

Durability of copper slag contained concrete exposed to sulfate attack

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ARTICLE INFO

Article history:

Received 14 July 2010

Received in revised form 13 October 2010

Accepted 13 November 2010

Available online 18 December 2010

Keywords:

Copper slag waste

Sulfate attack

Microstructural analysis

Ettringite

ABSTRACT

Sulfate attack is one of several chemical mechanisms of concrete deterioration. Exposure of concrete structures in the sulfate environments may lead to detrimental chemical, microstructural, and physical changes in the concrete matrix, resulting in serious deteriorations and service life reduction. Partial replacement of cement with slag is one of the efficient methods for improving concrete resistance against sulfate attack. In this paper the performance of copper slag contained concrete in sulfate solution is investigated. In this regard, an experimental study including expansion measurements, compressive strength degradation and microstructural analysis were conducted in sulfate solution on concretes made by replacing 0%, 5%, 10% and 15% of cement with copper slag waste. The results of this study emphasized the effectiveness of copper slag replacement in improving the concrete resistance against sulfate attack.

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1. Introduction

Climate change and global warming resulted by greenhouse gas emission have been a growing concern in recent years. The carbon dioxide, as a major environmental pollutant is a serious worldwide problem leading to the greenhouse effects. It was indicated that the largest growth in the CO₂ emissions has come from electricity generation, transport, industry and, above all, from building operations. One of the most important industries and building operations causing carbon dioxide emission is the cement and concrete related industries so that cement production (including direct fuel for mining and transporting raw material) consumes approximately 6 million Btus per metric-ton, and releases about 1 metric-ton of CO₂ [1]. Worldwide, the cement industry alone is estimated to be responsible for about 7% of all generated CO₂ [2]. By these considerations, the majority of European cement production is allocated to use of different supplementary cementitious materials (SCM) towards reducing the greenhouse gas emission [3].

On the other hand, many industrial wastes such as fly ash, silica fume, blast furnace slag and copper slag are pollutive; hence requiring proper collection, disposal and storage. Application of these materials in cement and concrete is environmentally friendly and economically beneficial, since such usage (1) decreases the depletion of natural resources, (2) reduces pollutant emissions and (3) increases the concrete durability [4–7], so industrial slag is known as one of the main constituents of supplementary cementitious materials which has been available since the inception of metal extraction from ores through metallurgical processes.

Copper slag is the waste material of matte smelting and refining of copper such that each ton of copper generates approximately 2.5 tons of copper slag. The amount of copper slag produced in the US and Japan are about four million and two million tons per year respectively [4,8–10]. The lower quantities of such waste are annually produced in Iran, Brazil and Oman, respectively about 360,000, 244,000 and 60,000 tons [4,11–15]. Consequently, conducting researches on the application of these environmental pollutant wastes in the concrete industry is of the most important movement towards sustainable development. Various research works can be found in the literature regarding the application of copper slag in concrete which a summary of them is presented in Table 1. As it can be seen, these researches have been usually focused on the mechanical properties of the copper slag as replacement of concrete aggregates [9,11,12,16] or cement [17–25]. Other research works paid some attentions on the application of copper slag in cement to solidify/stabilize its heavy metals [26–30].

Since 92% of the energy demand of concrete production is related to cement constituents, the application of copper slag as SCM has higher priorities than its usage as aggregates. In spite of some valuable researches conducted to investigate the mechanical properties of copper slag contained concrete as SCM, the durability properties; in particular alkali silica reaction, abrasion, freeze and thaw resistance, shrinkage and, above all, sulfate resistance of these concretes are rarely found in the literature.

Reviewing the aforementioned research works reveals the deficiency of investigations about the sulfate resistance of copper slag contained concrete. Sulfate attack, known as one of the most aggressive environments of concrete structures, causes serious deteriorations and results in service life reduction. The sulfate attack is generally defined as a deteriorative reaction of sulfate ions

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Table 1
Past researches of using copper slag in cement and concrete.

Properties	As supplementary cementitious materials	As aggregate replacement
Mechanical properties	Moura et al. [13], Al-Jabri et al. [15,20], Mobasher et al. [17], Tixier et al. [18], Ariño and Mobasher [19], Moura et al. [21], Sanchez de Rojas et al. [22], Alp et al. [25], Zain et al. [26], Deja and Malolepszy [33,34]	Caliskan and Behnood [9], Khanzadi and Behnood [11], Behnood [12], Al-Jabri et al. [16], Al-Jabri [36], Hwang and Laiw [37], Zong [39], Li [40]
Alkali-silica reaction	Tixier et al. [43]	–
Transport properties	Mobasher et al. [17], Tixier et al. [18], Moura et al. [21], Deja and Malolepszy [33,34]	–
Sulfate resistance	Tixier et al. [43], Tixier [44]	Ayano and Sakata [10], Hwang and Laiw [37]
Abrasion/freeze and thaw resistance	Dai et al. [35]	Ayano and Sakata [10], Tang et al. [38], Li [40], Shoya et al. [41,42]
Shrinkage	–	Ayano and Sakata [10], Hwang and Laiw [37]
Carbonation	Moura et al. [21]	Ayano and Sakata [10], Hwang and Laiw [37]
Pozzolanic activity	Sanchez de Rojas et al. [22], Zain et al. [26]	–

with calcium hydroxide and calcium aluminate hydrate to form gypsum and Ettringite. The reaction products, i.e. gypsum and Ettringite have 1.2–2.2 times more volumes than initial reactants [45] lead to expansion, cracking, and deterioration of concrete structures exposed to sulfate environment such as piers, bridges, foundations and concrete pipes. Degradation of calcium silicate hydrate (CSH) gel through leaching of the calcium compounds is another mechanism involved in sulfate attack. This process leads to loss of CSH gel stiffness and overall deterioration of the cement paste matrix [46]. The incorporation of supplementary cementitious materials such as slag, fly ash, and silica fume as a partial replacement of ordinary cement has been found a beneficial technique of enhancing the resistance of concrete to sulfate attack [45,47–50]. In this regard, this paper aims to study the effects of copper slag waste utilization as a supplementary cementitious material on durability performance of concrete in sulfate solution. To this aim, a comprehensive laboratorial study including expansion measurements, compressive strength degradation and micro-structural analysis in sulfate solution were considered by replacing 5%, 10% and 15% of cement with copper slag waste.

2. Materials and mixture proportions

An especial type of copper slag waste with chemical composition summarized in Table 2 was used as SCM. Unlike the reported researches having high SiO₂ (25–40%) and low CaO (0.6–10%) contents [4,11,16–22,25,26,31,32], the utilized copper slag has lower SiO₂ and higher CaO amounts respectively about 9.5% and 22%. Considering the availability of sufficient lime quantity required for hydration and strengthening (at early ages), this especial type of copper slag may be consid-

Table 2
Chemical composition of cement and copper slag.

