih modela za potencijalnu primenu u numeričkim simulacijama direktnog unošenja sprašenog sorbenta na bazi kalcijuma u ložište parnog kotla, sa osvrtom na složenost modela i potrebnim računarskim resursima. U zavisnosti od modela, moguća su odstupanja u rezultatima, izlaznim podacima i utrošenim računarskim resursima. Pojedini autori odvajaju model reakcija kalcinacije, uparen sa modelom sinterovanja, a nakon njih modeliraju sulfatizaciju. Drugi autori pretpostavljaju da je kacinacija trenutna, a trude se da modelima opišu reakciju sulfatizacije, dok efekte sinterovanja uzimaju kao parametar kroz koeficijent efikasnosti. Jednostavni modeli kvantifikuju sveukupne uticaje reakcije, dok se kod složenijih modela ulaže napor da se opiše i objasni unutrašnja struktura i reakcije čestice, kroz različite pristupe modeliranju unutrašnje strukture.

Ključne reči: sorbent, kalcijum, kalcinacija, sinterovanje, sulfatizacija, model