

## **Thermodynamic Modeling of the Effects of Wollastonite-Silica Fume Combination in the Cement Hydration and Sulfate Attack**

**Tarighat, A.<sup>1</sup>, Modarres, Y.<sup>2\*</sup> and Mohammadi, M.<sup>2</sup>**

<sup>1</sup> Associate Professor, Department of Civil Engineering, Shahid Rajaei Teacher Training University, Tehran, Iran.

<sup>2</sup> M.Sc. Student, Department of Civil Engineering, Shahid Rajaei Teacher Training University, Tehran, Iran.

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**ABSTRACT:** Sulfate attack is a series of physico-chemical reactions between hardened cement paste and sulfate ions. Sulfate ion penetration into the hydrated cement results in the formation of voluminous and deleterious phases such as gypsum and ettringite which are believed to cause deterioration and expansion of concrete. Concrete deterioration due to sulfate attack depends on many parameters, however, in experimental studies, the implementation of the parameters and obtaining the results in a short time are too difficult. In this paper the effect of wollastonite, with and without silica fume, on the performance of cement based materials during hydration and magnesium sulfate attack was studied by thermodynamic modeling. Thermodynamic modelling was carried out using the Gibbs free energy minimization program GEMS. By this method, in addition to investigating the type and volume of the produced materials, the optimal substitution percentage of wollastonite and silica fume were studied as well. In sulfate attack, especially at higher percentages of substitution, wollastonite is not very effective in itself. Wollastonite replacement has a reverse effect on monosulfate and ettringite phases. Volume of these phases increases with addition of the substitution percentage. Substituting a portion of the cement with wollastonite and silica fume would improve sulfate resistance. Substitution of 5% of wollastonite and 10% of silica fume has shown the best performance, highest increase in C-S-H gel volume and reduction in harmful phases such as gypsum, ettringite and brucite.

**Keywords:** Modeling, Silica Fume, Sulfate Attack, Thermodynamics, Wollastonite.

### **INTRODUCTION**

Sulfate attack comprises a series of physical and chemical reactions that occur between hardened cement paste and sulfate ions. Two important events that happen during a sulfate attack include loss of strength due to the decomposition of C-S-H gel and volume expansion as a result of the formed products

such as gypsum and ettringite (Tixier and Mobasher, 2003). These, in turn, cause cracking and deterioration in the structure of cement based materials. Natural or artificial pozzolans affect the microstructure and hydration kinetics of cement based materials and consequently could cause changes in the volume and porosity of them, the amount and types of hydrates that are formed and also

\* Corresponding author E-mail: yaghout.modarres@gmail.com

increase in the sulfate resistance through pozzolanic or hydraulic activities (Lothenbach et al., 2011). In addition, reducing the consumption of cement with simultaneous utilizing waste materials as cement replacement is preferred for reasons of environmental protection (Arshad et al., 2014; Askarinejad, 2017).

Wollastonite is a naturally occurring, acicular, inert, white mineral of high elastic modulus (Maxim and McConnell, 2005; Mathur et al., 2007). Wollastonite is formed at temperatures above 600 to 700 °C from calcite and quartz.  $\text{SiO}_2$  and  $\text{CaO}$  are the main components of this mineral material (Crooks, 1999). According to ASTM C 618, wollastonite could be classified as Class C pozzolan (ASTM, 2005); In the Rankin Chart, wollastonite has been located in the 'latent hydraulic' area (Jahim, 2010). The publication of the phase diagram  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  by Rankin and Wright in 1915 came as a great help for cement chemists for optimising raw mix composition for the production of Portland cement besides getting and insight for the possible phase composition one would expect to get by burning a bulk composition. As a matter of fact Rankin and Wright concluded the Portland cement clinker prepared in the ordinary way from lime, silica and alumina, would be essentially a mixture of  $\text{Ca}_3\text{SiO}_5(\text{C}_3\text{S})$ ,  $\text{Ca}_2\text{SiO}_4(\text{C}_2\text{S})$  and  $\text{Ca}_3\text{Al}_2\text{O}_6(\text{C}_3\text{A})$  with some  $\text{Ca}_5\text{Al}_6\text{O}_{14}(\text{C}_5\text{A}_3)$  and, possibly, a small amount of free lime (Gosh, 2002). In general, a very limited number of studies have been conducted on the effects of wollastonite, especially concerning the sulfate attack.

There have been reports by CRRRI of implementing wollastonite as a substitute for a portion of cement, sand or both. The results of the studies showed that presence of wollastonite in concrete increases the flexural and compressive strengths of concrete (Kalla et al., 2013).

Ransinchung and Kumar (2009) investigated the effect of wollastonite with and without silica fume as partial replacement of Portland cement mortars and concrete samples. According to the experimental data, application of a combination of silica fume and wollastonite increases the compressive strength. Considering the experiments which test the effect of wollastonite on durability of concrete, Mathour et al. (2007) investigated the effect of fly ash and wollastonite substitution on water absorption of concrete samples. They found that the samples containing wollastonite and fly ash had lower water absorption in comparison to the control samples. Also it was observed that mixtures' durability against sulfate attack, freezing/thawing cycles, drying shrinkage and abrasion, improved with addition of wollastonite.

