



Investigation of the effects of pH, aging and scrap tire content on the dissolution behaviors of new scrap tire-concrete mixture structures



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ABSTRACT

Scrap tires represent increasing environmental-pollution problems because they are not biodegradable and require a significantly long time for natural degradation, which is caused by the cross-linked structure of polymeric material and the presence of stabilizers and other additives. Potential use of scrap tires in construction is one of its important application areas and an alternative recovery method. In this study, a series of experiments was conducted to investigate the dissolution behaviors of new concrete-scrap tire mixture structures (brick) under different experimental conditions, such as scrap tire content, aging, and in acidic, basic and natural environments. The obtained results revealed different effects of adding scrap tires, aging and the existence of H^+ and OH^- on the dissolution of the brick structures. The added sulfuric acid dissolved calcium silicate hydrate, calcium aluminosilicate hydrate and calcium hydroxide of the brick via a naturalization reaction and released more soluble metal ions, particularly calcium, in the solution. Additionally, during acidic corrosion, the porosity significantly increased because calcium was removed from the structure; thus, the transport of other ions was enhanced in the corroded layer by diffusion. However, the addition of sodium hydroxide significantly decreased the solubility of calcium because the calcium silicate hydrate, calcium aluminosilicate hydrate and alkali-silica reaction products precipitated in the presence of calcium. The aging test showed that calcium was substantially dissolved from the brick structure in the first days and slightly slowed down in an acidic medium because the corrosion surface was gradually consumed, which caused the dissolution to occur in the lower part of the corroded region. The increase in scrap tire content increased the surface area and porosity, which resulted in more released calcium and silicon. The study affirmed that the use of granular scrap tires in concrete structures was feasible.

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1. Introduction

In recent years, the increasing amount of used tires generated worldwide has created serious environmental problems worldwide regarding the disposal of scrap tires. The estimated amount of annually discarded tires was approximately 200–300 million in the United States (Ahn and Cheng, 2014), more than 10,000,000 in Turkey (Yesilata et al., 2011) and 3.4 million tons in the European

Union (Sienkiewicz et al., 2012). The disposal of scrap tires throughout the world is usually performed with different methods: landfill, burning, reclamation and recycling. Landfill and burning cause serious environmental pollution to the soil, atmosphere and water, such as killing beneficial bacteria in soil, emission of toxic gases in the event of fire, occupying large volumes in landfills and providing breeding grounds for mosquitoes, rats and rodents, which spread many diseases (Issa and Selem, 2013; Jang et al., 1998). Recycling may appear to be the best method to dispose of scrap tires in large quantities. However, it is difficult because they are made of non-biodegradable materials and require a significantly long time for natural degradation due to the cross-linked structure of the polymeric material and presence of stabilizers and other additives (Adhikari et al., 2000; Fang et al., 2001).

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Therefore, only a small part of the generated scrap tires is currently recovered, but the remainder is left to the environment.

The potential use of granular scrap tires in construction is one of its important application areas and has recently been extensively investigated (Li et al., 2004; Pacheco-Torgal et al., 2012; Shu and Huang, 2014). The use of scrap tires in concrete is conferred and has been an advantageous method to solve these major recovery and recycling problems of scrap tires to safely and economically dispose of them and to improve the heat insulation, acoustic and elastic properties of concrete (Khaloo et al., 2008; Aiello and Leuzzi, 2010; Pelisser et al., 2011; Bravo and de Brito, 2012; Son et al., 2011; Al-Tayeb et al., 2013). Particularly, measurements of the thermal-insulation performance showed significant improvements in the insulation properties of the new concrete-scrap tire mixture structures (Yesilata and Turgut, 2007; Turgut and Yesilata, 2008; Yesilata et al., 2009; Corinaldesi et al., 2011). Yesilata and Turgut (2007) tested thermal properties of the rubberized concrete structure and found that the insulation performance of the rubberized concrete improved by 14.7% compared to the conventional concrete structure. Corinaldesi et al. (2011) investigated the mechanical behavior and thermal conductivity of mortars containing waste rubber particles and showed that the addition of rubber particles reduced both the material unit weight and the thermal conductivity. Turgut and Yesilata (2008) also investigated the physico-mechanical and thermal performances of the scrap tire-added bricks, and their test results satisfied the related standards.

