Thermodynamic and kinetic study of LC3 cement during sulfate attack

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ABSTRACT

Concrete is the most common materials for the construction. One of the most important issues about the concrete construction design is the service life of structure. The concrete sulfate attack as the well-known concrete deterioration problem reduces the service life of concrete structures. In this study, LC3 cement (limestone calcined clay cement) as an eco-friendly cement due to the reduction of clincker demand, and also as an effective solution for the increasing the cement durability in sulfate-rich environments has been studied. A thermodynamic simulation has been conducted to evaluate the performance of LC3 cement (limestone calcined clay cement) against the sulfate attack, with the consideration of the time parameter, using a thermodynamic software. The simulation results are compared with experimental and modeling results to the confirmation of present model accuracy. The comparison of result shows the suitable conformity. In this study, different kinetics level for ettringite and gypsum (as the main products of sulfate attack) formation has been introduced. Analyzing kinetics diagrams show that high Calcined Clay/ Calcined Clay + Limestone ratio leads to reduction of ettringite and gypsum formation amount and formation rate during the sulfate attack, however Calcined Clay/ Calcined Clay + Limestone ratio of 0.6 could be consider as the optimal ratio because of better kinetics performance.

KEYWORDS

LC3 cement, Sulfate attack, thermodynamics, Ettringite, Gypsum.

Introduction

One of the most important issues in the design and construction of concrete structures is their service life. Durable concrete structures increase the useful life of the construction, and also, decrease the irreparable damage to the environment. Sulfate attack can be mentioned as one of the most well-known deteriorations of concrete structures. The difference in the concentration of chemical phases between the internal and external environments of the concrete sample in saturated conditions, or the flow of sulfate-rich solution into the concrete sample in unsaturated conditions, causes the penetration and diffusion of sulfate ions into the concrete cement system. Penetration and diffusion of sulfate ions into the concrete cement system disturbs the equilibrium conditions of the system [1]. According to the second law of thermodynamics, the cement system returns to equilibrium due to the occurrence of chemical reactions between different phases. Finally, in order to return to the equilibrium state of the system, expanded phases such as gypsum, ettringite and under certain conditions, thaumasite are formed as a result of chemical reactions. Different theories with different approaches have emphasized the main role of the formation of expanding phases such as ettringite in the deterioration of concrete during sulfate attack. Therefore, one of the effective solutions for increasing sulfate resistance of concrete is to reduce the production of expanding phases in concrete during sulfate attack. The reduction of aluminum and calcium ions available in the cement system causes a reduction in the production of expanding phases. Due to its high pozzolanic property, calcined clay causes more portlandite to be consumed during the cement hydration process, and in this way, it significantly reduces the calcium in the cement system. The reduction of available calcium ions in the cement system, despite the presence of high amounts of aluminum ions, causes a decrease in the production of expanding phases such as ettringite during sulfate attack. Recently, a new type of tenary cement called LC3 has been presented, which is produced by replacing a part of cement clinker with calcined clay and stone-lime. LC3 cement, as an environmentally friendly cement, preserves natural resources and reduces carbon dioxide production [2]. LC3 cement is expected to perform well in sulfate environments due to the presence of calcined clay.

Despite extensive studies about the cement hydration or sulfate attack, the kinetic-chemical investigation of the cements, especially LC3 cement, as an eco-friendly cement, has received less attention during the attack. Sulfate. Therefore, in this study, the behavior of LC3 cement, kinetic changes of ettringite and gypsum as the main products of sulfate attack has been studied, using thermodynamic science and considering the time parameter.

Methology

In this study, the thermodynamic and kinetic simulation has been used to study the kinetic changes of ettringite and gypsum, as the main products of cement sulfate attack. The behavior of LC3 cement samples with different ratios of CC/CC+L (the ratio of calcined clay to the total amount of calcined clay and limestone) and different percentages of substituted cement have been investigated. Thermodynamic calculations have been done using PHREEQC geochemical code [3]. In addition to the equilibrium reactions, the kinetic reactions of the material during hydration and sulfate attack have also been modeled. The materials used in this research, as input parameters, include ordinary Portland cement, calcined clay containing 95% metakaolin and limestone. In this study, Portland cement sample (C100) is considered as a reference model. The characteristics of the studied cement samples are presented in Table 2. The physical characteristics and chemical composition of the materials and simulation conditions are given in Table 3. Cemdata18 software has been used as the thermodynamic database to define the thermodynamic properties of cement phases. The C-S-H phase is modeled using the CSHQ ideal model [5]. The alkaline members of the CSHQ model, has been used as a solution for simulating the absorption of alkalis. In addition to the absorption of sodium and potassium ions on the C-S-H surface, the absorption of other ions is also considered using DDL (diffuse-double layer) surfaces in PHREEQC. In this study, cement samples were exposed to a 30g/l sodium sulfate solution for 365 days, after 28 days of hydration. The results of cement hydration have been compared with the experimental [6], and numerical studies [7]. The validation results show that the present model is able to predict the composition of pore solution and precipitated phases very well.

