Cement & Concrete Composites 31 (2009) 186–194

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Hydro-mechanical behavior of a newly developed sulfur polymer concrete

Abdel-Mohsen O. Mohamed *, Maisa El Gamal

Department of Civil and Environmental Engineering, UAE University, P.O. Box 17551 Al Ain, United Arab Emirates

ARTICLE INFO

Article history:
Received 21 November 2006
Received in revised form 14 December 2008
Accepted 17 December 2008
Available online 25 December 2008

Keywords:
Sulfur
Fly ash
Sulfur polymer concrete
Durability
Hydraulic conductivity
Microstructure
Compressive strength

ABSTRACT

This study has focused on evaluating the durability of the newly manufactured sulfur polymer concrete (SPC) from recycled waste materials such as sulfur (by-product from oil industry), fly ash (recovered from the gases of burning coal during the production of electricity) and desert sand from abundant sand dunes quarries. The first step in such manufacturing process is the sulfur modification using polymeric additives to control sulfur crystallization and to prevent macro-crystals growth. In a controlled temperature surroundings, modified sulfur was mixed with elemental sulfur, fly ash and desert sand to form the newly SPC. The durability of the SPC was evaluated in: de-ionized water, acidic solutions of 20, 40, 70, and 98 wt% H_2SO_4 solutions, and saline solutions of 0.5, 1, 2, 3, 4, and 5 wt% NaCl, at different temperatures for different periods of time. To compare the SPC results with known material, normal Portland cement concrete (PCC) mortars were also studied. The results indicated that the manufactured SPC material has high compressive strength, low hydraulic conductivity, and high resistance to permeation of water, and particularly resistant to corrosion in acid and salt environments.

1. Introduction

In our day-to-day engineering practice, hydraulic cement based concrete materials are used for transporting and handling of troublesome fluids, such as acidic sewer wastes, industrial leach solutions, salt solutions, and acidic mine wastes. Hydraulic cement is a term used here since the water is the hydrating medium. Previous studies have indicated that concrete materials are subject to corrosion and disintegration, due to the reaction of the transporting fluids with the hydraulic cement binder material. Therefore, service life (i.e., durability) of concrete materials must be evaluated. Durability is an extremely complex subject and still going under extensive investigation by the scientific community.

Interest in sulfur cement, as an alternative to hydraulic cement, dates back to the early 20th century. Sulfur treated structural materials have been utilized for forming tanks or vents for holding leach or pickling solutions, for pipes or tiles for handling acidic sewer waters, flooring material for industrial plants and as patch material for concrete floors or walls. Its corrosion resistant properties made it a candidate for potential use as a construction material in the chemical industry.

Failures of sulfur cement products were encountered due to internal stresses set up by changes in the crystalline structure upon cooling. When unmodified sulfur and aggregate are hot-mixed, cast, and cooled to prepare sulfur concrete products, the sulfur binder, on cooling, from the liquid state, first crystallizes as monoclinic sulfur (S_β) at 114 °C with a volume decrease of 7%. On further cooling to below 96 °C, the S_β starts to transform to orthorhombic sulfur (S_α), which is the stable form of sulfur at ambient temperatures [1–4]. This transformation is rapid, generally occurring in less than 24 h. Since S_α is more dense than S_β high stresses are induced in the material. Hence, the sulfur binder can highly stressed and fail prematurely due to formation of micro-cracks.

Attempts were made by various investigators [5–12] to improve sulfur cement concrete products by using chemical additives for sulfur modification. Hence the term modified sulfur concrete (MSC) was introduced in the literature. Several substances have been tried, in order to inhibit the transformation of sulfur from monoclinic to orthorhombic states. The most common ones are: (1) dicyclopentadiene, or a combination of dicyclopentadiene, cyclopentadiene and dipentene [5–8], and (2) olefinic polysulfide additives [9–12]. The practical use of the former in commercial application has been limited because the reaction between sulfur and dicyclopentadiene is exothermic and requires close control; also the dicyclopentadiene-modified sulfur cement is unstable when exposed to high temperature. While the later had shown promise in these applications, their costs were deemed prohibitive for use in preparing sulfur concrete for large scale construction uses.

The preceding highlights the importance of the use of sulfur modifying agents in MSC manufacturing process. Therefore, this study is a continuation to previous studies, which reported by Mohamed and El Gamal [2] and Mohamed et al. [5], to produce an inexpensive MSC from waste recycled materials such as sulfur

---

* Corresponding author. Tel.: +971 3 767 5580; fax: +971 3 767 5582.
E-mail address: Mohamed.a@uaeu.ac.ae (Abdel-Mohsen O. Mohamed).

0958-9465/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2008.12.006

(by-product from oil industry), fly ash (by-product of burning coal), and desert sand from abundant sand dunes quarries. In the previous studies [2,5], olefin hydrocarbon polymeric material was used to modify sulfur, which upon solidification, remains in the monoclinic form and does not go through phase transformation to the orthorhombic form; hence the term sulfur polymer concrete was utilized (SPC). In this study, the durability of SPC is evaluated in terms of SPC ability to absorb water, and resist salt and acid penetration as a function of temperature and time.

2. Experimental

2.1. Materials

2.1.1. Sulfur

Elemental sulfur as a granular shape with purity of 99.9% was obtained from petroleum and natural gas, Al Ruwais refinery, United Arab Emirates (UAE).

Polymeric material, which is black oily, viscous, with specific gravity of 1.0289 g/C m^3, Kinematics viscosity at 135 °C of 431 cSt, and softening point of 48.8 °C, naturally-occurring as by-product of decomposed organic materials, achieved from the distillation of crude oil, and was obtained from Geo-Chem Middle East, Dubai UAE. From elemental analysis of the polymer, it contains 79% carbon, 10% hydrogen, 3.3% sulfur, and 0.7% nitrogen.

2.1.2. Fly ash

Fly ash is the ashy by-product of burning coal, in this work fly ash Class C was used, which was imported from India under trade No. 97/591 by Unibton ready-mix company UAE. Chemical analysis of fly ash was performed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) VISTA-MPX CCD simultaneous. The fly ash mainly consists of oxides of silica (59.31%), calcium (22.4%), aluminium (11.33%), iron (5.26%), magnesium (0.7%) potassium (0.5%), and sodium (0.31%). The cumulative grain size distribution is represented in Fig. 1.

2.1.3. Sand

The desert sand used in this production was obtained from a sandy dunes quarry in Al Ain area, UAE. The most common constituent of sand is silica (silicon dioxide), with specific gravity of 2.58 g/cm3, usually in the form of quartz, which because of its chemical inertness and considerable hardness, is quite resistant to weathering. Chemical analysis using ICP-AES indicate that the sand mainly consists of oxides of silica (74.4%), calcium (16.35%), magnesium (1.158%), iron (0.676%), aluminum (0.47%), and potassium (0.13%). The sand was screened to obtain grain sizes ranging from 0.08 to 0.43 mm. The cumulative grain size distribution is represented in Fig. 1.