However, because concrete is often in contact with water, it is exposed to the effects of acid and base ions (H^+ , OH^-) and corrodes over time, and its durability decreases, which reduces its service periods (Palvik and Uncik, 1997; Li et al., 1999; Macías et al., 1999; Pavlik, 2000; Beddoe and Dorner, 2005; Glass et al., 2000). For example, water channels and sewage pipes, which are built unprotected against corrosion, wastewater treatment plants, cooling towers, bridges, dams and other buildings, are exposed to these ions and are always under the risk of corrosion. If this exposure continues for a long period of time, these concrete structures gradually lose their mechanical strength, which results in cracking, mass loss, shrinkage of the corroded layers and eventually structural failure (Song et al., 2004; Hernandez-Olivares et al., 2007; Fan et al., 2010).

Concrete has been used as a main building material in construction for a long time. When Portland cement, water and aggregates, such as rock, sand, or gravel, are mixed together, this rock-like structure experiences a chemical reaction called hydration. The cement acts as a binding agent in this structure. The pH value of the pore solution in the concrete typically varies from 12 to 13.5 (Rasanen and Penttala, 2004; Jin et al., 2011) because of the chemical composition of Portland cement, which is provided in Table 1 (Anonymous, 2014). The hydration reaction of these oxides with water produces an alkaline mixture of paste, which increases the pH value of the pore solution (Li et al., 2005).

Table 1
Approximate chemical composition of a typical Portland cement.

Name	Chemical formula	Content, %
Lime	CaO	60–67
Silica	SiO ₂	17–25
Alumina	Al ₂ O ₃	3–8
Iron	Fe ₂ O ₃	0.5–6
Magnesia	MgO	0.1–4
Alkalies	Na ₂ O and K ₂ O	0.2–1.3
Sulfuric anhydride	SO ₃	1–3

Many studies have been performed to investigate the effects of acidic, basic and natural environments on the concrete structure and to elucidate the chemical reaction that produces soluble metal ions from the concrete structure. Their results show that the solubility of metal ions from concrete structures depends on the type and chemical composition of the cement and the pH of the attacking acid and base.

In an acidic environment, Beddoe and Dorner (2005) developed a computer model to elucidate the corrosion of concrete at a pH range of 4.0–6.5, and their simulation program comprises the effects of both the chemical reactions of the acid with the hydrated compounds of the concrete and the aggregate and the diffusion of ions in the pore system of the corroded surface. Their study concludes that the acidic environment can cause acidic corrosion, where calcium hydroxide, calcium silicate hydrates (CSH), and the calcium sulfoaluminate phases decompose and produce porosities. Palvik and Uncik (1997) introduced the usage of nitric acid and acetic acid solutions to determine the rate of corrosion of cement paste and cement mortars for different acid and concrete mediums. They observed that the corrosion of cement mortars was lower than that of cement pastes because sand particles did not allow the formation of long cracks in the layer of corrosion products. They also observed that nitric acid and acetic acid had different effects on the corrosion process. Xi et al. (2004) investigated the effects of simulated acid rain on the deterioration of cement concrete in laboratory tests and concluded that H^+ ions dissolved $Ca(OH)_2$ in the hardened cement paste, which reduced the concentration of $Ca(OH)_2$. They also remarked that SO_4^{2-} corroded the concrete and produced substances such as $Ca_3Al_6O_{12} \cdot CaSO_4$ and $CaSO_4 \cdot 2H_2O$, which significantly reduced the durability. If the results of their studies are summarized for acidic environment, acid attacks entirely decompose the hydrated and unhydrated cement paste components and aggregates, calcium hydroxide is dissolved, and hydrate silicate and aluminate phases are decomposed to produce Ca^{2+} ions in the concrete pore solution.

In a basic environment, Berube et al. (2004) summarized the presence of NaOH and KOH in the concrete pore solution, which indicated only a trace amount of calcium in the solution. They remarked that with time, Na^+ , K^+ , Ca^{2+} , $H_2SiO_4^{2-}$, $Al(OH)_4^-$ ions could release from the aggregates, which contained various common reactive silicate minerals, in the concrete pore solution and precipitate as (CSH), calcium aluminosilicate hydrate (CASH), and alkali-silica reaction (ASR) with reactive silica products in the presence of calcium ions because of their significantly low product of solubility at high pH.

The objective of this study is to investigate the feasibility of using granular scrap tires as a replacement for the aggregates in concrete structures and examine the effects of this replacement on the solubility of metal ions (Al^{+3} , Si^{+4} , Mg^{+2} , Ca^{+2} , Fe^{+3}) from the structure under acid and base attacks. It was believed that the investigation of the chemical-reaction mechanism of the new scrap tire-concrete structures under different experimental conditions, such as different scrap tire contents and aging in acidic, basic and natural environments, contributed new understanding to elucidate the dissolution mechanism.

