

## A modified grain model for the description of heterogeneous acid gas removal processes with incomplete sorbent conversion

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### Highlights

- Gas-solid reactions for acid gas treatment are hindered by incomplete solid conversion
- A nucleation submodel was integrated in the classical grain model to address the issue
- Experimental data on the  $\text{Ca}(\text{OH})_2/\text{HCl}$  system were interpreted with the modified model
- The main controlling parameters of the heterogeneous reaction process were identified

### 1. Introduction

Acid gases such as HCl,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  are typical pollutants related to the combustion of waste or biomass. Their removal via the injection of powdered basic sorbents, triggering gas-solid reactions of neutralization, is an effective method to curb acid gas emissions below emission limits. However, the efficiency of acid gas treatment systems is still hindered by lack of knowledge about the intrinsic limitations of the gas-solid reaction process. In particular, one of the main issues affecting acid gas removal by the widely used calcium-based sorbents is the low utilization of the solid reactant. Incomplete conversion has been ascribed either to pore blockage [1] or diffusional limitations [2], but no widely accepted theoretical explanation has been provided yet. Here, a fundamental model for gas-solid reactions is proposed to describe incomplete sorbent conversion as a result of a twofold resistance of product layer to gas diffusion and product nucleation. Model predictions were compared with measurements of HCl removal with calcium hydroxide,  $\text{Ca}(\text{OH})_2$ .

### 2. Methods

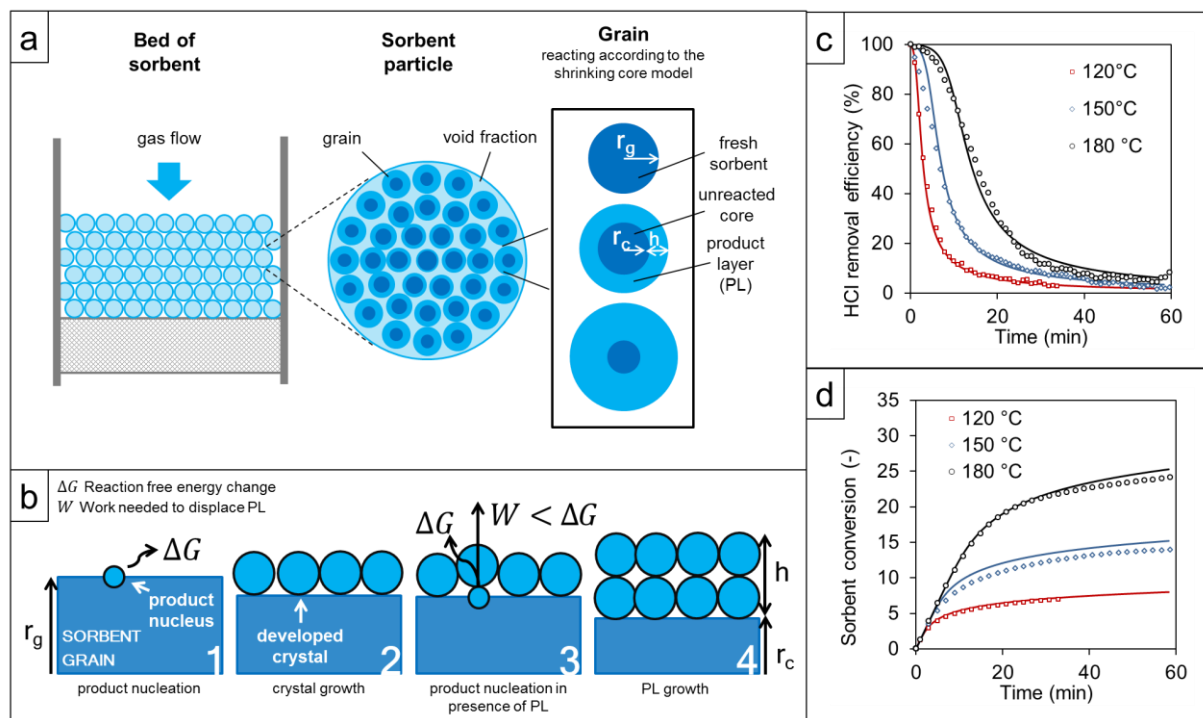
The experimental study of the reaction between  $\text{Ca}(\text{OH})_2$  and HCl was conducted in a fixed bed reactor, following the time-scale evolution of reaction by FTIR monitoring of the off-gas exiting the reactor. In addition, solid reaction products were analyzed via TGA to quantitatively verify the match between gas and solid conversion data.