Implementation of all the factors involved in sulfate attack and obtaining results in the shortest possible time is one of the problems associated with laboratory studies. Therefore, significance of the theoretical and software modeling along with the experimental studies, is in reducing the time and cost, and achieving reliable results. During the past decades, various methods have been developed for modeling hydration and sulfate attack, one of them is the thermodynamic model. Like any other chemical system, hydration of cement and physico-chemical processes which lead to changes in cement based materials, when exposed to an aggressive environment, all follow the thermodynamics laws. Several thermodynamic cement models (Kolani et al., 2012; Kunther, 2012; Lothenbach et al., 2012) have been developed and applied to cementitious systems in order to predict the long-term behaviour as envisaged in many countries for the disposal of low and intermediate level radioactive waste. Rothstein et al. (2002) applied thermodynamic calculations to obtain a better

understanding of the changes in fresh cement systems and compared the measured compositions of pore solutions with the calculated saturation indexes of different solids (portlandite, gypsum, ettringite, calcium monosulphoaluminate and C-S-H phase). Lothenbach et al. (2010a), De Weerd et al. (2011) and Kunther and Scrivener (2013) have performed a number of studies on the pure thermodynamic modeling and thermodynamic modeling implementing the transport code in the field of cement hydration and aggressive environments.

In this paper, the thermodynamic method was utilized to model the behavior of hardened cement paste, in order to better understand the hydration and external sulfate attack. It also examined the effect of wollastonite with and without silica fume. Thermodynamic modeling helps in predicting the composition of hydrated phases under

different conditions and also saving in time and cost.

## MATERIALS AND METHODS

### Materials

Portland cement type CEM I 42.5 N was used in this study (Lothenbach et al., 2010a). The chemical composition of cement, silica fume (Ramezani-pour et al., 2012) and wollastonite (Tarighat and Afzali, 2016) (from test results of X-ray fluorescence) are given in Table 1. The ratio of water to cementitious materials is 0.5, and the temperature is 20 °C. To check sulfate attack, magnesium sulfate solution with a concentration of 44 g/l is implemented, where the percentages of silica fume and wollastonite substitution are given in Table 2.

**Table 1.** Chemical composition and the physical characteristics of the clinker, wollastonite and Silica fume

	OPC <sup>a</sup>	Silica Fume <sup>a</sup>	Wollastonite <sup>a</sup>
SiO <sub>2</sub>	20.6	93.16	51.6
Al <sub>2</sub> O <sub>3</sub>	4.86	1.13	12
Fe <sub>2</sub> O <sub>3</sub>	3.37	0.72	5.6
CaO	63.56	-	22.7
MgO	2.18	1.6	1.8
SO <sub>3</sub>	2.3	0.05	0.2
Na <sub>2</sub> O	0.33	-	0.7
K <sub>2</sub> O	0.54	-	2.8
P <sub>2</sub> O <sub>5</sub>	-	-	0.2
TiO <sub>2</sub>	-	-	0.7
MnO	-	-	0.1
Free CaO	1.46	-	-
LOI	2.2	-	1.49

<sup>a</sup> XRF data

**Table 2.** Mix designation, % cement replacement

S. No.	Mix Designation	OPC	Silica Fume	Wollastonite
1	SF0 W0	100	0	0
2	SF0 W10	90	0	10
3	SF0 W20	80	0	20
4	SF5 W10	85	5	10
5	SF10 W5	85	10	5
6	SF10 W10	80	10	10
7	SF10 W20	70	10	20

### Thermodynamic Modeling

Thermodynamic modeling was first developed by chemists for calculation of complex multicomponent systems, which occur in nature. In the past, there was not any tendency toward using the knowledge of thermodynamics in cement hydration. Because they believed that C-S-H gel is metastable and would not exhibit thermodynamic behavior. On the other hand, enough thermodynamic data for cement phases were not available and properly depicting the formed phases was impossible (Lothenbach et al., 2010b; Lothenbach, 2010; Damidot et al., 2011).

In recent studies, the main aspects of cement chemistry are under focus of attention, and progress in this field has led many research teams around the world to develop thermodynamic models to further evaluate the complexity of the hydrated cement systems and improve the ability to predict their performance over time. It is therefore, possible to calculate the metastable equilibrium between C-S-H gel phase and other more stable crystalline phases (Lothenbach et al., 2010b; Damidot et al., 2011).

In this paper, thermodynamic modeling using Gibbs free energy minimization and GEM software have been employed. The GEM-Selektor code package is a multi-purpose Gibbs energy minimization code that solves complex multicomponent-multiphase equilibria involving non-ideal aqueous solutions, gas mixtures, solid solutions, supercritical fluids, melts, and sorption phases (Kulik et al., 2013). GEM-Selektor can be used for diverse geochemical modeling applications, including batch speciation and solubility calculations, solubility and PH titration diagrams, and various reaction path and mass transfer simulations. The GEM-Selektor package features a rich graphical user interface (GUI), modules for storage and maintenance of

thermodynamic data bases (both in thermochemical and reaction format), and a comprehensive selection of methods for correcting standard state data to elevated pressures and temperatures (Wagner et al., 2012).

Since 1965, several thermodynamic databases have been published for cement phases. One of the primary problems in many databases was that they were only appropriate for the environmental conditions. In this modeling, the cement database, called *cemdata14* is incorporated. This database is based on the geochemical database from Nagra/PSI (Thoenen et al., 2014), which contains thermodynamic data (Dissolution products, Gibbs free energy, enthalpy, entropy, heat capacity) for a number of cement phases such as C-S-H gel, hydrotalcite etc.

Sulfate attack was mimicked in the modeling by calculating the addition of increasing quantities of the sulfate solutions to the cement. It does not apply any restrictions on the calculated hydrate types. This method is based on the theory that states the core samples are never or hardly ever affected by sulfate while the outer layer is in contact with a large amount of sulfate solution. The advantage of this model is that the calculations are very fast but the calculated data are not time dependent. Modelling the sulfate attack is done by increasing the amount of sulfate in cement, and it is assumed that all the ions penetrate mortar with a similar rate.

