Numerical analysis of the hydration of calcium oxide in a fixed bed reactor based on lab-scale experiments^A

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Abstract

Thermochemical energy storage is gaining popularity as one possibility to integrate renewable energies into existing energy systems by providing large energy storage capacities at low costs. Systems based on the reversible reaction of calcium oxide and steam forming calcium hydroxide, are especially promising as the storage material is cheap, abundantly available, and non-toxic. Potential applications are the storage of industrial process heat, concentrated solar power, or novel power to heat concepts. Reactor design is increasingly accompanied by simulations. However, for indirectly heated fixed bed reactors, there currently exist only simulation models that are validated at 200 kPa. Therefore, a model coupling heat and mass transfer as well as the chemical reaction is set up and validated with recently published experimental data for an indirectly heated fixed bed with an operating range between 8.7 and 470 kPa. The simulation reveals that in this design with a thin reactive layer mass transfer is not limiting, while thermal losses have a significant influence and thus have to be accounted for in the model. Furthermore, at steam pressures above 200 kPa the reaction kinetics is not limiting and simplified kinetic models describe the reactor reasonably well. Whereas for lower pressures (below 50 kPa), the reaction kinetics becomes limiting and none of the analyzed kinetic models predict the reaction rate exactly. We conclude that the reaction kinetics at low steam pressures (8.7-50 kPa) is very sensitive towards pressure and temperature. The results can assist the design and upscaling of reactors for technical applications and show the necessity for further studies at low pressures.

Keywords: thermochemical energy storage; reaction kinetics; calcium oxide / hydroxide; fixed bed reactor; 2D simulation

1. Introduction

Thermal energy storage is considered an important component of the energy transition towards renewable energies as it can provide large storage capacities at comparatively low costs. Thermochemical energy storage is attractive due to its high energy densities. Systems based on the reaction of CaO with steam are promising for thermochemical energy storages as both reactants are cost-efficient [1] and non-toxic [2]. Besides energy storage, the application of CaO is also under development for heat pumps [3], carbon capture and storage [4] and sorption-enhanced hydrogen

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production [5,6]. The reaction $CaO_{(s)} + H_2O_{(g)} \rightleftharpoons Ca(OH)_{2(s)} + \Delta H$ was already addressed by several studies. Cycle stability of the material was proven in different works [7,8]. Various authors characterized the thermodynamic equilibrium of the reaction (see e.g. [9]) and its reaction enthalpy [7]. Lately, several different reaction kinetic models were proposed. Schaube et al. determined a model with measurements at steam partial pressures between 17.6 and 95.6 kPa for particles with a median size of $5.26 \,\mu m$ [7]. They split the model for the hydration into two parts depending on the distance to the thermodynamic equilibrium. A simplified model consisting of only one adjustable parameter was used by Shao et al. [10]. Criado et al. stated a model with a shrinking core mechanism based on measurements in a temperature range from 400 to 560°C and partial steam pressures between 50 and 100 kPa [9]. They also analyzed different particle sizes between 100 and 2000 µm and as a consequence introduced a factor accounting for the particle size. A first order model was proposed by Angerer et al. [11] based on measurements with a steam partial pressure between 50 and 500 kPa and a median particle size of 345.5 µm. Blamey et al. [4] analyzed the hydration and proposed a shrinking core model. They based their model on measurements with particle sizes larger than 500 µm at low steam partial pressures (0.002, 0.26 and 6.8 kPa) and temperatures of 200, 300 and 400 °C. Lin et al. [12] analyzed the hydration and dehydration at high temperatures up to 750 °C based on thermogravimetric measurements. They proposed a reaction kinetic model that was only slightly affected by the particle diameter (to the power of -0.11). In a later study, Lin et al. [13] investigated the effect of the cycle number and adapted the previous model. They found that the reaction rate was proportional to the exponential function of 1.088 divided by the number of cycles. Matsuda et al. [14] derived a reaction kinetic model based on measurements in a temperature range of 80 to 450 °C and steam concentrations between 1.5 and 15 vol%.

Currently, there are mainly three types of reactors addressing the hydration of CaO and also the reverse reaction experimentally. Firstly, fluidized bed reactors are used in experimental set-ups. Here, an inert gas is used to fluidize the bulk and supply or extract the reactant gas. Since the storage material is not easily fluidized, a significant fraction of easy to fluidize material has to be added [15] or the fluid inlet has to be designed in a special way [16]. This type of reactor offers high heat transfer coefficients. Secondly, there are directly permeated fixed bed reactors where gas streams directly through the bulk but the volume flow is too small to fluidize the bulk. Again, high heat transfer coefficients can be reached but channeling effects might become difficult [17]. Thirdly, in indirectly heated fixed bed reactors, the reactant gas is physically separated from the heat transfer fluid so there is no direct contact with the bulk. Therefore, this type of reactor has the lowest parasitic losses but also low heat transfer coefficients [18]. All reactor concepts have their specific advantages and disadvantages and the most suitable reactor concept varies, depending on the operation conditions of the intended process application. However, all concepts require further research to be applied broadly.

