



ALTERATION WITH REACTION PROGRESS OF THE RATE LIMITING STEP FOR SOLID-GAS REACTIONS OF Ca-COMPOUNDS WITH HCl

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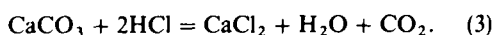
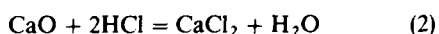
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(Received 11 April 1994; accepted in revised form 19 January 1995)

Abstract—Solid-gas reactions of calcium compounds with hydrogen chloride (HCl) are used in dry scrubbing of HCl from hot gases. The experimental data in the literature were analysed using the shrinking unreacted core model. It has been shown that the rate limiting step for the reactions alters with the extent of solid conversion in this time sequence: chemical reaction control, combined control, product layer diffusion control, and chemical reaction control again. The extent of solid conversion with time could not be predicted by the classical correlations obtained by assuming a single rate limiting step. A modified correlation was presented to obtain product layer diffusion coefficients. A new model, the crystallisation and fracture model, was proposed to describe the mechanism of the formation of the solid product layer. Based on free energy-mechanical work analysis, the model can fundamentally explain the reasons for the change of the rate limiting step, the existence of the maximum conversions of sorbent, the variation of the structure of the solid product layer with temperature, and the effect of gaseous products. The model may also be applicable to other solid-gas reaction systems.

INTRODUCTION

As one of the major sources of local and global environmental pollution, hydrogen chloride emissions (HCl) can be formed in combustion of certain fossil fuels such as chlorine-rich coals and in incineration of many forms of wastes. Calcium compounds such as lime and limestone have been considered as suitable materials for removal of HCl from hot fuel gases. Depending on the application, dry scrubbing of HCl may be designed to take place in entrained flow, in a fixed bed, or in both. The following reactions are involved in the processes:



Experimental studies on these reactions have been carried out using fixed-bed reactors (Uchida *et al.*, 1979; Karlsson *et al.*, 1981; Mura and Lallai, 1992; Weinell *et al.*, 1992; Peukert and Löffler, 1993), by thermogravimetric analysis (Daoudi and Walters, 1991a, b), or in a pneumatic transport system (Bandt *et al.*, 1992). Attempts have been made to simulate mathematically the process of dry scrubbing of HCl (Duo *et al.*, 1993a, b; Peukert and Löffler, 1993). A difficulty with the simulations is the lack of consistent kinetic data, e.g. the reaction rate constants, k_s , and the product layer diffusion (PLD) coefficients, D_s .

In most of the studies, k_s and D_s have been determined under the assumption that the overall rate is controlled either by chemical reaction (for k_s) or by PLD (for D_s). Alternatively, these parameters may also be obtained without this assumption if a sophisticated mathematical model is used. For example, Duo *et al.* (1993b) used their model to estimate the values for k_s and D_s based on the experimental data of Weinell *et al.* (1992). The estimated results support the assumption of Weinell *et al.* that PLD is the rate-limiting step. This is further supported by the observations that a product layer can be formed in a short time (e.g. < 1 s) (Bandt *et al.*, 1992) and the layer is impervious to gas diffusion.

Previous efforts were mainly focused on finding the rate limiting step for the whole process of reaction. However, it is possible that the rate limiting step alters with the progress of the reaction. If it does alter and this is not accounted for in the analysis, different and misleading conclusions can be drawn, since experimental data obtained by different researchers may not be taken at the same extent of reaction.

In order to demonstrate alteration of the rate limiting step with the progress of reactions of Ca-compounds with HCl, the experimental results taken from three independent investigations (Uchida *et al.*, 1979; Daoudi and Walters, 1991a; Weinell *et al.*, 1992) are analysed in the present study. For simplicity, the shrinking unreacted core model is employed.

As these three investigations will be referred to frequently, their experimental conditions are outlined in Table 1.

