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Technical Notes

The Kinetics Role of Gypsum in Limestone Calcined Clay Cement Exposing to Sulfate solution by the Thermodynamic Study

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Abstract:

In current research, the kinetics role of gypsum is evaluated during the sulfate attack by replacing cement with calcined clay and limestone. This study is done by geochemical code PHREEQC along with kinetics consideration. The results show that three stages can be considered for the kinetics change of gypsum. The first stage of gypsum production gets longer as calcined clay to cement replacement content ratio increases. This means that gypsum is produced with delay for the mixture with a greater calcined clay to cement replacement content ratio. The availability of more aluminum ions as a result of greater calcined clay leads to the continuation of ettringite production instead of gypsum formation. In LC3 cement the maximum amount of produced gypsum is reduced as well as the rate of gypsum production. The stress due to the gypsum formation is applied to the cement matrix with delay because of the prolongation of first stage.

Keywords: Thermodynamics, Kinetics, LC3 cement, Sulfate attack, Gypsum.

1. Introduction

The arrival of sulfate ions to the cementitious matrix leads to the production of expansive phases such as ettringite, and gypsum called external sulfate attack (ESA). Better sulfate resistance of concrete containing calcined clay has been reported by a few studies (Amiri et al. 2024, Cordoba et al. 2021, Rossetti et al. 2021, Cordoba et al. 2022, Dhandapani et al. 2022). The initial strength of concrete is positively affected by adding Limestone, and calcined clay as a fast-reacting pozzolan improves the initial strength (Krishnan and Bishnoi, 2020). Despite the fact that lot of researches focusing on the compressive strength of *LC3* cement, there are limited studies focusing on the sulfate resistance of *LC3* cement. In this research, the kinetics behavior of gypsum is evaluated in LC3 cement exposing to the sulfate solution. *LC3* cement with various calcined clay to cement replacement content ratio (*CC/CC+L*) and cement replacement content are studied by thermodynamic simulation. Thermodynamic simulation has no limitation about the prolonged-time test, measurement errors, and controlling test conditions in comparison to the experimental studies. Kinetics and thermodynamics sciences are complementary to each other for the monitoring of gypsum trends over a long period of sulfate attack time. Tkarhe kinetics performance results of the samples are investigated to evaluate the kinetics path of gypsum production, introducing the kinetics stage of gypsum while exposing to sulfate attack, and finding out how kinetics changes of gypsum improve the sulfate resistance in *LC3* cement.

2. Materials and methods

2.1. Thermodynamic model

In this research, geochemical code *PHREEQC* along with rate and kinetics coding data was used to perform the thermodynamics and kinetics calculations (Parkhurst and Appelo, 2013). Composition and characteristics of the materials and the mix proportion details are reported by authors (Karkhaneh et al. 2023, Zunino and Scrivener, 2021a). The simulation has been done at temperature equal to 20°C, and w/b, and RH equal to 0.4, 1% respectively. In this study, a constant water to cement ratio has been assumed for all samples. The constant water to cement ratio could be achieved by adjusting the dosage of superplasticizer based on the amount of limestone and calcined clay. CC/(CC+L) indicates the ratio of calcined clay to calcined clay and limestone, and C100 is considered as a reference sample.

2.2. Kinetics simulation

With the aim of kinetics simulation of hydration process without the restriction of initial dissolution, Parrot and Killoh hydration modelling is adopted (Krishnan and Bishnoi, 2020).

