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

Cataldo De Blasio, Jarl Ahlbeck, Frej Bjondahl
Åbo Akademi University, Faculty of Technology, Biskopsgatan 8, FIN-20500 Åbo, Finland

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 solid surface to the liquid bulk.
• Further dissolution of solid.

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.

$$\frac{dV_p}{dt} = -k_l \pi \rho \omega \left[2D\left(\frac{6V_p}{\pi}\right)^{\frac{1}{3}} + 0.13 \left(\frac{\varepsilon}{\rho_p}\right)^{\frac{1}{3}} \left(\frac{6V_p}{\pi}\right)^{\frac{1}{3}}\right]$$

Where $\rho_m$ 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 $\varepsilon$ is the kinematic viscosity of fluid, $\varepsilon$ is the agitation power per unit volume (W/l) and $\rho_p$ 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 maintained at constant room temperature.

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.

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.

Acknowledgements
Fortum Foundation, Finland.
Prof. Tapio Westerlund, Process Design Laboratory, Åbo Akademi University.
Prof. Heikki Ruskeepää, department of Mathematics, University of Turku.

Selected references: