



## Employing a step-wise titration method under semi-slow reaction regime for evaluating the reactivity of limestone and dolomite in acidic environment



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### ARTICLE INFO

#### Article history:

Received 11 May 2015

Revised 17 October 2015

Accepted 25 November 2015

Available online 10 December 2015

#### Keywords:

Gas desulfurization  
Limestone reactivity  
Mathematical modeling  
Transport phenomena

### ABSTRACT

Carbonate rocks are commonly utilized in Wet Flue Gas Desulfurization, WFGD, because of their capability to release calcium ions and precipitate as solid gypsum in an acidic environment. Studies on the reactivity of carbonate rocks and dissolution models can be employed for optimizing the WFGD process. The correct evaluation of limestone reactivity is therefore necessary for the design of the WFGD scrubbing process and for plant operation. In this study, after statistical considerations on evaluating the sample size threshold, a mathematical model and a detailed procedure are given for the estimation of the reaction rate constant and mass transfer coefficient.

Results are reported from testing limestone and dolomite samples with different formation periods and geological backgrounds. Samples were tested in a Batch Stirred Tank Reactor (BSTR) with a stepwise titration method using hydrochloric acid and non-steady state conditions. In the experiments particles were shown to be completely immersed in a defined viscous sub-layer. A parametric evaluation for the reaction rate was performed at each titration step using an implemented software procedure that handles hundreds of pH values and more than fifty particle size ranges. The experimental data were accurately fitted to the model. The second order model for dolomite and limestone samples accounts for both mass transfer and reaction rate terms, yielding values for the mass transfer coefficients that are congruent with values estimated by fluid-dynamics inspection.

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## 1. Introduction

Limestone has been used as binder for the manufacture of mortars and plasters since 7000 BC (Moropoulou et al., 2001). Additionally limestone is used in a number of industrial applications and is considered one of the world's most flexible minerals (Boynton, 1966). The sedimentary rock has been employed also in environmental protection, for example, as a filter for water purification and for acid remediation of process waters before being discharged; this process is known as acid water neutralization (Barton and Vatanatham, 1976; De Blasio et al., 2013; Komnitsas et al., 2004). The utilization of limestone and red mud to remove inorganic contaminants and the application of in-situ permeable reactive barriers has been investigated in literature

(Komnitsas et al., 2004), where limestone as a reaction medium was tested by setting up laboratory column experiments.

In environmental pollution control, Wet Flue Gas Desulfurization (WFGD) represents one of the most important technologies used for sulfur removal and gypsum precipitation. The process accounted for more than 90% of the FGD installation in recent years (Hrastel et al., 2007). The industrial process of WFGD consists of different sub-processes: the preliminary steps are limestone grinding, water–limestone slurry preparation and flue gas cooling. The absorption of gaseous SO<sub>2</sub> in droplets of a water–limestone slurry takes place in a suitable spray absorber tower and through successive reactions with limestone in dissolution and precipitation agitated chemical reactors. The oxidation of sulfite to sulfate is assured by forced convection of air into the bottom part of the scrubber. The precipitated gypsum is then removed. The energy required for WFGD can be up to 3% of the entire energy produced by the power plant (Hrastel et al., 2007).

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## Nomenclature

### Abbreviation

BSTR	Batch Stirrer Tank Reactor
ESR	Effective Surface of Reaction
PSD	particle size distribution
SEM	scanning electron microscopy
SHOS	Superhigh-Organic-Sulfur
SSA	specific surface area (m <sup>2</sup> /kg)
TOT	Time of Transfer (s)
WFGD	Wet Flue Gas Desulfurization
XRF	X-ray Fluorescence

### Symbols

$\Delta F_{ij}$	diameter frequency function (-)
$C_a^*$	non dimensional carbonate ion concentration (-)
$Re_\phi$	Reynolds number defined by Eq. (25)
$u_\phi$	shear stress velocity (m/s)
$Ar$	Archimedes number (-)
$C$	concentration (mol/m <sup>3</sup> )
$D$	diameter (m)
$D^*$	diffusivity, in Eq.(29) (m <sup>2</sup> /s)
$d_i$	mean diameter for the $i$ th particle class (m)
$d_p$	mean particle diameter (m)
$E'$	error, defined in Eq. (10)
$f_j$	frequency function for the $j$ th step (1/m)
$g$	acceleration of gravity (m/s <sup>2</sup> )
$K$	non dimensional constant (-)
$k_c$	mass transfer coefficient (m/s)
$k_r$	reaction rate constant (1/s)
$m$	mass (kg)
$n$	number of trials (-)
$P$	probability mass function (-)
$p$	probability (-)
$r$	reaction rate (mol/m <sup>3</sup> s)
$Re$	Reynolds number (-)
$S$	total reaction surface (m <sup>2</sup> )
$\hat{S}$	solubility (kg/m <sup>3</sup> )
$Sc$	Schmidt number (-)
$Sh$	Sherwood number (-)