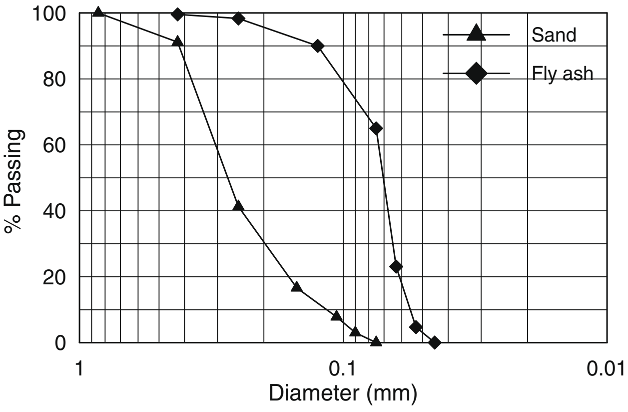

Fig. 1. Grain size distribution of the used fly ash and sand.

2.2. Preparation of modified sulfur cement

In an oil bath, 2.5 wt% of olefin hydrocarbon polymeric material and 97.5 wt% of molten sulfur were mechanically mixed at a controlled temperature of 140 °C for a period of about 45–60 min. The reaction progress was monitored by recording the temperature and viscosity variations during the mixing process. Then samples were allowed to cool at a controlled rate of 8–10 °C/min. The product is a sulfur containing polymer, which on cooling exhibits glass like properties. This product is commonly called modified sulfur cement (MSC). Distribution of the olefin hydrocarbon polymer in sulfur and free sulfur crystal type (orthorhombic or monoclinic) was evaluated using scanning electron microscopy, JSM-5600 Joel microscope, equipped with an energy dispersive X-ray detector (EDX). The specimen was sputter coated with 12 nm gold to render them conductive.

2.3. Preparation of sulfur polymer concrete

Sulfur polymer concrete (SPC) consisting of elemental sulfur, modified sulfur, fly ash, and sand was prepared according to the procedure described in [13]. The physical additives or aggregates (sand and fly ash) were dried in an oven from 170–200 °C for a period of 2 h. The specified amount of sulfur was melted in a heated mixing bowl that placed in oil bath with controlling temperature in the range of 132–141 °C. Fly ash was then transferred to the heated mixing bowl, and properly mixed with the molten sulfur for about 20 min, to insure complete reaction between sulfur and fly ash. Modified sulfur was then added and mixing continues for additional 5 min. Finally, desert sand was added, mixed and continued for about 20 min. In this process, we have used the proportions of 0.25 by wt% of modified sulfur cement, a ratio of 0.9 for sulfur to fly ash, and a ratio of one for sulfur to sand as recommended by [2,5]. At this stage of preparation, sulfur concrete mixture will be more viscous with a good workable consistency and can be easily bored into specified moulds for casting.

For specimen preparations, cubical steel moulds with dimensions of 50 × 50 × 50 mm, and cylindrical with dimensions of 85 × 38 mm were used. The moulds were preheated to approximately 120 °C before addition of the mixture. During the boring of SPC into the specified moulds the mixture was compacted using vibrator for 10 s. The surface of each specimen was then finished and the moulds were placed in an oven with a controlled cooling rate of five degrees per minute. After 24 h, specimens were demoulded and then cured in the tested solutions such as; de-ionized water, sulfuric acid solutions of; 20, 40, 70, and 98 wt% and sodium chloride solutions of 0.5, 1, 2, 3, 4, and 5 Wt% intended for different period. With respect to the reference samples, normal Portland cement concrete (PCC) mortars were prepared from sand and Portland cement with water to cement ratio of 0.5 Wt/Wt.

Specimens were then qualified by evaluating the changes in weight after immersion, ability to resist water flow, microstructure arrangements, mineralogical composition, and the ability to desorb ionic species via leaching tests.

2.4. Durability testing techniques

2.4.1. Moisture absorption

For SPC and PCC moisture absorption was determined by using the method described in [14]. Concrete samples were weighed, immersed in de-ionized water, and saline solution of 3% NaCl concentration at 24 °C for 24 h, surface dried, and reweighed.

2.4.2. Hydraulic conductivity

For of PCC and SPC samples, hydraulic conductivity was tested after immersion in different tested solutions; de-ionized water, saline solution of 3% NaCl concentration, and different concentrations of sulfuric acidic. The hydraulic conductivity was measured using the flexible membrane test apparatus, with replacing the flexible membrane accumulator with a free piston accumulator, to inject the solution at high pressure. This type of testing technique is highly recommended for testing intact core samples with low hydraulic conductivity. SPC cylindrical specimens were first saturated in tested solution for 24 h at room temperature. Specimens were encased inside a rubber membrane and water pressure was applied around the rubber membrane to prevent side leakage during hydraulic conductivity measurement. Then a water pressure of 2.2 MPa was applied across the tested specimen and the quantity of passing liquid was recorded as a function of time. The hydraulic conductivity was then calculated using Darcy's equation. Resistance of SPC to corrosive environments was achieved by testing the specimens in various aqueous environments such as 98% sulfuric acid, 50% phosphoric acid, 30% boric acid, and 10% acetic acid, at 24 °C.

2.4.3. Acid resistance

For SPC and PCC acid resistance testings were carried out for cylinder specimens with dimensions of 85 × 38 mm. The specimens were immersed: (a) in 40% sulfuric acid solution for 24 h for the visual inspection, (b) in 20, 40, 70, and 98% sulfuric acid, 24 h for determination of weight loss, and (c) in different acids such as sulfuric acid, phosphoric acid, boric Acid, and acetic acid for studying the effect of acid type on the hydraulic conductivity, loss weight, and strength loss. All specimens were removed from the acid solution and dried to determine the change in weight and physical properties.

2.4.4. Salt resistance

SPC salt resistance testing was evaluated through curing of SPC specimens for 7 days in different NaCl concentration solutions; 1, 2, 3, 4, and 5 wt% at 24 °C, and curing SPC samples at 3% NaCl solution for different intervals throughout one year time frame.

2.4.5. Compressive strength

For SPC specimens, compressive strength testing were conducted after immersion in different solutions using the Wykeham Farrance testing machine with maximum load of 200 kN.

2.4.6. Microstructure evaluation

Microstructure observation of SPC was examined using JSM-5600 Joel microscope equipped with an energy Dispersive X-ray detector for chemical analysis. The microstructure characterization performed for SPC was carried on the samples fragments. Samples were fasten on a sample rock and coated with a 12 nm gold layer for improved SEM imaging. The SEM analysis conditions are: voltage is 25 kV; working distance is 20 mm; void pressure is ultimate pressure system control with fully automatic setting of 10^{-4} Pa; mode of image is secondary electron; EDS system used is Link (oxford) ISIS ED system; and elements were quantified using normalization option.

2.4.7. Mineralogical evaluation

Changes in mineral composition of SPC were performed using X-ray Philips PW/1840, with Ni filter, Cu-Kα radiation ($\lambda = 1.542$ Å) at 40 KV, 30 mA and scanning speed 0.02°/S. The diffraction peaks between $2\theta = 2°$ and $2\theta = 80°$ were recorded and the newly formed minerals due to chemical reaction were determined manually by comparison with standard reference patterns and measurements (ASTM cards).

2.4.8. Leaching evaluation

Concrete chemical leached test were performed in accordance with the Accelerated Leach Test (ALT) procedures (ASTM C 1308), which were developed for evaluating the potential leachability from solidified matrices. The leached test was performed by testing SPC in various aqueous environments; three different aqueous systems were used for the test, de-ionized water (DIW), saline solution of 5% NaCl, and acidic solution of 70% H_2SO_4. Laboratory tests were performed by immersing SPC specimens in a transparent container filled with the tested solution. One millilitre from each aqueous solution was used for analysis by Inductively Coupled Plasma–Atomic Emission (ICP) to determine the total sulfate, calcium, aluminium, iron, and magnesium salts, leached in solutions. The remaining aqueous solutions were archived under room temperature conditions (24 °C). Each test was run in duplicate to ensure reproducibility.

3. Results and discussion

3.1. Modified sulfur cement

Addition of 2.5% by wt. of olefin hydrocarbon polymeric material to sulfur initiates chemical reactions whose type depends on the polymer content, heating temperature and the time of the reaction. It should be pointed out that, at $T < 95$ °C sulfur exists as a cyclooctasulfane crown with an S–S bond length of 0.206 nm, and S–S–S bond angle of 108°. At $T < 119$ °C sulfur crystallizes, when elemental sulfur heated to 119 °C, then cooled, with slower cooling rate <1.5 °C/min, resulted in the formation of a dense alpha sulfur crystal (S_α) with orthorhombic sulfur morphology as shown in Fig. 2a. At 119 °C (melting point of sulfur), the polymer thoroughly dispersed in the liquid sulfur and cyclooctasulfane turns partly into polymeric zigzag chains (bond length of 0.204 nm) [15].

At heating temperature less than 140 °C, elemental sulfur forms polysulfide compounds, which initiates formation of a network. Such structures differ considerably in the chemical and thermal stability from unmodified sulfur. At 119–159 °C, molten sulfur exists essentially as cyclooctasulfane (λ–S). Above 159 °C, eight-member ring rapidly break down into bi-radicals, which are recombined to form polymeric chains with a maximal length of up to 10^6 of sulfur atoms. However, above 140 °C, dehydrogenation of saturated polymer components can occur and linear polysulfide compounds can transform into stable cyclic thiophene structures [16]. Keeping in mind that modified sulfur should be produced within its recommended mixing temperature range of 135–141 °C.

The internal microstructures are affected by some factors as chemical reaction of sulfur with polymer components and its dissolution or dispersion. The crystallization features of modified sulfur displayed from SEM revealed the role of polymer in: (a) controlling the crystallization of sulfur, (b) reaction of sulfur with the olefin hydrocarbon polymer, and (c) limiting and controlling the crystal growth in such a way that all crystals are plate-like of micron dimension as monoclinic sulfur crystal of beta form ($S_ß$) as shown in Fig. 2b. These plate-like microstructure crystals of micron size play a major role in: (a) relieving stresses produced from thermal expansion mismatch in concretes, (b) helping to resist cracking, (c) tolerating any thermal expansion, and (d) developing less residual stresses and less shrinkage upon cooling [9].

3.2. Sulfur polymer concrete

The raw materials used in these preparations have some specific known characteristics. The main aspects of the concrete performance that will be improved by the use of fly ash are increased long-term strength and reduced hydraulic conductivity

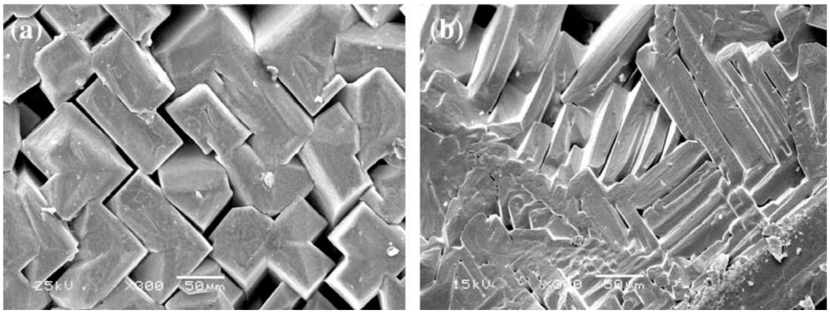

Fig. 2. SEM images display the microstructures morphology of; (a) elemental sulfur heated to 120 °C then slower cooling, a dense orthorhombic alpha sulfur crystal (S_α) is revealed, (b) sulfur after modification with the polymer, plate-like monoclinic beta sulfur crystal (S_β) is revealed.

of the concrete resulting in potentially better durability. The use of fly ash in concrete can also overcome some specific durability issues such as sulfate attack and alkali silica reaction. The desert sand was found to be of good quality showing a low concentration of impurities and grains with an irregular geometry. This quality of sand grains may reduce the workability of the mortar but on the other hand enables the molten sulfur to adhere more easily on the surface of the sand grains [17]. The molten sulfur acts as binder for these aggregates. Mortar with modified sulfur shows high viscosity, which has an important effect on the crystallization of sulfur. The modified sulfur is very efficient in binding and strengthening the aggregates. The microstructure characterization performed by scanning electron microscopic has revealed how the sulfur covers and very well binds the aggregates and also fills the inner spaces in such a way that the matrix is homogeneous with high degree of packing as shown in Fig. 3.

The determined physical and chemical properties of the prepared SPC materials show high dense structure density of 2.21–2.37 Mg/m^3, having a comparable density with that of hydrated Portland cement; therefore this material should provide similar radiation-shielding properties. Setting or hardening of SPC takes place on cooling to about 110 °C. The hot mix may be poured at either very high or very low ambient temperatures without any problems as compared with the placing of hydraulic cement concrete. Additionally, the hot mix may be maintained in the fluid form for many hours without deterioration. SPC does not support combustion. Sulfur present in the surface will slowly burn when exposed to direct flame but it self extinguishes when the flame is removed. The low thermal conductivity of sulfur results in slow penetration of heat. A further important characteristics of SPC are: (a) low hydraulic conductivity, and (b) void spaces (pores) are not connected, which contributed to the observed low hydraulic conductivity.

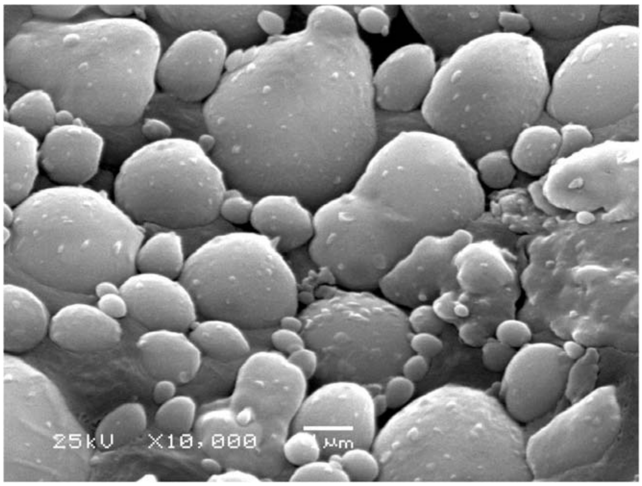

Fig. 3. SEM image of sulfur polymer concrete illustrating how sulfur and modified sulfur bind, coat, and penetrate deep and in between the aggregates.

3.3. Durability testing results

3.3.1. Moisture absorption

The moisture absorption results of SPC and PCC after immersion in de-ionized water, and 3% NaCl solutions, at 24 °C for 24 h, indicate that for PCC, the % water absorption in water and saline solution reached 12.5% and 7.7%, respectively, which are considered very high while, for SPC, the recorded water absorption values were 0.17% and 0.25%, respectively; indicating that SPC has low water absorption character in comparison with PCC. To explain such results, one has to realize that the existing sulfur and the added polymer prevent water penetration because they are hydrophobic in nature. Also, the majority of the matrix is composed of sulfur coated aggregates and sulfur accumulated in the voids between particles. This in turn will lead to SPC having impermeable characteristics [18]. These results are in agreement with recommended specifications [13], where the maximum moisture absorption of SPC should be less than 1% for coarse aggregates and less than 2% for fine aggregates.

3.3.2. Hydraulic conductivity

Measured hydraulic conductivities of SPC and PCC indicated that SPC has very low water permeation. Under a pressure of 2.2 MPa, SPC has a hydraulic conductivity in the order of 1.456×10^{-13} m/s, while PCC has a hydraulic conductivity in the order of 8.39×10^{-8} m/s, after being immersed in water. It is interesting to note that some researchers [19] have evaluated the volume of pore spaces of SPC and PCC and indicated that they have approximately the same volume however; the pores in SPC concrete are not connected providing low hydraulic conductivity characteristics, while the pores of PCC concrete are connected. It should be noted that the hydraulic conductivity of a material is highly dependent on the size of pore spaces, degree of connectivity between pores, grain shape, degree of packing, and cementation [20,21].

To evaluate the effect of acid attack on the hydraulic conductivity, SPC specimens were immersed in 98% sulfuric acid, 50% phosphoric acid, 30% boric acid, and 10% acetic acid, at 24 °C. Experimental results revealed that hydraulic conductivity values of SPC specimens are in the range of 10^{-11}–10^{-13} m/s indicating that SPC is an impermeable material. Table 1 summarizes the experimental results of hydraulic conductivity, loss in weights

Table 1
Effect of acid type on hydraulic conductivity measurements, weight loss and compressive strength loss, of SPC after 7 days immersion in corrosive acids.

Acid type	Hydraulic conductivity (m/s)	Weight loss (%)	Strength loss (%)
Water	1.456×10^{-13}	0.00	0.0
98% Sulfuric	7.660×10^{-11}	0.23	13.5
50% Phosphoric	3.103×10^{-12}	0.08	7.9
30% Boric	8.176×10^{-13}	0.07	4.0
10% Acetic	2.196×10^{-12}	0.14	16.0

due to chemical reaction, and compressive strength loss. These data have revealed that SPC exhibits high resistance to aggressive acidic environment, under the same conditions Portland cement concrete specimens, in most of these cases, were destroyed.

Immersed PCC specimens in 40% sulfuric acid solutions for 24 h showed high effervescence, and the specimen became soft and white due to formation of calcium sulfate hydrate. By contrast, SPC specimens remained structurally stable with no signs of corrosion or carking as shown in Fig. 4. This in turn indicates that SPC offers better protection to acid attack compared with PCC.

3.3.3. Loss in weight

The mass change calculations of PCC and SPC, immersed for 1 and 7 days in different sulfuric acid solutions of 20%, 40%, 70%, and 98% H_2SO_4 are shown in Fig. 5. The results indicated that: (1) there is no significant loss in weight for SPC specimens especially that immersed in dilute sulfuric acid; (2) a little loss in weight of about 0.29% after immersion in 98% H_2SO_4 solution, for 24 h; and (3) no more loss in weight with immersion of SPC specimens for 7 days at different sulfuric acid solutions. For PCC specimens, there is weight loss in the amount of 2.7% particularly in the case of 40% sulfuric acid solution concentration.

3.3.4. Durability in acidic environment

Evaluation of the effect of the acid concentration on the durability of SPC was studied through immersion of SPC specimens in 20, 40, 70, and 98 wt% sulfuric acid solutions, for 7 days at 24 °C. Specimens were then washed, dried and examined by SEM as well as chemical analysis using energy dispersive X-ray spectroscopy (EDX). The results shown in Table 2 indicated that SPC samples were composed mainly of silicon and sulfur containing compounds, and various metals such as calcium, aluminium, iron, and potassium.

The EDX observation revealed that with an increase of sulfuric acid concentration, the percentage of elemental sulfur increases, because of the formation of metal sulfates due to the reaction of the basic oxides (in the fly ash and sand) with sulfuric acid. It is known that most bases dissolve in water releasing hydroxide ions (OH^-) which react with acids to form salts. For the base calcium oxide, the oxide accepts hydrogen ions, so one could say that a base is a proton acceptor as indicated in Eqs. (1)–(3). With an increase of sulfuric acid concentration a reduction in the capillary porosity of the system could be obtained due to salt formation that precipitated on the SPC surface and in the pore spaces.

$$\text{Acid} + \text{Basic Oxide} \rightarrow \text{Salt} + \text{Water} \tag{1}$$

$$H_2SO_4\ (aq) + CaO\ (s) \rightarrow CaSO_4\ (aq) + H_2O\ (l) \tag{2}$$

$$Ca^{2+} + Al^{3+} + 2SO_4^{2-} + 12H_2O \rightarrow CaAl(SO_4)_3 \cdot 12H_2O\ (s) \tag{3}$$

Compressive strength of SPC was determined for cubic specimens measuring 50 × 50 × 50 mm. Fig. 6 shows the variations of compressive strength of SPC specimens cured in the air and de-ionized

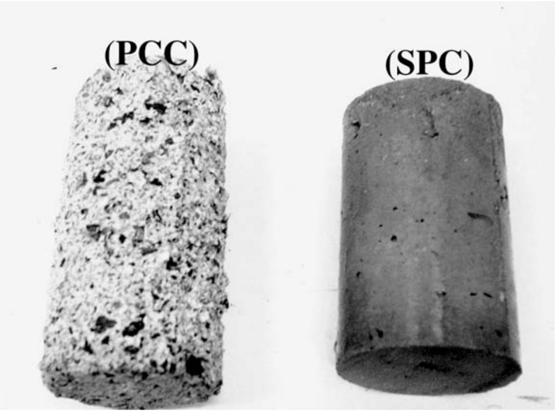

Fig. 4. Appearance of concrete specimen's immersed one day in 40% sulfuric acid solution.

