Coupled thermodynamic modelling and experimental study of sodium hydroxide activated slag

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HIGHLIGHTS

- Influence of Na_2O was studied through thermodynamic modelling and experiments.
- Reaction kinetics was quantified as a function of time.
- Thermodynamic modelling was performed in a time scale.
- Experimental data were used to evaluate the thermodynamic modelling results.

GRAPHICAL ABSTRACT
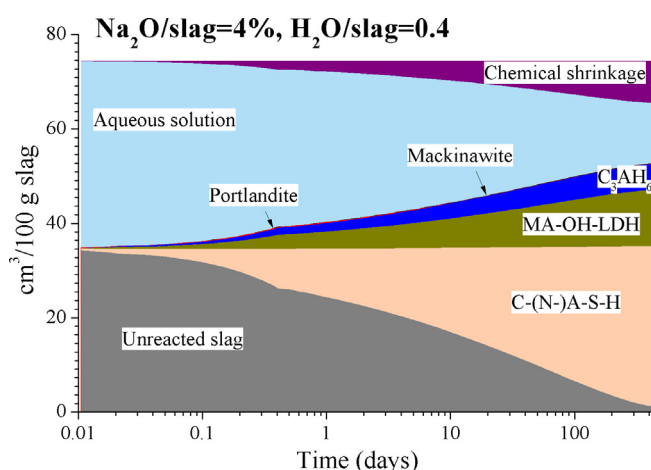
ABSTRACT

In previous researches, the thermodynamic modelling of alkali-activated slag was conducted as a function of the degree of reaction of slag, which makes it difficult to compare the modelling results with the experimental results in a time scale. In this study, the reaction kinetics of sodium hydroxide activated slag was studied using isothermal calorimetry and quantified using the Ginstling-Brounshtein equation. With the quantified reaction kinetics, the hydration of slag was thermodynamically modelled in a time scale. Based on the thermodynamically modelled phase assemblage, chemical shrinkage and phase evolution were derived as a function of time.

Besides the isothermal calorimetry, a series of experimental techniques were used to evaluate the thermodynamic modelling results. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to investigate the pore solution composition. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were used to study the reaction products. Energy-dispersive X-ray spectroscopy (EDX) was used to examine the elemental composition of reaction products. The experimental results were presented, discussed, and used to evaluate the thermodynamic modelling results in terms of pore solution composition and reaction products. The modelled pore solution composition matched the experimentally measured data within ± 1 order of magnitude. The thermodynamic modelling and experimental results were in agreement regarding bound water, type and amounts of reaction products.

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1. Introduction

Thermodynamics plays an important role in the understanding of chemical reactions. It is able to predict whether a reaction can take place and to calculate the solid phase assemblage and the aqueous phase composition at the final state once the reaction is completed. In particular, the thermodynamic modelling has been extensively used in the research of Portland cement hydration [1,2]. For thermodynamic modelling, it is crucial to obtain the thermodynamic database for the reaction products before performing the thermodynamic calculations. In alkali-activated slag, a calcium-sodium aluminosilicate hydrate (C-(N)-A-S-H) is identified as the primary reaction product [3]. Besides, crystalline reaction products, such as hydrotalcite [4], tetracalcium aluminate hydrate (C_4AH_{13}) [4], katoite (C_3AH_6) [5], and stratlingite (C_2ASH_8) [6], are identified as the secondary reaction products. The thermodynamic data for the secondary reaction products have been reported in the literature [1,2,7], such as equilibrium solubility product, enthalpy and entropy etc. However, the thermodynamic data were scarcely determined for C-(N)-A-S-H in the literature. This is because of the amorphous nature of C-(N-)A-S-H and the complex chemical environment (highly alkaline pore solution) in alkali-activated slag. Due to the insufficient thermodynamic data, the hydration of alkali-activated slag is seldom studied via thermodynamic modelling when compared to the hydration of Portland cement.