Compound/property	Cement	Copper slag
<i>Chemical analysis (%)</i>		
Calcium oxide (CaO)	62.89	22.25
Silica (SiO ₂)	20.19	9.57
Alumina (Al ₂ O ₃)	3.84	4.43
Iron oxide (Fe ₂ O ₃)	3.99	57.42
Manganese oxide (MnO)	0.20	–
Magnesium oxide (MgO)	3.56	1.56
Sodium oxide (Na ₂ O)	0.20	1.47
Potassium oxide (K ₂ O)	0.72	–
Titanium dioxide (TiO ₂)	0.26	–
Sulfur trioxide (SO ₃)	1.87	–
Cu as CuO	–	1.24
Zn as ZnO	–	0.94
Pb as PbO	–	0.51
Ba as BaO	–	0.23
Ni as NiO	–	0.06

ered as a reactive cementitious material. The summation of silica, alumina and iron oxide in the copper slag is 71.4%, slightly exceeding the 70% limit for Class N raw and calcined natural pozzolans, according to ASTM C618. The strength activity index of copper slag was measured based on ASTM C618. The results presented in Table 3 reveal that the strength activity of copper slag is slightly higher than the natural pozzolan and fly ash requirements of 75% according to ASTM C618. Besides, as a well-known pozzolanic activity measurement, thermo-gravimetric analysis was performed on copper slag to evaluate calcium hydroxide consumption. This method is based on the thermal decomposition of crystalline calcium hydroxide in a temperature range of 400–500 °C to calcium oxide and water. The pozzolanic activity were measured by combining 50% copper slag and 50% calcium hydroxide powder in presence of enough water for pozzolanic reactions. The results of this test which are presented in Table 3 for 7 and 28 days, suggest a mediocre pozzolanic activity.

Table 3
Strength and pozzolanic activity of copper slag.

Test	7 days	28 days
Strength activity index, % of control	78	81
Thermo-gravimetric measurement ^a (%)	26	31

^a Thermo-gravimetric analysis is done by combining 50% copper slag with 50% Ca(OH)₂ powder.

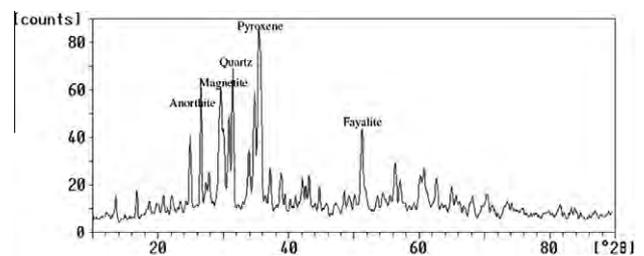


Fig. 1. X-ray diffraction of copper slag.

Table 4
Mechanical and physical properties of cement.

Tricalcium silicate (C ₃ S) (%)	54.02
Dicalcium silicate (C ₂ S) (%)	16.41
Tricalcium aluminate (C ₃ A) (%)	4.01
3 day compressive strength (MPa)	18.2
7 day compressive strength (MPa)	28.5
28 day compressive strength (MPa)	42.6
Initial setting time (min)	85
Final setting time (min)	210
Specific surface (m ² /kg)	331.4
Specific gravity (g/cm ³)	3.15
Loss on ignition (975 °C) (%)	3.81
Loss on drying (105 °C) (%)	0.24

Table 5
Aggregate properties.

Aggregate type	Specific gravity	Absorption (%)	Fineness modulus	% <75 μm
Fine (0–4.75 mm)	2.53	2.60	3.2	1.1
Coarse (4.75–19 mm)	2.56	1.46	–	0.2

Table 6
Mixture proportions of concretes and fresh concrete properties.

Mixture identification	Copper slag (%)	Cement (kg/m ³)	Copper slag (kg/m ³)	Slump (mm)	Density (kg/m ³)
CS ₀ (control)	0	360	0	70	2308
CS ₅	5	342	18	75	2312
CS ₁₀	10	322	36	70	2315
CS ₁₅	15	306	54	70	2328

Note: all mixtures are made by w/cm = 0.5, water = 180 kg/m³, fine aggregate = 870 kg/m³ and coarse aggregate = 870 kg/m³.

Table 7
Compressive strength of concrete specimens.

Immersion in water/sulfate solution (days) ^a	Normal condition				Sulfate attack condition			
	CS ₀	CS ₅	CS ₁₀	CS ₁₅	CS ₀	CS ₅	CS ₁₀	CS ₁₅
0	29.7	27.5	25.2	23.3	29.7	27.5	25.2	23.3
7	–	–	–	–	33.7	31.9	26.1	24.7
14	–	–	–	–	35.4	33.6	30.3	28.7
21	40	37.5	36	35.2	35.7	34.5	32.1	30
28	–	–	–	–	35.4	36	33.1	32.8
61	–	–	–	–	34.5	37.6	35.2	35.0
83	44	43	41.7	39.5	–	–	–	–
90	–	–	–	–	33.8	35.6	33.0	31.5
120	45	44.6	43.2	41.2	32.4	34.9	32.0	31.5

^a After 7 days curing in water.

Table 6 summarizes the concrete mixture proportions and fresh concrete properties. In addition to the control concrete without incorporating the copper slag (CS₀), three mixtures were made by replacing 5%, 10% and 15% of cement with copper slag named as CS₅, CS₁₀ and CS₁₅ respectively. Copper slag has minor influence on concrete workability; slumps of all mixtures were almost equal, while presented a minimal effect on concrete density, attributed to its higher specific gravity in comparison with cement.

3. Sulfate solution exposure effects

In order to investigate the effects of sulfate attack, of each mixture, three concrete prisms (75 × 75 × 285 mm) and 33 concrete cubes (100 × 100 × 100 mm) were prepared. From them, nine cubes were used for determining the compressive strength of concrete continuously immersed in water (normal condition), while 24 cubes and 3 prisms were applied for measuring the compressive strength and length expansion of concretes immersed in sulfate solution (sulfate attack condition), respectively.

Especially curing and exposure regime were adopted to study the sulfate attack on the concrete. Concrete cubes and prism specimens were cured in water for 7 days and after that immersed in the sulfate solution having 50 g per liter of Na₂SO₄.

3.1. Expansion measurements

To study the influence of copper slag replacement on the sulfate expansion, the length of concrete prisms immersed in sulfate solution was measured during the immersion time. The expansion due to sulfate attack (*S_E*) is determined by using the following equation adopted from ASTM C1012 [51]:

$$S_E = [(L_t - L_0)/L_0] \times 100 \tag{1}$$

where *L_t* is the length of specimen at time *t* after immersion in sulfate solution and *L₀* is the initial length before immersion in sulfate.

