Calcium based sorbent calcination and sintering reaction models overview

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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

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-SOx 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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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.

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 penetration in 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\textsubscript{3} [9,14,15,17,21–23], or Ca(OH)\textsubscript{2} [13,15]) the endothermic calcination reaction is modeled as:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]  
\[ \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \] (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]:

\[ \text{CaO} + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4 \] (2)

In this exothermic reaction, CaO particles react with SO\textsubscript{2} and oxygen from the surrounding gas so that CaSO\textsubscript{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:

\[ R_c = R_{c0} e^{-\frac{E_a}{RT}} \] (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 \text{CO}_2 in the mixture and the equilibrium pressure \(P_{eq}\), by the equation [25]:

\[ R_c = k_c(P_{eq} - P_i-cP) \] (4)

Silcox et al. [19] also related the calcination rate with the \text{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):

\[ R_c = k_c(P_{eq} - P_i) \] (5)

Dependences of the rate coefficient \(k_0(ke=1.22\ e^{-4026/\text{T}}[25])\) 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:
The correction (6) corresponds to the research of Barker [28], as the CO₂ concentration was found to negligibly influence the calcination rate if the partial pressure of CO₂ 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:

\[ R_e = k e^{-\frac{P}{P_{eq}}} \]  

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:

\[ X(t) = 1 - \left( 1 - e^{-k t} \right)^3 \]  

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]:

\[ \frac{d(N_{CaO_3})}{dt} = -k N_{CaO_3} S_{CaO_3} M_{CaO_3} \]  

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):

\[ X(t) = 1 \cdot e^{-k t} \]  

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

\[ \sum_{k=1}^{n} S_{CaO_3}^k \left( X_k(t_k) \cdot X_i(t_{i-1}) \right) \]  

### 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]:

\[ \begin{pmatrix} S_k \ - \ S \\ S_k \end{pmatrix} = k t \]  

Coefficients \( \gamma \) and \( k_s \) are correlated to partial pressures of H₂O and CO₂, 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:

\[ S_{CaO_3}^k = S_{CaO_3} \left( 1 - \left( K_i t_i \right)^{1/\gamma} \right) \]  

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:
\[
\frac{ds}{dt} = -k_s (S - S_m)^2
\]  \hspace{1cm} (14)

In this model the value of the coefficient \(k_s\) is a function of CO2 partial 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 \(S_m\), 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 CaSO4 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:

\[
r = \frac{1}{W} \frac{dn}{dt} = \eta \frac{k_{\text{surf}} c^n}{\rho}
\]  \hspace{1cm} (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:

\[
\eta_{\text{eff}} = e^{\frac{\Delta H}{RT}} \left( \frac{k_0}{k_0 + \frac{C_{\text{ref}}}{C'}} \right)
\]  \hspace{1cm} (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 SO2 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 CaSO4, 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.

\[
r_{\text{SO2}} = \frac{c_{\text{SO2}}}{k_v S_z + \frac{L}{D_z} S_{\text{avg}}}
\]  \hspace{1cm} (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:

\[
S_i = \frac{3(1 - \varepsilon)\left(2g_i^2 - n_{i\text{eff}}f\left(g_i, \lambda_i\right)\right)}{r_0\left(2 - n_{i\text{eff}}\left(1 + \frac{3}{2}\lambda_i\right)(1 - \lambda_i)^2\right)}
\]  

(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 Borgwardt 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:

\[
k_{\text{b}} = 2.655 S_8^2 p_{SO_2}^{0.64} e^{\frac{-36600}{RT}}
\]  

(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 Koçafı and coworkers [35]. Simons and Pigford [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.
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### Table 1: Overview of major equations governing calcination, sintering and sulfation rates in models by different authors

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<td>Sintered calcium oxide surface at time step ( k )</td>
<td></td>
</tr>
<tr>
<td>[11]</td>
<td>Calcination ( \frac{dR_c}{dt} = \frac{M}{\rho} k_c A )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \left( \begin{array}{c} P_{eq} - P \end{array} \right) P_{eq}^{-1} &lt; P &lt; P_{eq} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 ( P_s &lt; P_{eq} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[15,21]</td>
<td>Calcination extent ( X=1 - \left( 1 - k \frac{t}{d_{\text{calc}}} \right)^{1} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaCO(<em>3) rate constant ( k</em>{CaCO_3} = 10.303 e^{\frac{10380}{T}} )</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>CaCO(<em>3) rate constant ( k</em>{CaCO_3} = 10.303 e^{\frac{10380}{T}} )</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Ca(OH)(<em>2) rate constant ( k</em>{Ca(OH)_2} = 53.87 e^{\frac{8100}{T}} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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$_2$ in surrounding gas
- $c_{ref}$ / 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
REFERENCES

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SAŽETAK

Pregled modela reakcija kalcinacije i sulfatizacije sorbenta na bazi kalcijuma

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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