Mathematical modelling of limestone dissolution in batch stirred tank reactors in presence of a diluted strong acid.

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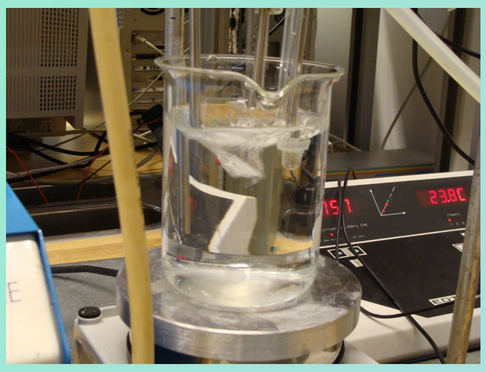
Abstract

In the present work a mathematical model describing the transport phenomena occurring in limestone-strong acid reaction in small BSTRs (Batch Stirred Tank Reactors) was developed and evaluated.



Introduction

The correlation between the *pH* value and limestone dissolution rate has been studied . In addition, a model for FGD performance as a function of limestone reactivity was developed. Few studies have discussed the variation of the particle size distribution during dissolution. In this study a more general mathematical model has been developed; it takes into consideration the particle size distribution and transport phenomena as the main factors affecting the dissolution.

Theory

The entire phenomenon is constituted of three main steps:

- Diffusion of the reagents from the liquid bulk to the solid surface.
- Reaction of the reagents with the solid.
- Diffusion of the reaction products from the particle surface to the liquid bulk.
- Further dissolution of solid.

Phenomena	Reactions
Dissolution of limestone	$CaCO_3(s) \rightarrow Ca_2^+ + CO_3^{2-}$
Carbonate ions react with the hydronium ions according to:	$H_3O^+ + CO_3^{2-} \rightarrow HCO_3^- + H_2O$
Carbonic ions react with hydronium ions	$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$
Final products	$H_2CO_3 \rightarrow CO_2(g) + H_2O$

The mechanism of reaction and the limestone dissolution have been studied and it has been demonstrated that the mass transfer is the limiting factor for the chemical reactions

The correlation between volume V_p and time t is considered to be a function of the mass transfer coefficient related to the liquid film k_L, for the particular case of limestone-acid system.

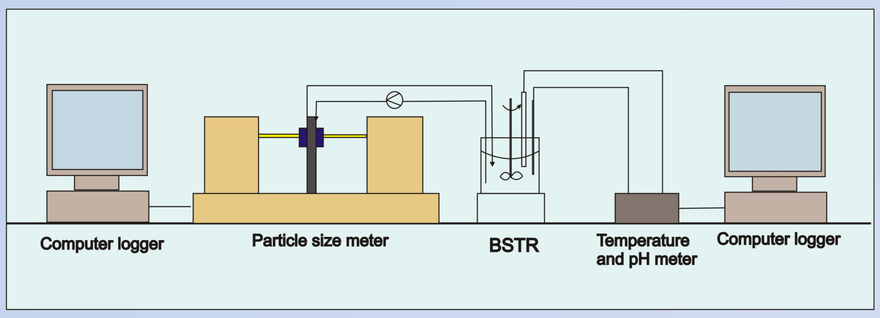
$$\frac{dV_p}{dt} = -K\frac{\pi C_h}{\rho_m}\left[2D\left(\frac{6V_p}{\pi}\right)^{\frac{1}{3}} + 0.13\left(\frac{\varepsilon \upsilon_c}{\rho_c^2}\right)^{\frac{1}{4}}\left(\frac{\upsilon_c}{D}\right)^{-\frac{2}{3}}\left(\frac{6V_p}{\pi}\right)^{\frac{2}{3}}\right]$$

Where ρ_m is the molar density of the limestone and C_h is the concentration of hydronium ions and d_p is the diameter of the particle υ_c is the kinematic viscosity of fluid, ε is the agitation power per unit volume (W/l) and ρ_c is the fluid density. The *K* parameter is dimensionless and indicates the dissolution rate constant of limestone.