In order to design thermochemical energy storage reactors for technical applications, simulation models which couple reaction kinetics with heat and mass transfer in the reactor are required. Some simulation models of this reaction system with the different reactor concepts have already been analyzed. Previous numerical studies predominately focused on fluidized beds or directly permeated bulks. Criado et al. [19] modelled their bubbling fluidized bed reactor with two homogenous phases, a gas phase and an emulsion phase. Both phases were perfectly mixed and interchanging mass. By adjusting the mass transfer factor between both phases, they validated their model with their experimental data. A similar

model was used by Angerer et al. [11] to propose a design for an up-scaling of a bubbling fluidized bed. Schaube et al. [20] set up a model for a CaO bed that was permeated by a nitrogen/steam mixture. Heat and mass transfer as well as the chemical reaction were modelled. Furthermore, they compared the simulation to measurements of the reactor [21]. In cases that were not limited by the reaction rate they observed good agreement with the experiment. However, it was found that in cases of high gas flows, the reaction was limited by the reaction kinetics and in these cases the reaction rate was overestimated, indicating that the system is sensitive to the correct kinetic expression. Nagel et al. described a general model for a permeated fixed bed reactor [22]. They coupled the heat and mass transfer between the solid and gaseous phase considering the chemical reaction and local non-equilibrium. Shao et al. [10] used a simplified form of that model and applied it on a CaO/Ca(OH)₂ fixed bed that was permeated by a nitrogen/steam mixture. They found that the influence of the kinetics was small. Furthermore, the consideration of local non-equilibrium was only relevant for larger particles (500 μ m). Nagel et al. [23] compared the kinetic model by Shao et al. to the more detailed model by Schaube et al. in a 1D simulation and found that the reactor was mainly limited by heat transfer and consequently, the results of both models were similar. However, their results have not been validated by experimental data.

In case of indirectly heated fixed bed reactors for CaO/Ca(OH)₂ the literature is scarce. A fixed bed reactor that was indirectly heated by air [24] was modelled by Linder et al. [25] as well as by Ranjah and Oztekin [26]. The first authors used a 2D model and after the introduction of a loss term, the simulation matched the experiment reasonably well. Ranjah and Oztekin set up a 3D model of the reactor and showed that 3D effects are not distinct at high porosities of 0.8. When the mass transport becomes limiting due to low porosities, this effect is more dominant. However, they validated the model only qualitatively. The two simulation models of an indirectly heated fixed bed reactor have been validated only for a single hydration pressure of about 200 kPa and used data from a 20 kg pilot scale reactor [24]. Therefore, our aim for this study is to set up a model for the hydration of CaO in an indirectly heated fixed bed reactor and validate it for a more comprehensive operating range. The dehydration is beyond the scope of this paper. Schmidt et al. recently published the results of a 2.4 kg $Ca(OH)_2$ bulk for an extended operating range between 8.7 and 470 kPa steam pressure [27,28]. The specific design of this reactor minimizes heat and mass transfer resistances to a realistic large scale design limit and is therefore chosen to provide validation data for the simulation. In addition, previous studies did not compare the influence of different reaction kinetic models at operating conditions where the reaction kinetics becomes limiting. Thus, we tested different reaction kinetic models and their extrapolations to the conditions of the experiments. This is especially important for the pressure range between 8.7 to 50 kPa as no model has been validated there, yet. As the reaction kinetics is independent of the reactor type, the achieved results can also be transferred to other reactor concepts.

2. Model formulation

In this section, firstly the reactor and the experimental procedure are described. Then, modelling equations as well as boundary and initial conditions are stated. Finally details of the numerical implementation are given.

2.1 Reactor description

The modelled indirectly heated fixed bed reactor as well as the conducted experiments is already described in [27,28]. All parameters of the reactor and the experimental procedure that are relevant for



Figure 1 Scheme of the cross section of the simulated reactor and pressure vessel.

modelling are given here. Further details (e.g. regarding instrumentation, dehydration experiments or the overall setup) can be found in the corresponding studies.

Fig. 1 shows the reactor in its pressure vessel. The steam inlet connects the pressure vessel via a valve with the evaporator. Since we solely analyze the hydration reaction, the reactant gas only flows into the bulk and is consumed by the reaction. There are two 1600 mm x 150 mm x 10 mm loose powder bulks containing about 1.8 kg CaO (corresponding to 3600 kJ_{chem}) situated at the up- and downside of a pillow plate heat exchanger. The pillow plate hermetically separates the bulk and reaction gas (steam) from the air which serves as heat transfer fluid (HTF). Seven thermocouples are placed equidistantly in the middle of one bulk (the detailed position is given in Fig. 3), two others at the air inlet and outlet, respectively. A probe measuring the steam pressure is located inside the vessel. As the reaction bed is very thin in this reactor design, heat and mass transport resistances have been minimized to application relevant values. Thus if these mechanisms are limiting for this design, they will be even more distinct for future upscaling. Furthermore, results regarding the reaction kinetics from this set up can be transferred to any other reactor because the reaction kinetics does not depend on the reactor design. To account for thermal losses, electric heat tracings are installed around the pressure vessel except for the air outlet flange. Furthermore, the whole pressure vessel is insulated with 45 mm mineral wool (thermal conductivity of 0.1 W/(m K)).

2.2 Experimental procedure

Before the start of each experiment, the air flow and the heat tracings were set to the temperatures given in Tab. 1 and heated the reactor until a steady state was reached. Experiments from two different measurement series were chosen for the validation. For the high pressure range the initial temperature and the mass flow was kept constant, and hydration has been performed at three different pressures (200, 270 and 470 kPa compare Tab. 1). In the low pressure range a measurement series has been performed where the difference between the preheating temperature and the equilibrium temperature at the respective water vapor pressure has been kept constant (for more details on the experimental conditions please refer to [27,28]).

During the heating phase, the pressure vessel was under vacuum and disconnected from the evaporator. Steam at the respective pressure was prepared in the evaporator. When the temperatures in the reaction bed reached a steady state, the state was held for another three minutes. Then, the reactor was connected to the evaporator and the steam induced the exothermal hydration of CaO. The local increase of temperatures in the bulk and at the air outlet was measured. The conversion was measured by the decrease of the filling level of the evaporator. The decrease of the liquid water volume in the evaporator corresponds to the steam that is consumed by the hydration since the pressure is held equal. Consequently, the conversion is an integral measurement of the whole reaction bed. Experiments were finished when all temperatures reached a steady state, again.