It has been noted that the hydration process is assumed to continues without being restricted by space limitation which can occur in LC3 cement as a theoretical calculation. The kinetics reaction of supplementary cementitious materials of LC3 cement and their effect on the rate of hydration process has been considered by a sigmoid function presented by *Kunther et al*. (2016). Sulfate attack is simulated in such a way that samples are exposed to a 30 g/l Na_2SO_4 solution for 365 days, after the 28 days of hydration. The hydration model was used to determine pore solution concentration, phase assemblage, solid solution, and porosity. Then, chemical composition and physical properties of hydrated samples have been used for transport and thermodynamic equilibrium calculations. The diffusion coefficients of cations, anions, and neutral species in a solution vary, influencing the diffusive flux of a specific ion. This flux is determined by concentration gradients, electrical potential differences, and the effect of chemical activity. Nernst-Plank equation (Appelo and Postma, 2009) has been used to calculate the multi-component diffusion using multi_d keyword in Phreeqc. In the simulation, the diffusion calculation has been combined with the phase equilibrium model to simulate ionic profile and chemical reaction. The self-diffusion coefficient of ions in free water at a given temperature were used as the diffusion coefficients and tortuosity value as 1. In this research, kinetics simulation of sulfate attack including precipitation and dissolution of phases are modeled by the rate equation proposed by *Lasaga et al*. (1994).

2.3. Model verification

The results of this study have been compared with other numerical and experimental studies. The cement hydration results of experimental research (Lothenbach et al. 2008), and numerical research (Elakneswaran et al. 2016) shows the similarity with the current results, as shown in Figures 1 and 2. More detail reported by authors (Karkhaneh et al. 2023).

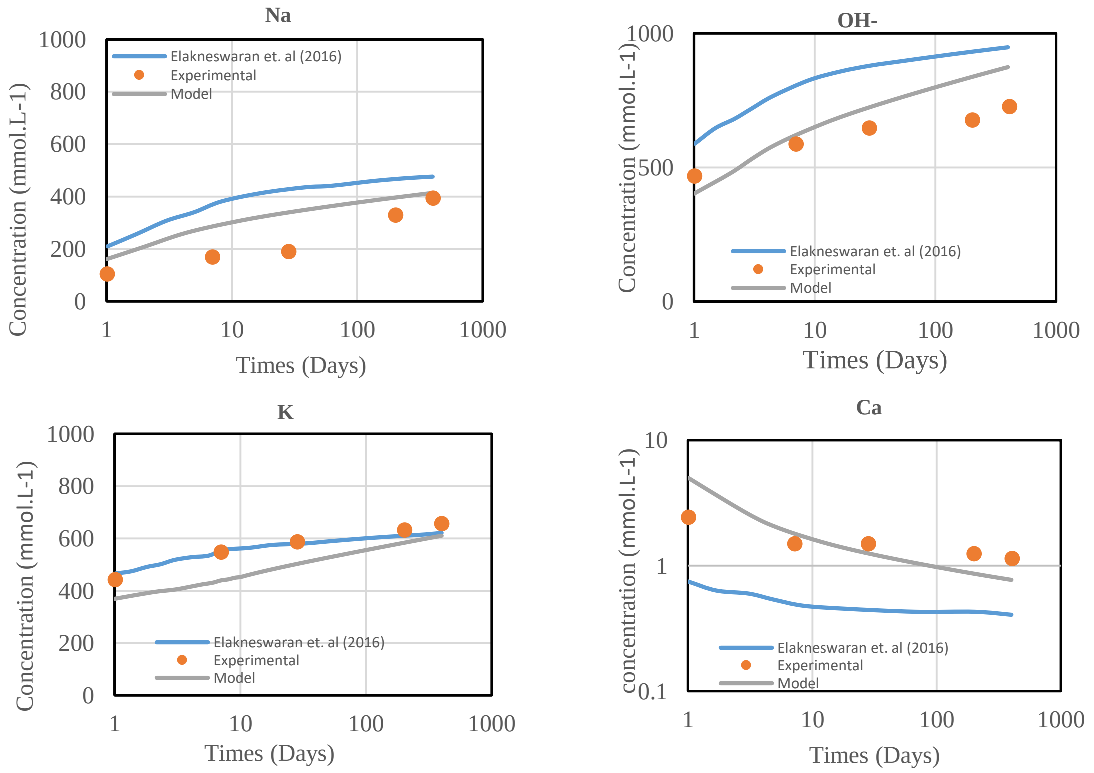


Fig. 1 Kinetic changes of elements concentration of pore solution during hydration time