2. Materials and methods

2.1. Preparation of the scrap tire-concrete bricks

In this study, four different fresh scrap tire-concrete mixtures for brick production were prepared: (1) a brick (R-0) without scrap tires and (2) three different types of bricks (R-20, R-40, R-60) with different volumes of granule scrap tire additives. The mixture calculations were determined based on the volume of materials, and

according to these calculations, the weights of the materials were obtained to prepare the bricks. For example, in a mixture of R-20, 20% volumetric granulated scrap tires were replaced instead of 20% of the aggregate volume. Again, in a mixture of R-60, the aggregate that constituted 60% of the total aggregate volume was removed from the mixture, and granular scrap tires were added instead of the aggregate that corresponded to the removed aggregate volume. The amount of materials of the concrete mixture, which was calculated based on the volume, is provided in Table 2. The effects of the scrap tire volume on the brick properties were investigated while maintaining constant cement and water contents (W/C mass ratio was 0.45) in all mixtures. The grading curves of the aggregate and scrap tire used to make the bricks are shown in Fig. 1. The cumulative passing amount of the aggregate in this study complies with the standards. The used cement was CEM I 32.5 and provided from the daily production of SanliurfaTurkerler Cement Factory. The chemical composition of the cement was determined according to American Society for Testing and Materials (ASTM) C114. The grain size of the selected sand was taken as a maximum of 4.75 mm particle diameter to provide good adhesion between the tire surfaces and the concrete. The sand used in this study had a saturated surface dry unit weight of 2.73 g/cm³, and the granular scrap tire had a saturated surface dry unit weight of 1.05 g/cm³ according to American Society for Testing and Materials (ASTM) C128.

Materials with certain mixing ratios were placed in a 50-L pan-type concrete mixer and mixed as dry for two minutes. Then, the sedimentation and compression factor values of the fresh mixture were obtained by slowly transferring some water into the dry mixture after a total mixing time of three minutes, while the 50-L pan-type concrete mixer was rotating. The resulting fresh mixture was compacted into steel molds with internal dimensions of 105 mm × 225 mm × 75 mm as two layers. After compaction was completed, the upper surface of the fresh brick mixture was finished with a trowel.

2.2. Physico-mechanical and thermal properties for the feasibility of the scrap tire-concrete bricks

Physico-mechanical and thermal properties of scrap tire-concrete bricks used in this study were investigated for their feasibility and explained by Turgut and Yesilata (2008). They measured the water absorption and the porosity of the structure, and they observed a monotonic increase with the scrap tire percentage. However, the unit weights and the values of ultrasonic pulse velocity decreased with increasing scrap tire. These results revealed that a decrease in the unit weights led to an increase in water absorption, and similarly, an increase in the porosity led to a decrease in the values of ultrasonic pulse velocity. Water absorption values of the samples satisfied the standards set by the American Society for Testing and Materials (ASTM) C140. The compressive strength values of the samples for both load-bearing and non-load-bearing masonry units complied with the American Society for Testing and Materials (ASTM) C129 and (ASTM) C90. The flexural strength values of all samples considered in this study also

Table 2
Mixing ratios for the concrete briquette samples.

Sample name	Cement (Kg/m ³)	Water (Kg/m ³)	W/C	Sand (Kg/m ³)	Scrap tire (Kg/m ³)	Total (Kg/m ³)
R-0	537	242	0.45	1478	0	2257
R-20	537	242	0.45	1182	114	2075
R-40	537	242	0.45	889	227	1895
R-60	537	242	0.45	591	341	1711

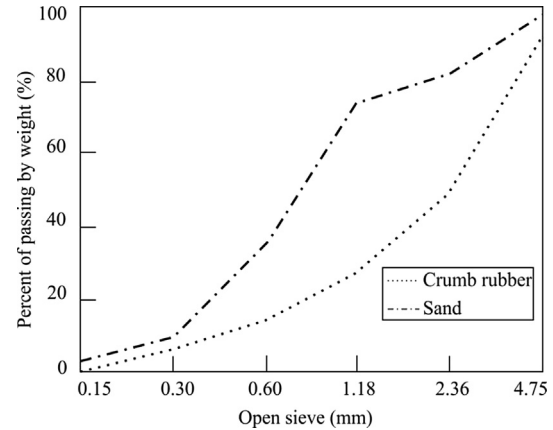


Fig. 1. Grading curves of the tires and sand that were used to make the concrete bricks.

satisfied the requirement described in British Standards Institution (BS) 6073.

The properties of the samples after freezing–thawing were also investigated. The results of the investigation showed that there was a potential for using scrap tire as a freeze–thaw resisting agent in the brick structures. The bricks with crumb rubber performed significantly better under freezing–thawing conditions than with the control mix.

2.3. Cost analysis for the feasibility of the scrap tire-concrete bricks

The estimated production cost of scrap tire-concrete brick was determined from the present annual costs of various items, including material (cement, sand, and granulated scrap tire), energy, salaries and wages, insurance, and other operations/maintenance costs. The cost-analysis of fired clay brick was performed according to the report of the Brick Industry Association in Turkey (Lokman et al., 2008). In this report, the percentage of production cost of fired clay brick per cost components was given. The cost-analysis of R-60 brick was calculated according to the existing concrete brick plant.

The production costs of R-60 brick and traditional fired clay brick, per 1000 bricks, are summarized in Table 3. The production cost of traditional fired clay brick was approximately \$265 per 1000 bricks, while that of R-60 brick was only \$201 per 1000 bricks. The costs of raw materials (including transport cost) as granulated scrap tire, sand, Portland cement, and water in R-60 brick were 171, 4.48, 58.99 and 0.18 \$/t, respectively. The price of the granulated scrap tire was more expensive than that of sand. Compared to the market price of traditional fired clay brick produced in Sivas-Kangal in Turkey, the composite brick with FA, LP and 20% SF (i.e., LFS-20) was a low-cost product. Therefore, the estimated production cost of new scrap tire-concrete brick was cheaper than that of traditional fired clay brick.

Table 3
Analysis of production cost for per 1000 bricks.

Cost components	Traditional fired clay brick, US \$	R-60 brick, US \$
Raw material	26.50	166.90
Labor	119.25	19.95
Electricity	13.25	2.45
Fuel	18.55	1.75
Coal (for firing)	47.70	–
General expenses	26.50	6.30
Depreciation	13.25	3.50
Total cost	265.00	201.00

2.4. Investigation of solubility behaviors of metal ions

The brick samples for solubility tests of metal ions were cut using a diamond cutter bench with the size of 20 mm × 30 mm × 40 mm in the laboratory. They were washed with distilled water before testing to remove any dust and small particles from the surface and dried in an oven overnight to maintain them at 60 °C. After the samples cooled to room temperature, their masses were determined using a high-precision (± 0.001 mg) digital scale. Because the solubility tests were conducted at three different pH values for four different types of brick samples, which contained different amounts of scrap tire, twelve brick samples were selected in total for the experiments. The average measured mass values and scrap tire amounts are provided in Table 4.

The solubility experiments were started by placing the brick samples in glass beakers that contained 150 ml of distilled water and allowing the solubility to occur at different pH values. In practice, H₂SO₄ and NaOH are used as pH modifiers to adjust the pH of the experimental medium. Therefore, in this work, they were used as pH modifiers. For the acidic environment, the H₂SO₄ solution was used drop wise to adjust the pH value of the experimental medium to 3.6. To minimize any dilution error of the H₂SO₄ addition, the acid concentration was maintained as high as possible. The test samples were placed in the test medium and left for specified time intervals. For the analysis, 3-ml test solutions were removed from the medium; then, the pH was readjusted to 3.6 repeatedly. The pH of the medium for the basic study was adjusted to 10.5 using NaOH as a pH modifier with an identical procedure. The pH was only adjusted in one direction. For the natural pH studies, the brick samples were immersed into the distilled water and left for certain time intervals without adding any pH modifier.

To determine the dissolved metal ions from the structure under various experimental conditions, such as pH, aging and the amount of scrap tire additive, 3-ml test solutions were taken at each different sampling time and put into different glass bottles. Then, these solutions were left overnight in a cooler to allow any remaining insoluble particles to settle. All samples were analyzed for aluminum, silicon, and other metal ions, such as calcium, magnesium, and iron, using a Perkin Elmer Optima 5300DV ICP-OES type instrument. The concentration of the dissolved metal ions other than calcium and silicon was not significant in all of the analyzed samples in this work; therefore, the solubility of calcium and silicon ion concentrations of the brick samples was more focused. The experimental conditions of the solubility tests and the concentration of metal ions are summarized in Table 5. The metal ion concentrations of Al³⁺, Si⁴⁺, Mg²⁺, Ca²⁺, Fe³⁺ are reported as mg/l (ppm) in the solution. The pH values provided in the results are the measured values before the pH adjustments.