Materials and methods

The used limestone is from the Parainen quarry in SW Finland. The carbonate rock is a 1900 million-year-old limestone metamorphosed to marble during the Svecofennian orogeny 1830 million years ago (metamorphosed limestone). Mineralogically it is almost pure calcite and texturally an even grained marble.

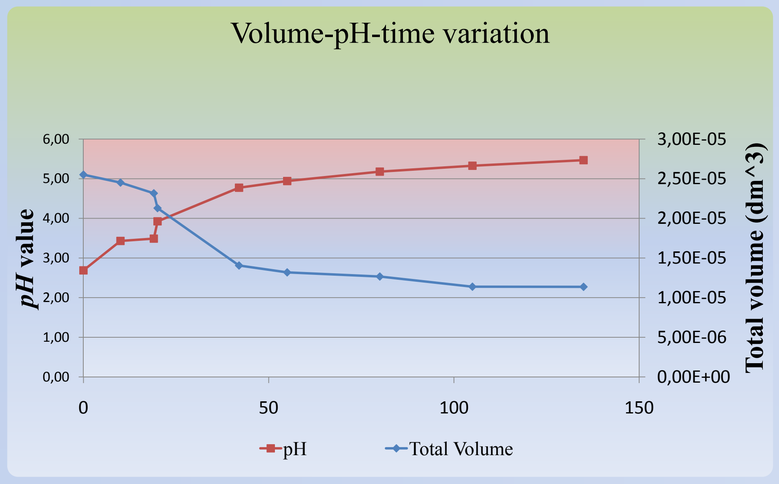
The experimental apparatus is constituted by a batch stirred tank reactor, a laser-beam diffractometer with a particle size meter and one temperature and *pH* meter. The temperature has been mantained at constant room temperature.



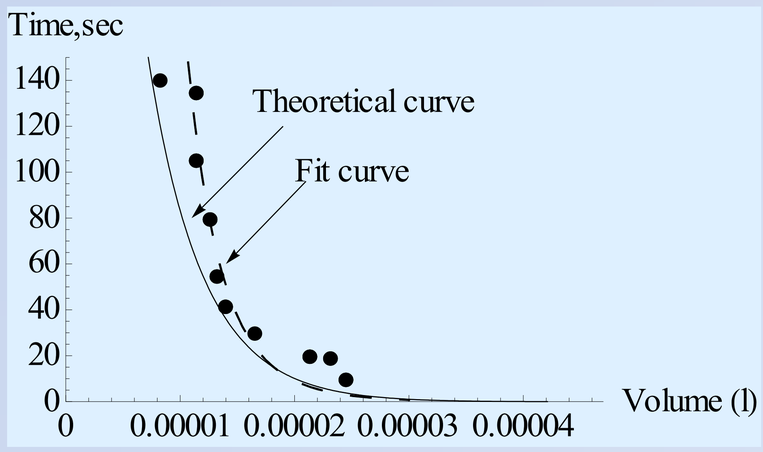
For each size range, the limestone fraction in volume was given. Furthermore it was possible to control all the BSTR parameters by computer device. The two computer loggers were synchronized together.

Results

Volume-time dependency as a function of the hydronium concentration.



The technique and the model presented in this work eliminate uncertainties and errors encountered when the *pH* of the solution is maintained unchanged. Constant *pH* is a condition difficult to obtain



The mathematical model was sensitive to the *pH* variations: at small differences of hydronium concentration there was a sensible increase of the time needed to have the measured changes in volume. This behavior is perfectly in accordance with the model reported here.

Conclusions

The dissolution rate model gives results in good agreement with the experimental data, according to this work, it is possible to evaluate the reactivity of high calcium limestone with specified particle size distribution. The model and the experimental procedure provide a more complete tool for measuring the properties of the gas desulfurization chemicals.

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