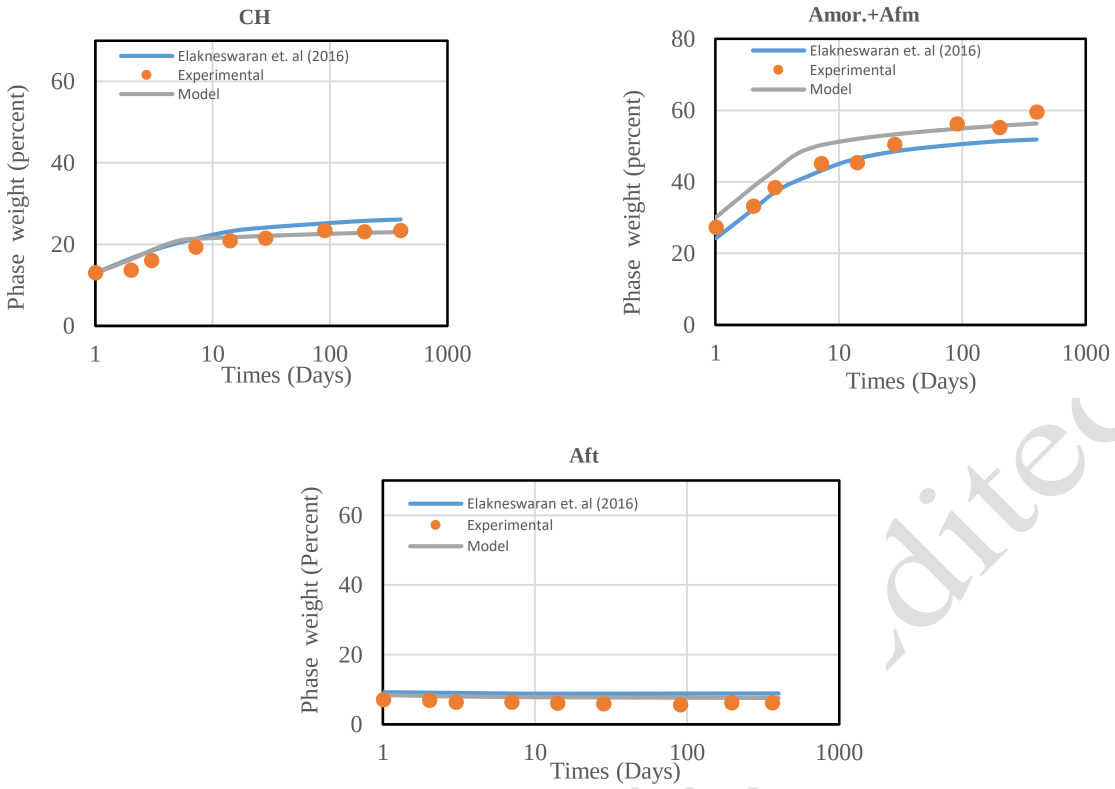
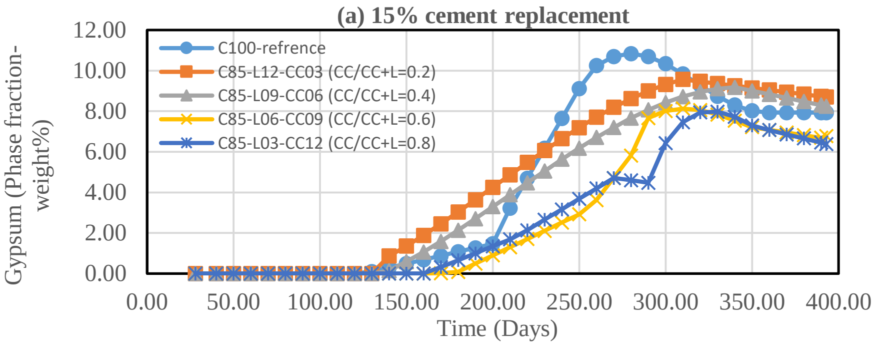