Steam pressure	Air inlet temperature	Air mass flow	Initial bulk temperature
in kPa	in °C	in kg/h	in °C
470	500	25.8	490
Reference: 270	500	25.8	490
200	500	25.8	490
50	350	15.5	340
20	310	15.5	300
8.7	280	15.5	280

Table 1 Parameters of the analyzed experiments.

2.3 Governing and kinetic equations

The following assumptions are made in order to derive reasonable simplifications for the model:

- A two dimensional model is sufficient to describe the reaction bed (a previous study showed that the 3D effects of geometry and flow profile for reaction beds with a porosity greater than 0.8 can be neglected [26])
- (2) There is a symmetry plane in the middle of the air channel (despite the single-sided steam inlet, pressure probes indicate isobaric conditions on the surface of both bulks)
- (3) The CaO/Ca(OH)₂ bulk can be considered as a continuum which fills the whole space between heat exchanger plate and filter plate
- (4) Effective heat conductivities of CaO and Ca(OH)₂ bulks are the same and constant (independent of the temperature, steam pressure and cycle number)
- (5) Heat transfer based on thermal radiation is negligible for the used small particles (based on [20])
- (6) The thermal mass of the steam can be neglected compared to the much higher reaction enthalpy. It was calculated that the sensible heating up of the steam to equilibrium temperature, requires between 2 % and a maximum of 5 % of the released enthalpy of reaction.
- (7) The filter plate can be modelled as a metal plate with the same mass
- (8) The heat transfer in the HTF channel can be approximated by correlations for flat plates

The model consists of 3 different domains. The air domain represents the air flow through the heat exchanger. One steel domain is used for the heat exchanger and one for the filter plate. The most important domain is the bulk describing also the conversion of CaO to $Ca(OH)_2$. Based on the assumptions and simplifications, the governing and kinetic equations were derived as follows. For each

domain mainly energy balances are required to describe the reactor. A general form is given in eq. (1) for all domains:

$$\rho_{i}c_{p,i}(T)\frac{\partial T}{\partial t} - \nabla \cdot (\lambda_{i}\nabla T) + \rho_{i}c_{p,i}(T)\boldsymbol{u} \cdot \nabla T = \Delta H(T) \cdot \frac{\partial X}{\partial t} \cdot \frac{n_{\text{CaO}}(t=0)}{V_{\text{bulk}}}, \quad i$$
(1)
$$\in \{\text{bulk, steel, air}\}.$$

 ρ_i describes the density of the domain material i, $c_{p,i}(T)$ its temperature dependent isobaric heat capacity, T the temperature, t the time, λ the thermal conductivity and u the vector of velocities. $\Delta H(T)$ is a function for the molar reaction enthalpy, $X = 1 - (n_{CaO}(t)/n_{CaO}(t=0))$ is the conversion and $n_{CaO}(t=0)/V_{bulk}$ the molar density of CaO at time 0. According to assumption (6) the steam phase is not considered in the energy balance. Depending on the domain different terms can be removed in eq. (1). In the bulk there is no movement (u = 0) and consequently only heat conduction and the reaction heat lead to a temperature change of the sensible CaO/Ca(OH)₂ mass. For the air and steel domains, there is no reaction ($\frac{dX}{dt} = 0$). In the steel domains, the velocity is additionally zero. For the air domain, the velocity is determined by a mass balance

$$\frac{\partial \rho_{\rm air}}{\partial t} + \nabla \cdot (\rho_{\rm air} \boldsymbol{u}) = 0 \tag{2}$$

to account for density changes due to temperature gradients. Compared to solving the full Navier-Stokes equations, a simpler approach is sufficient here. Due to the pillow plates and the high volume flow the air is well mixed and the heat transfer coefficient from the air to the heat exchanger is not limiting.

Mass transfer for the steam phase can be considered by a mass balance of the steam with incorporation of Darcy's law:

$$\frac{\partial}{\partial t}\epsilon\rho_{\text{steam}} - \nabla \cdot \left(\rho_{\text{steam}} \cdot \frac{K}{\mu} \cdot \nabla p\right) = Q_{\text{m}} \quad . \tag{3}$$

 ϵ is the porosity, p the pressure, μ the dynamic viscosity, K the permeability and $Q_{\rm m} = -\frac{\partial X}{\partial t} \cdot \frac{n_{\rm CaO}(t=0)}{V_{bulk}} \cdot M_{\rm steam}$ the mass sink due to the hydration. The permeability can be calculated with the particle diameter $d_{\rm p}$ and the porosity ϵ by the Carman-Kozeny relationship $\left(K = \frac{d_{\rm p}^2 \epsilon^3}{180(1-\epsilon)^2}\right)$.

To solve eq. (1) for the bulk domain, a model that describes the conversion rate is required. The general form of most published kinetic models is [29]

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k(T) \cdot h(p, p_{eq}) \cdot f(X). \tag{4}$$

Here, k(T) is a function accounting for the temperature, usually described by the Arrhenius equation $k(T) = A \cdot \exp(-E/(RT))$ where A is the pre-exponential factor, E the (apparent) activation energy and R the universal gas constant. The function h depends on the steam pressure p and the equilibrium pressure p_{eq} and describes the influence of the distance to the thermodynamic equilibrium. There are also formulations based on the local temperature and thermodynamic equilibrium temperature T_{eq} . f(X) is a function of the conversion describing the growth mechanism during the reaction. An overview of the applied kinetic models is given in Tab. 2. Fig. 2 shows the conditions of the underlying measurements of these models as well as the temperature ranges and pressures occurring in the

analyzed experiments. Angerer et al. used non-isothermal measurements and therefore the dotted lines represent the pressures of their measurements.