### Mechanism of Magnesium Sulfate Attack

The PH of the magnesium sulfate solution is acidic (PH = 5.7 at a concentration of 1 mol/dm<sup>3</sup>). Solubility of this salt is relatively high (30.8 g/100 gH<sub>2</sub>O). The impact of magnesium sulfate on concrete is a double chemical attack because each of the ions SO<sup>2-</sup> and Mg<sup>2+</sup> forms its usual product. Therefore, magnesium sulfate attack is dangerous for

cement composites. As a result of  $MgSO_4$  solution influence, the main products (ettringite, gypsum) of sulfate attack and hydroxide  $Mg(OH)_2$  in exchange reaction with  $Ca^{2+}$  ions are formed. Due to the lower solubility of  $Mg(OH)_2$  as compared to  $MgSO_4$ , magnesium hydroxide gel is precipitated in all reactions of magnesium sulfate with calcium hydroxide and other calcium phases. Gel  $Mg(OH)_2$  and then brucite is formed on the sample surface or in large pores. It may affect the progress of the attack. The compact cover of brucite may retard the attack a little. However, it means that cation  $Mg^{2+}$  leaves solution lowering its PH value. Thus, the acidity of solution is sustained and it results in acceleration of calcium ions dissociation in the solution and formation of gypsum (Piasta et al., 2014).

## RESULTS AND DISCUSSION

### Hydration Products

Before exposure to the sulfate solution, phases of clinker in cement paste samples are

hydrated and hydration products, such as C-S-H gel, portlandite, hydrotalcite, hemihydrate, ettringite, monosulfate and hydrogarnet are formed (Figure 1). Further details are given in the appendix. Thermodynamic modeling of cement hydration in terms of increasing of wollastonite percentage shows that by increasing wollastonite, portlandite would decrease to the extent that by 24 percent replacement it is fully consumed and consequently, C-S-H gel would increase. It is because when wollastonite reacts, silica and alumina enter the system. Silicates react with portlandite and by its consume create extra C-S-H gel. So C-S-H gel increases. Also ettringite would be slightly reduced and turned into monosulfate which increases its volume. It is due to this fact that after sulfates are finished, the remaining of aluminates and ferrite react with ettringite and convert to monosulfate. Hemihydrate and hydrotalcite would remain unchanged and hydrogarnet would slightly increase which is negligible.

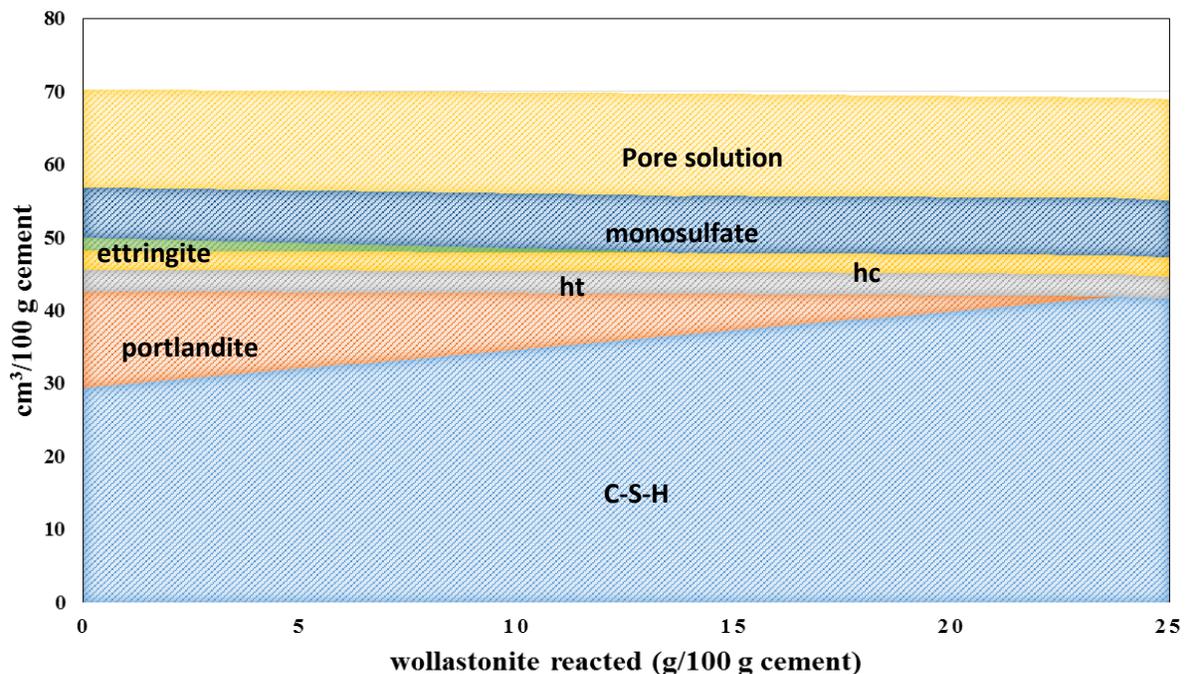


Fig. 1. Changes in the modelled phases with increasing substitution of wollastonite

### Study of Magnesium Sulfate Solution

Magnesium sulfate could react with all the hydrated cement products and is generally known as the most destructive sulfate. Thermodynamic modeling at the core of hydrated samples, predicts the presence of C-S-H gel, portlandite, hydrotalcite and monosulfate (Figure 2). In this solution, even at concentrations less than 44 g/l, gypsum is present. Near the surface where the concentration of sulfate solution is much more than the core samples, gypsum, brucite and with a significant amount hydrotalcite is formed. In addition, it is present also near the surface of other amorphous and weak crystals such as SiO<sub>2</sub>. Ettringite formed in high concentration in the solution, would be unstable near the surface.