A model for the description of the reaction was developed, by coupling the conventional grain model [3] for gas-solid reactions concerning porous sorbents (Fig. 1a) with a crystallization and fracture submodel [4] (Fig. 1b). The grain model attributes the decline of reactivity to the increase of the characteristic length for solid-state diffusion, owing to the growth of the product layer (PL). It neglects that, for reactions involving volume expansion in the solid phase, the nucleation of a product crystallite at the reaction interface requires the displacement of the PL. Therefore, further nucleation is only possible if the energy released by reaction ( $\Delta G$ ) is higher than the mechanical work  $W$  required to displace PL. The present model integrates this aspect in the grain model framework [5], by introducing a reduction factor for the active reaction surface, which takes into account the inhibition of nucleation due to the accumulation of the PL around the sorbent grains via a population balance for product nuclei. The application of the model requires the measurement and the calculation of a set of morphological and thermodynamic input data, while three key model parameters remain to be determined by experimental data fitting: the chemical reaction rate constant ( $k_s$ ), the PL diffusivity of the gaseous reactant ( $D_s$ ), and the mechanical coefficient ( $K$ ) determining the work involved in product nucleation. A sensitivity analysis was conducted with the variance-based method [6], in order to study the relative weight of the three parameters in determining the model output at different reaction stages.

### 3. Results and discussion

The experimental results evidenced that final sorbent conversion is mainly affected by the reaction temperature, while concentration of the gaseous reactant and sorbent-to-HCl ratio have only minor influence.

A set of experimental runs at temperatures of 120, 150 and 180 °C was used to calibrate the temperature dependence of the kinetic and diffusion coefficients in the model, while runs with different amounts of gaseous and solid reactants were used as validation set. As expected, chemical reaction rate and diffusivity increase exponentially with temperature, while the mechanical resistance of the PL has a log-linear decrease with temperature, in line with the temperature trend of the elastic modulus of metal oxides. The calibrated model satisfactorily reproduced the experimental data of dechlorination efficiency (Fig. 1c) and sorbent conversion (Fig. 1d). The sensitivity analysis highlighted that the controlling parameters of the process are  $D_s$  in the initial stage and  $K$  at later stages, with only minor role of  $k_s$ .



**Figure 1.** Model layout and application to data: (a) grain model framework; (b) crystallization and fracture submodel; examples of model application to removal efficiency (c) and sorbent conversion (d) data for the runs with 2500 ppm HCl in gas phase and 100 mg  $\text{Ca}(\text{OH})_2$  in the sorbent bed (dots: exp. data; continuous lines: model results).

#### 4. Conclusions

A phenomenological model for the description of gas-solid reactions in acid gas removal processes was developed to interpret experimental data collected for the  $\text{Ca}(\text{OH})_2/\text{HCl}$  system. The model simulations showed good agreement with data and allowed to identify the main controlling parameters for the process. The obstacle to sorbent conversion generated by PL growth is arguably the cause of the low utilization of  $\text{Ca}(\text{OH})_2$  observed in industrial acid gas treatment systems. Proper design and operational measures should be envisaged to reduce PL hindrances.

#### References

- [1] T. Chin, R. Yan, D.T. Liang, J.H. Tay, *Ind. Eng. Chem. Res.* 44 (2005) 3742-3748.
- [2] F. Montagnaro, M. Balsamo, P. Salatino, *Chem. Eng. Sci.* 156 (2016) 115-120.
- [3] J. Szekeley, J.W. Evans, H.Y. Sohn, *Gas-Solid Reactions*, Academic Press, London, 1976.
- [4] W. Duo, J.P.K. Seville, N.F. Kirkby, R. Clift, *Chem. Eng. Sci.* 49 (1994) 4429-4442.
- [5] G. Antonioni, A. Dal Pozzo, D. Guglielmi, A. Tugnoli, V. Cozzani, *Chem. Eng. Sci.* 148 (2016) 140-154.
- [6] A. Saltelli, P. Annoni, I. Azzini, F. et al., *Comput. Phys. Commun.* 181 (2010) 259-270.

#### Keywords

Acid gas; gas-solid reactions; flue gas cleaning; modelling.