As a reference, a simple kinetic model regarding a term for conversion, a term for the distance to the equilibrium as well as a constant factor is postulated (eq. 5), which yields a high reaction rate, and is from now on called "Fast". It is used in the simulations unless otherwise stated.

$$\frac{\mathrm{d}X}{\mathrm{d}t} = 15\frac{1}{\mathrm{s}} \cdot \frac{T_{\mathrm{eq}} - T}{T_{\mathrm{eq}}} \cdot (1 - X). \tag{5}$$

Besides kinetic models there are also different formulations for the equilibrium pressure. In this study, the equilibrium line of Samms and Evans [30] is used as the equilibrium formulation for all kinetic models:

$$p_{\rm eq} = 100 \,\mathrm{kPa} \cdot \exp\left(-\frac{11375 \,\mathrm{K}}{T_{\rm eq}} + 14.574\right).$$
 (6)

Table 2 Parameters of kinetic models for the hydration of CaO.

	A in 1/s	E in J/mol	$h(p,p_{ m eq})$ or $h(T,T_{ m eq})$	f(X)
Fast	15	0	$rac{T_{ m eq}-T}{T_{ m eq}}$	1-X
Criado et al. 2014 [9]	$\frac{3.5\cdot10^{-4}}{d_{\rm p}[\mu{\rm m}]}$	-59,400	$\frac{p_{\rm H_2O}-p_{\rm eq}}{p_{\rm total}}$	$3(1-X)^{\frac{2}{3}}$
Angerer et al. 2018 [11]	390,827	87,460	$\left(\max\left\{\frac{1}{\left(\frac{p_{H_2O}}{p_{eq}}\right)}\right\}-1\right)^{3.43}$	1-X
Schaube et al. 2012 far from eq. [7]	13,945	89,486	$\left(\frac{p_{H_2O}}{p_{\rm eq}}-1\right)^{0.83}$	$3(1-X)[-\ln(1-X)]^{\frac{2}{3}}$
Schaube et al. 2012 close to eq. [7]	$1.0004 \\ \cdot 10^{-34}$	-443,427	$\left(\frac{p}{10^5 \text{Pa}}\right)^6$	1-X



Figure 2 Compilation of the analyzed experiments (solid line) and the underlying measurements of the used kinetic models (dots and squares). Angerer et al. used dynamic measurements therefore the analyzed pressure levels are shown as dotted lines.

2.4 Initial and boundary conditions

Fig. 3 shows the geometry modeled in the simulation with the applied boundary conditions. Due to the symmetry boundary condition (B1) in the middle of the air channel, only one half of the reactor needs to be considered. At the air inlet (B2), the measured temperature and mass flow of the air is used. At the air outlet (B3) ambient pressure is assumed. All other external boundaries are adiabatic (B4). According to assumption (8) a correlation for a parallel plate duct is used [31] for the heat transfer from the air flow to the heat exchanger plate (yielding e.g. 250 W/(m² K) for an air mass flow of 25.5 kg/h). The heat transfer coefficients between bulk and steel (heat exchanger or filter plate) are assumed to be large-1000 W/(m²K) are arbitrarily chosen. Calculations based on the VDI heat atlas [31] indicate that the used value is rather an underestimation due to the small particle sizes. However, an exact determination of the value is not required since it is much larger than the heat transfer inside the reaction bed, thus the heat conduction inside the bed will always dominate the overall heat transfer. The pressure measured during the experiment by the pressure probe inside the vessel is used as an input. Therefore, the first measured pressure is the initial value of the simulation. Initially, the bulk consists solely of CaO with a bulk density of 378 kg/m³, resulting in a porosity of about 88.5 %. At the beginning, the temperatures of the filter, the bulk, and the heat exchanger plate are set to the mean measured bulk temperature.



Figure 3 Scheme of the 2D model including the position of the thermocouples. Boundary conditions are: symmetry (B1), measured mass flow and temperature (B2), ambient pressure (B3), adiabatic boundaries (B4).

2.5 Numerical procedure

A structured rectangular mesh is used with smaller elements at the bottom and top of the bulk. The mesh consists of 330 vertical elements (i.e. approximately 5 mm per element). 1 horizontal element is employed for the air domain, 10 for the heat exchanger, 100 for the bulk and 10 for the filter plate. For a mesh refinement study, the simulation at a steam pressure of 270 kPa is used and the time until 95 % of CaO is converted is employed as the characteristic value. A refinement of the mesh by a factor of 10 results in a change of the characteristic value below 0.1 %. Hence, the used mesh is assumed to be sufficiently fine. Along with the boundary conditions, the parameters listed in Tab. 3 are applied. For the properties of air and steam, built-in material properties of COMSOL Multiphysics 5.3a are used. The bulk density and the isobaric heat capacities are average values depending on the state of conversion.

Table 3 Used parameters

Parameter	Unit	Symbol	Value		Reference
Heat conductivity CaO/ Ca(OH) ₂	W/(m K)	$\lambda_{ m bulk}$	0.4		[32]
Isobaric heat capacity CaO	J/(kg K)	$c_{\rm p,bulk}(T)$	923	at 450 °C	[33]
Ca(OH) ₂		•	1504	at 450 °C	
Bulk density CaO	kg/m³	$ ho_{ m bulk}$	378	Porosity	
Ca(OH) ₂			500	$\epsilon = 0.8$	
Reaction enthalpy	kJ/mol	$\Delta H(T)$	101	at 450 °C	[33]
Particle diameter	μm	d_p	5.5		[28]
Ambient temperature	°C	$T_{\rm ambient}$	25		
Gas constant	J/(mol K)	R	8.314		
Heat conductivity steel	W/(m K)	$\lambda_{ m steel}$	20.8	at 450 °C	
Density steel	kg/m³	$ ho_{ m steel}$	8000		
Isobaric heat capacity steel	J/(kg K)	C _{p,steel}	500		