Magnesium sulfate attack mechanism is so that first, magnesium sulfate reacts with portlandite, so gypsum and brucite are formed. Brucite formation needs a lot portlandite, so when portlandite is consumed, magnesium sulfate would go after more calcium and is decalcified and consequently C-S-H gel degradation occurs. Brucite formation also results into reduced PH in the pore solution. Reducing the PH in ettringite is followed by instability near the surface. On the other hand, C-S-H gel has a tendency to release calcium in order to raise the PH to maintain balance. This process helps accelerate decomposition of C-S-H gel near the surface (Al-Amoudi, 2002; Zelic et al., 2007; Piasta et al., 2014).

### The Effect of Wollastonite

Portlandite has plate-like crystals, which does not play an important role in the strength and C-S-H gel with its three-dimensional crystals maintains the main strength. The use of mineral materials, helping to minimise both ettringite and gypsum formation and aids sulfate resistance in three ways (Whittaker and Black, 2015): a) Diluting the clinker species. Reducing tricalcium

aluminate and tricalcium silicate contents results in less aluminate hydrates and portlandite to react with sulfates. b) They further reduce the portlandite content as they hydrate. As such, less portlandite is available to form gypsum or to provide calcium to form ettringite. c) Blended systems usually exhibit a finer pore structure, reducing permeability, and thereby improving resistance. By substituting wollastonite, the predicted products in thermodynamic model, are the same but the volume of the products is changed (Figure 3).

Adding wollastonite causes portlandite consumption, production of C-S-H gel and reduction in the volume of some harmful phases. With increasing the replacement of wollastonite, more portlandite is consumed which is turned into C-S-H gel. Formation of gypsum and brucite needs great amounts of portlandite, because by increasing the percentage of wollastonite substitution, portlandite volume decreases (Figure 4), and a decline could be observed during these two phases. However, with a 10% substitution, there is no significant change in these phases (Figure 5a,b).

The results of monosulfate, ettringite and hydrotalcite phases are different. By increasing the substitution of wollastonite, the volume of these phases increases. By increasing the substitution percentage, monosulfate phase in the core sample is slightly decreased (Figure 6a). But, with advancing from core to the surface, in the presence of high sulfate solution concentrations, this phase increases. Naturally, the increase of monosulfate, also results into increase of ettringite (Figure 6b). Resistance to sulfate attack depends on several factors, the most important of them seems to be the available amount of Al<sub>2</sub>O<sub>3</sub> for the formation of ettringite. In addition to aluminum released during hydration, it is also distributed between the C-S-H gel, AFt and AFm phases. It seems that the only significant

direct source of available  $Al_2O_3$  is in AFm phase. In general, to investigate the cause of increase in these phases there is need for understanding the Aluminum ions

distribution (Gollop and Taylor, 1992). According to the obtained results, more replacement of wollastonite in high percentages is not desirable.

