



The mechanism of dissolution of minerals in acidic and alkaline solutions: Part II Application of a new theory to silicates, aluminosilicates and quartz



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ABSTRACT

The kinetics of the dissolution of silicates, aluminosilicates and quartz is described by a novel theory of dissolution. The experimental data for the rate of dissolution of these minerals shows a remarkable pattern: for many of these minerals, the order of reaction with respect to H^+ is close to 0.5 in the acidic region, and the order of reaction with respect to OH^- is close to 0.5 in the alkaline region. It is proposed that the site of bond breaking in the rate-determining step of dissolution is the weakest bond, and this is frequently the metal–oxygen bond because of the higher bond energy of silicon–oxygen bonds. Alternatively, the least number of silicon–oxygen bonds is broken. This means that silicate groups react intact as a unit. Both metal atoms and silicate groups react and are removed independently. The rates of these independent processes are coupled by the potential at the surface. In the acid region, H^+ reacts with silicate groups at the surface. In the alkaline region, OH^- ions react with the metal atom at the surface. The proposed theory of dissolution correctly predicts the observed orders of reaction with respect to H^+ ions and OH^- ions in solution. The order of reaction of forsterite with respect to H^+ changes from 0.5 in the acidic region to 0.25 in the region above a value of pH of approximately 6. The proposed mechanism suggests that the reason for the change in order of reaction is that the H^+ needs to be positioned at the inner Helmholtz plane to be effective in alkaline solutions.

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1. Introduction

The dissolution of minerals in acidic and alkaline solutions is of interest in a large number of fields, including geochemistry, minerals processing, hydrometallurgy and materials science. The dissolution of rock-forming minerals is important in establishing an understanding of many geochemical processes. The dissolution of protective films on materials continues to be of interest in materials science. The dissolution of minerals that contain valuable metals is the key process in hydrometallurgy. The study of dissolution and leaching continues to drive much of the research interest in hydrometallurgy.

The dissolution of silicate ores to recover valuable metals is not frequently practised in hydrometallurgy. One notable exception is in the recovery of zinc. Zinc is recovered at the Skorpion mine in Namibia from saucanite and hemimorphite minerals, which are silicate minerals (Borg et al., 2003). Another possibility, although economically unattractive at present, is the dissolution of clay minerals such as kaolinite, which has been investigated as an alternative source of aluminium (Ford, 1991).

For hydrometallurgists, though, the dissolution of silicates is important in the whole-ore processing of other minerals. Silicates are almost

always present in economic ores because they are such an abundant mineral group. During leaching, the silicates may not be inert, and can contribute to the impurities that need to be removed from solution. For example, aluminosilicates contribute aluminium, colloidal silica and other metal ions to whole-ore and heap-leaching circuits. Aluminium needs to be removed from copper plants in Zambia and the Democratic Republic of Congo by precipitation to prevent build-up in the circuit. Silica in solution and colloidal silica may contribute to crud formation in solvent extraction plants.

Fractional orders of reaction, particularly with respect to H^+ and OH^- , are frequently observed for silicate minerals. A general mechanism for the dissolution of minerals in non-oxidizing solutions was proposed by Crundwell (2014). This mechanism accounts for the effect of the potential difference across the interface between the mineral and the solution, which leads to the fractional orders of reaction reported for the silicates.

The purpose of this paper is to apply the proposed mechanism of dissolution to the kinetics of dissolution of the silicate and aluminosilicate minerals and quartz. In particular, this paper demonstrates that the mechanism of dissolution derived by Crundwell (2014) describes the dissolution of the silicates.

The paper is structured in the following manner. In the next section, classification of the silicates based on their structure will be presented.

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The types of dissolution behaviour will be described next. Following this, the experimental results reported by others are summarized. Finally, the proposed theory of dissolution is applied to the dissolution of these minerals.

2. Classification of the silicates

Silicon forms a tetrahedral unit with four oxygen atoms, SiO_4^{4-} , in silicate minerals. These tetrahedral units can be arranged in several different ways by sharing the oxygen atoms on the corners of the tetrahedral structure, resulting in the six classes of silicates that are shown in Table 1.

The silicates present a wide range of structural arrangements, from independent tetrahedra, through ring, chain and sheets to a continuous three-dimensional polymer.

The behaviour of these structures during dissolution is discussed in the next section.

3. Dissolution behaviour of the silicates

The dissolution of silicates in acid or alkaline solutions results in either (i) the complete breakdown of the silicate structure, (ii) the partial breakdown of the structure, usually experienced as the dissolution of the cations leaving a siliceous residue behind, or (iii) no dissolution (Terry, 1983b,1983c).

The dissolution of silicates, particularly in the context of weathering, is frequently classified as congruent or incongruent. Congruent dissolution occurs when no new phases are formed; incongruent dissolution occurs when new solid phases form with dissolution. Incongruent dissolution implies the formation of a partially leached zone or an alteration layer.