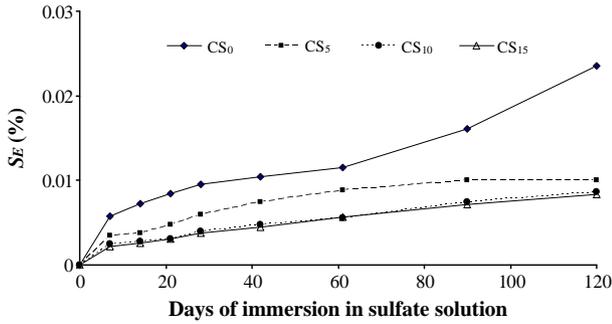


Fig. 2. Expansion in sulfate solution versus age.

The mineralogical compounds of this slag identified by XRD analysis is shown in Fig. 1. The main components are identified as Pyroxene (CaZnSi₂O₆), Fayalite (SiO₄Fe₂), Anorthite (CaAl₂Si₂O₈), Quartz (SiO₂) and Magnetite (Fe₃O₄), while the previous researches showed the presence of only Fayalite, Magnetite and Quartz [17–19,21,22,25]. The specific gravity of utilized copper slag was 3.49 g/cm³, about 10% more than 3.15 g/cm³ of cement.

Type I Portland cement meeting the requirements of ASTM C150 and fine (0–4.75 mm) and coarse aggregates (4.75–19 mm) which met the requirements of ASTM C33 were used in this investigation. The chemical composition and physical properties of cement are presented in Tables 2 and 4, respectively. Also, the physical and mechanical properties of aggregates are reported in Table 5.

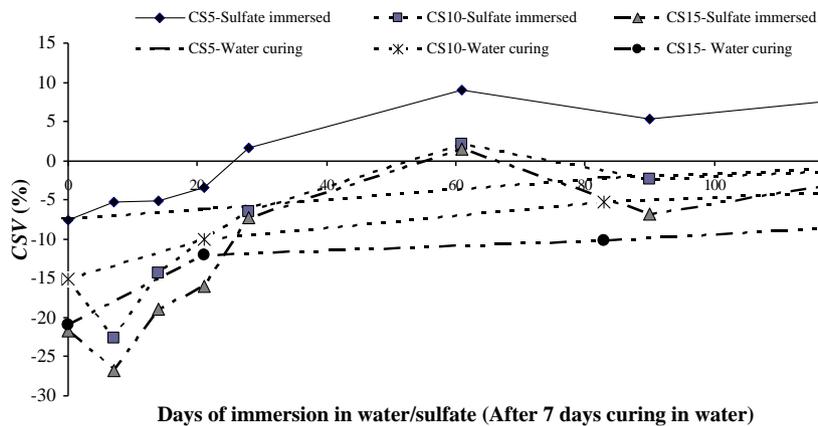


Fig. 3. Compressive strength variation versus immersion time.

S_E curves of specimens are illustrated in Fig. 2 for CS_0 , CS_5 , CS_{10} and CS_{15} containing 0%, 5%, 10% and 15% of copper slag respectively. The expansions of CS_5 , CS_{10} and CS_{15} were 76.5%, 48.7% and 49.6% of CS_0 expansion after 61 days immersion, whereas after 120 days immersion these values decreased to 42.6%, 36.6% and 35.3% respectively. These observations emphasize that concretes containing copper slag (CS_5 , CS_{10} and CS_{15}) showed better performance than control concrete (CS_0), in particular by proceeding the sulfate solution exposure time. Besides, by increasing the amount of copper slag from 5% to 10%, the observed expansion de-

creased, while the expansions of samples containing 10% and 15% of copper slag were almost similar.

3.2. Compressive strength

Compressive strength of cubes was measured for both normal and sulfate attack conditions and the results are presented in Table 7. As it can be seen, the compressive strength of concrete specimens in sulfate condition experienced a decreasing trend in comparison with the specimens in normal condition. After 21 days in sulfate solution, the amount of this decrease was 10.8%, 8%, 10.8%, and 14.8% for CS_0 , CS_5 , CS_{10} and CS_{15} respectively, whereas after 120 days, these values reached to 28%, 21.7%, 25.9% and 23.5%.

To provide a tool for more illustrative explanations of copper slag utilization on the strength properties, compressive strength variation factor (CSV) is defined by Eq. (2) [52].

$$CSV(t) = [CS_{\alpha}(t) - CS_0(t)] \times 100 / CS_0(t) \quad (2)$$

where $CS_{\alpha}(t)$ is the compressive strength of concrete containing $\alpha\%$ of copper slag at time t ; $CS_0(t)$ is the compressive strength of control concrete at time t and t is the time of immersion in sulfate attack or normal condition just after 7 days curing in water.

In fact, CSV compares the compressive strength results of concrete containing copper slag with control concrete. CSV of specimens cured in water or immersed in sulfate solution, is shown in

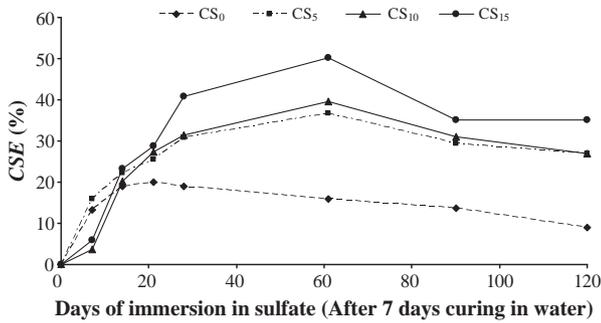


Fig. 4. Compressive strength evolution versus sulfate immersion time.

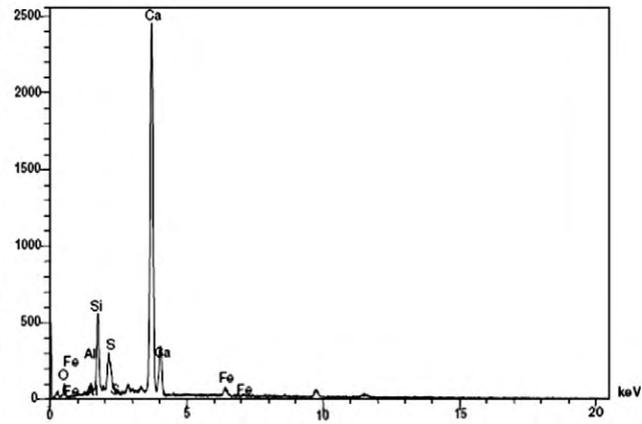
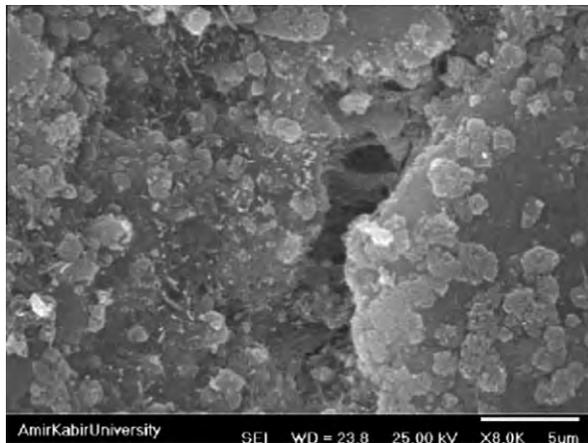


Fig. 5. SEM/EDX of CS_{15} after 120 days in normal condition.

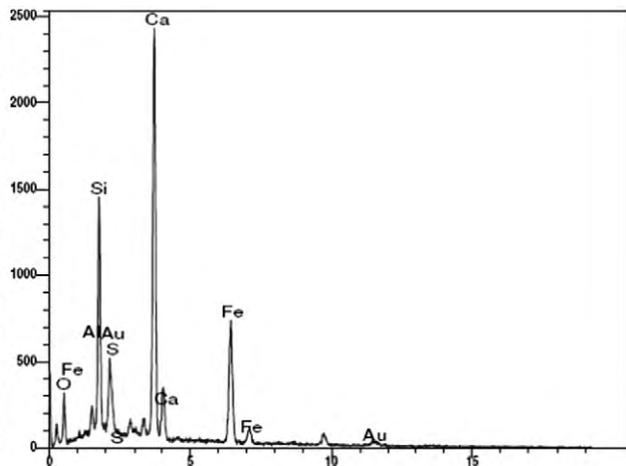
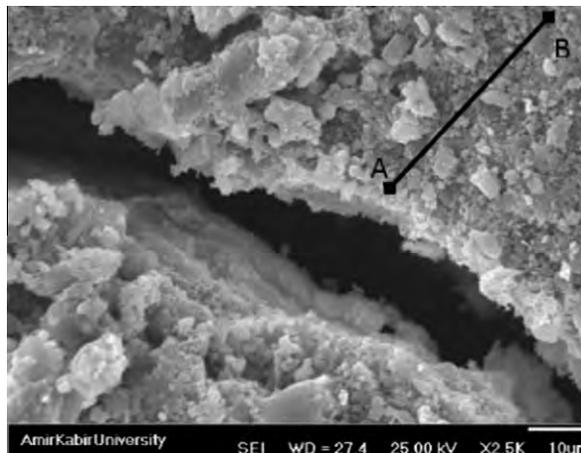


Fig. 6. SEM images of CS_0 after 61 days immersion in sulfate solution.

Table 8
 Chemical components of concretes in normal and sulfate attack conditions.

Identification		Chemical components					
		C	O	Al	Si	S	Ca
Normal condition	CS ₁₅	8.21	25.35	0.51	7.26	1.74	52.80
After 61 days immersion in sulfate	CS ₀	9.37	31.18	0.71	12.17	6.56	32.34
	CS ₅	26.54	27.70	7.97	25.03	4.85	2.13
	CS ₁₀	24.08	26.25	5.4	30.2	2.02	5.2
	CS ₁₅	20.08	35.45	0.12	1.71	1.94	32.49
After 120 days immersion in sulfate	CS ₀	14.37	34.25	5.5	3.12	6.3	32.34
	CS ₅	21.81	28.04	4.87	27.48	2.56	8.31
	CS ₁₀ -section 1	24.94	33.07	1.57	28.89	2.19	7.71
	CS ₁₀ -section 2	13.79	21.19	1.92	4.89	1.89	42.46
	CS ₁₅ -section 2	14.96	40.26	1.34	6.34	1.97	31.01

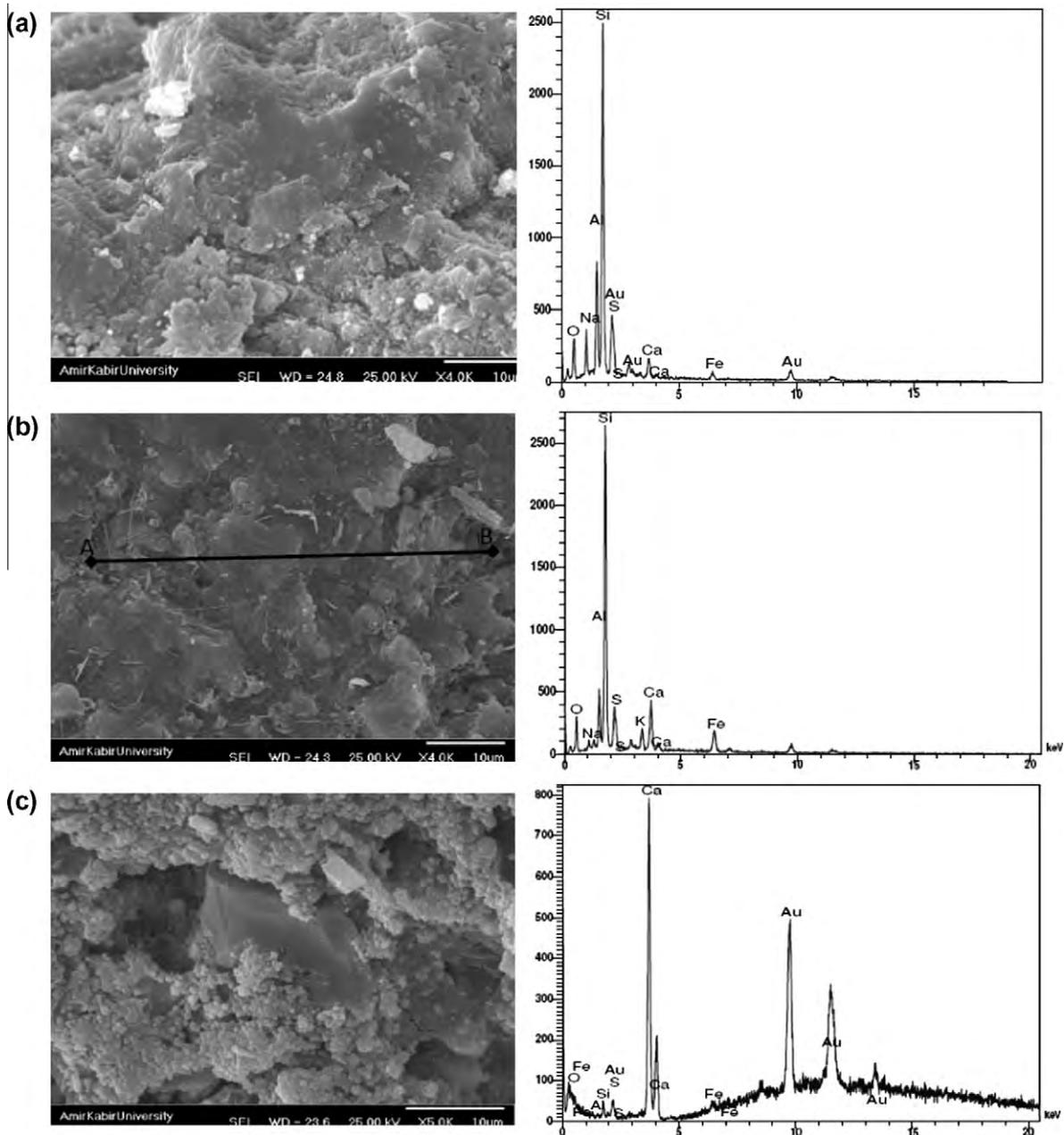


Fig. 7. SEM images of concretes containing copper slag after 61 days immersion in sulfate solution: (a) 5% copper slag-CS₅, (b) 10% copper slag-CS₁₀, (c) 15% copper slag-CS₁₅.

Fig. 3. As it can be deduced from Table 7 and Fig. 3, concrete containing copper slag stored in normal condition always presented lower compressive strength in comparison with control concrete. By increasing time of immersion, the aforementioned reduction decreased. The compressive strength of CS₅, CS₁₀ and CS₁₅ were 92.5%, 85% and 80% of CS₀ at 7 days, while their 90 days corresponding compressive strength increased to 97.5%, 95% and 90% of CS₀.

Copper slag contained specimens exhibited a better performance when exposed to the sulfate attack condition, in a manner that their corresponding compressive strength was closer to CS₀ and even they gained more compressive strength than CS₀ after 61 days. The compressive strength of CS₅ was about 10% more than CS₀, while CS₁₀ and CS₁₅ presented values comparable to CS₀ after 120 days immersion.

Moreover, another index is defined to relate the compressive strength of concretes in sulfate exposure to the initial state after

7 days curing in water. The compressive strength evolution factor (CSE) for specimens immersed in sulfate solution, determined by using Eq. (3), is shown in Fig. 4 [53].

$$CSE(t) = [CS_{\alpha}(t) - CS_{\alpha}(0)] \times 100 / CS_{\alpha}(0) \quad (3)$$

where CS_α(t) is the compressive strength of concrete containing α% of copper slag at time t; CS_α(0) is the compressive strength of concrete containing α% of copper slag before moving the specimens to sulfate and t is the time of exposure in sulfate, just after 7 days curing in water.

As it can be seen, CSE of all specimens is developed in the initial stages, whereas it degrades with proceeding of the exposure time. These results suggest two processes in concrete; hydration increases the compressive strength, while deteriorative chemical reactions between sulfate solution and concrete components results in the production of expansive agents and thus decreases the compressive strength.

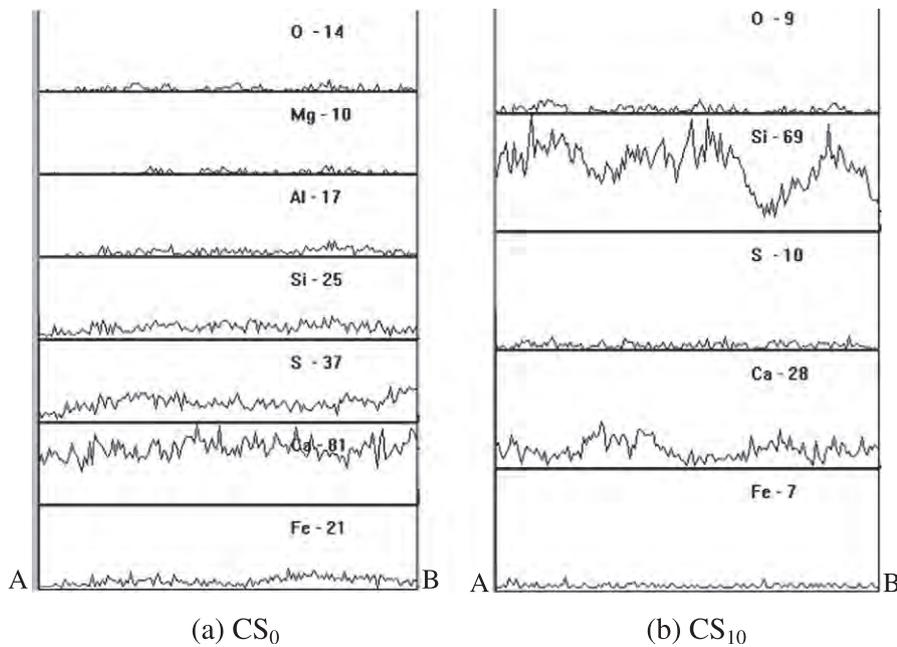


Fig. 8. EDX of line AB for: (a) CS₀ and (b) CS₁₀.

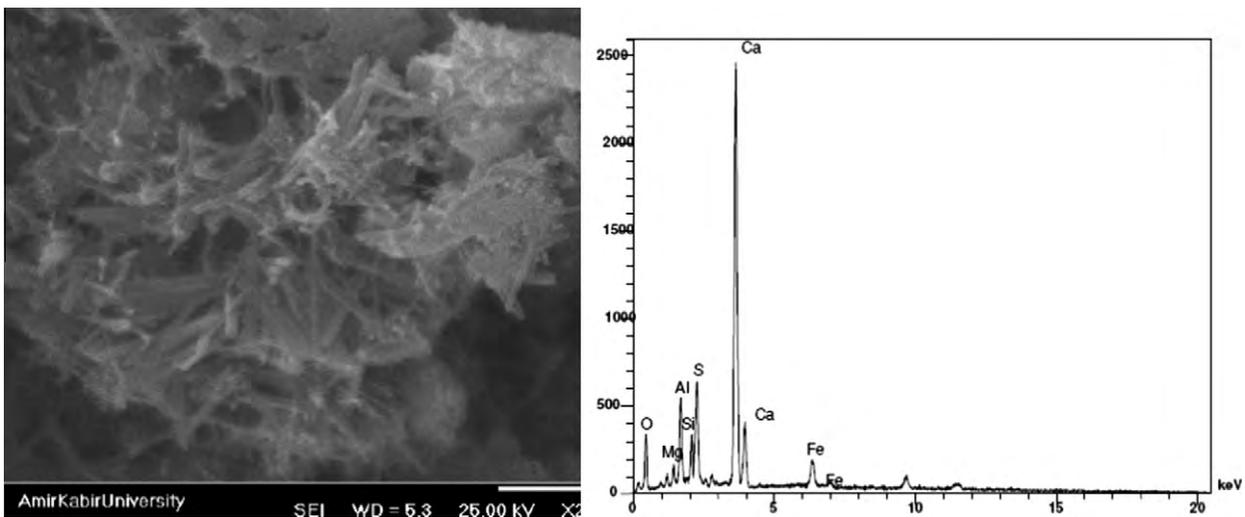


Fig. 9. SEM/EDX of CS₀ after 120 days immersion in sulfate solution.

