Chemical Engineering Science 148 (2016) 140–154

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Enhanced modelling of heterogeneous gas–solid reactions in acid gas removal dry processes

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HIGHLIGHTS

- A low temperature-dependent final conversion of solid is reported in acid gas dry removal processes.
- An improved model was developed for acid gas reactions with dry powdered solid sorbents.
- A grain model approach was integrated with a crystallisation and fracture submodel.
- The model was validated against literature data on the $Ca(OH)_2$/HCl system.
- The model is able to account for the temperature-dependent final conversion of solid reactant.

ARTICLE INFO

Article history:
Received 9 January 2016
Received in revised form
7 March 2016
Accepted 13 March 2016
Available online 24 March 2016

Keywords:
Flue gas treatment
Acid gas removal
Dry sorbent adsorption
Gas–solid reactions
Crystallization and fracture model

ABSTRACT

Acid gases as hydrogen halides and sulphur oxides are typical pollutants of combustion processes. Their removal from flue gas can be performed via the injection of dry powdered sorbents, as calcium hydroxide. However, the efficiency of dry treatment methods is hindered by the limited final conversion of the solid reactant, due to an abrupt decline of its reactivity during the reaction process. Fundamental gas–solid reaction models such as the shrinking core model and the grain model are able to reproduce this phenomenon only introducing an arbitrary value of the final conversion or an adjustable value of the solid-state diffusivity of the gaseous reactant. In the present study, the conventional grain model approach was integrated with a crystallisation and fracture (CF) submodel, which links the chemical potential of nucleation to the work needed to displace the layer of solid product formed on the reaction interface. The decline in reactivity of the sorbent was accounted by a twofold effect of the product layer growth: (i) the increase of the characteristic length for solid-state diffusion, accounted for in the grain model, and (ii) the increase of the mechanical work required for nucleation as a function of product layer thickness, accounted for in the CF submodel. This approach, validated against literature data on the $Ca(OH)_2$/HCl system, allowed reproducing the conversion of the solid reactant at different operating temperatures.

1. Introduction

Hydrogen halides and sulphur oxides are formed in several combustion processes, including municipal solid waste incineration (MSWI) (Niessen, 2010). Among the different removal processes available and applied in current industrial practice, in recent years Dry Sorbent Injection (DSI) processes (Marocco and Mora, 2013) became increasingly attractive due to the improved removal efficiency and the easy management of process waste streams (Gutiérrez Ortiz and Ollero, 2008). DSI processes are based on the injection of dry powdered calcium-based sorbents (calcium hydroxide, calcium carbonate or calcium oxide), or sodium-based alkali (carbonate or bicarbonate), into the flue gas where solid sorbent particles and gas molecules react by gas-solid heterogeneous reaction processes. Particulate matter, including converted or partially converted sorbent particles, is then removed in gas-solid separators (typically by the use of a fabric filter).

Despite the satisfying performance shown by DSI processes in reducing outlet concentrations of acid gases far below current legislative requirements (European Commission, 2006), industrial practice is still mostly empirical and DSI systems are often not operated at their optimum (De Greef et al., 2013). Detailed process

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http://dx.doi.org/10.1016/j.ces.2016.03.009
0009-2509/

modelling would allow a full-aware process optimisation, reducing sorbent consumption, waste production and operating costs. However, to date only few studies attempted the modelling of DSI performance. Chisholm and Rochelle (1999) adopted a semi-empirical approach to determine kinetic parameters and to simulate the performance of a dry treatment system using data from laboratory-scale experiments on hydrogen chloride removal by calcium hydroxide. Other authors modelled in-duct desulphurisation by applying empirical kinetic equations (Kaiser et al., 2000; Gutiérrez Ortiz and Ollero, 2008). An operational model based on a simplified description of the acid gas removal process was proposed by Antonioni et al. (2011). Its implementation allowed the identification of the optimal operating conditions of the flue gas treatment section of an existing MSWI (Antonioni et al., 2014). Nevertheless, the model required specific operational and/or design data for its calibration. Recently, an attempt was done to study such systems by computational fluid dynamics, yet applying a simplified model to the chemical reaction process (Marocco and Mora, 2013).

Actually, acid gas neutralisation with sorbent particles is a complex process, which results from the superimposition of different effects, such as flow through a porous fixed bed of particles, diffusion in the particle pores and reaction with the sorbent, where also equilibrium thermodynamics plays an important role. Several studies addressed single aspects of the process. Thermodynamic calculations to identify the theoretical limit for HCl removal by calcium- and sodium-based sorbents was addressed in several studies (Shemwell et al., 2001; Verdone and De Filippis, 2004; Chin et al., 2005a). Weinell et al. (1992) carried out a comprehensive investigation of the reactivity of $Ca(OH)_2/CaO$ towards HCl considering a wide range of operating conditions (temperature, moisture, surface area of the solid reactant). Daoudi and Walters (1991) and Yan et al. (2003) focused on the determination of the chemical reaction rate respectively for the CaO/HCl and the $Ca(OH)_2$/HCl systems, while Duo et al. (1995) and Fonseca et al. (1998) studied the role of the solid-state diffusion of the gaseous reactant in controlling the process over longer reaction times.