One of the earliest models for the dissolution of silicates is the proposal that the rate of dissolution is controlled by the diffusion of ions through an alteration layer. Alteration layers, of several Angstroms thick, have been observed on the surface by XPS and other studies, which presumably supported the observation of parabolic kinetics (Brantley, 2008; Tsomaia et al., 2003). The diffusional view is no longer predominant. The evidence against the diffusional view is two-fold: (i) the observed orders of reaction are close to one-half, whereas diffusional processes can only be first order; and (ii) the dissolution often becomes congruent at longer reaction times, particularly at conditions far from equilibrium.

Even if diffusion through the alteration layer does not control the rate of dissolution, alteration layers are present on the surface, particularly at lower pH values. Such alteration layers may be the result of preferential leaching leading eventually to a layer of constant thickness at

steady state, or due to the re-precipitation of material after dissolution (Brantley, 2004).

This study is focused on the dissolution of the silicates under conditions where dissolution is congruent and the products are in the same stoichiometric ratio as in the mineral. Oelkers (2001) and Oelkers and Gislason (2001) argue that the partial breakdown of the silicate structure is part of the initial stages of dissolution, a “provisional part of the dissolution process” that continues until congruent dissolution is established. In other words, this study is not concerned with the initial processes where non-stoichiometric dissolution might dominate prior to dissolution under stoichiometric conditions. The rates of dissolution of the silicates are frequently determined by measuring the concentration of Si in solution, which implies the measurement of the complete breakdown of the silicate structure.

Generally, the dissolution reactions are assumed to be dependent on the phenomena occurring at the interface, rather than on the diffusion of material through the alteration layer. One model of the reaction pathway envisages the dissolution occurring in four steps as the bridging bonds between the Si are broken by reaction with protons. This means that the silicon tetrahedral with four oxygen atoms departs from the surface by breaking bonds with other Si atoms. This possible pathway is shown in Fig. 1 (Brantley, 2008; Tsomaia et al., 2003).

The pathway shown in Fig. 1 seems plausible; however, like all proposals concerning chemical pathway, it does not describe the kinetics of dissolution. In other words, the pathway does not indicate how the rate of reaction is increased or retarded, or the factors that influence the rate of reaction. In contrast, the aim of a kinetic mechanism is to identify the step or steps that are the slowest in the reaction pathway. These slow steps ‘control’ the rate of the overall reaction. As is argued later, these rate-controlling phenomena have not been satisfactorily identified for the dissolution of silicates.

The kinetic factors that influence the rate of dissolution are discussed in the next section.

4. Kinetics of dissolution of silicate minerals

The rate of dissolution is affected by the concentration of the reagent in solution and the temperature (Crundwell, 2013). This dependence is usually expressed mathematically in the following form for an irreversible reaction:

$$\text{rate} = k[c]^n \exp(-E_A/RT) \quad (1)$$

where $[c]$ represents the activity or concentration of a reactant, k the rate constant $[\text{mol}/(\text{mol}/\text{m}^3)^{-n}/(\text{m}^2/\text{s})]$, n the order of reaction $[-]$, E_A the activation energy $[\text{kJ}/\text{mol}]$, R the gas constant $[\text{kJ}/\text{mol}/\text{K}]$, and T the temperature $[\text{K}]$. The units of rate are $\text{mol}/\text{m}^2/\text{s}$.

Table 1
Classification of silicates (Terry, 1983a).

Class	Structural arrangement	Si:O ratio	Silicate group	Example
Nesosilicates (orthosilicates)	Independent tetrahedra	1:4	SiO_4^{4-}	Forsterite, Mg_2SiO_4 Willemite, Zn_2SiO_4
Sorosilicates (pyrosilicates)	Two tetrahedral that share a common oxygen atom	2:7	$\text{Si}_2\text{O}_7^{6-}$	Hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$
Cyclosilicates (ring silicates)	Closed rings of tetrahedral sharing two oxygen atoms each	1:3	$\text{Si}_3\text{O}_9^{6-}$ $\text{Si}_4\text{O}_{12}^{8-}$ $\text{Si}_6\text{O}_{18}^{12-}$	Beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
Inosilicates (chain silicates)	Pyroxene group: continuous single chain of tetrahedral each sharing two oxygen atoms Amphiboles: continuous double chain of tetrahedral alternately sharing two and three oxygen atoms	1:3 4:11	$(\text{Si}_2\text{O}_7^{6-})_n$	Enstatite, MgSiO_3 Diopside, $\text{CaMgSi}_2\text{O}_6$ Anthophyllite, $(\text{Mg}, \text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ Hornblende, $(\text{Ca}, \text{Na})_{2-3}(\text{Mg}, \text{Fe}, \text{Al})_5\text{Si}_6(\text{Al}, \text{Si})_2\text{O}_{22}(\text{OH})_2$
Phyllosilicates (sheet silicates)	Continuous sheets of tetrahedral each sharing three oxygen atoms	2:5	$(\text{Si}_2\text{O}_5^{2-})_n$	Chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (serpentine) Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ Biotite, $\text{K}(\text{Mg}, \text{Fe})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$
Tectosilicates (framework silicates)	Continuous framework of tetrahedral each sharing all four oxygen atoms	1:2	$(\text{SiO}_2)_n$	Quartz, SiO_2 K-feldspar, KAlSi_3O_8 Albite, $\text{NaAlSi}_3\text{O}_8$

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