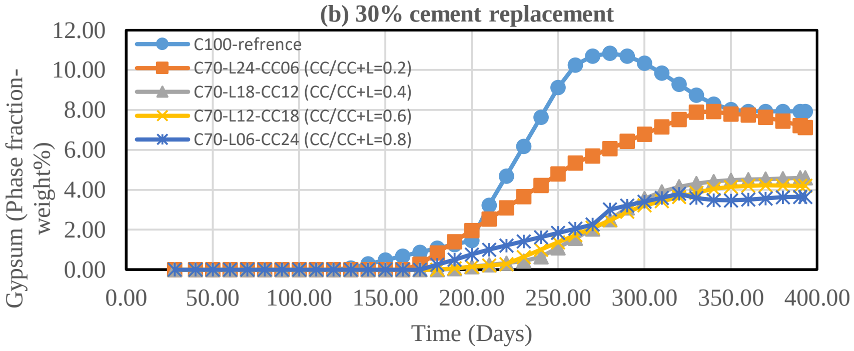
Fig. 2 Kinetic changes of phases in the cementitious matrix during hydration time

3. Results and discussion

3.2. Kinetics changes of gypsum

Figure 3 shows the kinetics changes of gypsum, one of the main sulfate attack production, for the binder mixtures during 365 days of sulfate attack. The change of gypsum is studied during the sulfate attack, because of the consumption of gypsum after the hydration process. A brief analysis of Figure 3(a) to (c) indicates that the final produced gypsum is decreased by the increase of two parameters which are calcined clay to cement replacement content ratio, and cement substitution percentage. Although, the kinetics path of gypsum slightly changes in the samples with 15% of cement substitution, the kinetics change of gypsum significantly improved in samples with greater cement substitution percentage. Also, three kinetics stages could be considered for the gypsum changes while exposing to the sulfate attack, according to the gypsum kinetics diagrams (Figure 3). Figure 4 shows three stages considered for kinetics changes of gypsum related to the reference sample, in the duration of sulfate attack. The first stage is a quiescent part in which no gypsum is produced nor consumed. it is obvious that a longer period of the first stage leads to the later exertion of stress to the cement matrix because of the delay in gypsum production. gypsum starts to be produced up to the maximum amount in the second stage. In the second stage, gypsum is usually produced in two-part with low, and high rate formation. Finally, gypsum tends towards stability in the third stage.





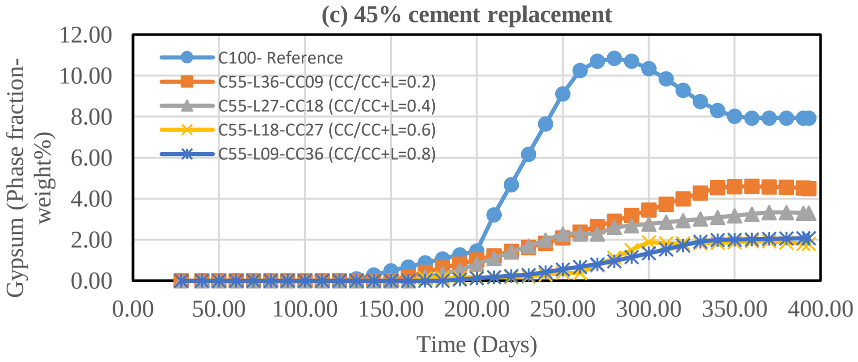


Fig. 3 Kinetics path of gypsum for different cement substitution percentage (a) 15% (b) 30% (c) 45% over a 365 days of sulfate attack (30 g/l Na_2SO_4)

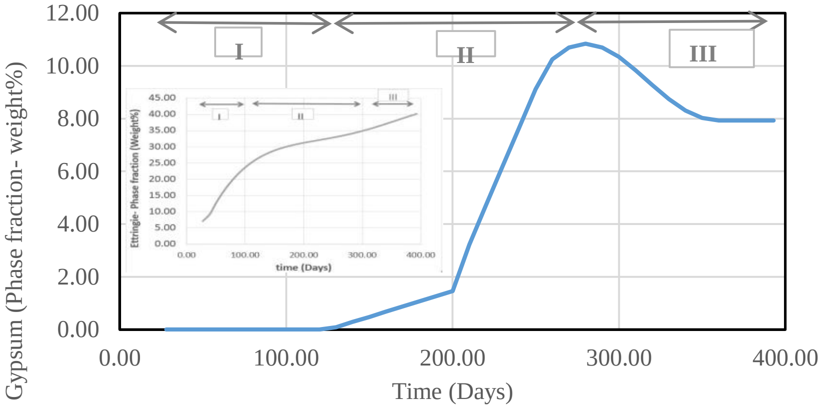


Fig. 4 Three kinetics steps of gypsum evolution in the duration of sulfate attack