In spite of the relevant work carried out in the field, to date no detailed model is available to describe the gas-solid heterogeneous reaction process and the associated transport phenomena taking place in acid gas removal processes with calcium-based sorbents. Actually, an unreacted shrinking core model (Levenspiel, 1998) for gas–solid reactions is not able to correctly predict the incomplete conversion of the solid sorbent observed in several experimental studies (Weinell et al., 1992; Fonseca et al., 1998; Chisholm and Rochelle, 1999; Yan et al., 2003). Coupling the shrinking core model to a grain model (Szekely et al., 1976) to describe particle behaviour improved the quality of results, but still such approach is not able to reproduce experimental findings, and in particular the limited temperature-dependent final conversion of the solid sorbent (Duo et al., 1994). Presently, available models use empirical parameters derived from data fitting to introduce an arbitrary maximum conversion or an ultimate conversion value based on experimental data fitting (Chisholm and Rochelle, 1999). Alternatively, the diffusivity of the gaseous reactants through the layer of solid product is decreased introducing an empirical dependency on sorbent conversion as reaction proceeds (Wang and Teng, 2009). Such empirical approach allows the model to reproduce the abrupt decrease in the reactivity of the solid reactant observed experimentally (Standardo and Foscolo, 2010).

In the present study, an improved model to simulate the heterogeneous reaction process between acid gases and solid reactants was developed. The model addressed specifically the incomplete conversion of the solid reactant. A crystallisation and fracture model derived from that originally proposed by Duo et al. (1994) was developed for the heterogeneous reaction among calcium hydroxide and hydrogen chloride. The model takes into account the formation and break-up of crystals on the surface of the solid grains, and was integrated into a shrinking core and grain model to describe reactions in the porosity of the solid particles. The model was validated against experimental data reported in the literature to assess its ability to predict the conversion of solid sorbent particles and the final conversion of the solid sorbent.

2. Model description

2.1. Calcium hydroxide/hydrogen chloride reaction process

The overall reaction between $Ca(OH)_2$ and HCl leads to the formation of calcium chloride ($CaCl_2$), in anhydrous (R1) or dihydrate form (R2):

$$Ca(OH)_2(s) + 2{\cdot}HCl(g) = CaCl_2(s) + 2{\cdot}H_2O(g) \tag{R1}$$

$$Ca(OH)_2(s) + 2{\cdot}HCl(g) = CaCl_2{\cdot}2{\cdot}H_2O(s) \tag{R2}$$

The formation of dihydrate calcium chloride besides that of anhydrous calcium chloride was evidenced by X-ray diffraction tests carried on by Gullett et al. (1992) and by Jozewicz and Gullett (1995). However, Partanen et al. (2005) observed that, given the highly hygroscopic nature of calcium chloride, it is possible that the actual reaction product is anhydrous $CaCl_2$, that is then rapidly hydrated when the sample is extracted from the reactor and cooled at room temperature for XRD analysis.

Several authors also reported the formation of calcium hydroxychloride (CaOHCl) as solid product at the typical temperatures of industrial acid gas removal treatments (150–200 °C):

$$Ca(OH)_2(s) + HCl(g) = CaOHCl(s) + H_2O(g) \tag{R3}$$

Weinell et al. (1992) and Gullett et al. (1992) stated that CaOHCl is an intermediate product that can further react with HCl to form $CaCl_2$:

$$CaOHCl(s) + HCl(g) = CaCl_2(s) + H_2O(g) \tag{R4}$$

Conversely, some studies (e.g. see Bausach et al. (2006) and Chin et al. (2005b)) suggest that CaOHCl is the final product of the reaction between $Ca(OH)_2$ and HCl. Allal et al. (1998), confirming the study of Jozewicz and Gullett (1995), evidenced that $Ca(OH)_2$ and $CaCl_2$ can react to form CaOHCl:

$$Ca(OH)_2(s) + CaCl_2{\cdot}2{\cdot}H_2O(s) = 2{\cdot}CaOHCl(s) + 2{\cdot}H_2O(g) \tag{R5}$$

Bodenan and Deniard (2003) analysed air pollution control (APC) residues of the flue gas treatment systems of 12 European MSWIs and found CaOHCl as the only product of the chlorination process. However, it is still unclear if the formation CaOHCl from $CaCl_2$ takes places during flue gas treatment or after the APC residues are removed from the process and stored at ambient conditions. Therefore, there is still a lack of knowledge about efficiencies and yields of the HCl removal process by reaction with $Ca(OH)_2$, and, as a consequence, of the entire flue gas treatment section (Yassin et al., 2007), that is also highly influenced by transport phenomena.

The overall reaction process does not require catalysis and no catalytic effects from impurities are reported in the literature.

In the following, reaction R1 was considered as the main reaction process taking place in hydrogen chloride removal from flue gases in DSI operating conditions, since this was the reaction considered in a number of relevant previous studies (Weinell et al., 1992; Fonseca et al., 1998; Chisholm and Rochelle, 1999; Yan et al., 2003). Nevertheless, different reaction stoichiometries may be