



Review

Variability of crystal surface reactivity: What do we know?

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ABSTRACT

A multitude of natural processes and technical applications require our ability to provide a reliable prediction of crystal surface reactivity. During the last decades, the detailed analysis of crystal surface reactions revealed the existence of intrinsic variability in surface reactivity. This reactivity acts in addition to extrinsic factors, such as inhibitors, background electrolytes, or pH variations. The nature of this intrinsic variability is poorly understood. In any case, it must represent complex energetic contributions from and interactions between reacting mineral surfaces and dissolved and particulate materials in the fluid.

Consequently, single rate constants and homogeneous surface area normalization are problematic constraints for the explanation and prediction of surface reactions of both, natural and artificial materials. Here, we review various aspects of intrinsic variability of crystal surface reactivity from experimental and modeling results including the fundamental role of microscopic kink site distribution. Important reaction processes include crystal dissolution and sorption of small particles, i.e., nanoparticles and colloids.

A key means of understanding these variations lies in understanding the relationship between surface energy distribution and surface roughness. Rough surfaces are well-known to control the retention of colloids and nanoparticles under unfavorable adsorption conditions. This review provides an integrated view on an important feedback process that includes surface reactivity, kink site distribution, surface roughness, particle retention, and surface inhibition as critical components. Also, we review briefly the methods used to quantify surface roughness variability over a wide range of scales. It is our goal to highlight the multiple facets that may both reflect or influence the intrinsic variability of reactions over time.

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1. Introduction

1.1. Aim of the paper

Many applications require our ability to predict rates of fluid–crystal reactions with high precision. Such predictions are complicated to make because critical reaction rates show broad variations, often several orders of magnitude (e.g., Becker et al., 1996; Casey et al., 1993; Daval et al., 2013; Maher et al., 2006; Swoboda-Colberg and Drever, 1993; Velbel, 1999; White et al., 1996; White and Brantley, 2003). Even under well-constrained and constant chemical conditions in the laboratory variations can be easily two orders of magnitude (e.g., Arvidson et al., 2003; Asta et al., 2008; Eggleston and Hochella, 1994; Liang and Baer, 1997; Morse et al., 2007; Rimstidt et al., 2012). Several aspects of this *intrinsic* rate variability have been discussed during the last few years in the literature (e.g., Dove and Platt, 1996; Eggleston and Hochella, 1992; Harries et al., 2013; Hiemstra and van Riemsdijk, 1999; Higgins et al., 2002; Hochella et al., 1990; Levenson and Emmanuel, 2013; Madden et al., 2006; Sanders et al., 2010; Stumm, 1997; Teng and Dove, 1997). For a brief summary see Lutge et al. (2013).

The main objective of this review is an attempt to analyze, discuss, and finally connect these aspects of variability of crystal–fluid reactions. This attempt may have to remain unfinished, yet, because important questions that are related to this topic are still not fully answered. A few examples are: How large is the intrinsic variability of crystal surface reactivity? Is it correct to apply a single (mean) rate constant for the prediction of material release from a crystal surface during dissolution? What evolution of surface reactivity over reaction time do we have to expect? Does crystal surface roughness correlate with surface reactivity? And how can we implement information about the variability of reactivity into predictive approaches?

These questions are all related to the *intrinsic* variability of surface reactivity. Additionally, *extrinsic* factors are able to inhibit or catalyze surface reactions significantly. There might be also an opportunity that extrinsic factors, such as adsorbing nanoparticles or colloids could “map” certain reactive sites of a crystal surface. Many fluid–solid reactions in natural and technical environments occur as a sum of diverse and, in part, concurrent reactions. The reacting fluid contains dissolved and particulate matter. The concurrent reactions will continuously impact the evolution of surface roughness and topography. The interaction of small particles (colloids) with crystal surfaces alters surface chemistry, charge, roughness, and, more importantly, the surface reactivity. However, such

changes occur often heterogeneously distributed on crystal surfaces. Thus, the local differences in surface reactivity may change dramatically over reaction time. How do such changes impact the overall reactivity of natural and technical systems? The answer to this question has important consequences for our ability to predict reaction rates correctly.

The overarching framework that provides thorough understanding, meaningful quantification, and robust prediction of surface reactivity is provided by the concept of surface energy (e.g., Yudin and Hughes, 1994), including its spatial distribution. Surface energy and its fluctuations initiate surface reactions and govern their evolution over time. Critical insight in this framework is provided by different types of reactions, such as dissolution or adsorption.

Within this scope, the objectives of our paper are:

- (i) to discuss the experimental data exhibiting intrinsic variability;
- (ii) to provide information about the respective impact of intrinsic and extrinsic factors that govern reaction rate variability;
- (iii) to review results from kinetic Monte-Carlo (KMC) modeling approaches that inform about spatial and temporal variability of intrinsic reactivity;
- (iv) to discuss approaches to analyze and quantify the evolution of surface topography;
- (v) to review the impact of surface roughness on the resulting interaction energy between collector surfaces and small particles (colloids).

1.2. Organization of the present study

We discuss important attributes of surfaces: reactivity (“reactive surface area”) and topography. Quantification of surface topography evolution requires a robust concept of surface roughness analysis. The approach of converged roughness parameters is discussed and employed to quantify the topography evolution of common non-fractal mineral surfaces. This approach enables the meaningful adaptation of roughness parameters, well-known in material science, for a characterization of natural, complex crystal, mineral, and rock surfaces. Crystal surface roughness is able to modify the effective surface energy potential and therefore the resulting forces according to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. As a consequence, spatial and temporal fluctuations of the DLVO interaction forces occur over the periods of crystal surface reactions. Thus, important consequences for adsorption reactions of both molecules and particles are expected. As an example, the interaction of

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