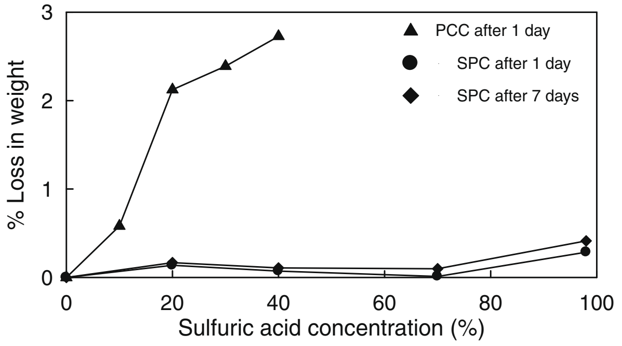

Fig. 5. Effect of sulfuric acid concentration on the weight loss of PCC and SPC after being immersed in 40% sulfuric acid solutions for 1 and 7 days.

Table 2
Effect of acid concentration on the % element of SPC composition, the data obtained from the EDX.

Element (%)	Sulfuric acid concentration			
	20 (%)	40 (%)	70 (%)	98 (%)
O	34.9	26.6	20.44	25.06
Al	7.64	11.98	8.06	4.84
Si	28.21	29.76	21.93	11.51
S	24.6	26.85	44.49	56.01
K	0.93	0.89	1.25	0.54
Ca	1.87	1.02	0.39	0.42
Fe	1.84	2.89	3.43	1.63

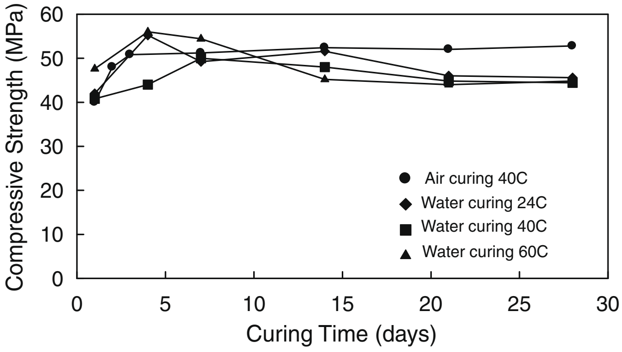

Fig. 6. Compressive strength of SPC as a function of the curing medium and curing temperature.

water, at different temperatures. It is clear that SPC reaches hardening and gains its strength over short time resulting in high strength material with an average compressive strength of 54 MPa. It is also clear that, for SPC cured in the air, 76% of its ultimate compressive strength was developed within one day and 97% after three days. However, at later ages up to 28 days, there was no clear trend for the compressive strength development suggesting that the maximum strength was developed during the early days. Similar results were reported by [10,22].

The variations of compressive strength with time, for SPC samples cured in water, at different temperatures are shown also in Fig. 6. The strength increases in the first three days of immersion, as water temperature increases. It is also shown that, after 3 days, the strength loss was happened up to 15 days, and then the strength remains almost constant up to 28 days. The strength increase could be attributed to the formation of cementing agents due to water availability. Considering the special chemical characteristics of fly ash and sand used in the manufacturing process, one recalls, from sand composition where it has high percent of SiO_2 (74.4%) and CaO (16.35%), and low amounts of Al_2O_3 (0.47%) and Fe_2O_3 (0.676%) while fly ash has high amounts of SiO_2 (60.9%) and Al_2O_3 (32.4%), and low amounts of Fe_2O_3 (4.34%) and CaO (0.46%). The availability of these types of oxides could lead to the formation of tricalcium silicate ($CaO \cdot SiO_2$), tricalcium aluminate ($CaO \cdot Al_2O_3$), and tetracalcium alminoferite ($CaO \cdot Al_2O_3 \cdot Fe_2O_3$). With water availability, the following reactions will take place and new minerals or cementing agents such as calcium silica hydrate (CSH), tricalcium aluminate hydrate (C_3AH_6) and calcium aluminoferrite hydrate (C_6AFH_{12}) could be formed, as indicated by Eqs. (4)–(6),

$$\begin{aligned}&2(3CaO\cdot SiO_2)+6H_2O \rightarrow 3CaO\cdot SiO_2\cdot 3H_2O+3Ca(OH)_2\\&\text{Tricalcium Silicate}+\text{Water}\rightarrow\text{Tombermonte gel}+\text{Calcium Hydroxide}\\&2C_3S+6H\rightarrow C{-}S{-}H+3CH\end{aligned} \tag{4}$$

$$\begin{aligned}&3CaO\cdot Al_2O_3+6H_2O\rightarrow 3CaO\cdot Al_2O_3\cdot 6H_2O\\&\text{Tricalcium Aluminate}+\text{Water}\rightarrow\text{Tricalcium Aluminate Hydrate}\\&C_3A+6H\rightarrow C_3AH_6\end{aligned} \tag{5}$$

$$\begin{aligned}&4CaO\cdot Al_2O_3\cdot Fe_2O_3+10H_2O+2Ca(OH)_2\\&\qquad\rightarrow 6CaO\cdot Al_2O_3\cdot Fe_2O_3\cdot 12H_2O\\&\text{Tricalcium Aluminoferrite}+\text{Water}+\text{lime}\\&\qquad\rightarrow\ \text{Calcium Aluminoferrite Hydrate}\\&C_4AF+10H+C_2OH\rightarrow C_6AFH_{12}\end{aligned} \tag{6}$$

A comparison between the losses in strength, after 28 days of SPC cured in air and SPC immersed in water, indicated that curing of SPC in water resulted in some decrease in compressive strength. The strength reduction has been investigated via microstructure studies by SEM. Fig. 7a and b shows the micrograph images of SPC fractured surfaces, cured in air and de-ionized water after aging time of 28 days at 40 °C.

The fractured surfaces of SPC reveal a different morphology, SPC cured in the air results in a homogenous sulfur distribution with good binding and coating of the aggregates as shown in Fig. 7a. For specimens cured in de-ionized water, one observes that no homogenous distribution of sulfur, where parts of the aggregate surfaces were uncoated with sulfur as shown in Fig. 7b. this observation appears to explain the small strength reduction of SPC cured in water, which is in complete agreement with reported studies by various investigators [8,23,24].

Table 3 summarizes the compressive strength results of SPC samples cured in water for different periods, up to 18 months at 24 °C, and the strength loss of SPC as a result of curing in acid solutions. The results suggested that SPC is stable and durable in water because of its ability to maintain its high strength even at very concentrated acidic environments.

3.3.5. Durability in saline environment

Durability of SPC specimens in saline environments was evaluated through immersion of SPC specimens in: (1) different NaCl concentration solutions of 1, 2, 3, 4, and 5 wt% for 7 days, and (2) at 3% salinity for 24 months. All cases were tested at 24 °C. As shown in Fig. 8, higher resistance to saline environment was achieved even with a small loss in compressive strength at high salinity of 5% NaCl. As the test period increases, the compressive strength of SPC showed insignificant decrease during immersion period of 12 months, as shown in Fig. 9. The lower water absorption and the high salt tolerance of SPC made it difficult for saline solution to penetrate the surface, thus maintaining its high strength.