3. Results and discussion

3.1 Estimation of thermal losses and model calibration

Fig. 4 presents the initial simulation results (solid lines) and the corresponding experimental measurements (solid lines with symbols) for the temperatures and the conversion in the reactor without consideration of thermal losses. The conducted experiment was a hydration of CaO at a starting temperature of 490 °C with steam at a pressure of 270 kPa. For clarity, only three temperatures (T1, T3, and T7, highlighted points in Fig. 3) are plotted. In the experiment the evacuated reactor is connected to the evaporator after 3 minutes and the steam pressure rises within seconds to 270 kPa. Consequently, CaO reacts exothermally with steam forming Ca(OH)₂. Accordingly, the temperatures in the reaction bed increase rapidly. Within the first five minutes simulated and experimental temperatures rise simultaneously and reach the same maximum temperature. The reached maximum temperatures accord to the thermodynamic equilibrium temperature (dotted line) of the reaction at the measured pressure. Subsequently, temperature plateaus are hold for different length of time according to the direction of the HTF flow. At T1 (beginning of the reaction bed) the cooling load is high due to the incoming air flow thus the reaction proceeds fast and after 20 minutes the temperature starts to decrease again. The temperature decrease indicates that most of the material in the region has completely reacted and therefore the heat released by the reaction decreases. In the middle of the reactor (T3) the temperature plateau is held longer, while at the end of the reaction bed (T7) the plateau is held for the longest time since cooling load is initially lower in this region of the reaction bed. The qualitative temperature courses accord well to the results of other simulations of indirectly heated fixed beds [25,26]. These courses are characteristic for reactions limited by heat transfer which was also reported by [20] and [23]. As the reaction is not limited by mass transport and the reaction rate is sufficiently high, the temperatures rise until the equilibrium temperature is reached. The temperature and conversion courses are then largely determined by how fast the heat is transported out of the reactive bulk. It is obvious that heat is removed far quicker in the experiment than in the simulation. An energy balance for the air domain shows that only about 0.21 kWh of the reaction enthalpy that accounts for 1 kWh were taken up by the air flow. Consequently, this first simulation revealed that even though huge efforts have been made to avoid heat losses (insulation and heat tracings) thermal losses of the reactor largely affect the reaction progress. Therefore, a method to account for the thermal losses of the reactor has been determined in the next step.



Figure 4 Temperature profiles (top) and global conversion (bottom) of simulation (sim.) and experiment (exp.) for the hydration at a steam pressure of 270 kPa.

An exact representation of the physical heat loss mechanisms of radiation, convection and conduction, in this reactor is rather complex and would require a detailed 3D simulation. Furthermore, the required measurements to validate such a thermal loss model, like the temperature of the pressure vessel and the gas phase at various locations, are not available from the experimental set up. Therefore, we integrated two simplified global thermal loss mechanisms and determined the respective heat transfer coefficients by the available experimental data.

The first implemented equation represents thermal losses which are prevalent during the ongoing exothermal hydration reaction. It is assumed that due to the large temperature difference between the reaction temperature in the bulk (e.g. in Fig. 4 560 °C after hydration is initiated) and the preheating temperature of the pressure vessel (500 °C) convective heat transfer through the gas phase is dominating. Since the bulk is highly porous (88.5 %) it is further assumed, similar to the approach of Linder et al. [25], that free convection occurs in the whole volume of the bulk. Consequently, the heat transfer is described by a driving temperature difference between the pressure vessel and the bulk temperatures as well as by a volumetric heat transfer coefficient $k_{v,global}^*$ (compare eq. 7):

$$\dot{Q}_{\text{global}} = k_{\text{v,global}}^* \cdot \left(T_{\text{pressure vessel}} - T_{\text{bulk}} \right)$$
 (7)

In addition to the losses which occur while the exothermal reaction proceeds, it can be seen from Fig. 4 that when the experiment reaches steady state conditions (minute 90 to 100), the bulk temperatures stabilize around 491 °C (T1) , 493 °C (T3) and 485 °C (T7). This reveals that, even though the reactor is equipped with heat tracings and insulation, parts of the set up must be colder than the set temperature of 500 °C. Additionally, it is obvious that the losses are slightly different at different regions in the reaction bed since different temperature plateaus arise for T1, T3 and T7. To account for these heat losses, a second equation is implemented and the reaction bed is split into three regions (left, middle and right, shown in Fig. 3):

 $\dot{Q}_{\rm local,j} = -k_{\rm v,j}^* \cdot (T_{\rm bulk} - T_{\rm ambient})$ j \in {left, middle, right} (8) As both loss mechanisms are superimposed, they had to be determined together. Therefore, a two-step approach was chosen. In the first step we varied $k_{\rm v,global}^*$ in a range from 1000 to 1750 W/(m³K) in steps of 250 W/(m³K) and $k_{\rm v,left}^*$ and $k_{\rm v,middle}^*$ in the range of 0 to 100 in steps of 20 W/(m³K) as well as $k_{\rm v,right}^*$ in 25 W/(m³K) steps between 50 and 200 W/(m³K) in order to match the steady-state part after the reaction. In the second step, parameters fitting the measurements best were additionally used in a sensitivity study covering the step width of each parameter in order to match the overall conversion best. The parameters $k_{\rm v,global}^* = 1400 \text{ W/(m³K)}$, $k_{\rm v,left}^* = k_{\rm v,middle}^* = 60 \text{ W/(m³K)}$ and $k_{\rm v,right}^* = 125 \text{ W/(m³K)}$ were determined in this way.

