論文の内容の要旨

論文題目　　Thermo-Hygro Stability of Solidified Pozzolans in Aqueous Medium

（湿潤環境下におけるポゾラン硬化体の熱力学的安定性に関する研究）

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The production rate of by-product has been greatly exceeded an attempt to reduce this abundant material by its utilization in many segments. The remains become problems when hundred of million tons is disposed on soil foundation and pollutes the biosphere. The application of by-product as cement replacement is considered as a great consensus to obtain some advantage both for concrete performance and environmental issues comprising economical problems. Considering the stability and ensuring their general application to the macro-scale system for long term serviceability are of important contemplation in many fields. Therefore, a comprehensive analysis of the multi-scale thermodynamics stability of by-product applications requires its clarification, simplification and investigation in micro-sized level at laboratory-scaled specimens.

The thermodynamic stability under aqueous medium was discussed for suitable treatment of blast furnace slag (BFS) and fly ash in this research. The discussion was directed to the gas-phase stability coupling with kinematics which is associated with vapor pressure inside the micro-pores of the solidified materials. Concerning the harmful substances to human health, especially boron in fly ash, liquid-phase stability related to ion dissolution and adsorption of boron was also investigated in line with the thermo-hygro stability. A sustainable waste material application in some point of views has immense value to the contribution in society.

Gaseous-phase stability in porous media such as cementitious material is specified with diffusion of humidity for the vapor pressure which represents the micro-climate in pores of hardening cementitious composites. Using BFS as a by-product at low water-to-cement ratio (W/C) to develop high strength concrete can cause early-age cracks as a consequence of autogenous shrinkage when self-desiccation induces more stress under restrained conditions. In this study, moisture distribution in mortar having 40% cement replaced with BFS at low W/C was investigated with a specific measurement. Embedded sensors are introduced in this study to deal with problems on measuring relative humidity in mortars containing BFS since dissolves sulphate during hydration becomes a troublesome to obtain a reliable measurement.

The proposed method is verified to be applicable under the sulfate gaseous conditions during the early hydration when BFS is partially mixed with the ordinary Portland cement (OPC), where the previous sensing system is impossible. Moreover, a comprehensive procedure with detailed explanations to measure internal relative humidity was proposed. The experimental results were then compared with the analytical ones by the thermo-hygo simulation system named *DuCOM*. Lower W/C has a considerable effect on moisture diffusion in concrete since the pore structure of concrete becomes finer, especially when BFS is used. The moisture loss and drying shrinkage of mortar specimens having W/C of 25% and 35% made with 40% blast furnace slag is much greater than those made with pure OPC.

The rapidity of hygro-states of BFS was identified in terms of the volumetric mechanistic stability which investigated with shrinkage measurement using two types of embedded strain gauges. The purpose of this study is to investigate autogenous shrinkage of mortar using different commercial slag cements, which are categorized in slag cement type B (JIS standard). A caution procedure to use embedded gauges was proposed in detail. A problem to deal with accuracy results has been considered comprehensively to obtain a reliable measurement. In this study, mortar specimens made from seven industrial slag cements were prepared with the same mix proportion and curing condition. The results were then compared with the shrinkage of OPC mortar and the one made with 40% BFS replacement. Compressive strength and autogeneous shrinkage were analyzed at a certain age. The effect of high temperature of curing to shrinkage was also considered and was thought to increase the hydration process in the early age. The results show that autogeneous shrinkage of slag cements varies in reactivity and the maximum shrinkage in the slag cement mortar is about three times larger that in the specimen made with OPC. Furthermore, by analyzing the results, a comprehensive benchmarking was considered on slag content in the mixture, the particle size distributions and chemical properties of cement slag. A linear relation between the autogeneous shrinkage and the compressive strength of slag cement mortar is obtained. This fact may bring comprehensive information to the material designs in practice, where some influential factors should be considered, such as the creation of the early hydrated products, the greater chemical shrinkage, finer pore structure of blended cement containing BFS, and the particle shapes of blended cement.

