

# Dissolution Mechanism of Silicate Mineral Phases into Water by Considering Silicate Network Structure

著者	RUAN FANG
学位授与機関	Tohoku University
学位授与番号	11301甲第19869号
URL	<a href="http://hdl.handle.net/10097/00135742">http://hdl.handle.net/10097/00135742</a>

氏名	らん ふあん 阮 方
研究科, 専攻の名称	東北大学大学院工学研究科 (博士課程) 金属フロンティア工学専攻
学位論文題目	Dissolution Mechanism of Silicate Mineral Phases into Water by Considering Silicate Network Structure (シリケートネットワーク構造に基づくケイ酸塩結晶鉱物相の水への溶出機構解明)
論文審査委員	主査 東北大学教授 柴田 浩幸 東北大学教授 植田 滋 東北大学教授 長坂 徹也

## 要約

### • Chapter 1: Introduction

More than 40 million tonnes of the blast furnace slag and steelmaking slag are produced annually in Japan, which are a byproduct in the metallurgy industry. Their excellent physical and chemical characteristics, for example, hydraulic proper bearing capacity, wear resistance and heavy weight of unit volume, make this secondary structural material possess huge potential in the field of resource recycling. Almost all the blast furnace slag has been recycled in the society, however, an environmentally-friendly and high-efficient recycling of steelmaking slag has not yet been achieved. Although the steelmaking slag has been applied in many aspects in society, the potential environmental risks due to the excess alkali elution have attracted much attention. Because steelmaking slag consists of various silicate minerals and/or glass phases, knowing the Ca leaching property of each phase is crucial. In addition, the environmental risk can be mitigated by investigating the dissolution mechanism of silicate mineral phases into water. However, the effect of silicate network structure of silicate mineral phases on their dissolution behaviors into water has not yet been revealed. Therefore, the research objective is to clarify the dissolution mechanism of silicate mineral phases into water by considering silicate network structure. This research investigated the dissolution behaviors of 15 kinds of silicate mineral phases into water, revealed the relationship between the elution ratios of Ca and the polymerization degree of the silicate network structures, clarified the elution kinetics of the network modifiers (NWM) and the network formers (NWF) in the silicate structure according to the non-steady diffusion model and the detachment reaction model, respectively. Subsequently, the dissolution mechanism of silicate mineral phases into water was proposed. Eventually, the prediction models of the short-term elution ratios of Ca and Si were established. The following is described for details.

### • Chapter 2: Effect of Silicate Skeleton Structure on the Dissolution Behaviors of CaO-SiO<sub>2</sub> Silicate Mineral Phases in Water

In the investigation of the effect of silicate skeleton structures on the dissolution behaviors of 5 kinds of CaO-SiO<sub>2</sub> quasi-binary mineral phases into water, silicate mineral phases with different silicate skeleton structure including isolated

[SiO<sub>4</sub>]<sup>4-</sup> tetrahedrons structures, dimer [SiO<sub>4</sub>]<sup>4-</sup> tetrahedrons structures, three-membered ring structures and the single chain structures were synthesized according to the phase diagram, and then identified by X-ray diffraction method. The short-term leaching tests using powder mineral samples with the particle size under 53 μm were conducted to analyze their dissolution behaviors. The results obtained from the leaching tests revealed that the pH of each solution greatly increased in the first 5 minutes, which was caused by the intense elution behavior of Ca from target mineral phases, and the elution amount of Ca was in the following order: Ca<sub>3</sub>SiO<sub>5</sub> > γ-Ca<sub>2</sub>SiO<sub>4</sub> > Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> > α-CaSiO<sub>3</sub> > β-CaSiO<sub>3</sub>. This suggested that the elution behavior of Ca is the main reason of the increase in pH of solution. Furthermore, the elution ratios of Ca after 1 hour's leaching decreased when the basicity of the silicate mineral phases decreased, and the elution ratios of Ca decreased when the polymerization degree of the silicate skeleton structures increased.