As seen in Figure 3(a) to (c), the period of quiescent stage gets longer as calcined clay to cement replacement content ratio increased. Figure 5 indicates the first stage of gypsum change and the second stage of ettringite production for the reference sample in the duration of sulfate attack. According to Figure 5, the gypsum production is started almost in the middle of the second step of ettringite evolution, when most of the *Al* contained phases convert to ettringite, and the presence of sulfate and calcium ions leads to the production of gypsum. The beginning of gypsum formation and the second step of ettringite production are indicated in Figure 6 for the different mixtures during the sulfate attack. It is obvious that a sample with a high *CC/CC+L* ratio contains more calcined clay content which means that more aluminum ions enter the cement matrix. The presence of more aluminum ions leads to more formation of ettringite instead of gypsum. In fact, the calcium ions as the result of leaching of portlandite, and the sulfate ions entered because of the sulfate attack produce gypsum, in the absence of aluminum ions.

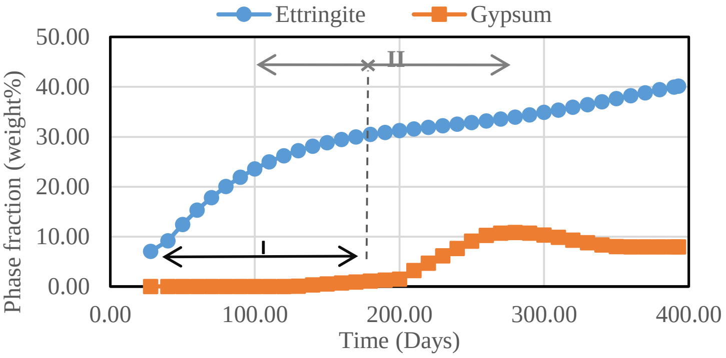
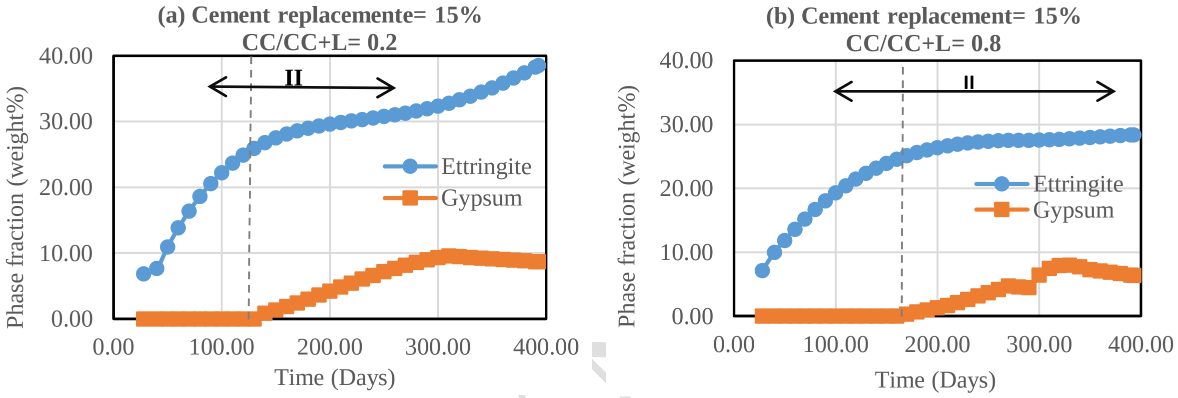
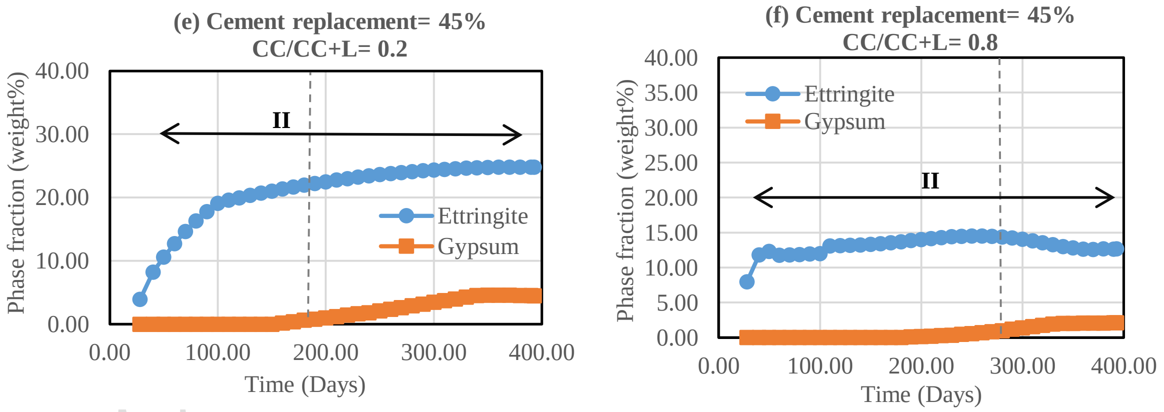