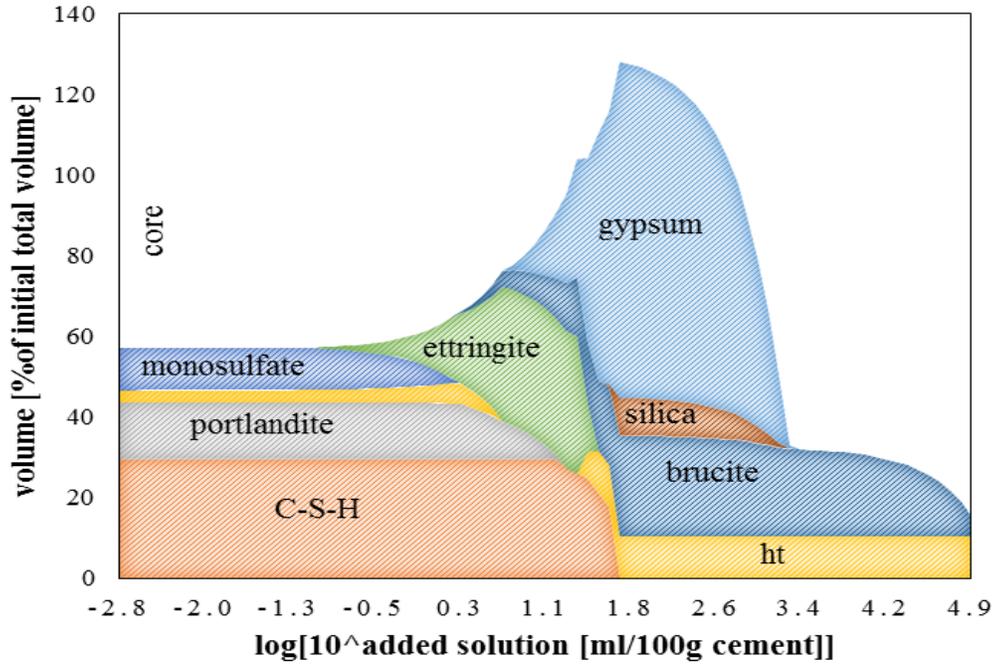


Fig. 2. Phase assemblage of the mortar sample (SF0 W0) immersed in 44 g/l MgSO4

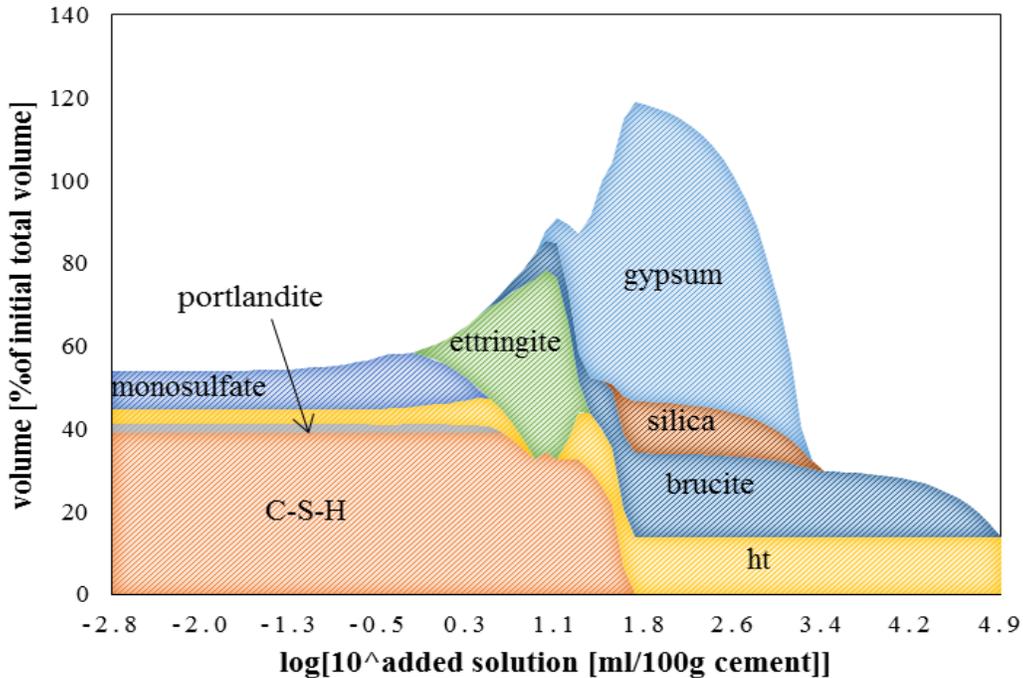


Fig. 3. Phase assemblage of the mortar samples by substituting 20% wollastonite immersed in 44 g/l MgSO4

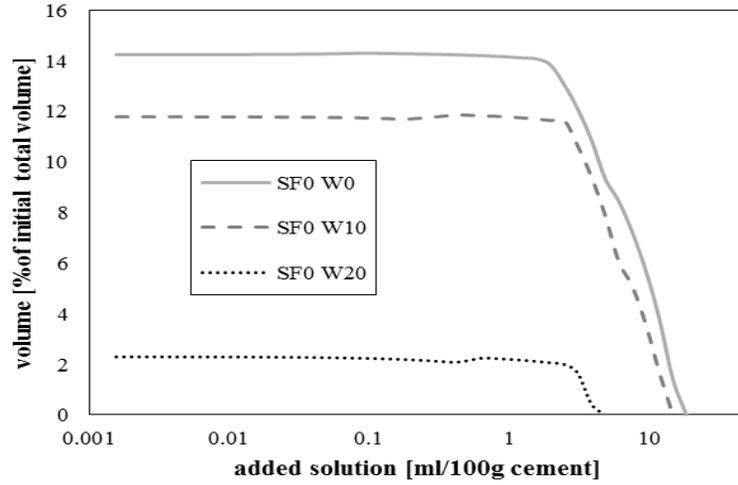


Fig. 4. Comparison between effects of various wollastonite mixes in portlandite

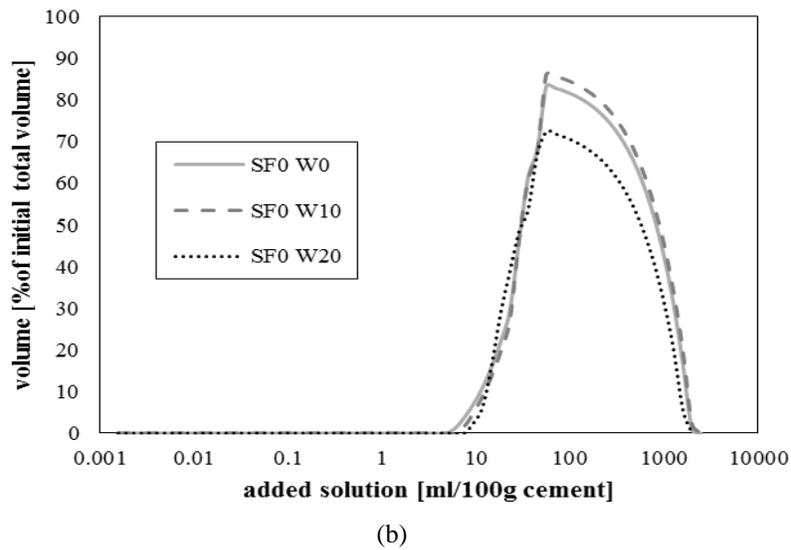
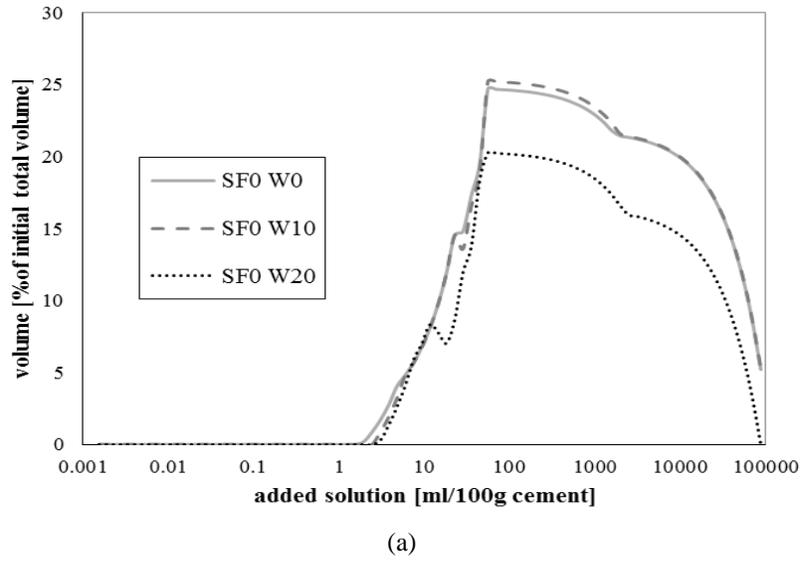