• Chapter 3: Clarification of the Dissolution Mechanism of CaO-SiO<sub>2</sub> Silicate Mineral Phases in Water

As for the clarification of the dissolution mechanism, 4 kinds of CaO-SiO<sub>2</sub> quasi-binary mineral phases with different silicate skeleton structures were prepared in the form of bulk samples. After the leaching tests, the changes in surface condition were analyzed to reveal the dissolution mechanism. The elution kinetics of Ca and Si were analyzed by combining the experimental results collected in the leaching solution and on the surfaces of the bulk mineral samples. The time dependence of the Ca-Si relative release ratio during leaching indicated the preferential elution of Ca to Si in the initial stage of dissolution, and the degree of the preferential elution was enhanced when the complexity of the silicate skeleton increased. Correspondingly, the formation of a Ca-depleted layer on the surface of the leached sample was also confirmed by X-ray photoelectron spectroscopy and time-of-flight secondary-ion mass spectrometry. This suggested the occurrence of an ion-exchange reaction between Ca<sup>2+</sup> and H<sub>3</sub>O<sup>+</sup> in the initial stage of the leaching test. In addition, the nanoscale amorphous layers were observed on the surfaces of bulk minerals for all the target mineral phases by transmission electron microscopy, and the thickness of this layer decreased with the increase in the complexity of the silicate skeleton structure. Based on these experimental results, the rate-determining steps of Ca and Si were determined as the semi-infinite diffusion step in the Ca-depleted layer and the detachment reaction step of the intermediate phase (amorphous layer) that is formed on the surfaces of the bulk mineral samples by hydration, respectively. Therefore, the dissolution of the silicate mineral phase into water includes the ion-exchange reaction between Ca<sup>2+</sup> and H<sub>3</sub>O<sup>+</sup> in the initial stage, then the Ca<sup>2+</sup> started to diffuse in the Ca-depleted layer. Subsequently, the regularly arranged crystalline structure changed in amorphous layer with the attack of protons, which can be seen as an intermediate product. At last, the detachment reaction of this amorphous layer happened, hydrated Si species released from the mineral surface. The diffusion coefficient of Ca in the leached layer and the reaction-rate coefficient of Si were also evaluated according to the elution kinetics of Ca and Si, respectively, and their variation trends showed that they decreased with the increase in the polymerization degree of the silicate skeleton structure in the following sequence: γ-Ca<sub>2</sub>SiO<sub>4</sub> > Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> ≈ β-CaSiO<sub>3</sub> >

$\alpha$ -CaSiO<sub>3</sub>.

• Chapter 4: Effect of Additives (MgO, FeO, Al<sub>2</sub>O<sub>3</sub> or CaF<sub>2</sub>) on the Elution Behavior of Ca from Silicate Mineral Phases in Quasi-ternary System in Water