Discussion and results

Figures (1) and (2) show the process of kinetic changes of ettringite phase during the hydration p and sulfate attack. The production rate of ettringite increases at the beginning of the hydration process and sulfate attack, and after that, the kinetics of ettringite production gradually decreases. During the sulfate attack, due to the entry of a large amount of sulfate ions into the cement system, the monosulfate phase enters into a chemical reaction. This chemical reaction begins with the influx of a large number of sulfate ions. It leads to the monosulfate conversion into the secondary ettringite. Sulfate, calcium

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and aluminum ions are the main components required to produce ettringite phase. The production of ettringite is gradually limited by the consumption of the main components required for the production of ettringite phase. Therefore, the production kinetics of ettringite gradually decreases after an initial peak. The replacement of cement clinker with calcined clay and limestone leads to a decrease in the production of ettringite phase compared to the reference sample. LC3 cement has more effect on the production of the secondary ettringite rather than primary ettringite. The Control of the first stage of secondary ettringite production leads to reduction of sudden stress due to the sudden formation of large amounts of ettringite with a high production. The uniformity of the ettringite formation rate is disturbed in samples with CC/CC+L ratio, higher than 0.6. Therefore, CC/CC+L ratio equal to 0.6, can be considered as the optimal value.

Table 1. Characteristics of cementitious mixture samples

Cement replacement amount	CC/(CC+L)	Mixture ID
0	-	C100
15%	0.2	C85-L12-CC03
	0.4	C85-L09-CC06
	0.6	C85-L06-CC09
	0.8	C85-L03-CC12
30%	0.2	C70-L24-CC06
	0.4	C70-L18-CC12
	0.6	C70-L12-CC18
	0.8	C70-L06-CC24
45%	0.2	C55-L36-CC06
	0.4	C55-L27-CC18
	0.6	C55-L18-CC27
	0.8	C55-L09-CC36

Table 2. Physical characteristics and chemical composition (XRF) of portland cement, limestone and calcined clay and simulation conditions as input parameters of the model [4]

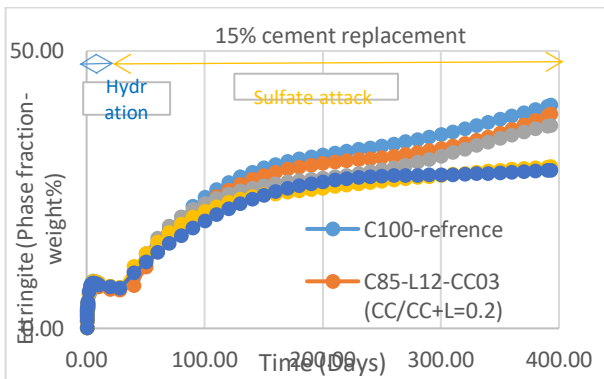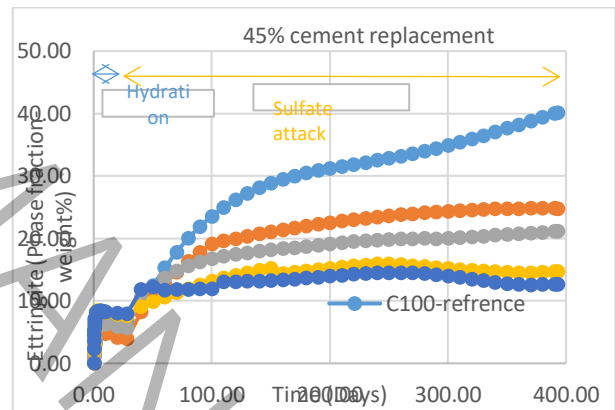| wt.%	Cement	Limestone	Calcined clay
SiO_2	19.51	0.11	52.00
Al_2O_3	4.42	0.00	43.80
Fe_2O3	3.12	0.04	0.33
CaO	63.85	54.96	0.03
MgO	2.10	0.15	0.01
SO_3	3.25	0.03	0.10
Na_2O	0.19	0.06	0.14
K_2O	0.83	0.00	0.29
TiO_2	0.31	0.00	1.53
P_2o5	0.33	0.00	0.16
MnO	0.05	0.00	0.01
Physical composition			
Loss on Ignition (LOI)	1.54	42.25	1.47
Specific Surface Area (A) (m^2/g)	1.41	3.60	13.56
Mixing conditions			
w/b	0.4		
T (°C)	20		
RH (%)	1		

Figure 2. The process of kinetic changes of ettringite phase for 45% replacement of cement exposed to 30 g/l sodium-sulfate solution (Na_2SO_4) during 28 days of hydration and 365 days of sulfate attack