These parameters are mainly a mathematical fit. Nevertheless, the magnitude can be discussed physically. $k_{v,global}^*$ represents the interaction with the casing pipe that has the largest heat transfer area. As the loss parameters are based on the bulk volume this parameter becomes the largest. Thermal losses to spots of the casing pipe that were not heated sufficiently (e.g. the frame or flanges) are described by $k_{v,left}^*$, $k_{v,middle}^*$ and $k_{v,right}^*$. While it is a coincidence that $k_{v,left}^*$ and $k_{v,middle}^*$ have the same magnitude, $k_{v,right}^*$ is larger because the flange on the right side was not heated.

Fig. 5 shows the temperature and conversion trends of the simulation with implemented loss terms. The course of the simulated temperatures matches the experimental data very well, showing similar reaction times. Small differences occur for T3 and T7 as in the experiment the thermodynamic equilibrium temperature is hold for a shorter duration followed by a lower decreasing rate, indicating that the Fast model overestimates the reaction rate for high conversions. Nevertheless, the match of the global conversion profile is very good. It is clear, that the determined parameters for the thermal losses are only strictly valid for the presented reactor at the applied operating conditions (temperature, pressure). However, the description of the losses is a reasonable first approximation since validated models for the exact representation of, for example the convective heat transfer in the reacting bulk, are not yet available and furthermore could not be validated by this set up. Moreover, the analysis revealed that heat losses had a large effect on the performance of the presented reactor. This is an important finding in order to obtain a comprehensive understanding of the experimental data. In general it can be concluded that if the hydration reaction is induced by a sudden pressure increase, the resulting large temperature difference between reaction temperature and the colder reactor casing can cause significant thermal losses. Thermal losses should therefore always be considered carefully for the design of future thermochemical reactors and additional experimental set ups are required to validate the physical loss terms.



Figure 5 Hydration simulation with incorporated loss mechanisms at a steam pressure of 270 kPa.

3.2 High pressure simulations

3.2.1 Model validation

As the loss terms have been determined only for a single steam pressure (270 kPa), it has to be tested whether extrapolations to lower or higher steam pressures (with associated bulk temperatures) are valid. Fig. 6 displays the pressure variations between 200, 270 and 470 kPa. Apart from the pressure all other parameters remain unchanged. In general, with higher steam pressures the maximum temperatures, given by the thermodynamic equilibrium, increase. With higher temperatures the thermal losses also increase and consequently, the reaction duration at 470 kPa is the shortest. The initial increase and the maximum temperatures are matched very well by the simulation. Since the thermodynamic equilibrium temperature is reached at all pressures, there is no limitation of the mass transport or the reaction kinetics in the experiment, because both limitations would lead to temperatures below the thermodynamic equilibrium. So the reaction is limited by the heat transfer.

The profiles for T1 are close to the experimental results except for a slightly steeper temperature decrease during the cooling phase at 200 kPa. The maximum deviations between simulation and experiment trends have been determined. In general, deviations range between 1.7 % and 3.5 %. However, there are two major exceptions. Firstly, the measurement of T3 at 470 kPa deviates 8.7 % from

the simulation. This difference can be attributed to changes of the bulk in the middle of the reactor which were observed after cycling in the experiments (for details refer to Fig. 10 in [27]). The steam inlet is situated in the middle of the reactor so that the pressure shock after opening the valve might explain a change in the bulk that is more pronounced for T3 than for the other positions. The pressure shock is especially large at the highest pressure of 470 kPa. Consequently, assuming that the bulk fills the whole space between heat exchanger and filter plate with a constant height leads to a small overestimation of the amount of material present in the middle region in the simulation model. Secondly, for T7 also a major deviation of 10.9 % occurs at the 470 kPa experiment where the temperature plateau is longer in the simulation than in the experiment. In contrast, the temperature plateau of T7 at 200 kPa is shorter in the simulation than in the experiment. This indicates that the influence of the loss term on the reaction time is guite sensitive in this region of the reaction bed. Due to the temperature dependence of the loss terms, thermal losses at the higher maximum temperature of 600 °C (470 kPa) at T7 are slightly underestimated in the simulation. Thus, this results in a later temperature decrease resulting in a comparatively large deviation. Accordingly, at the lower temperature of 540 °C (200 kPa) thermal losses are slightly overestimated. This is not the case for the beginning of the reaction bed (T1) because in this area the influence of the cooling load of the incoming cold air on the reaction time is more pronounced than in the rear region of the reactor.

Despite the differences in the local temperature profiles, the maximum errors are usually within the measurement uncertainty of the experiments and the overall conversion courses, displayed in Fig. 7, correspond well. Therefore, the implemented loss mechanisms can be considered valid for the present reactor design in a pressure range between 200 and 470 kPa which is currently the broadest pressure range for an indirectly heated fixed bed.



Figure 6 Comparison of the simulated and measured temperature profiles at pressures of 200, 270, and 470 kPa.



Figure 7 Overall conversion profiles at 200 and 470 kPa.

3.2.2 Variation of kinetic equations

At high pressures between 200 and 470 kPa and high temperatures the experimental results revealed that the kinetics of the reaction is very fast, even very close to the thermodynamic equilibrium temperature. As also Nagel et al. [23] showed, in this case the use of a simplified kinetic equation is appropriate. Our results agree and the simple Fast kinetic equation represented a sufficiently fast reaction rate so simulated temperature trends also showed plateaus at the thermodynamic equilibrium temperature. The reaction times then only depend on the correct reproduction of the heat transfer out of the reaction bed, which was achieved after implementing the thermal losses in the simulation. In the following, it has been investigated whether published kinetic equations (given in Tab. 2) also correctly predict the evolution of the temperature plateaus.

