



Mechanism and kinetics of wollastonite fibre dissolution in the aqueous solution of acetic acid

Petr Ptáček*, Magdaléna Nosková, Jiří Brandštetr, František Šoukal, Tomáš Opravil

Centre for Materials Research, Faculty of Chemistry, Brno University of Technology, Purkyňova 464/118, Brno, CZ-621 00, Czech Republic

ARTICLE INFO

Article history:

Received 1 August 2010

Received in revised form 17 September 2010

Accepted 28 September 2010

Available online 28 October 2010

Keywords:

Wollastonite

CaSiO₃

Acetic acid

Dissolution of silicates

Dissolution mechanism

Dissolution kinetics

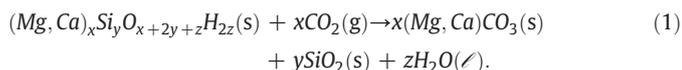
ABSTRACT

The dissolution of fibrous wollastonite (CaSiO₃) in the aqueous solution of acetic acid (3 mol dm⁻³) was investigated in the temperature interval from 25 to 50 °C using mixed batch-type reactor. An incongruent dissolution of wollastonite proceeds under applied acidic condition. The pH of solvent was increasing during leaching of calcium and its actual value depended on the concentration of Ca²⁺ ions in the solution according to the Henderson buffer equation. That enabled the monitoring of dissolution kinetics via concentration of Ca in the dispersion medium of suspension of wollastonite measurement. The kinetic parameter of the process was evaluated from measured dissolution rates of wollastonite at constant temperature using the empirical Arrhenius equation. The apparent activation energy and pre-exponential factor estimated from the Arrhenius plot are 47 ± 1 kJ mol⁻¹ and (1.8 ± 0.9) × 10³ s⁻¹. The kinetics analysis of the process indicates that the process is driven by the stationary two-dimensional diffusion (D₂).

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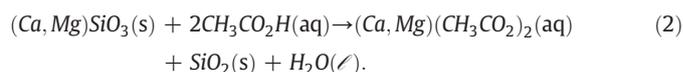
1. Introduction

Carbon dioxide capture and storage (CCS) technologies are considered as one of the main options for reducing the atmospheric emissions of CO₂ from human activities [1]. Carbonation of natural silicate minerals is an alternative to geological [2–6] or ocean storage [7–12] of anthropogenic CO₂. Mineral carbonation traps carbon dioxide as environmentally stable solid carbonates, which can be described by the following overall chemical reaction [1,13]:

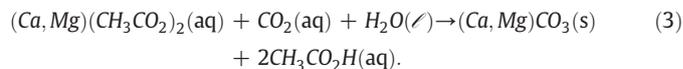


Alkaline-earth oxides, such as MgO and CaO, are present in large amounts and high concentrations in naturally occurring silicate minerals. The natural carbonation of silicate minerals is very slow so the carbonation reaction must be accelerated considerably to be a viable large-scale storage method for capturing CO₂. One of the most promising methods suggested for carbonation involves the leaching or dissolution of calcium and magnesium rich silicates in the liquid media and subsequent precipitation of magnesium or calcium carbonates from the leachate through the subsequent carbonation [1].

The process consists of two main steps. First, calcium or magnesium ions are extracted from a natural silicate mineral by leaching in acetic acid:



After filtrating silica from the solution, CO₂ is introduced into the leachate, forming calcium or magnesium carbonate that precipitates from the solution (Eq. (3)). Acetic acid is next recovered to the extraction step [14,15].



The theoretical background concerned to the dissolution of silicates in the acidic environment is well described in the literature. The course of silicates dissolution was influenced by the type of applied solvent and its concentration in the solution [1]. Furthermore the temperature [16,20,24,26], pH [16,20,24,26], and ionic strength [16,17] of the solvent and the crystallographic direction [18] affected the dissolution. Some data on the kinetics of dissolution of calcium and magnesium containing silicates published in the literature are listed in Table 1.

The present paper summarizes the results of kinetic study concerned to dissolution of wollastonite in the aqueous solution of acetic acid. Leaching of calcium from fibrous wollastonite was investigated within the temperature range from 25 to 50 °C. The morphological model

* Corresponding author. Fax: +420 541 149 389.
E-mail address: ptacek@fch.vutbr.cz (P. Ptáček).

suitable for the description of a leaching process in the solution of acetic acid was found. This work ties into previous work [27] aimed at the investigation of the effect of temperature on the amount of extracted calcium and the properties of residual silica particles.

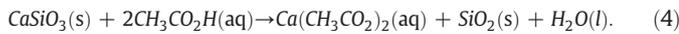
2. Experimental and methodology

2.1. Sample characterization and measurement

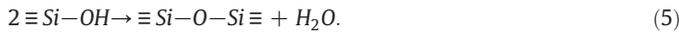
The wollastonite obtained from Ankerpoort NV: The Mineral Company (Netherlands), with specific surface area of $0.66 \text{ m}^2 \text{ g}^{-1}$ (Chembet 3000) was used in this study. The particles of $90 \mu\text{m}$ undersize were employed without other treatments. The wollastonite properties and the dissolution experiments were described elsewhere [27]. The temperature of leaching batch ranged from 25 to $50 \text{ }^\circ\text{C}$. All tests were repeated at least four times. If outlier results were identified, the values were discarded from the set of results and the experiment was repeated.