Figure 1. The process of kinetic changes of ettringite phase for 15% replacement of cement exposed to 30 g/l sodium-sulfate solution (Na_2SO_4) during 28 days of hydration and 365 days of sulfate attack
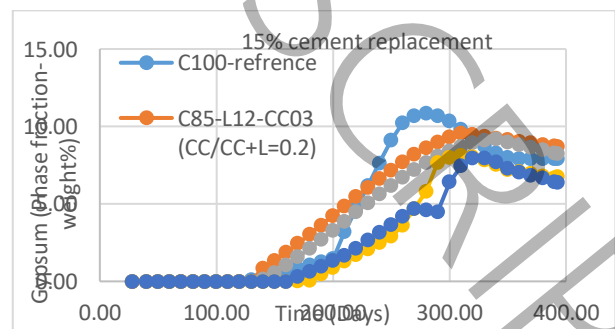

Figure 3. The process of kinetic changes of gypsum phase for 15% replacement of cement exposed to 30 g/l sodium sulfate solution (Na_2SO_4) during 365 days of sulfate attack
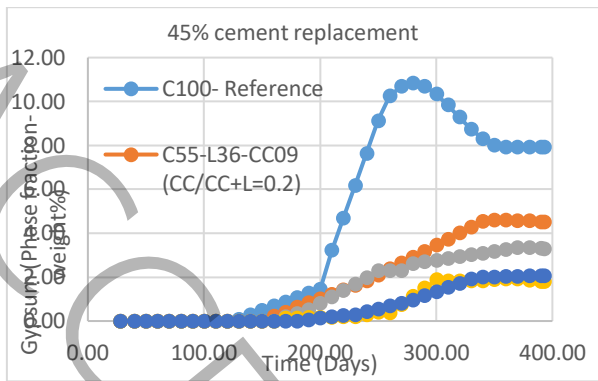
Figure 4. The process of kinetic changes of gypsum phase for 45% replacement of cement exposed to 30 g/l sodium sulfate solution (Na_2SO_4) during 365 days of sulfate attack

Figures (3) and (4) show the process of kinetic changes of the gypsum phase. The amount of gypsum production decreases with the increase of two parameters, the percentage of cement replacement and CC/CC+L ratio, during sulfate attack. At first, the diagrams of kinetic changes of the gypsum phase indicate a period of quiescent stage. In this stage, no amount of the gypsum phase is consumed or produced during the sulfate attack (the first stage of the kinetic changes of the gypsum phase). Obviously, the expanding and destructive gypsum is produced later when the path of the first stage of gypsum production is longer. Therefore, the longer path of the first stage of gypsum changes (quiescent stage) leads to a delay in the gypsum production, and a delay in the development of stress caused by the production of the expanding phase of gypsum in the cementitious system. Then, in the next stage, the gypsum phase starts to be produced during the sulfate attack (second stage). Gypsum phase is produced to the maximum amount in the second stage. In this stage, gypsum phase is formed with two different production rates, low and high rates. The second stage of kinetic changes of gypsum phase is the stage of starting production of gypsum up to the maximum value. At this stage, gypsum phase starts to be produced and the production rate of gypsum phase accelerates to the final amount of gypsum phase production. The increase of two parameters, cement replacement percentage and CC/CC+L ratio, decreases the amount of gypsum production rate kinetically, in addition to the final amount of gypsum phase production. Finally, the gypsum phase moves towards a stable value (third stage). In the third stage of the kinetic changes of gypsum, the amount of gypsum remains constant or decreases slightly. It finally tends to a constant value and reaches equilibrium during sulfate attack. The conversion of the gypsum phase to ettringite phase is the reason of gypsum reduction in the third stage.

Conclusions

The results of this study show that three different kinetic stages can be considered for the formation of secondary ettringite and gypsum during sulfate attack. In general, the increase of two parameters, percentage of cement replacement and the ratio of calcined clay to the total of calcined clay and limestone, leads to a decrease in the amount and production rate of destructive phases of ettringite and gypsum in LC3 cement, during sulfate attack. The first stage of ettringite formation has a high rate. By increasing the ratio of calcined clay to total calcined clay and limestone, the production of secondary ettringite is kinetically controlled in the first stage of ettringite formation. Therefore, the initial sudden stress due to the rapid formation of the expanding phase of ettringite, no longer occurs during the sulfate attack. In LC3 cement, the production of the gypsum is delayed during sulfate attack due to the increase in the duration of the first stage of the kinetic change of the gypsum. Therefore, the sudden stress resulting from the production of the expanding phase of gypsum is also delayed and controlled kinetically. Due to the production of secondary ettringite phase in a lower amount and with a more uniform production rate, the parameter of the ratio of calcined clay to the total of calcined clay and limestone equals 0.6 (not the higher ratio, equal to 0.8) can be introduced as the optimal value in LC3 cements.

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