$T$	non-dimensional parameter in Eq. (29) (-)
$t$	time (s)
$u_\infty$	reference velocity (m/s)
$V$	volume of reaction (m <sup>3</sup> )
$x$	number of successes in Bernoulli trials (-)
$Y$	proportion of successes in Bernoulli trials (-)
$y$	non dimensional carbonate ion concentration (-)
$Z$	standard normal variable (-)
$z$	upper percentage point of the standard normal distribution

### Subscripts

$\infty$	refers to a distance sufficiently large
$a$	related to the concentration of the dissolving component
$a_i$	refers to concentration of the dissolving component at interface.
$F$	fluid
$i$	diameter class
$j$	titration step
$p$	particle
$s$	solid
$st$	stirrer
$v$	refers to the vessel in Eq. (25)

### Greek symbols

$\nu$	kinematic viscosity of the fluid (m <sup>2</sup> /s)
$\rho$	density of the particle (kg/m <sup>3</sup> )
$\tau$	(Time of Transfer) <sup>-1</sup> (1/s)
$\omega$	angular velocity (1/s)
$\Gamma$	gamma function
$\alpha$	(1 - $\alpha$ ) defined as confidence coefficient (-)
$\phi$	subscript in Eq. (24). Refers to the shear stress
$\gamma^{LW}$	Lifshitz-van der Waals tension (J/m <sup>2</sup> )
$\gamma^+$	solid surface free energy acid parameter (J/m <sup>2</sup> )
$\gamma^-$	solid surface free energy base parameter (J/m <sup>2</sup> )
$\Omega$	indicates the samples tested. Is followed by the sample number

The process involves mass transfer and reaction phenomena involving gas, liquid and solid phases as follows (Carletti et al., 2013; Dou et al., 2009): The gaseous SO<sub>2</sub> is first absorbed by the slurry droplets giving SO<sub>2</sub> in liquid phase; SO<sub>2</sub> then reacts with water to give hydronium ions and this determines the typical acidic environment of the dissolution tank, where the common pH value is 5.5 (Dou et al., 2009). In order for precipitation of gypsum to take place, calcium carbonate compounds have an important role in the formation of the required calcium ions, Ca<sup>2+</sup>, which are then able to react with sulfate and water and form the solid precipitate, which is then collected. If limestone dissolution is enhanced, the Ca<sup>2+</sup> ions are more readily available in solution and the process becomes more effective. For this reason limestone dissolution has been reported to be a major parameter affecting the SO<sub>2</sub> absorption yield (Guelli et al., 2010) and one of the determining steps of the process (Pepe, 2001).

The main reactions, including the reaction of gypsum formation, are reported in Table 1 and a more detailed description of the process can be found in literature (Stultz and Kitto, 1992).

The study of mineral dissolution and the modeling of its kinetics is significant for WFGD and also for other fields of study. For instance, hydrochloric acid is used to dissolve carbonate rocks to facilitate the extraction of oil; additionally carbonate dissolution

at different pH values influences the natural CO<sub>2</sub> accumulation in marine sediments.

Various technologies have been applied in WFGD and diverse sorbents are commonly used as shown in Table 2 (Takeshita and Soud, 1993).

The WFGD technology is not a new technology; nevertheless the increasing global consumption of coal emphasizes the need for additional research and the optimization of the WFGD process. Coal may contain sulfur in organic as well as inorganic form. The

**Table 1**

Main steps and reactions in WFGD (De Blasio et al., 2013).

Rate determining steps	Reactions
Absorption of gaseous SO <sub>2</sub> in liquid water	SO <sub>2</sub> + H <sub>2</sub> O ⇌ H <sup>+</sup> + HSO <sub>3</sub> <sup>-</sup> HSO <sub>3</sub> <sup>-</sup> ⇌ H <sup>+</sup> + SO <sub>3</sub> <sup>2-</sup>
Oxidation of HSO <sub>3</sub> <sup>-</sup> (liquid phase)	HSO <sub>3</sub> <sup>-</sup> + ½ O <sub>2</sub> ⇌ H <sup>+</sup> + SO <sub>4</sub> <sup>2-</sup>
Solid limestone is dissolving in acidic environment (pH 5.5, Industrial process)	HSO <sub>4</sub> <sup>-</sup> ⇌ SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup> CaCO <sub>3</sub> ⇌ Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup> CO <sub>2</sub> + H <sub>2</sub> O ⇌ HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> HCO <sub>3</sub> <sup>-</sup> ⇌ CO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup> H <sub>2</sub> O ⇌ H <sup>+</sup> + OH <sup>-</sup>
Crystallization of gypsum	Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> + 2H <sub>2</sub> O ⇌ CaSO <sub>4</sub> · 2H <sub>2</sub> O

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