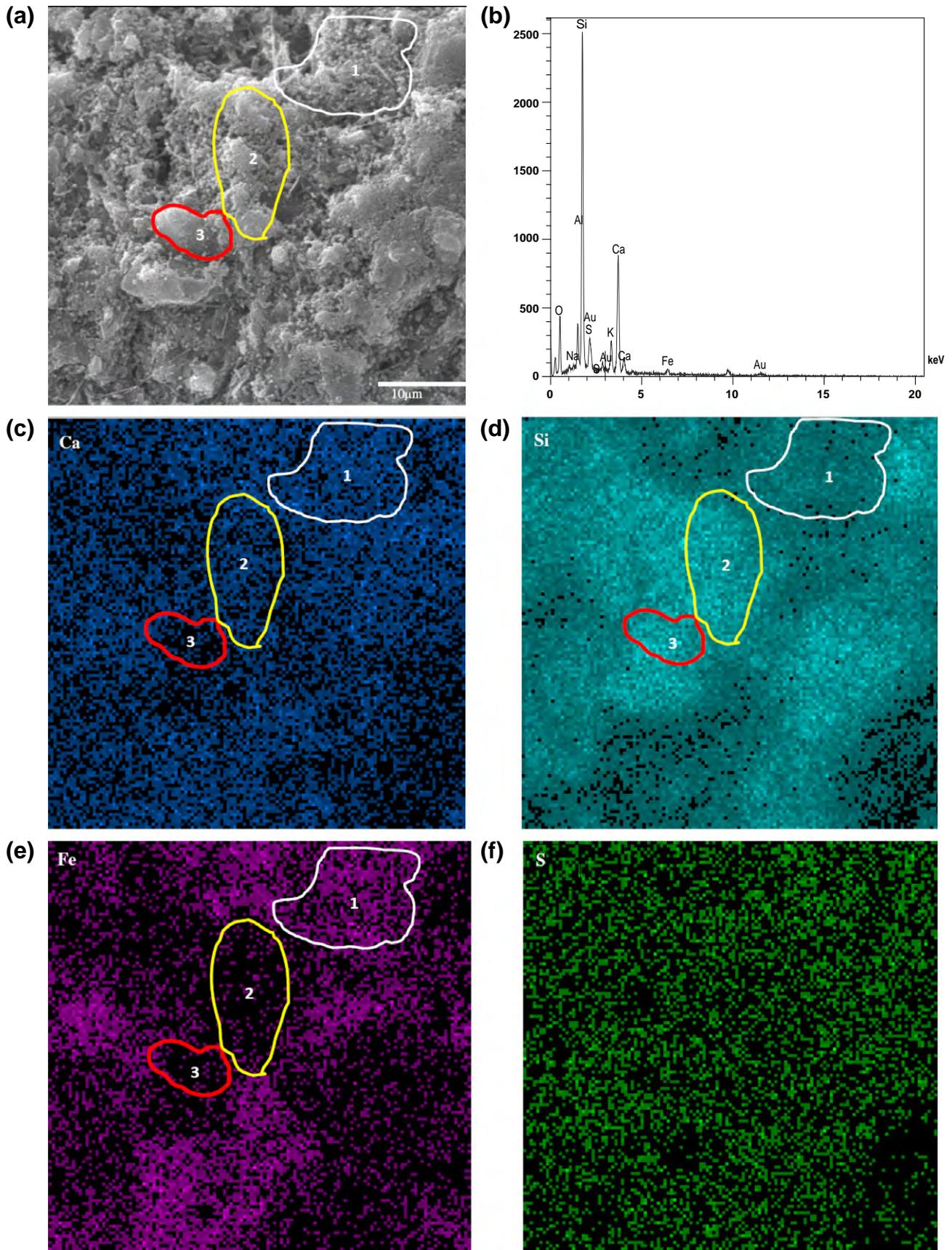


Fig. 10. SEM/EDX after 120 days immersion in sulfate solution for CS₅: (a) SEM, (b) EDX, (c) Ca, (d) Si, (e) Fe and (f) S.

From the foregoing processes, the first is supposed to be dominant at the early ages, leading to compressive strength development, whereas at later ages the second process is the governing factor resulted in strength reduction.

Besides, the observed trend shown in Fig. 4, proposes an initiation time for sulfate attack deterioration (ITD) for control and copper slag contained concretes, as the compressive strength increases until ITD and then a decreasing trend occurs. According to this figure, for concretes containing copper slag, ITD took place after 61 days immersion in sulfate solution, while for the control concrete IDT is recognized to be 21 days.

3.3. Microstructural analysis

The scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis were considered for microstructural and material component identification studies, respectively. To carry out SEM/EDX analysis, samples were prepared at the depth of 10 mm of understudied concretes.

3.3.1. Normal condition

Fig. 5 presents the SEM micrograph of CS₁₅ after 120 days immersion in water. Ca(OH)₂ deposits (CH) can be easily detected in this figure. Since copper slag showed a mediocre pozzolanic activity, the presence of remaining CH is inevitable. However, the

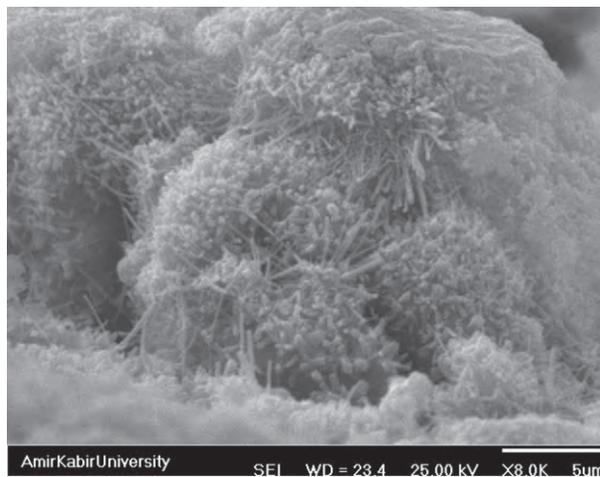
dense texture of concrete containing copper slag can be recognized in this figure. The chemical components of this concrete identified by EDX analysis is shown in Table 8. As it can be observed the sulfur (S) content of CS₁₅ in normal condition was 1.74%.

3.3.2. 61 days in sulfate attack condition

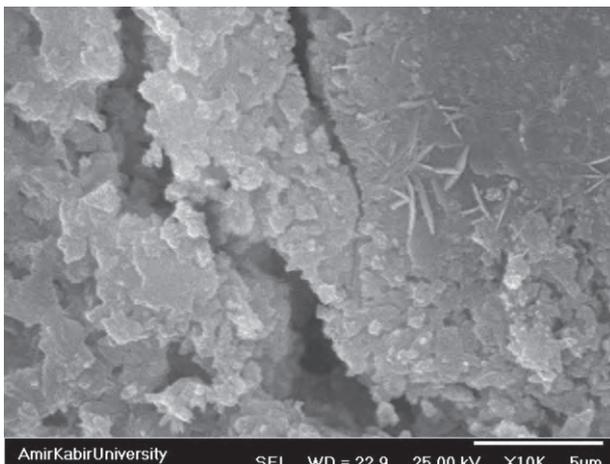
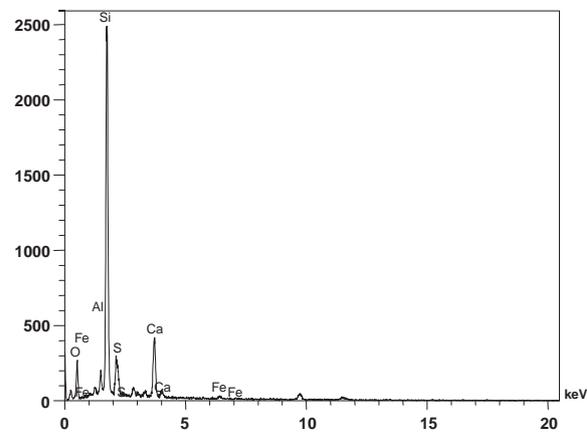
The microstructure of control concrete (CS₀) after 61 days immersion in sulfate solution is shown in Fig. 6. A crack can be observed, occurring in the CH formation. Ettringite needle shaped crystals are not detectable in this micrograph. Absence of Ettringite could be attributed to the specimens' ages, in a manner that specimens had inadequate time to form the expansive agents. However the high amount of sulfur emphasized the potential of Ettringite formation in CS₀.

Fig. 7 presents the SEM images of concretes containing 5%, 10% and 15% copper slag (CS₅, CS₁₀ and CS₁₅). As it can be seen, these concretes had denser textures than CS₀. The preceding observation could be related to the pozzolanic activity and filling properties of copper slag.

The amount of S in CS₀ was about 6.56%, while CS₅, CS₁₀ and CS₁₅ had about 4.85%, 2.02%, and 1.94% respectively (see Table 8). The sulfur content in CS₁₀ and CS₁₅ after 61 days immersion in sulfate solution was almost equal to specimens normally cured in water, while CS₀ presented higher sulfur content. This trend is more recognizable in Fig. 8 by comparing the sulfur content in



(a) CS₁₀-section 1



(b) CS₁₀- section 2

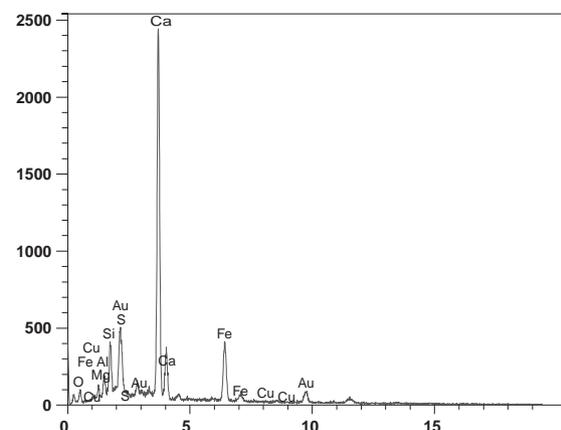


Fig. 11. SEM/EDX of CS₅ and CS₁₀ after 120 days immersion in sulfate solution.

EDX line AB of CS₀ and CS₁₀. Therefore CS₀ is justified to be more prone to deterioration comparing with the copper slag contained concretes. The higher potential to react with sulfates observed for CS₀ could be attributed to its higher permeability, which confirmed by the increasing S_E in CS₀ from 90 to 120 days (see Fig. 2). Moreover, nearly uniform distribution of sulfur in CS₀ of line AB (Fig. 8) demonstrates the ingress of external sulfur.

By considering the EDX analysis of CS₅, it seems that this concrete also has some potential for Ettringite formation due to the amounts of sulfur (S) and aluminum (Al) components. However, CS₁₀ and CS₁₅ exhibited different performance than CS₀ and CS₅. Based on the chemical compositions summarized in Table 8 and presented in Fig. 8, the amount of penetrated sulfur in CS₁₀ and CS₁₅ was low which emphasized low permeability. In this regard, the observed CH crystals in Fig. 7c, was denser than what seen in Fig. 6 for CS₀.

Since the sulfate attack mechanism is considered to be on base of penetration [54–57], CS₁₀ and CS₁₅ have lower potential for Ettringite formation and deterioration in comparison with CS₀ and CS₅.

3.3.3. 120 days in sulfate attack condition

According to the Table 8, the fair condition for Ettringite formation (5.5% Al and 6.3% S) was already existed for CS₀ after 120 days immersion in sulfate solution. The microstructure study confirmed this phenomenon as presented in Fig. 9. Based on the observed

micrographs, needle shaped Ettringite could be observed for CS₀, confirming the ascending 90–120 days trend of S_E shown in Fig. 2. Considering the sulfate expansion (Fig. 2), compressive strength variation (Fig. 3), and microstructural studies, the formation of Ettringite probably took place in period of 90–120 days immersion in sulfate solution.

The microstructure and EDX curves of CS₅ are shown in Fig. 10. Calcium silicate hydrates (CSH) products are recognizable in different parts of Fig. 10a. Assessment of Fig. 10c–e, reveals that the source of CSH detected in the regions 1 and 2 were different. CSH detected in region 2 is supposed to be as a result of cement hydration, whereas the one recognized in region 1 might be due to pozzolanic reactions of copper slag with CH. This could be confirmed by the concentration of ferrous (Fe) in region 1. Although CS₅ exhibited potential for Ettringite formation as detected in 61 days, and sulfur uniformly distributed (see Fig. 10f), there was no evidence for this phenomenon after 120 days. This might be attributed to the consumption of CH through pozzolanic reaction of copper slag.

The microstructure and EDX curves of CS₁₀ are presented in Fig. 11. In section 1 of CS₁₀, CSH products are seen in companion with the CH deposits (Fig. 11a). In spite of the observed remained CH crystals for CS₁₀ in Fig. 11b, the formation of Ettringite was not detected which could be related to the lower permeability.