Fig. 5. Comparison between various wollastonite mixes: a) brucite, b) gypsum

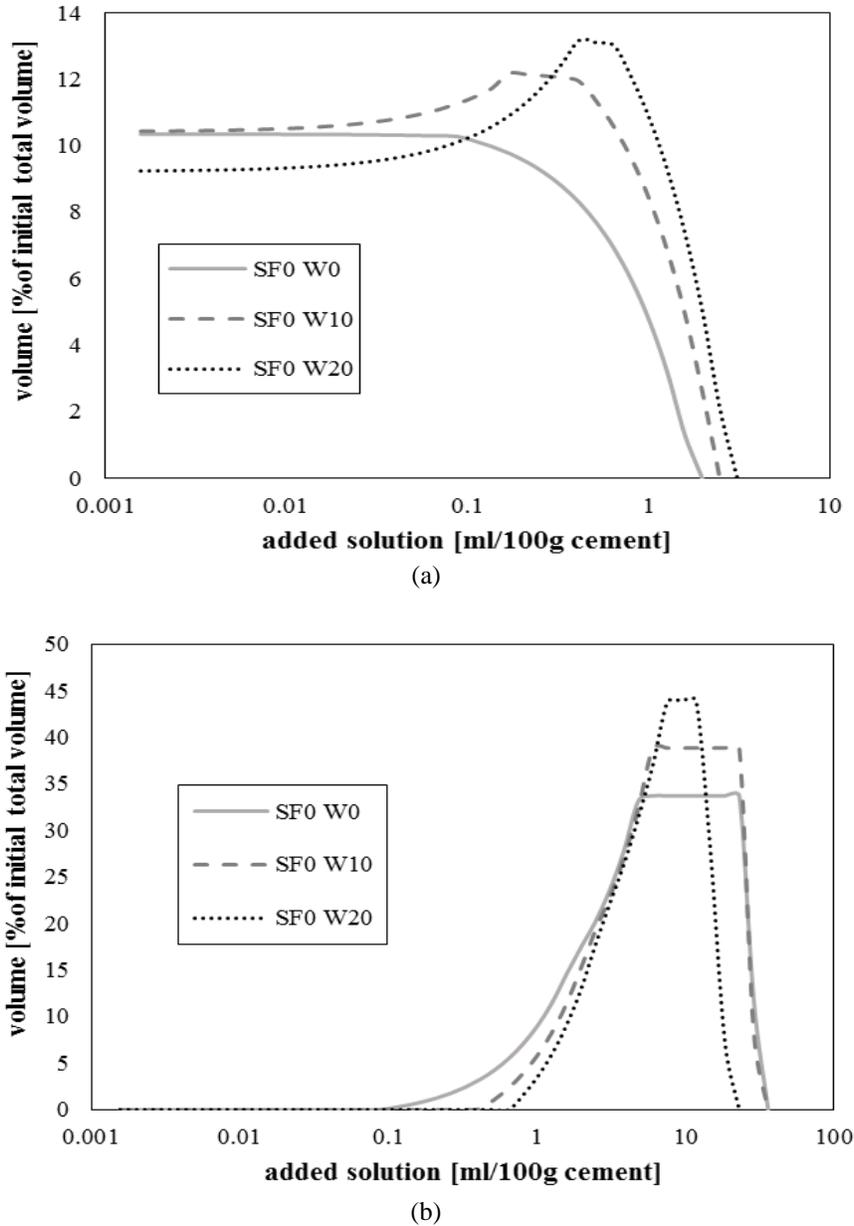


Fig. 6. Comparison between the effects of various wollastonite mixes: a) monosulfate, b) ettringite

### Effect of Wollastonite and Silica Fume

In order to improve the effect of wollastonite in sulfate attack, using silica fume with wollastonite is studied in this paper. Silica fume consists of  $\text{SiO}_2$  of very fine particle sizes and has a relatively high pozzolanic activity. Use of cement systems containing silica fume, is the best way to illustrate the effectiveness of such compositions as silica- rich material on the phase assemblage of Portland cement,

especially in thermodynamic calculations (Lothenbach et al., 2011).

