Use of carbonate rocks for flue gas desulfurization: Reactive dissolution of limestone particles

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ABSTRACT

Sedimentary rocks, such as limestone, are widely utilized in flue gas desulfurization (FGD) processes because of their ability to form sulfur compounds. The most common system adopted for FGD is the wet scrubbing process, in which the dissolution rate of sedimentary rocks represents one of the most important factors. Evaluation of the dissolution and the reactivity of solid particles involved is therefore a key factor for FGD process design and plant operation. The rate of dissolution affects the cost of makeup and waste disposal. For this reason a method to test different qualities of raw materials can give us a better understanding of the desulfurization process and reasonable economical effects. In the present work the dissolution of carbonate rocks was investigated by utilizing hydrochloric acid and the mass transport phenomena involved in batch stirred tank reactors (BSTRs) were modeled. By evaluating the ratio of convective to diffusive mass transport and the ratio of momentum and mass diffusivity, it was possible to relate the quality of raw materials in terms of a defined Time Of Exposure (TOE). The model involved takes into account the variation of the particle size distribution derived from the allocation of the scattered light energy using the Fraunhofer diffraction theory. Improvements from previous studies were done [1].

1. Introduction

Fossil fuels and oil are widely utilized all around the world for energy supply and the increase in energy demand will bring to a reasonable raise of pollutants emissions. Coal and oil contain sulfur in organic as well as inorganic form and sulfur dioxide, SO_2 is then obtained from the combustion with oxidation of the above mentioned fuels. Sulfur dioxide has a number of hazards to human health and it is able to react in the atmosphere giving the formation of acid rains. For this reason the legislation in many countries has begun more and more strict about SO_2 emissions [2]. Flue gas desulfurization is for these motivations increasingly important and different kind of industrial solutions are adopted. Wet scrubbers are among the most used FGD plants representing the 80% of the market share [3]; limestone is reacting with sulfate (SO_4) in acidic environment with water giving gypsum in solid form which is then collected. Studies about the dissolution of limestone in presence of acids have been done previously [4,5], mathematical models were obtained for different geometries [6] and it was tried to attain a general method for testing FGD raw materials. The objective of this study was to investigate different kind of sedimentary rocks in acidic environment, simulating the conditions of the holding tank in a wet FGD packed tower [7]; and provide a better estimation of surface renewal time as well as modeling of transport phenomena involved in two phase systems.

2. Theory

2.1. Background

Different methods in sulfur dioxide reduction have been developed over the years. Common solutions on the market involve a gas–liquid contact with forced oxidation, where air is used in order to ensure the oxidation of sulfite in sulfate. Solid limestone particles are usually used to obtain calcium ions able to react with sulfate and water to give gypsum that crystallizes as solid. A more accurate description of the reactions involved is presented in Table 1 [3].

In order to build an applicable mathematical model for the dissolution dynamics of limestone rocks some approximations are required. The rate of reaction between acid and solid is generally considered to be of the first order [8]. In addition the system is considered to be isothermal and without viscous generation of heat. A schematic representation of an industrial wet FGD packed tower is shown in Fig. 1 [3].

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Nomenclature

$[A^*]$ molar concentration at saturation for the generic component A (mol/m^3)
B_0 initial concentration of hydronium ions (mol/m^3)
C BET constant
C_{ai} interface molar concentration (mol/m^3)
C_∞ solute molar concentration in the liquid region (mol/m^3)
ΔC difference in concentration of the dissolving component (mol/m^3)
D mass diffusivity (m^2/s)
D_a mass diffusivity of the generic component A (m^2/s)
d_p diameter corresponding to one particle having the total surface of reaction (m)
k_c mass transfer coefficient (m/s)
$k_{mn}[B_0]^n$ pseudo first order reaction rate constant k_1 (1/s)
K_1 reaction rate constant for first order chemical reactions (1/s)
L integration length along the x (m)
m order of reaction toward the generic component A
$\dot{m}$ mass transfer rate (mol/s)
n order of reaction toward the generic component B; amount of the adsorbate in Eq. (12) (mol)

N_A Avogadro number (1/mol)
N_i mass flux over a particular surface (mol/m^2)
n_m monolayer capacity (Pa)
p equilibrium pressure related to the adsorbates (Pa)
P_0 saturation pressure of adsorbates (Pa)
R_A average specific rate of transfer for the component A ($mol/(s \cdot m^2)$)
Re Reynolds number
Sc Schmidt number
Sh Sherwood number
t time (s)
t_E time of Exposure (s)
v_i velocity at the interface (m/s)
x spatial coordinate (m)

Greek letters
μ_∞ viscosity of the liquid medium at a large distance from the axes origin (Pa s)
μ_w viscosity of the liquid medium (Pa s)
σ molecular cross-sectional area (m^2)

The holding tank of a full scale FGD tower represents a Continuous Batch Stirred Tank Reactor (cBSTR) in which we have three phases and acidic surroundings (Table 1). The degree of acidity influences the limestone dissolution and modifies the performance of the FGD plant. The utilization of HCl for testing the reactivity of limestone has been already performed in previous studies [9,10]. Reactions between limestone and HCl are reported in Table 2, which describes more accurately all the reaction steps occurring, this shows that considering the above mentioned effects as an overall first order reaction is a simplification.

2.2. Mathematical modeling

Our results indicate that there are other properties related to the carbonate rocks other than $CaCO_3$ content affecting the reactivity. Rocks with similar $CaCO_3$ contents react in different ways with acids. There is evidence that geological parameters like porosity (degree of compaction of sedimentary limestone) and crystal size and shapes may have an important impact on the capability to release calcium ions.

The mathematical model related to solid particles consumption considers shrinking particles because of the dissolution and reaction with hydronium ions into the bulk solution. The shrinking core
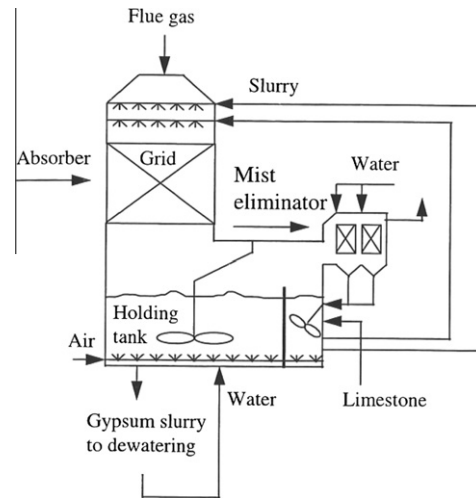

Fig. 1. Illustration of a FGD packed tower with co-current gas slurry contacting.

model [11] is applied and the limiting factor is considered to be the mass transport of cations to the solid surface. Experimental results

Table 1
Main reactions involved in wet FGD with forced oxidation.

Gas phase	Liquid phase	Solid phase	Rate determining steps
$SO_2 \rightarrow\rightarrow$	$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^-$ $HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$		Absorption of SO_2
$O_2 \rightarrow\rightarrow$	$HSO_3^- + 1/2O_2 \rightleftarrows H^+ + SO_4^{2-}$ $HSO_4^- \rightleftarrows SO_4^{2-} + H^+$		Oxidation of HSO^{3-}
$CO_2 \rightarrow\rightarrow$	Ca^{2+} $CO_2 + H_2O \rightleftarrows HCO_3^- + H^+$ $HCO_3^- \rightleftarrows CO_3^{2-} + H^+$ $H_2O \rightleftarrows H^+ + OH^-$	$CaCO_3$	Dissolution of limestone
	$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow\rightarrow$	$CaSO_4\,2H_2O$	Crystallization of gypsum