The effect of ternary additives (MgO, FeO, Al<sub>2</sub>O<sub>3</sub> or CaF<sub>2</sub>) on the dissolution behaviors of 10 kinds of quasi-ternary silicate mineral phases was investigated by the powder leaching test. The quasi-ternary silicate mineral phases showed relatively lower elution ratios of Ca than those of CaO-SiO<sub>2</sub> quasi-binary mineral phases. As for the chemical additives of MgO and FeO, the elution ratios of Ca of these related silicate mineral phases decreased when the replacement ratios of Mg<sup>2+</sup> increased for silicate mineral phases with isolated [SiO<sub>4</sub>]<sup>4-</sup> tetrahedron silicate skeleton structures, suggesting that the addition of MgO in nesosilicates have an effect to suppress the elution ratio of Ca. The replacement of Fe<sup>2+</sup> also showed an effect to reduce the elution ratio of Ca for silicate mineral phases with single chain structures. As for the chemical additive of CaF<sub>2</sub>, it showed an effect to remove the face-sharing connection between CaO<sub>x</sub> polyhedrons in the sorosilicate group, which was considered as one of the reasons to explain the relatively lower elution ratio of Ca for the case of Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>. As for the chemical additive of Al<sub>2</sub>O<sub>3</sub>, the crystal structures of these ternary silicate mineral phases were confirmed by the crystallographic information files, and it was found that the Al and specific Mg atoms could form the [AlO<sub>4</sub>]<sup>5-</sup>, [AlO<sub>6</sub>]<sup>9-</sup> and [MgO<sub>4</sub>]<sup>6-</sup> polyhedrons as the NWF like Si atoms, and they linked to the silicate skeleton structure to form a more complicated silicate network structure with higher polymerization degree, which corresponded to the chemical stability of silicate mineral against water. Moreover, the variation trend of the elution ratios of Ca roughly decreased when the polymerization degree of silicate network structure increased for all the target silicate mineral phases (**Fig. 1**). Furthermore, the effect of the silicate network structure on the dissolution mechanism of the quasi-ternary silicate mineral phases was also investigated by applying the dissolution mechanism for CaO-SiO<sub>2</sub> quasi-binary mineral phases, the elution kinetics of NWM (Ca, Mg, etc.) and NWF (Si, Al, etc.) were confirmed to follow the non-steady diffusion model and detachment reaction model well, respectively. The relationship between the polymerization degree of the silicate network structure and the diffusion coefficient of NWM, and the reaction-rate constant of NWF were summarized. The diffusion coefficient of Ca and the reaction-rate constant of Si for the quasi-ternary silicate mineral samples were lower than that of CaO-SiO<sub>2</sub> quasi-binary silicate mineral samples in most cases. The diffusion coefficients of Mg and Fe showed relatively lower values than those of Ca, suggesting that it is more difficult for Mg and Fe to diffuse through the diffusion layer than Ca. The reaction-rate constant of Si was lower than that of Al for the Ca<sub>2</sub>Al(AlSi)O<sub>7</sub>.

• Chapter 5: Correlation between the Elution Behavior of Ca from Silicate Mineral Phases into Water and the Possible Influencing Factors based on Multivariate Analysis

The correlations between the elution ratios of Ca obtained from all the target silicate mineral phases into water and the possible

influencing factors were studied based on the multivariate statistical analysis. The possible influencing factors including the corrected basicity, polymerization degree of the silicate network structure, lattice energy and the average neighboring distance of Ca-O bonds. These influencing factors were calculated by investigating the crystal structures of the silicate mineral phases according to their crystallographic information files. The correlations suggested that the elution ratio of Ca roughly increased when the corrected basicity and lattice energy index increased for all the target silicate mineral phases. In contrast, the variates of lattice energy and the neighboring distance of Ca-O bonds showed relatively weaker correlation to the elution ratio of Ca. Moreover, the empirical formulas were proposed to predict the elution ratios of Ca and Si from the silicate mineral phases in water after 1 hour's leaching. By dividing the target mineral phases into quasi-binary and quasi-ternary systems, the specific prediction formulas were obtained on the basis of multiple linear regression analysis for each system. Furthermore, the practicalities of the prediction formulas were verified by predicting the short-term elution ratios of Ca from solid-solution silicate mineral phases of  $\text{Ca}_2\text{SiO}_4\text{-Ca}_3\text{P}_2\text{O}_8$  into water. The predicted elution ratios of Ca decreased when the content of  $\text{Ca}_3\text{P}_2\text{O}_8$  increased, which agreed well with the variation trend in the previous research, suggesting the validity of the prediction empirical formulas.

#### • Chapter 6: Conclusions

Results obtained in each chapter are summarized, and the impacts of this research in academic and industrial fields are suggested. With the clarification of the dissolution mechanism of silicate mineral phases by considering the silicate network structure, the understandings in the dissolution behavior of silicate materials will be promote in the academical field. In industrial field, by applying the prediction formulas of the short-term elution ratio of Ca, the design for chemical modification of the melt steelmaking slag would be suggested according to the effective selection of the durable mineral phases. It is meaningful to propose the guideline of the chemical modification to produce a kind of new slag product with more stable structures. This study is expected to support some hints that could help to develop the effective technologies to suppress the excess alkali elution from the steelmaking slag in the field.