Fig. 5 Comparison of the first stage of gypsum changes with the second stage of ettringite changes while exposing to the sulfate attack for the reference cement



(a) Cement replacemente= 15% CC/CC+L= 0.2

(b) Cement replacement= 15% CC/CC+L= 0.8



(e) Cement replacement= 45% CC/CC+L= 0.2

(f) Cement replacement= 45% CC/CC+L= 0.8

Fig. 6 Matching of the beginning of gypsum formation with the second step of ettringite evolution for the mixtures with the cement replacement of ((a), (b)) 15%, ((c), (d)) 30%, and ((e), (f)) 45%; and CC/CC+L= ((a), (c), (e)) 0.2, and ((b), (d), (f)) 0.8

However, the late consumption of aluminum ions due to the presence of high content of this element in the mixture leads to the continued ettringite production, and the gypsum production is delayed and slowed down, which can be seen by comparing Figure 6(a) with (b), 6(c) with (d), and 6(e) with (f). As seen in Figure 6, the beginning of gypsum production happens later, and the line representing the beginning of gypsum formation moves towards the second step of ettringite evolution as calcined clay to cement substitution percentage increased. In addition to increment of calcined clay to cement substitution percentage (*CC/CC+L)*, the higher level of cement replacement also results in the delaying of gypsum formation, according to the comparison of Figure 6(a) to (e), and 6(b) to (f). More production of the intermediate phases leads to the extending of the second step of ettringite formation for the mixtures with higher level of cement replacement. The presence of large amounts of intermediate phases causes a higher rate of phases transformations. The intermediate phases are first convert to each other and eventually, they convert to ettringite phase at various conversion rates. When most of the Al-contained phases convert to ettringite, gypsum starts to form. So, the presence of more Al-contained phases causes the alteration of intermediate phases to ettringite, which takes longer period (extending the second step of ettringite formation), and the beginning of gypsum production is postponed. Therefore, the extended path and the existence of more calcined clay results in the delaying of gypsum formation for the mentioned mixtures. In the second stage, gypsum starts to form and the production accelerates until the maximum level of gypsum production (see Figure 4). According to Figure 3, both increment of calcined clay to cement substitution percentage (*CC/CC+L*), and the cement replacement amount reduce the maximum amount of formed gypsum. The important point is that as well as the decreasing of maximum amount of gypsum production, the formation rate has also reduced significantly which means that the sudden production of gypsum until the maximum amount at a high rate, and consequently, the creation of sudden stress doesn't happen anymore. The main reason for decreasing gypsum formation is the reduction of portlandite in LC3 cement after the hydration process. In the hydration process, portlandite is produced at the lower level due to the existence of calcined clay and limestone. Figure 7 shows the portlandite production during the 28 days of hydration. As seen in Figure 7, the amount of portlandite related to the reference cement is more than other mixtures. Increasing the cement replacement decreases the amount of produced portlandite at a positive rate however, increment of calcined clay to cement substitution percentage(*CC/CC+L*) leads to further reductions of produced portlandite at a negative rate due to the greater amount of calcined clay (see Figure 7(a), and (b)). In the presence of limestone, calcium carbonate reacts with C_3A to produce carboaluminates. Therefore, the production of portlandite is rising but in the lower quantities. Calcined clay consumes portlandite to produce the *CSH* phase by the pozzolanic reaction. It means that portlandite is produced at first and then consumed by calcined clay. So, the synergic effect of limestone and calcined clay leads to the production of portlandite in the lower quantities because of limestone, and consumption of formed portlandite in the larger quantities because of calcined clay in *LC3* cement. In the third stage, the amount of gypsum remains constant or it is decreased negligibly until finally tends toward stability (Figure 3). Very low conversion of gypsum to ettringite is the reason for gypsum amount reduction in the third stage.