Many authors did not consider the change of the size of a reacting particle with the conversion of solid reactants when they took the shrinking unreacted

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Table 1. References from which experimental data are taken

Authors	Reaction	T (°C)	d_p (μm)	S_p (m^2/g)
Weinell <i>et al.</i> (1992)	(1)	100–250	2.1–20.5	20
Daoudi and Walters (1991a)	(2)	310–670	≤ 45	9
Uchida <i>et al.</i> (1979)	(3)	200–400	274	Unknown
Uchida <i>et al.</i> (1979)	(2)	700–900	274	Unknown

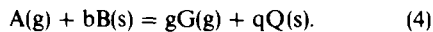
core model to explain their results. This may be tolerable if the volume expansion ratio, α , the molar volume of solid product to solid reactant, is within 0.5–2 (Szekely *et al.*, 1976). For reactions (1), (2) and (3), $\alpha = 2.37$ ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is assumed as the initial form of the product), 3.04, and 1.45, respectively. The effect of volume expansion on the reaction rate is considered in the present paper.

An analysis of free energy and work, based on a model of reaction, crystallisation, and product layer fracture, is proposed to explain the mechanism of formation of the solid product layer.

CORRELATIONS FOR DETERMINING RATE LIMITING STEPS

Gas–solid reactions may be controlled by each of the following steps or by combinations of them (Levenspiel, 1972): (gaseous) film diffusion, (intraparticle) pore diffusion, PLD, and/or chemical reaction on the surface of unreacted cores. It has been shown that for the reactions of Ca-compounds with HCl under the conditions applied in the experiments listed in Table 1, the resistances of the former two steps are too low to be rate limiting. This has also been confirmed by a mathematical simulation (Duo *et al.*, 1993b). Thus, only chemical reaction and diffusion through the product layer are considered as possible rate limiting steps in this paper.

Suppose a single irreversible gas–solid reaction is concerned (reversible reactions can be treated in a similar way), which is represented in a general form as follows:



It is assumed that the chemical reaction occurs on the surface of a “particle” if it is non-porous, or on the surface of “grains” inside the particle if it is porous (the grain model applied) (Szekely *et al.*, 1976). It is also assumed that the particles and grains are spherical and that the gas concentration is constant in the bulk flow, C_A , to which the reacting particles are exposed.

For chemical reaction control, according to Levenspiel (1972), the following equation predicts the radius of the unreacted core, R_c , and the degree of solid conversion, X , at any time, t :

$$\frac{t}{\tau_r} = 1 - \frac{R_c}{R_p} = 1 - (1 - X)^{1/3} \quad (5)$$

where τ_r represents the time required for complete

conversion:

$$\tau_r = \frac{\rho_B R_p}{bk_s C_A} \quad (6)$$

where ρ_B is the molar density of the solid reactant, k_s the reaction rate constant, and b is a stoichiometric constant given in eq. (4). The initial size of the reacting particles (or grains) is given as $R_p = d_p/2$ (non-porous), or as $R_p = 3/(\rho_s S_p)$ (porous), where ρ_s is the sorbent density.

For PLD control with a constant diffusion coefficient, D_s , if any change in particle size with conversion is ignored ($\alpha = 1$),

$$\frac{t}{\tau_s} = 1 - 3(1 - X)^{2/3} + 2(1 - X) \quad (7)$$

where τ_s equals the time required for complete conversion of B. If a change in particle size is considered ($\alpha \neq 1$) (Szekely *et al.*, 1976),

$$\frac{t}{\tau_s} = 3 \frac{\alpha - [\alpha + (1 - \alpha)(1 - X)]^{2/3}}{\alpha - 1} - 3(1 - X)^{2/3} \quad (8)$$

where α is the volume of solid product formed from unit volume of solid reactant. For eqs (7) and (8), τ_s is given by

$$\tau_s = \frac{\rho_B R_p^2}{6bD_s C_A} \quad (9)$$

Although the product layer (CaCl_2) is relatively impervious, as has been suggested by previous studies (Bandt *et al.*, 1992; Daoudi and Walters, 1992; Weinell *et al.*, 1992), the overall rate in the initial or early stages of the reactions may not be controlled by PLD. This is because a continuous product layer has not been formed at short times. When a significant conversion of the solid reactant has been reached, diffusion through the product layer is expected to overtake chemical reaction as the rate limiting step.

Thus, we propose that the rate limiting step alters with progress of reaction, with chemical reaction control in the initial or early stages, followed by combined control of chemical reaction and PLD, and PLD control in the later stages. As will be discussed later, chemical reaction again controls the overall rate in the final stage before the reactions cease. Under these assumptions, the reaction rate constants and the PLD coefficients may be obtained from the initial and later parts of the conversion–time curve, respectively.

In the regime of PLD control, the rate of diffusion through the product layer is equal to the rate of

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