Concerning the microstructure of SPC specimens, Fig. 10 is SEM image showing the contact regions between sulfur and the physical aggregates (fly ash and sand). The growth of sodium chloride crystals leads to a partial detaching between sulfur and physical aggregates, which in turn results in slight reduction of compressive strength.

The chemical analysis performed by ICP, for SPC specimens immersed for 7 days in 5% NaCl solution, indicated the presence of 0.049% Na atoms at the surface (i.e., 0.125% NaCl molecules) while, for SPC section at depth of 10 mm from the surface, the analysis does not show any sodium atoms indicating that NaCl penetration is only limited to the outer surface of SPC specimens. The implication of such finding is that SPC is salt resistant material and could be reinforced. In addition, low hydraulic conductivity makes SPC a good candidate for stabilization of waste and barrier system design.

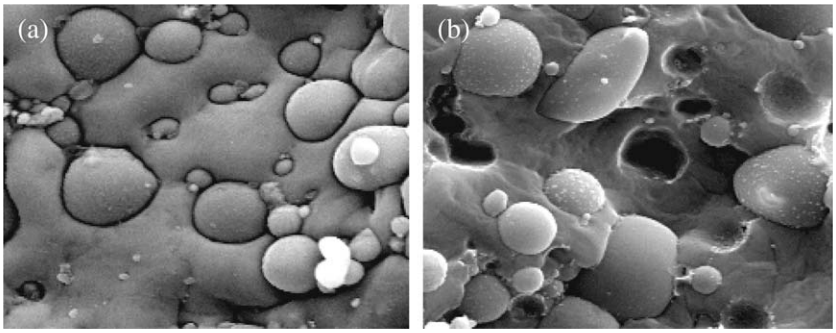

Fig. 7. SEM images of SPC fracture surface after curing 28 days, at 40 °C: (a) air, (b) water.

Table 3
Loss in the compressive strength of SPC cured in water, and in different sulfuric acid solution, at 24 °C.

Curing medium	Time	Loss strength (%)
Water	1 Month	1.3
Water	6 Months	2.1
Water	12 Months	3.1
Water	18 Months	5.2
0% Sulfuric acid	7 Days	0.0
40% Sulfuric acid	7 Days	2.1
70% Sulfuric acid	7 Days	3.3
98% Sulfuric acid	7 Days	7.5

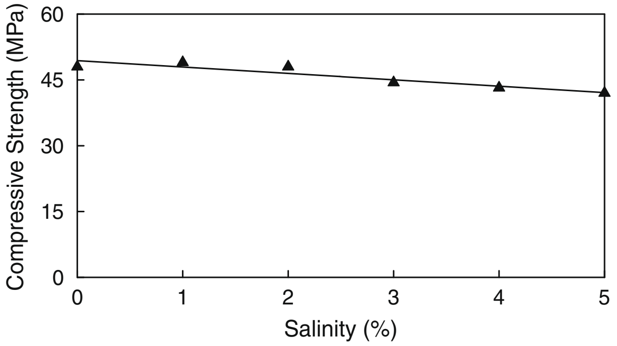

Fig. 8. Compressive strength of SPC cured for 7 days in different salinity, at 24 °C.

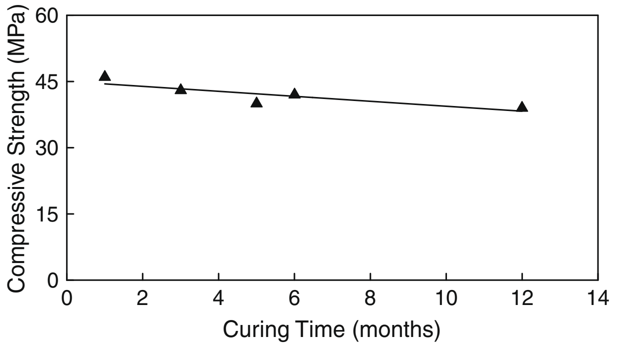

Fig. 9. Compressive strength of SPC cured in 3% saline solution for one year, at 24 °C.

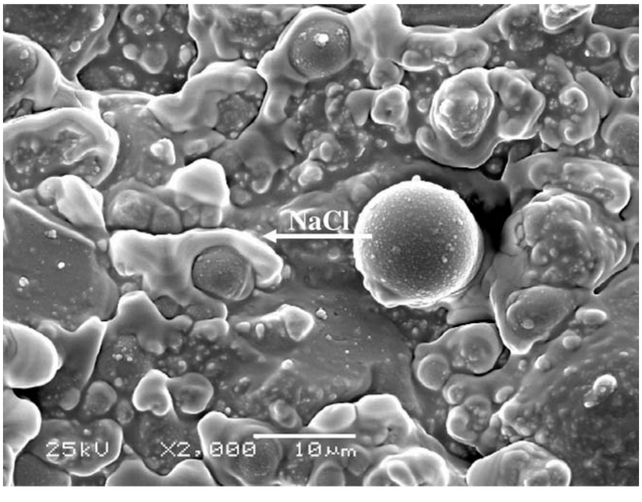

Fig. 10. SEM image of SPC cured for 7 days in 5% saline solution at 24 °C.

3.4. Mineralogy

Mineralogical composition of SPC was tested using X-ray diffraction analysis, to evaluate the potential formation of minerals during manufacturing and curing conditions. Fig. 11 shows the mineral composition of SPC samples which cured in water for 28 days at 24 °C. The major constituents in decreasing order are quartz (SiO_2), and sulfur. The minor constituents in decreasing order are calcium silicate hydrate ($Ca_{1.5}SiO_{3.5}!xH_2O$), plagioclase ($CaAlSi_3O_8$), calcite ($CaCO_3$), aluminium oxide hydrate ($5Al_2O_3!H_2O$), hematite (Fe_2O_3), dolomite ($CaMg(CO_3)_2$), and calcium aluminium oxide hydrate ($Ca_3Al_2O_6!H_2O$).

It is likely that the source of detected minerals by X-ray diffraction analysis is the following:

(1). the silica derived from two sources; quartz (SiO_2), plagioclase (calcium aluminium silicate) and newly formed calcium silicate hydrate mineral from the reaction of tricalcium silicate with water;
(2). aluminium is detected in the three phases; plagioclase (calcium aluminium silicate) derived from desert sand, aluminium oxide hydrate derived from the reaction of aluminium oxide with water, and calcium aluminium oxide hydrate derived from the reaction between tricalcium aluminate with water;
(3). iron appeared in the form of hematite (Fe_2O_3) and derived from fly ash and desert sand;
(4). calcium appeared in the phase of calcite ($CaCo_3$), dolomite ($CaMg(CO_3)_2$, calcium silicate, calcium aluminium oxide hydrate and plagioclase (calcium aluminium silicate); and
(5). magnesium found in minor proportion and concentrated mainly in dolomite ($CaMg(CO_3)_2$). Such minerals are stable and contribute to the observed SPC compressive strength increase.