Lothenbach and Gruskovnjak used a solid solution model to simulate C-(N-)A-S-H in alkali-activated slag [8]. They described C-(N-)A-S-H as a system of two concurrent solid solution systems, based on which the uptake of Al was considered using the Al/Si ratio of 0.1 and the uptake of Na was considered using the ratio of the Na in C-(N-)A-S-H relative to the Na in the aqueous solution. The simulation results showed that the pore solution composition and assemblage of reaction products were consistent with the experimental results in the different alkali-activated slag systems. Later on, this approach was further improved to study the influence of slag composition in terms of MgO [9] and Al_2O_3 [10] on the hydration of alkali-activated slag. In the approach [9,10], the uptake of alkalis by C-S-H was modelled by using an ideal solid solution model between jennite, tobermorite, $[(KOH)_{2.5} \cdot SiO_2 \cdot H_2O]_{0.2}$ and $[(NaOH)_{2.5} \cdot SiO_2 \cdot H_2O]_{0.2}$ as proposed by Kulik et al. in [11]. The uptake of Al by C-S-H was considered based on the energy-dispersive X-ray spectroscopy (EDX) measurement.

For thermodynamic modeling of alkali-activated slag, it is of great significance to account for the uptake of Al and Na into C-S-H. Myers et al. [12], for the very first time, proposed a calcium-alkali aluminosilicate hydrate ideal solid solution model (CNASH_ss) to explicitly account for the structurally-incorporated Al and Na into C-S-H, and applied it to simulate the chemistry of C-(N-)A-S-H in alkali-activated slag. In this approach, a set of eight end-members were used to describe C-(N-)A-S-H based on the sublattice solid solution model. The thermodynamic properties were estimated through the optimization of the equilibrium solubility products for their dissociation reactions. The uptake of Al and Na were considered as an independent substitution in the formation of C-(N)-A-S-H. Afterwards, several researches were carried out using this model to study the hydration of alkali-activated slag.

Myers et al. used the CNASH_ss model to describe the solubility and chemical composition data for C-(N-)A-S-H in sodium silicate and sodium carbonate activated slag [5]. Later on, they used this model to determine the phase diagrams for alkali-activated slag binders with various alkaline activators [13], by which the phase assemblages and chemical properties of these materials can be controlled. By applying the CNASH_ss model, Ye and Radlinska simulated the phase assemblage and chemical shrinkage of alkali-activated slag [14]. However, the aforementioned thermodynamic modelling studies did not take into account the reaction kinetics. As a result, it was not possible to compare the modelling results with the experimental results as a function of time. For this reason, the reaction degree of slag at a given age has to be approximated before performing thermodynamic modelling.

This study investigated the reaction kinetics of sodium hydroxide activated slag through the measurement of heat evolution rate. The quantification of the reaction kinetics as a function of time was performed by using the Ginstling-Brounshtein equation. The quantified reaction kinetics enabled the correlation between the time and reaction degree of slag, by which the hydration of slag was thermodynamically modelled in a time scale. According to the modelled phase assemblage, chemical shrinkage and phase evolution were derived.

Besides the isothermal calorimetry, a series of experimental techniques were used to study the hydration of slag. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to measure the elemental concentration in the pore solution. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were used to study the reaction products. Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) was used to examine the elemental composition of reaction products. The experimental results were presented and discussed. By comparing to the experimental data, the thermodynamic modelling results were evaluated in terms of pore solution composition and reaction products. The obtained results contribute to new insights regarding thermodynamic modelling of alkali-activated slag.

2. Materials and methods

2.1. Materials and mixtures

Ground granulated blast furnace slag was used in this study to prepare sodium hydroxide activated slag paste. The chemical composition of slag was determined by X-ray fluorescence spectrometry (XRF) as seen in Table 1. Sodium hydroxide (analytical grade, >98%) was mixed with distilled water to prepare sodium hydroxide activator. The mix compositions of the pastes are listed in Table 2. The mixtures were denoted as AAS4, AAS6 and AAS8 corresponding to the mixtures with Na_2O/slag = 4%, 6% and 8%, respectively.

The slag and sodium hydroxide activator were mixed in a commercial Hobart mixer with two minutes low-speed, followed by two minutes high-speed mixing. Subsequently the mixed slag paste was cast into cylinder polyethylene jars

Table 2
Mix composition of the slag paste per liter.

Mix	Slag (g/L)	Na₂O (g/L)	Water (g/L)
AAS4	1360	54	544
AAS6	1360	82	544
AAS8	1360	109	544

Table 1
Chemical composition of blast furnace slag.

Oxide	SiO₂	CaO	Al₂O₃	MgO	Fe₂O₃	SO₃	K₂O	TiO₂	L.I.[*]
Weight (%)	32.91	40.96	11.85	9.23	0.46	1.61	0.33	1.00	1.15

[*] L.I. refers to loss on ignition.