Fig. 12 presents SEM/EDX images of CS₁₅ after 120 days immersion in sulfate solution. Along with line AB, Fig. 12a, CH and CSH

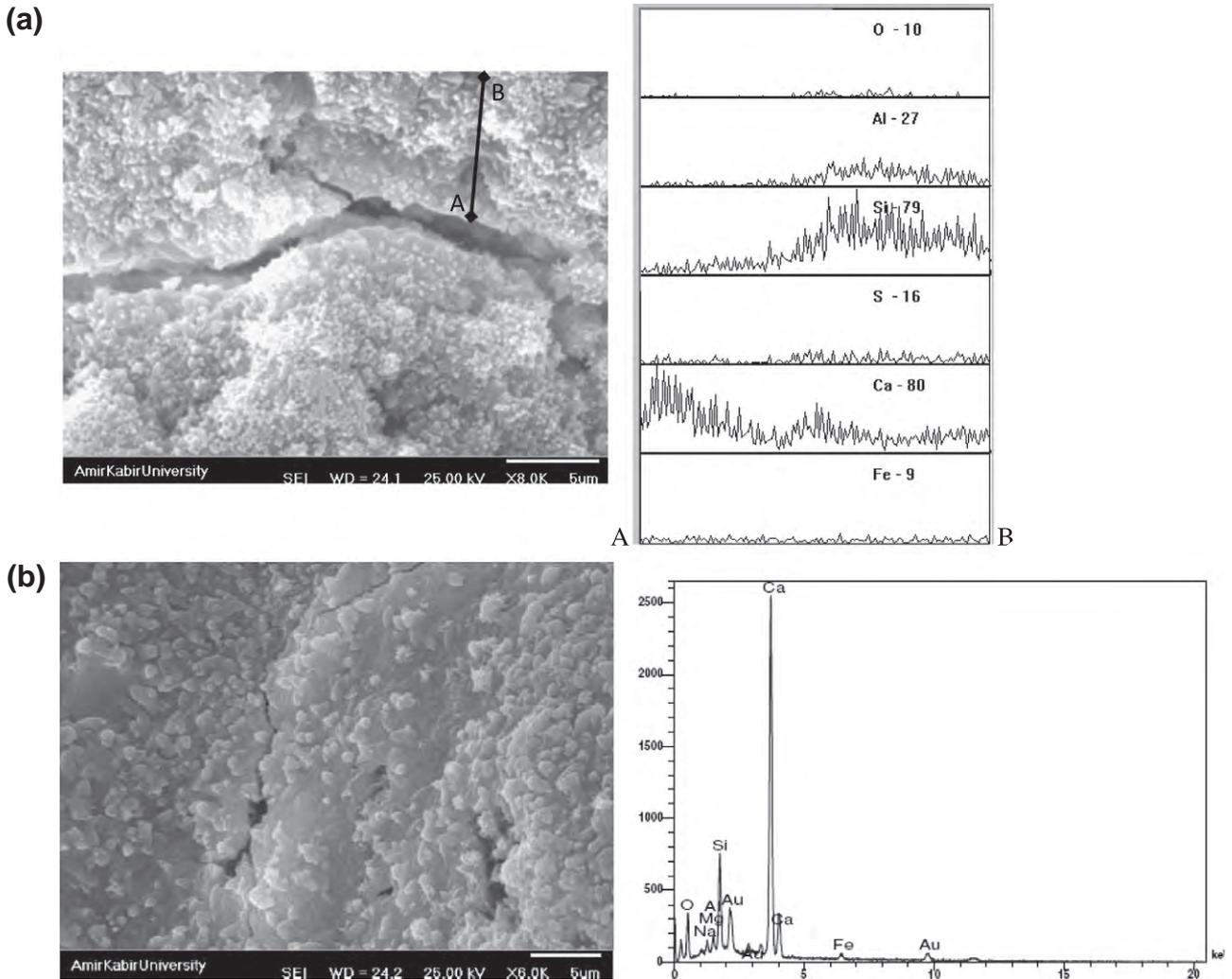


Fig. 12. SEM/EDX of CS₁₅ after 120 days immersion in sulfate solution: (a) CS₁₅-section 1, (b) CS₁₅-section 2.

could be observed which starts by CH at A and leads to formation of CSH at B. A crack is also observed in the location of CH crystals which is related to the lower strength of these crystals. It should be noted that the crack in CH crystals was also seen in Fig. 6 for CS₀. However the Ettringite formation was not detected until 120 days immersion.

4. Discussion

Based on the aforementioned results, the application of copper slag in concrete production makes a noticeable improvement in sulfate resistance. In this regard, replacement of cement with copper slag up to 15% led to more than 50% decrease in sulfate expansion. This improvement accompanied with less strength degradation of concrete samples as seen in Fig. 3 and Table 8. In addition, microstructure studies showed the Ettringite formation in control concrete, however, it had not occurred in copper slag contained concretes. According to ACI 233 [54], the observed improvements could be discussed as follows:

- (1) The decrease in C₃A due to cement replacement with slag [54,58]. This mechanism might not involve in this study due to the low content of C₃A in the utilized cement (Table 4).
- (2) Through the reduction of soluble calcium hydroxide, the environment for the formation of calcium sulfoaluminate, the primary cause of deterioration due to sulfate attack is reduced [54]. According to thermo-gravimetric analysis (Table 3), copper slag presented a mediocre pozzolanic activity, so it could consume calcium hydroxide. Therefore, a portion of improvement regarding sulfate resistance could be attributed to the reduction of calcium hydroxide.
- (3) Investigations indicate that resistance to sulfate attack depends greatly on the permeability of the concrete or cement paste [54–57]. Concrete with permeable structure is more vulnerable to the sulfate attack. By reviewing the amount of sulfur content and water penetration in Table 8 and Fig. 13, the less permeable microstructure of concrete was gained by application of copper slag. Therefore, this mechanism was the most governing phenomena for the observed improvements of this study.

5. Conclusion

This paper addressed the application of copper slag waste as supplementary cementitious materials to be used as a key element regarding the sustainable development. In this study, the sulfate resistance of concrete made with 5%, 10% and 15% of copper slag

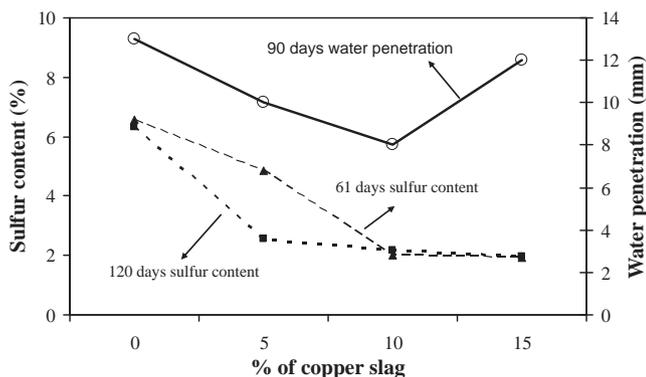


Fig. 13. Sulfur content and water permeability.

were studied in comparison with concretes without copper slag replacement.

The following conclusions can be drawn from this investigation:

1. The application of copper slag waste effectively reduced the deteriorative sulfate expansions as much as replacing of cement by 5%, 10% and 15% of copper slag led to 57.4%, 63.4% and 64.7% lower expansion than that of concrete without copper slag.
2. The copper slag contained concretes showed better compressive strength performance in sulfate comparing with the control concrete specimens. Although the strength of copper slag contained concretes observed to be lower than control concretes in normal condition, they could develop their strength up to or even more than the control concrete mixture in sulfate attack condition.
3. Microstructural studies detected the formation of deteriorative Ettringite in concrete without copper slag while those destructive crystals were not seen in copper slag contained concretes.

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