Fig. 8 shows the influence of different kinetic models on the simulation results for T7 at a hydration pressure of 200 to 470 kPa. T7 has been chosen because here the temperature plateau is hold the longest. It can be observed that the temperature profiles simulated with the kinetic equations of Schaube et al. (blue line), and Angerer et al. (green line) evolve at different temperatures below the thermodynamic equilibrium temperature for each pressure level. Temperature trends which show an obvious distance to the thermodynamic equilibrium temperature indicate that in the kinetic models the rate of reaction becomes too slow close to the thermodynamic equilibrium temperatures are limited by the rate of reaction. Consequently, there is a thermal equilibrium of the released heat of the reaction and thermal losses or the heat taken by the air stream.

Schaube et al. based their model on measurements with a maximum steam pressure of up to 97.5 kPa. The extrapolated reaction rates at a pressure of 270 kPa are too slow to match the experimental results. As a consequence, the extrapolation of the model to higher pressures is not valid. Even though Angerer et al. determined their kinetic model in the range of 50 to 500 kPa the simulation shows that the predicted reaction rate is also too slow to reach a plateau temperature close to the thermodynamic equilibrium temperature. A reason for this might be that they used larger particles (mean particle diameter 345.5 μ m). Smaller particles (5 μ m), as they were used in the experiments, offer a larger surface area which increases the rate of reaction. As a consequence, the generalization of the kinetic model of Angerer et al. to much smaller particle sizes seems not valid.

The kinetic model of Criado et al. predicts the experimental results correctly. Although the equation was determined with thermogravimetric analysis measurements only up to 100 kPa an extrapolation to higher pressures seems valid. The reason for this could be related to the consideration of different particle sizes in the range from 100 μ m up to 2000 μ m and a derived kinetic model that is inversely proportional to the particle diameter. Due to the small particles used in the experiment, this reaction kinetics becomes quite fast and leads to approximately the same results as the Fast kinetics.

For future applications with indirectly cooled reaction beds, it can be concluded that even in a design with very thin bulk layers heat transfer will become the main limiting factor, as kinetics are always sufficiently fast in the high pressure range.



Figure 8 Influence of different kinetic models on the simulation of the temperature course of T7 at a steam pressure of 200 - 470 kPa.

3.3 Low pressure simulations

The high pressure analysis revealed that an exact description of the heat transfer out of the reaction bed, including thermal losses, is the most important point in order to obtain valid simulation results. However, at low steam pressures, this might be different since the reaction kinetics become significantly slower at lower temperatures according to the Arrhenius equation and the gas transport into the reaction bed might cause relatively large pressure drops. Therefore, we analyzed the influence of the gas transport as well as the reaction kinetics on the simulation results in the pressure range of 8.7 to 50 kPa.

3.3.1 Model validation

Fig. 9 shows that for the low pressure experiment at 8.7 kPa, a simulation with the assumption of a fast kinetic, leads to a significant deviation from the measurements. Again, the simulated temperatures reach the thermodynamic equilibrium within seconds after opening the valve. However, the measured temperatures are about 12 to 23 °C below these temperatures. In general, there are two possible explanations for this. Firstly, there is a mass transport limitation. This means that the steam flow into the bulk is hindered, resulting locally in a lower steam pressure. A locally lower steam pressure would directly cause a lower reaction equilibrium temperature. Secondly, the reaction kinetics is too slow and there is thermal equilibrium between released heat by the reaction and the heat absorbed by the air flow or thermal losses. Additionally, a combination of both effects is also possible.



Figure 9 Measurements and simulation with Fast kinetics at a steam pressure of 8.7 kPa.

For the experiments a mass transport limitation could be excluded by a variation of the cooling load. The measured temperature plateau at T7 remained approximately the same even though the air flow was varied from 15.5 to 25.8 kg/h showing that the local steam pressure is not reduced by a faster conversion rate due to a faster heat removal (for details refer to [28]). To verify this result and to ensure there is also no mass transport limitation in the simulation model, the pressure distribution of the reaction gas in the reaction bed was analyzed. The occurring Reynolds-particle numbers were in the order of 0.02 and therefore sufficiently small so that the pressure gradient could be described by Darcy's law [34]. After opening the valve, there is a pressure difference of over 800 Pa. Here, high velocities occur as the steam flows from the pressurized evaporator into the evacuated bulk. However, with increasing pressure in the bulk the velocities and consequently also the pressure differences decrease. After 20 s the maximum pressure difference is 200 Pa and after two minutes it declines to 120 Pa, corresponding to a temperature difference of the thermodynamic equilibrium of 1 and 0.5 K, respectively. Fig. 10 shows the pressure distribution over the height of the reaction bed after 395 s. Here, the maximum pressure difference is 110 Pa. The maximum pressure at the top of the bulk is 8.45 kPa. The lowest pressures of 8.34 kPa are measured at the reaction front at the bottom left. Here, heat is taken by the air stream and the reaction proceeds the fastest. Therefore, the pressure decreases as the reaction consumes steam and the steam flow causes a pressure drop according to Darcy's law. However the analysis proofed that the difference between the measured pressure in the reactor and the pressure in the reacting bulk is negligible. As a consequence, the difference between the equilibrium temperature (calculated by the measured pressure) and the plateau temperatures can certainly be dedicated to a limitation of the intrinsic reaction kinetics.



Figure 10 Simulated pressure distribution for the 8.7 kPa experiment after 395 s

3.3.2 Variation of kinetic equations at 8.7 - 50 kPa

Since the correct representation of the temperature plateaus during the low pressure hydration relies on a correct prediction of the reaction rate, simulations performed with different kinetic models stated in Tab. 2 were analyzed. Fig. 11 shows the results for T7 at a steam pressure of 8.7, 20, and 50 kPa. For the whole pressure range, measured temperatures do not reach the thermodynamic equilibrium albeit the difference decreases with increasing pressure. Nevertheless, the Fast kinetics as well as the one by

Criado et al. reach the thermodynamic equilibrium temperature at all pressures and thus overestimate the reaction rate. Even though the kinetic equation by Criado et al. was derived including measurements at 45 kPa as shown in Fig. 2, the reaction rate in the 50 kPa experiment is overestimated. The reason for this might be that the particle size term has a big influence on the reaction rate. The extrapolation to particle sizes of 5 μ m, which is far below their lower measured boundary of 100 μ m, leads to a too high acceleration of the reaction rate.