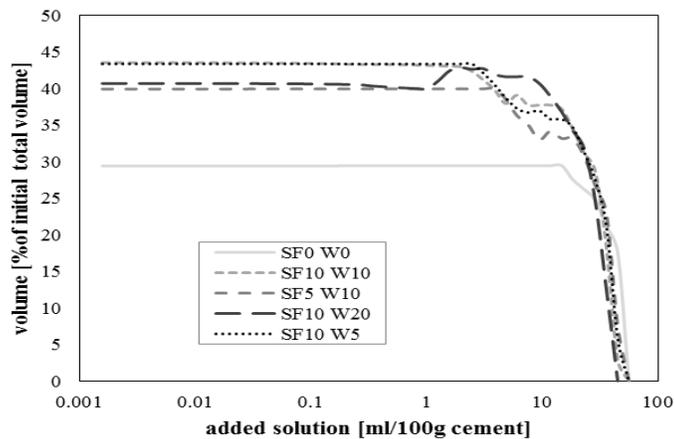
In all intended mixes, SF10 W10 to SF10 W5, portlandite is reduced and C-S-H gel is increased (Figure 7a). Most of the increase in the volume of C-S-H gel corresponds to mix SF10 W5 and the lowest corresponds to the mix SF5 W10. This reflects the role of silica fume in C-S-H gel. In mixes SF10 W20 and SF10 W10, (mixes that include the highest amount of additives replacement) portlandite

is completely consumed (Figure 7b). Full consumption of portlandite in magnesium sulfate is not desirable. Because, as mentioned before, due to reduced PH in this solution, decomposition of C-S-H gel occurs faster in comparison to other sulfate solutions (sodium and potassium sulfate). On the other hand, full consumption of portlandite phase provides a good opportunity for direct interaction of the sulfate ions with C-S-H gel which intensifies degradation of C-S-H gel and as a result, loss of strength would follow. So the remaining small quantities of portlandite is important. That is why mix SF10 W5 is a desirable option among others.

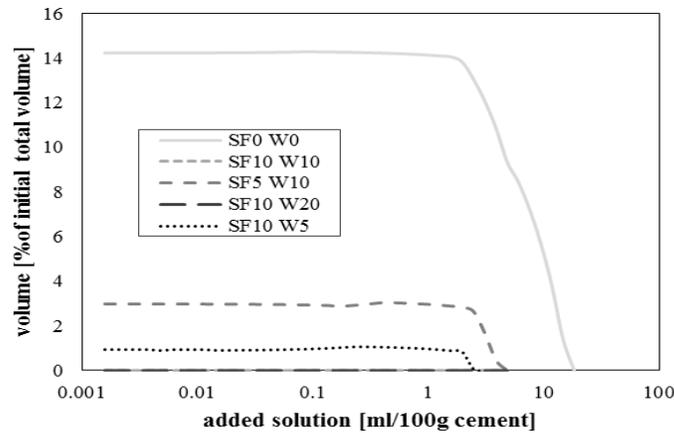
The amount of monosulfate in mix SF10 W5 is close to mix SF0 W0 (the initial state) (Figure 8a). In mix SF10 W20 due to the high percentage of replacement of silica fume and

wollastonite, monosulfate is completely consumed. Mix SF5 W10, due to increase of monosulfate in high concentration compared to the initial state, is not favorable. Proper decrease in this phase is only visible in mix SF10 W10. Due to complete consumption of monosulfate in mix SF10 W20, the lowest formed ettringite belongs to this mix, too (Figure 8b).

As a whole, gypsum and brucite phases are reduced (Figure 9). The highest reduction in these phases belongs to mix SF10 W20 and the lowest belongs to mix SF5 W10. This amount is in fact in a direct relationship with the portlandite consumption. Hydrotalcite phase is also increased in all mixes and only mix SF10 W5 is desirable and is close to the initial state.

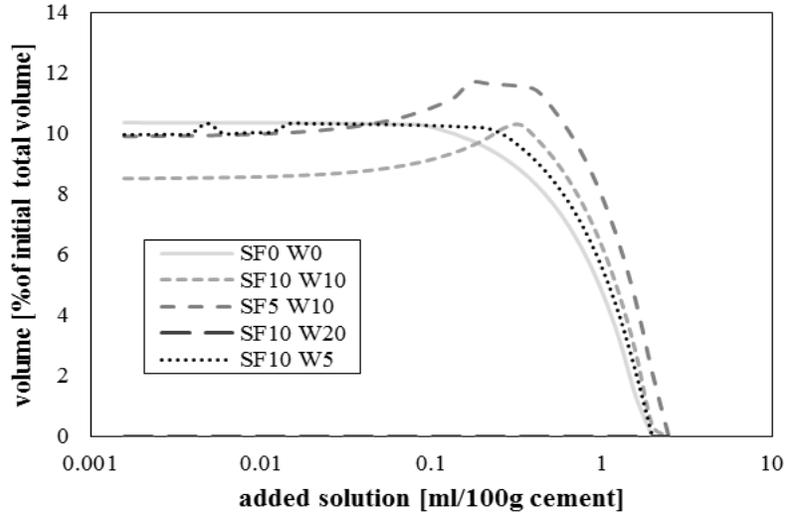


(a)

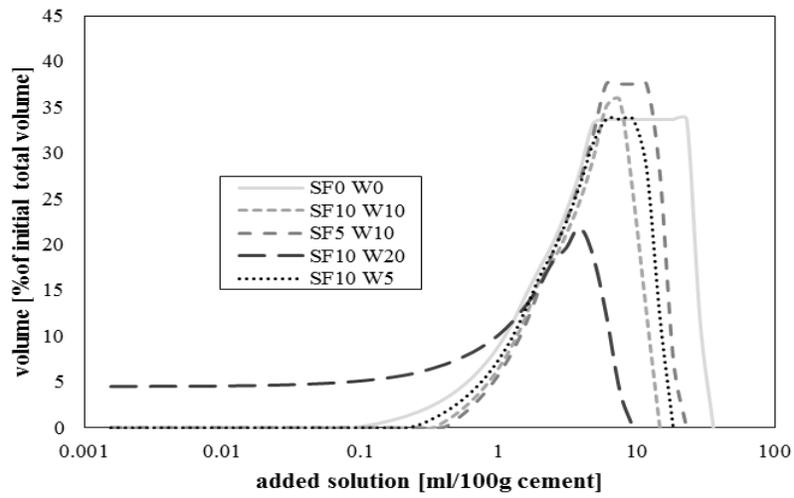


(b)

