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SciVerse ScienceDirect

Procedia Earth and Planetary Science 7 (2013) 179 – 182

Procedia
Earth and Planetary Science

Water Rock Interaction [WRI 14]

Pitfalls in the measurement of the true dissolution kinetics of soft minerals

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Abstract

The study of dissolution can face pitfalls at all length-scales, other phenomena being able to blur the investigated reaction. We present here two situations where an a posteriori analysis of the experimental results enables recovery of the true dissolution behavior free from external influences. In standard solution chemistry dissolution experiments, the measured dissolution rate is the result of a combination of the reaction kinetics and of mass transport due to the convection of the flowing solvent. We show here how to circumvent this mass transport contribution to recover the true dissolution rate constant. Moreover, in AFM dissolution experiments, the stress applied by the tip to the surface modifies the velocity of the atomic steps, the migration of which is at the origin of dissolution. We show here how to obtain stress-free, true dissolution velocities.

Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

Keywords : dissolution; reaction kinetics; boundary layer; pressure solution; holographic interferometry; AFM.

1. Introduction

Among water-mineral interfacial processes, dissolution is present in countless problems: durability of mineral materials, management of nuclear wastes, sequestration of atmospheric CO_2, pollution of drinking water, etc. In all these situations, the use of predictive models or the optimization of industrial processes requires the knowledge of values of the kinetic parameter of dissolution as accurate as possible. But the delicate nature of the measurement of dissolution rates has often led to satisfy oneself with orders of magnitude.

In a study of the influence of humidity on the mechanical aging of gypsum boards, the elucidation of the exact microscopic origin of the phenomenon has needed the knowledge of dissolution rate constants

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Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013
doi:10.1016/j.proeps.2013.03.128

with accuracy of the order of 20% [1]. In this context, we have searched for methodologies to remove parasitic phenomena from dissolution measurements.

These measurements are of two kinds:

- Usual dissolution measurements are performed with solution chemistry experiments. The working product dissolves in the stirred solvent, and the dissolution rate is deduced from the increase of the concentration in the vessel. With this technique, the measured reaction rate is blurred by the flowing of the solvent, inducing a hydrodynamic contribution to the rate.
- More recent techniques try to deduce the dissolution rate from atomic observations, the velocity of atomic steps at the dissolving surface or the normal retreat velocity of this surface. Atomic force microscopes are often used for these measurements and the influence of the force applied by the tip of the microscope to the surface is neglected, without proof.

In both cases, the access to the pure dissolution kinetics is made difficult by the presence of another field (fluid flow, mechanical stress), modifying the reaction kinetics. We detail below methods to get rid of these disturbances with the example of the dissolution of gypsum in water.

2. How to measure the pure dissolution kinetics in a stirred solvent?

In standard measurement of dissolution rates, as used in chemistry, geology, pharmaceutical science … the mineral, usually in the form of powder, dissolves in a vessel where the solvent is flowing, or put in motion by a stirrer [2]. In the vicinity of the dissolving grain, a mass transport boundary layer develops, making the transition between the surface where the velocity of the fluid is zero, and the bulk flowing liquid. In this boundary layer, the dissolved solid migrates by Fickian diffusion from the interface toward the upper limit of the boundary layer, where it is mixed with the bulk liquid and eventually advected to the measurement device. Therefore, the dissolution rate, i.e., the velocity of increase of the concentration, results from the combination of the reaction rate at the solid-liquid interface, and of the diffusion speed in the boundary layer. The latter depends on the layer thickness, which in turn is a consequence of the geometry of the solid and of the stirring intensity.

As mentioned above, to gain accuracy in the knowledge of the dissolution rate constant of soft minerals, we have proposed a hydrodynamic analysis of the phenomenon that has led to an expression of the dissolution rate including the contributions of the chemical reaction and of the diffusion. Both factors can then be disentangled and the pure chemical reaction rate constant can be isolated, free from any mass transport contribution [3].

We have tested our model with all experimental dissolution rates of gypsum in water available in the literature. Our method requires the knowledge of the boundary layer thickness in the experiment. This quantity is generally not provided and we had to deduce it from the geometry of the device. The uncertainty of this quantity is therefore too large to compute a reliable value of the pure dissolution rate constant from one experimental dissolution rate. But all the existing devices show various boundary layer thicknesses. So computing one pure dissolution rate constant from all the experiments amounts to probe numerous boundary layer thicknesses, then lowering the uncertainty.

The value obtained from the literature with this method has been compared to the value measured with a non-standard measurement technique, holographic interferometry. This measurement has two advantages: it is carried out in quiescent water (so no hydrodynamics disturbs the phenomenon) and it permits to measure the concentration directly at the solid-liquid interface [4]. This experimental value agrees perfectly with the value deduced from the literature, thus validating our analysis.

This study has shown that the dissolution rate measured in standard solution chemistry experiments is blurred by mass transport phenomena. But it has also indicated a mean to get rid of these phenomena, thus giving access to the pure chemical reaction rate constant.