3.5. Sulfur leaching

Chemical investigations on possible leaching of sulfur from SPC specimens immersed in de-ionized water and saline solution of 5% NaCl were conducted. Decomposition products were measured as sulfates, using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Figs. 12 and 13 show the percentage of leached sulfur and calcium during 64 days, in DIW and saline solution. The results indicated that at room temperature, SPC was very stable and insoluble in water through the test duration, where no pH change or weight loss was observed. As the duration time of leached test increases, it was found that; the total leached sulfur in DIW was nearly steady. The data represented in Fig. 14 indicated that SPC is stable in aqueous environment, which is consistent with the previous observation where there was no weight loss observed.

It is postulated that homo-nuclear polymeric anions of sulfur are formed in the presence of moisture. The soluble calcium polysulfate so formed can then be leached by water. It was reported in the literature that the leached product is a mixture of calcium sulfate, sulfite and elemental sulfur [25,26]. In the presence of oxygen and water, sulfur is slowly oxidized to sulfite and then to sulfate [27]. The oxidation process can be explained as follows. From the fact that elemental sulfur exists in different allotropic forms and has different densities that are sensitive to cooling rates, one may expect micro-cracking of the surfaces of large monoliths on cooling. Such stress induced cracks, pores, or other surface imperfections are excellent areas for oxidation and formation of expansive sulfate minerals.

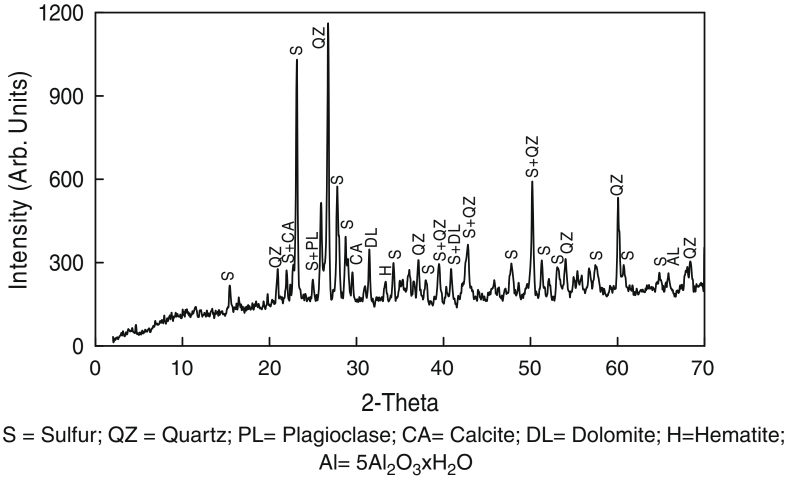

Fig. 11. X-ray diffraction of SPC which cured for 28 days in de-ionized water at 24 °C.

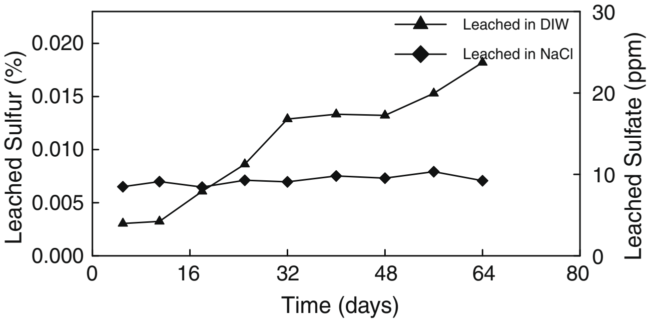

Fig. 12. Variations of the amount of sulfur and sulfate leached from SPC in de-ionized water and 5% salt solution.

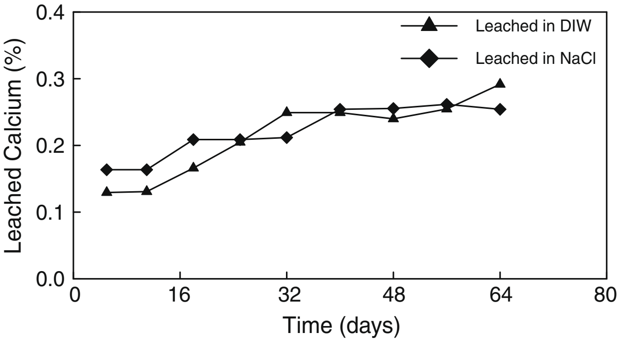

Fig. 13. Variations of the amount of calcium leached from SPC in de-ionized water and 5% salt solution.

As discussed above calcium and sulfate are leached away by the aqueous solutions of de-ionized water (DIW) and saline solution from SPC. The total sulfur content leached in each solution, as sulfate, appears to be low as shown in Fig. 12. Also, the tested solutions have extremely low concentrations of dissolved calcium sulfate as shown in Fig. 13. Saline water contributed to calcium leaching from SPC, approximately the same quantity as that leached in the case of DIW. While the leached sulfate in saline solution is significantly lower than that in DIW, it means that there is another source of calcium in saline water, rather than calcium sulfate. By using the US Environmental Protection Agency (US EPA) titration test method for determination the soluble carbonates and bicarbonates after 64 days, it was found that in DIW, the carbonates and bicarbonates were 0, and 24.3 mg/l, respectively, while in saline solution, they were 3.6 and 112 mg/l, respectively. This indicates that the leached calcium in DIW comes mainly from dissociation of calcium sulfate while, in saline solution the major leached calcium comes from dissociation of calcium bicarbonate. Also, it can be noted that decomposition of sulfur in SPC in salt solution is significantly slower than that in water, which is compatible with previously reported studies [26].

Attack of SPC by 70% sulfuric acid solution resulted in the formation of calcium, aluminium, iron, and magnesium sulfates, which when they are soluble, they might be leached away by the aqueous solution, as indicated in Fig. 15. Sulfuric acid reacts with most metals in a displacement reaction to produce metal sulfates. Dilute H_2SO_4 attacks calcium, aluminium, magnesium and iron. The calcium sulfate is a major soluble salt, and the acidic environment accelerated salt solubility and leaching process. Water acts as a solvent and a transport medium for aggressive agents and reaction products. The degree of reaction of an acid is dependant on the chemical character of anions present. The strength of acid, its dissociation degree in solutions and, mainly the solubility of the salt formed are dependent on the chemical character of anion. The acidic attack is based on the processes of decomposition and leaching of the constituents of concrete matrix. This effect contributes to the progress of acidic attack. Fig. 15 indicates that, metals leached in acidic solution, depending on to the percentage of each metal oxide in the mixture and the level of concentrations in the leachate, are below the standards set by environmental agencies for solidification of hazardous waste.

4. Conclusions

In this study, an inexpensive sulfur polymer concrete (SPC) was manufactured from waste recycled materials such as sulfur (by-product from oil industry), fly ash (by-product from coal-fired electric generating plants), and desert sand from abundant sand dunes quarries. An olefin hydrocarbon polymeric material was used to modify sulfur; sulfur remains in the monoclinic form and does not go through phase transformation to the orthorhombic form. The durability of SPC specimens was evaluated in terms of its ability to absorb water, resist acid and salt penetration, and leachability as function of medium and time.