3. Results

3.1. Effect of the pH modifiers on the solubility of metal ions

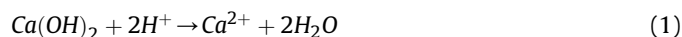
In this part of the study, the effect of pH on the solubility of metal ions in the brick structures was investigated while

Table 4
Mass of the concrete briquette samples in acidic, neutral and alkaline media.

Sample name	Scrap tire volume (%)	The mass of concrete sample for pH 3.6	The mass of concrete sample for pH 7	The mass of concrete sample for pH 10.5
R-0	0	129,519	131,199	136,620
R-20	20	132,690	127,453	135,024
R-40	40	101,079	109,227	104,017
R-60	60	104,943	96,493	100,173

maintaining the other factors of experimental condition constant. First, H₂SO₄ was added to the experiment medium drop wise until the medium reached pH 3.6; then, the solubility experiments were performed and repeated for different time periods over approximately two weeks; the results are shown in Table 5. The pH values of the medium, which were measured before each sampling, increased to approximately 10.8, which indicated that the H⁺ ions added to the medium were consumed and reacted with the concrete structure that contained alkali materials because the cement was composed of an abundance of metal ions, as shown in Table 1 and there were aggregates in the brick structure.

Three samples were analyzed and mean values were calculated for the each scrap addition. The age of all samples tested was 28-day. As observed in Fig. 2, the dissolution of CSH, CASH, ARS products and calcium hydroxide released more Ca²⁺ and Si⁴⁺ ions at low pH values than the release of Fe³⁺, Mg²⁺ and Al³⁺ ions from ferrite, aluminate and other hydrates in the brick structures. These overall reactions could be summarized by combining three basic dissociation reactions among CSH, CASH, ARS products and calcium hydroxide minerals of the brick and the aqueous species in the pore solution, which had sulfuric acid (Yuan et al., 2013). These minerals were significantly affected by the addition of H₂SO₄ acid, which increased the corrosion of the brick surface. At a pH value of 3.6, the neutralization reaction can be postulated to govern the chemical reaction between the acid and Ca(OH)₂, which consumes two H⁺ ions in the solution when the hydroxyl ions transfer one calcium ion from the brick structure to the test solution. The proposed neutralization reaction to release Ca²⁺ ion is as follows:



The neutralization reaction of the acid at different points in the brick structure dissolved the soluble solid hydration products, which resulted in more porosity, and the released Ca²⁺, Si⁴⁺, Mg²⁺, Fe³⁺ and Al³⁺ entered the pore solution. The porosity increased when calcium was removed from the brick structure, which enhanced the transport of ions in the corroded layer via diffusion. Mg²⁺, Fe³⁺ and Al³⁺ ions were not present in the pore solution because their concentrations were less than Ca²⁺ and Si⁴⁺ in cement composition and because they had significantly low solubility product constants. For example, aluminum has a solubility product value of 1.3×10^{-33} and appears as an Al(OH)₃ precipitate at pHs below 4.5. These results were consistent with the results of the simulation studies of Beddoe and Dörner (2005), who examined the corrosion of the concrete surface in acidic environment. They also suggested that the dissolved Ca²⁺ ions formed pores on the concrete surface and caused the other ions to join. However, the medium lost its acidic character via the neutralization reaction, and the pH of the solution increased to approximately 10.8. This condition describes why the pH of the test solution continuously became approximately 11, which indicated an alkaline state.

At high pH values, the dissolution of Ca(OH)₂ significantly decreased compared to that in acidic medium, as shown in Fig. 2. The absence of H⁺ ions indicates low Ca²⁺ ions in the medium because the neutralization reaction did not occur. Berube et al. (2004) explained the low solubility of Ca²⁺ ions in the pore solution of concrete in an alkaline medium significantly well. They affirmed that different ionic species, such as Na⁺, K⁺, Ca²⁺, H₂SiO₄²⁻, Al(OH)₄⁻, and so on, could be released into the concrete pore solution from minerals with time, and the CSH, CASH and ASR products precipitated because of their significantly low product of solubility and the presence of dissolved calcium in the solution. This explanation confirmed the results of this study.

The concentration of dissolved calcium at the natural pH values were less than the concentration in the acidic medium and more

Table 5
Experimental conditions of the solubility tests with the concentration of metal ions from the scrap tire-concrete structure (mg/l).