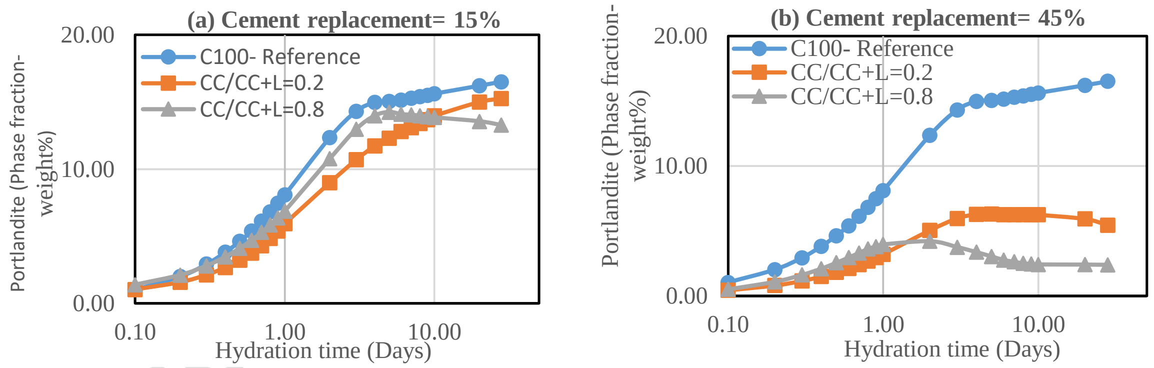


Fig. 7 Kinetics changes of portlandite for reference cement and the mixtures with cement replacement of (a) 15%, and (b) 45%, during 28 days of hydration

4. Conclusion

A thermodynamics and kinetics study have been done to evaluate the gypsum role for cement samples containing limestone and calcined clay (LC3 cement) in the sulfate-rich environment by a geochemical modeling program *PHREEQC*. Samples with various cement substitution content, and calcined clay to cement substitution percentage (*CC/CC+L*) were evaluated. The kinetics diagrams have been analyzed to get more information about the kinetics path of gypsum production during sulfate attacks. The results show that the final produced gypsum is decreased by the increase of calcined clay to cement replacement content ratio, and cement substitution percentage (*CC/CC+L*). Although, the kinetics path of gypsum slightly changes in the samples with 15% of cement substitution, the kinetics change of gypsum significantly improved in samples with greater cement substitution percentage. Three stages can be considered as the kinetics change of gypsum in the duration of sulfate attack. The first stage of gypsum production gets longer by the increment of *CC/CC+L* ratio. It means that gypsum is produced with delay for the samples with a higher ratio of calcined clay to cement substitution (*CC/CC+L*). The availability of more aluminum ions due to the existence of more calcined clay leads to the continuation of ettringite production instead of gypsum formation. The first stage of gypsum production takes longer by increasing of cement substitution content, due to the extending of ettringite second stage path. In *LC3* cement, the stress due to the gypsum formation is applied to the cement matrix with delay because of the prolongation of the first stage. The maximum amount and rate of produced gypsum is decreased by increasing the ratio of calcined clay to cement substitution, especially with more cement substitution content, in the second step of gypsum production, due to the lack of available portlandite. In *LC3* cement, the production of portlandite is significantly reduced because of the synergic effect of calcined clay and limestone during the hydration. The lower rate of gypsum formation leads to the prevention of sudden stress into the cement matrix.