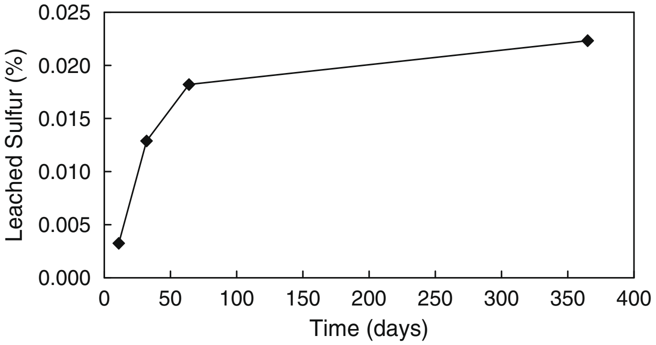

Fig. 14. Variations of the amount of sulfur leached from SPC in de-ionized at 24 °C, as function of time.

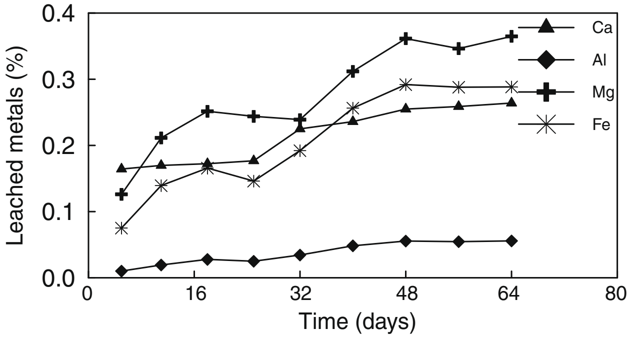

Fig. 15. Variations of the amount of metals leached from SPC in 70% sulfuric acid solution at 24 °C.

The results indicated that the manufactured SPC material has high compressive strength, low hydraulic conductivity, and high resistance to permeation of water, sulfuric acid and salt solutions, and very low leachability potential. This in turn will make such material a good candidate for its use in construction industry for subsurface installations and in waste management for stabilization of hazardous waste and waste barrier systems.

Acknowledgments

This study was financially supported by a grant from the Research Affairs of the United Arab Emirates University.

References

[1] Vroom H, Whitmore DW. Sulfur concrete for high corrosion resistance. In: Proceedings, national association of corrosion engineers, Saskatoon, Canada, February; 1991.

[2] Mohamed AMO, El Gamal M. Compositional control on sulfur polymer concrete production for public works. In: Mohamed, editor. Reclaiming the desert: towards a sustainable environment in arid lands. London: Taylor & Francis Group; 2006. p. 15–26.

[3] Mc Bee WC, Sullivan TA, Patrick OB. Structural materials. US Patent No. 4,022,626 May 10; 1977.

[4] Mc Bee WC, Weber HH. Sulfur polymer cement concrete. In: Proceedings of the twelfth atinual department of energy low-level waste management conference, CONF-9008119, national low-level waste management program, Idaho Natl. Engineering Lab., Idaho Falls, Idaho; 1990.

[5] Mohamed AMO, El Gamal M, Elsaiy AK. Thermo-mechanical behavior of newly developed sulfur polymer concrete. In: Mohamed, editor. Reclaiming the desert: towards a sustainable environment in arid lands. London: Taylor & Francis Group; 2006. p. 27–38.

[6] Currell BR. The importance of using additives in the development of new applications for sulfur. Symposium on new users, for sulfur and pyrites, Madrid; 1976. p. 105–103.

[7] Bordoloi BK, Pierce EM. Plastic sulfur stabilization by copolymerization of sulfur with dicyclopentadiene. Advances in chemistry series no. 165. Washington DC: American Chemical Society; 1978. p. 31–53.

[8] Beaudoin JJ, Feldmant RF. Durability of porous systems impregnated with dicyclopentadiene-modified sulfur. Int J Cem Compos Lightweight Concr 1984;6(1):13–7.

[9] Lin SL, Lai JS, Chian ESK. Modification of sulfur polymer cement (SPC) stabilization and solidification (S/S) process. Waste Manage 1995;15(5/6):441–7.

[10] Vroom AH. Sulfur cements process for making same and sulfur concretes made there form. U.S. Patent No. 4,293,463; 1981.

[11] Vroom AH. Sulfur polymer concrete and its application. In: Proceeding of seventh international congress on polymers in concrete, Moscow; 1992. p. 606–21.

[12] Nnabuife EC. Study of some variables affecting the properties of sulfur-reinforced sugarcane residue based boards. Indian J Technol 1987;25:363–7.

[13] ACI Committee 548. Guide for mixing and placing sulfur concrete in construction (ACI 548.2R-93). Farmington Hills, Mi: American Concrete Institute; 1993.

[14] ASTM C128-97. Specific gravity and absorption of fine aggregate; 1997.

[15] Voronkov MG, Vyazankin NS, Deryagina EN. Reaction of sulfur with organic compounds. Novosibirsk: Nauka; 1979.

[16] Syroezhko AM, Begak OYu, Fedorov VV, Gusarova EN. Modification of paving asphalts with sulfur. Russ J Appl Chem 2003;76(3):491–6.

[17] Gemelli E, Cruz AAF, Camargo NHA. A study of the application of residue from burned biomass in mortars. Mater Res 2004;7(4):545–56.

[18] Darnell GR. Sulfur polymer cement, a new stabilization agent for mixed and low-level radioactive waste. 7.1.1-7.1.11. In: Moghissi AA, Benda GA, editors. Proceedings of the first international symposium on mixed waste, Baltimore, MD., August 26–29, 1991, Univ. of Maryland, Baltimore; 1991.

[19] Vroom AH. Sulfur concrete goes global. Concr Int 1998;20(1):68–71.

[20] Mohamed AMO, Hogan HE. Geoenvironmental engineering. Amsterdam (The Netherlands): Elsevier; 1998. 707 p.

[21] Yong RN, Mohamed AMO, Warkentin BP. Principles of contaminant transport in soils. Amsterdam (The Netherlands): Elsevier; 1992. 327 p.

[22] Mc Bee WC, Sullivan TA, Jong BW, 1983, Corrosion-resistant sulfur concretes. BuMines Report No. 8758, vol. 28. Washington DC: US Bureau of Mines; 1983.

[23] Czarneckt B, Gillott JE. Effect of different admixtures on the durability of sulfur concrete made with different aggregates. Eng Geol 1990;28:105–18.

[24] Abdel-Jawad Y, Al-Qudah M. The combined effect of water and temperature on the strength of sulfur concrete. Cem Concr Res 1994;24:165–75.

[25] Berry EE, Soles JA, Malhotra VM. Leaching of sulfur and calcium from sulfur infiltrated concrete by alkaline and neutral aqueous media. Cem Concr Res 1977;7(2):185–9.

[26] Lusty JR. Chemical investigations on leaching of sulfur from sulfur infiltrated concretes. Cem Concr Res 1983;13(2):128–233.

[27] Mattus CH, Mattus AJ. Evaluation of sulfur polymer cement as a waste form for the immobilization of low level radioactive or mixed waste. OAK Ridge National Laboratory; 1994.