2.2. Methodology and mathematical background

The crystal structure of wollastonite (CaSiO_3) is build up from single unbranched chains which consist of $[\text{Si}_3\text{O}_9]^{6-}$ units. Chains are held together via positively charged Ca^{2+} ions. These ions are replaced by H_3O^+ during dissolution. The incongruent dissolution of wollastonite in the aqueous solution of acetic acid can be generally expressed as follows:



The dissolution of solids in liquids (or melts) consists of a surface chemical reaction and transport of the reaction components to the reaction boundary [28]. Many multicomponent silicate minerals were dissolved incongruently. The Ca^{2+} ions were replaced by H_3O^+ ions and leached layer of silica was formed. This layer wasn't homogeneous and its structure was changing with time as a consequence of polymerization of silanol groups [29]:



Besides the temperature the solubility of an amorphous silica layer depends on pH and shows the minimum at pH 7. The accurate data are

still missing because there is an extreme variation in the forms in which the amorphous silica can occur. The rate of dissolution is proportional to the concentration of H_3O^+ and OH^- ions in the range from 0 to 2 and from 3 to 6, respectively. The rate of diffusion or desorption of the silicic acid from the surface limits the rate of dissolution if pH is higher than 6 [30].

The evaluation of dissolution experiments reflects the following facts and presumptions:

- The amount of calcium passed into the solution is much higher than other elements released from wollastonite during leaching experiments, i.e. the amount of other metals in the solution is negligible;
- Large excess of acetic acid in the system ensures its stable concentration level;
- Henderson–Hasselbalch buffer equation (Eq. (6)) can be applied for the reaction mixture;
- Incongruent dissolution process, where leached layer covers collapsed wollastonite core continuously so that the shape of particle is preserved. In other words, the dissolution of wollastonite is a heterogeneous process;
- The reaction is proceeding until total dissolution of wollastonite. Therefore, the time dependence of the process can be described by dimensionless parameter denoted as the degree of conversion (y).
- Leached calcium was instantaneously transported out of surface by intensive stirring of the system;
- The sample of wollastonite contains a certain amount of calcite (5.6%) which was dissolved immediately after acetic acid was introduced into the reactor.

The validity of these terms was discussed already in the previous paper [27].

$$\text{pH}(T) = \text{p}K_a(T) + \log \frac{2[\text{Ca}^{2+}]}{[\text{CH}_3\text{CO}_2\text{H}]} \quad (6)$$

The $\text{p}K_a$ is the dissociation constant of acetic acid. All variables in Eq. (6) depend on the temperature. The steady-state dissolution rate for applied temperature $r_+(T)$ can be calculated using equation [21]:

$$r_+(T) = \frac{([\text{Ca}^{2+}]_i - [\text{Ca}^{2+}]_t)V}{\nu_{\text{Ca}} \cdot S \cdot (t - t_i)} = \frac{\Delta[\text{Ca}^{2+}]V}{S \cdot \Delta t} \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right]; \quad (7)$$

where $[\text{Ca}^{2+}]_i$ and $[\text{Ca}^{2+}]_t$ are an initial t_i and general time t concentrations of Ca^{2+} ions, respectively. The initial time of the process means the beginning of an induction period, so that the amount of Ca released during dissolution of calcite can be excluded. The quantities V , ν_{Ca} and S are a volume of the system, stoichiometric number of calcium in Eq. (4) ($\nu_{\text{Ca}} = 1$) and total surface area of sample introduced into the reactor, respectively. The term $\Delta[\text{Ca}^{2+}]/\Delta t$ of Eq. (7) can be determined as the slope of the linear part of the plot of concentration vs. time.

The variation of mineral dissolution rates with temperature is commonly described using the empirical Arrhenius law given by [21,31]:

$$r_+ = A \exp\left(-\frac{E_A}{RT}\right); \quad (8)$$

where A , E_A and R are the pre-exponential factor, the apparent activation energy and the universal gas constant, respectively. The estimation of the apparent activation energy and the pre-exponential (frequency) factor (A) is based on the logarithmic form of the Arrhenius law:

$$\ln r_+ = \ln A - \frac{E_A}{R} \frac{1}{T}; \quad (9)$$

Table 1
Data about dissolution of silicates collected from the literature.

Mineral	Solution properties	E_A [kJ mol ⁻¹]	Rate limiting step of process	Reference
Wollastonite	pH 3–8	79.2	Diffusion ^a	[19]
	Diluted acetic acid, pH 2–3.5	47.1	Two-dimension diffusion	This article
Enstatite	pH 1–11; 28–168 °C	48.5	Reaction ^b	[20]
Forsterite	pH 2; 25–65 °C	63.8	Reaction ^b	[21]
Olivine	pH 2–5; 65 °C	125.6	Reaction	[22]
	3 M H ₂ SO ₄ ; 60–90 °C	66.5	Reaction	[23]
Serpentine	2 M H ₂ SO ₄ ; 30–70 °C	68	Diffusion	[1]
	2 M HCl; 30–70 °C	70		
	2 M HNO ₃ ; 30–70 °C	74		
Talc	pH 1–10.6; 25–150 °C	45.0		[24]
Anorthite	pH 2.4–3.2; 45–95 °C	18.4 ^c		[25]
Diopside	pH 2–12; 25–70 °C	40.6	Surface reaction	[26]

^a Under low pH values.

^b Forming of rate-controlling precursor complex.

^c Under pH = 2.6.

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