Liquid stability of waste material was further examined by investigation of fly ash hydration in aqueous medium. Liquid stability with regard to the ion leaching and adsorption was experimentally investigated by focusing on boron from both the solidified and non-hardened fly ash. In this study, fly ashes obtained from the Japanese district were dissolved with de-ionized water until a certain time. Boron content in suspension was then assessed in time with Inductively Coupled Plasma (ICP) depending on water contact with fly ash. The effect of temperature is considered by mixing fly ash with hot water. The pH of solution was also observed to investigate the tendency of alkalinity of suspension in releasing soluble boron from fly ash in aqueous media. The solid part of the extracted suspension was analyzed with XRD to compare minerals binding boron in fly ash after contact with water. The result was then compared with an initial condition

when there was no contact of fly ash with water. The experimental results show that chemical stability of boron ion in aqueous media is rapid so that the solid-liquid relation of boron in solid and saturated conditions can be assessed in a simple equation. Boron ions are also adsorbed rapidly by the surface of fly ash particles. Process of sorption and de-sorption of boron ions was found less than one week. The thermodynamic complexity of leaching is explained by coupling the irreversible ionization process with the recoverable course of adsorption-desorption action.

The experimental results were assessed to develop a mathematical model of boron leaching from fly ash. The requirement of mass conservation was formulated to simulate the boron release from fly ash to the natural environment. A computational approach to predict both release and capture of the boron ion is presented based upon the finite element discretization. This computational method was validated by using experimentally identified material parameters. i.e., the final adsorption capacity, dissolution capacity of leaching from solid and their intrinsic half time which represents the stability and transient process of these chemical events. The leaching of boron ion was simulated as a multi-phase equilibrium of adsorption-desorption coupled isothermal equilibrium. For verification, simple one dimensional finite element was used to simulate migration of boron ion into the liquid. The model exposed a good prediction of boron leaching in de-ionized water as compared with the experimental result. The proposed model could be a powerful tool to simulate boron migration in various media. It is also clarified that the proposed test can deal with the overall adsorption-desorption process of cement-soil mixtures. This versatility is regarded as the critical point since the method is intended to be employed to the aqueous underground environment. The model shows that in dense media, boron ion migrates slower than in porous media. When a barrier system is introduced, boron ion is retained in the contaminant area. Boron leaching in time based on different adsorption capacity of media and the variation of ion diffusion in different media can be also predicted. The higher the capacity of media to boron the more boron ion leaching from the contaminant can be shown by the proposed model.

Finally, some efforts in laboratory scale to create the artificial barriers adopted from geopolymer method were applied to prevent the interaction between fly ash and the nature. The specimens were provided by preparing fly ash in containers with the same weight. The top of the surface was injected with a combination of sodium silicate and sodium hydroxide solution. It showed that solidification of fly ash by alkali injection creates a strong barrier. The specimens were then immersed in the water and the boron concentration in time was determined with ICP measurement. The corrosive base solution made with a combination of 2M to 14 Molars of sodium hydroxide and sodium silicate showed variation effect to retain boron leaching from fly ash. It can be concluded that some barriers made from solidified-injected fly ash with different concentration from 4M to 8M of sodium hydroxide demonstrate an optimum result. Mechanistic stability of geopolymer paste was investigated with shrinkage measurement. Based on the same procedure developed to measure autogeneous shrinkage of BFS mortars, shrinkage of geopolymer

pastes was then compared with OPC and BFS pastes. As the result shown by shrinkage measurement, geopolymer pastes harden rapidly and show less volumetric deformation. Consequently, the binders formed by injecting alkalis into fly ash are solidified rapidly as the liquid diffused into the powder. Therefore, geopolymer technique is expected to be used as one of the solutions to prevent boron leaching from fly ash.

The idea behind this study to investigate thermodynamic stability is to elucidate the behaviour of by-product both in solid and liquid phases throughout a comprehensive study and above all, to provide a proposed analytical calculation method based on the experimental results.