Statements and Declarations

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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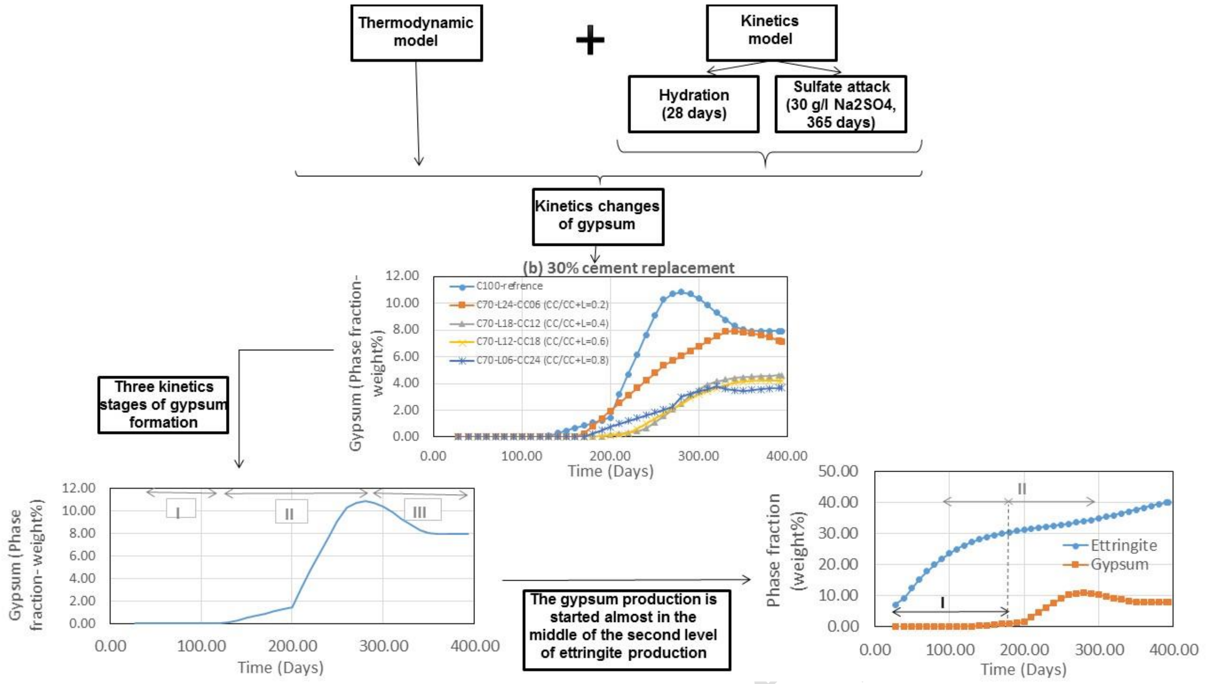
Graphical abstract


Thermodynamic model
+
Kinetics model
Hydration (28 days)
Sulfate attack (30 g/l Na2SO4, 365 days)
Kinetics changes of gypsum
(b) 30% cement replacement
Gypsum (Phase fraction-weight%)
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00
100.00
200.00
300.00
400.00
Time (Days)
C100-refrence
C70-L24-CC06 (CC/CC+L=0.2)
C70-L18-CC12 (CC/CC+L=0.4)
C70-L12-CC18 (CC/CC+L=0.6)
C70-L06-CC24 (CC/CC+L=0.8)
Three kinetics stages of gypsum formation
Gypsum (Phase fraction-weight%)
I
II
III
Time (Days)
The gypsum production is started almost in the middle of the second level of ettringite production
Phase fraction (weight%)
50.00
40.00
30.00
20.00
10.00
0.00
Ettringite
Gypsum
I
II
Time (Days)