The models by Angerer et al. and Schaube et al. result in temperature courses below the thermodynamic equilibrium. So these models show correctly, that there is a reaction kinetics limitation. The extrapolation of the reaction kinetic model by Angerer et al. matches the maximum temperatures best for each pressure level. The heat released by the reaction decreases according to the growth mechanism term (eq. 5). Therefore, the thermal equilibrium temperature decreases over time during the reaction affecting also the Arrhenius and the pressure related term. In the experiment, the thermal equilibrium temperature declines faster than in the simulation with the Angerer reaction kinetics meaning that the reaction rate is slower in the experiment. Consequently, the reaction time is longer.

Applying the reaction kinetic model from Schaube et al. yields always temperatures below the measured ones. An explanation for a lower thermal equilibrium could also be an overestimation of thermal losses. Therefore, for this reaction kinetic model simulations without thermal losses were run (blue dotted lines). Even then, the reached plateau temperatures are underestimated, indicating too slow reaction rates. However, the overall reaction times are predicted correctly and especially for 8.7 kPa, the temperature course is qualitatively similar, apart from a temperature offset.

This simulation study revealed that at low pressures the influence of the reaction kinetics significantly affects the reactor performance. From the analyzed kinetic models no extrapolation could predict the plateau temperature correctly, which was shown for the first time. However, for real applications the low pressure range is especially important if only low temperature thermal energy is available to supply steam (50 kPa corresponds to about 80 °C evaporation). Consequently, for future system design it will be crucial to develop expressions for the reaction kinetics of CaO/Ca(OH)₂ also at steam pressures between 8.7 and 50 kPa and validate them at larger scales. This can be achieved either by a lab scale set up that can exactly quantify the thermal losses or by further thermogravimetric measurements at these pressures. Both will be addressed in future work.



Figure 11 Pressure variation at low pressures between 8.7 and 50 kPa.* indicates simulations without consideration of thermal losses.

4. Conclusions

A model for an indirectly cooled fixed bed reactor, coupling heat and mass transfer as well as the chemical reaction, has been developed and the hydration of CaO has been numerically analyzed. The model has been adjusted with experimental data, to account for thermal losses, and validated for different steam pressures (200 - 470 kPa). The pressure range of previous simulations has been extended considerably to higher pressures up to 470 kPa as well as to lower pressures of 8.7 kPa. Recently published kinetic models by Angerer et al. (2018), Criado et al. (2014), and Schaube et al. (2012) have been applied to the model to determine whether extrapolations to different pressures and smaller particle sizes (5 µm) are valid.

At high pressures (200 – 470 kPa) the analysis revealed that the reaction kinetics is generally fast and the mass transport resistance over the reaction bed negligible. Consequently, the performance of reactors in this operating range is mainly dominated by the heat transfer out of the reaction bed. Thus, an exact description of the heat transfer is required in order to obtain valid simulation results. While the conductive heat transfer from the reaction bed to the heat transfer fluid can be described reasonably well, it was found that convective heat transfer in the reactor also has a major influence. This can be attributed to the reactor design and the operating mode of triggering the reaction with a large pressure increase, yielding a large temperature increase. However, in general not all parameters to describe the physical loss mechanisms, in particular the free convection of the steam between the reactive bulk and the pressure vessel, are known sufficiently. Future works should therefore address a validation of models for this physical loss terms. Summarized, it can be stated that for the high pressure range simple reaction kinetic and mass transport models can be used, but the heat transfer in the reactors, in particular thermal losses due to the temperature jump during hydration, should be considered carefully.

Experiments in the low pressure range (8.7 - 50 kPa) were simulated for the first time. It could be proven by the simulation that the pressure drop over the thin reaction bed is negligible. Moreover, the simulation study verified that the reached hydration temperatures in the reactor are limited by the reaction rate. As a consequence, we could prove that for low pressure simulations an exact model of the reaction kinetics is essential. We found, that the models by Schaube et al. and Angerer et al. could describe the slowdown of the reaction rate qualitatively, but none could reproduce the measured temperature plateaus exactly. Therefore, a new model for the reaction rate for the CaO/Ca(OH)₂ system in the pressure range of 8.7-50 kPa is still required and the model has to be validated with experimental data at larger scales which will be addressed in future studies.

Declaration of interest: none

Nomenclature

Symbol and indices	Unit
A	1/s
Cp	J/(kg K)
d_p	m
E	J/mol
eq	

Pre-exponential factor Isobaric heat capacity particle size Apparent activation energy Equilibrium

exp.		Experiment
ΔH	kJ/mol	Reaction enthalpy
HTF	-	Heat transfer fluid
К	m²	Permeability
k_{v}^{*}	W/(m³ K)	Volumetric heat transfer coefficient
m	kg	Mass
<i>M</i> _{Steam}	g/mol	Molar mass of Steam
n	mol	Mole number
Р	kPa	Pressure
Q	W/m³	Volumetric loss/gain
$Q_{\rm m}$	kg/(m³ s)	Mass sink
sim.		Simulation
t	S	Time
Т	К	Temperature
u	m/s	Velocity
ν	m/s	Seepage velocity
Х	-	Conversion
V _{bulk}	m³	Volume of the bulk
ρ	kg/m³	Density
ϵ	-	Porosity
λ	W/(m K)	Heat conductivity
μ	Pa s	Dynamic viscosity

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