Fig. 7. Comparison between the effects of various wollastonite- silica fume mixes: a) C-S-H gel, b) portlandite



(a)



(b)

Fig. 8. Comparison between the effects of various wollastonite- silica fume mixes: a) monosulfate, b) ettringite

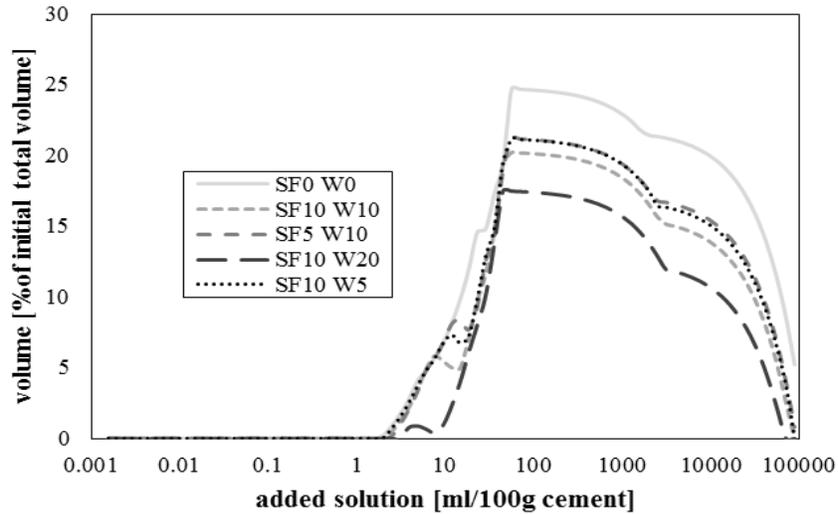


Fig. 9. Comparison between the effects of various wollastonite- silica fume mixes in brucite

## CONCLUSIONS

- GEM software helps in studying the microstructure of cement, volume and type of phases formed in sulfate solutions under different conditions. In this paper, the effect of wollastonite and silica fume on performance of the cement based materials during hydration and magnesium sulfate attack was studied.
- The results show that substituting wollastonite with a part of cement would result in increased portlandite consumption, increase of C-S-H gel and decrease of ettringite volume during hydration. During the magnesium sulfate attack, it causes reduced volume of formed harmful products like gypsum and brucite. Although when replacement is done in low percentages, a significant change in the volume of these phases is not observed.
- By increasing the substitution percentage of wollastonite, volume of monosulfate and ettringite phases would increase. This increase could be attributed to the aluminum ion distribution between phases. So wollastonite alone does not have a positive effect on sulfate attack.
- Substitution of a part of cement by wollastonite and silica fume has a desirable effect on magnesium sulfate attack. Mixes SF10 W10 and SF10 W20 which have a high percentage of silica fume and wollastonite, are not suitable due to the complete consumption of portlandite and monosulfate. As in this case, there is an opportunity of reaction between magnesium sulfate and C-S-H gel.
- Among the proposed mixes, mix SF10 W5 that contains 5% wollastonite and 10% silica fume, has exhibited the best performance. C-S-H gel possesses the highest increase in volume in mix SF10 W5. In contrast to other mixes, monosulfate and hydrotalcite have not changed much in this mix and reduction of formed ettringite is also desirable.

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## Appendix

The solid phases in hydrated cement systems consist mainly of portlandite and a gel like phase, a calcium silicate hydrate termed C-S-H. Alumina combines with water, calcium and sulfate to form mainly AFt (ettringite) and AFm phases. Commercial Portland cement pastes contain ~5-15% of (AFm+AFt) (Balonis, 2010).

**AFm:** is shorthand for a family of hydrated calcium aluminate hydrate phases (aluminate-ferrite-monosubstituent phases). Its crystalline layer structure is derived from that of portlandite, Ca(OH)<sub>2</sub>, but with one third of the Ca<sup>2+</sup> ions replaced by a trivalent ion, nominally Al<sup>3+</sup> or Fe<sup>3+</sup>. The resulting charge imbalance gives the layers a positive charge which is compensated by intercalated anions (e.g. SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, Cl<sup>-</sup> etc.); the remaining interlayer space is filled with H<sub>2</sub>O. Its general formula is [Ca<sub>2</sub>(Al,Fe)(OH)<sub>6</sub>].X.xH<sub>2</sub>O, where X represents a monovalent ion or 0.5 of a divalent interlayer anion and x represents the number of water molecules (Balonis, 2010).

**Aft:** [Ca<sub>3</sub>Al(OH)<sub>6</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·(24+2)H<sub>2</sub>O (conventional cement shorthand notation: C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>) or ettringite, crystalline - trigonal. Product of hydration of C<sub>3</sub>A and gypsum. AFt (aluminate-ferrite-trisubstituted) compound is typically needle-shaped. It is stable at 20 °C down to ~4 percent relative humidity. Various analogues (carbonate, iron, hydroxide, etc.) and solid solutions have been reported (Balonis, 2010).

**Hydrotalcite:** blast furnace slag introduces Mg to the system which upon hydration gives a hydrotalcite - like phase characteristic for slag cement blends (Balonis, 2010).