Days	pH	0% Scrap tire	20% Scrap tire	40% Scrap tire	60% Scrap tire
0	3.6	Al ⁺³ = 0.486	Al ⁺³ = 0.588	Al ⁺³ = 0.520	Al ⁺³ = 1334
		Si ⁺⁴ = 6114	Si ⁺⁴ = 3893	Si ⁺⁴ = 6914	Si ⁺⁴ = 4916
		Ca ⁺² = 25.52	Ca ⁺² = 35.29	Ca ⁺² = 31.96	Ca ⁺² = 43.89
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	7	Al ⁺³ = 1056	Al ⁺³ = 0.762	Al ⁺³ = 1075	Al ⁺³ = 1043
		Si ⁺⁴ = 6171	Si ⁺⁴ = 5578	Si ⁺⁴ = 6888	Si ⁺⁴ = 7083
		Ca ⁺² = 20.14	Ca ⁺² = 5723	Ca ⁺² = 24.08	Ca ⁺² = 27.94
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	10.5	Al ⁺³ = 0.830	Al ⁺³ = 0.707	Al ⁺³ = 1266	Al ⁺³ = 1063
		Si ⁺⁴ = 5486	Si ⁺⁴ = 5880	Si ⁺⁴ = 7655	Si ⁺⁴ = 8766
		Ca ⁺² = 9744	Ca ⁺² = 4001	Ca ⁺² = 19.13	Ca ⁺² = 14.60
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
1	3.6	Al ⁺³ = 0.502	Al ⁺³ = 0.727	Al ⁺³ = 0.562	Al ⁺³ = 0.604
		Si ⁺⁴ = 8726	Si ⁺⁴ = 10.05	Si ⁺⁴ = 9322	Si ⁺⁴ = 4591
		Ca ⁺² = 57.11	Ca ⁺² = 94.74	Ca ⁺² = 84.95	Ca ⁺² = 93.63
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	7	Al ⁺³ = 1669	Al ⁺³ = 1322	Al ⁺³ = 1496	Al ⁺³ = 1392
		Si ⁺⁴ = 9248	Si ⁺⁴ = 9935	Si ⁺⁴ = 6971	Si ⁺⁴ = 9256
		Ca ⁺² = 77.26	Ca ⁺² = 34.31	Ca ⁺² = 104.1	Ca ⁺² = 57.15
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	10.5	Al ⁺³ = 0.807	Al ⁺³ = 1311	Al ⁺³ = 1490	Al ⁺³ = 1383
		Si ⁺⁴ = 11.83	Si ⁺⁴ = 14.47	Si ⁺⁴ = 9067	Si ⁺⁴ = 11.13
		Ca ⁺² = 4710	Ca ⁺² = 20.31	Ca ⁺² = 33.98	Ca ⁺² = 45.80
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
2	3.6	Al ⁺³ = 1181	Al ⁺³ = 0.539	Al ⁺³ = 0.831	Al ⁺³ = 1493
		Si ⁺⁴ = 11.17	Si ⁺⁴ = 15.33	Si ⁺⁴ = 13.46	Si ⁺⁴ = 7538
		Ca ⁺² = 88.06	Ca ⁺² = 155.7	Ca ⁺² = 123.0	Ca ⁺² = 135.9
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	7	Al ⁺³ = 1636	Al ⁺³ = 1607	Al ⁺³ = 1650	Al ⁺³ = 1482
		Si ⁺⁴ = 11.09	Si ⁺⁴ = 6531	Si ⁺⁴ = 6922	Si ⁺⁴ = 7585
		Ca ⁺² = 58.96	Ca ⁺² = 114.1	Ca ⁺² = 121.8	Ca ⁺² = 94.01
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	10.5	Al ⁺³ = 0.606	Al ⁺³ = 0.920	Al ⁺³ = 1842	Al ⁺³ = 1369
		Si ⁺⁴ = 17.38	Si ⁺⁴ = 16.35	Si ⁺⁴ = 9002	Si ⁺⁴ = 13.58
		Ca ⁺² = 7638	Ca ⁺² = 25.87	Ca ⁺² = 13.72	Ca ⁺² = 19.49
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
5	3.6	Al ⁺³ = 0.686	Al ⁺³ = 0.672	Al ⁺³ = 0.691	Al ⁺³ = 0.811
		Si ⁺⁴ = 14.30	Si ⁺⁴ = 20.24	Si ⁺⁴ = 19.35	Si ⁺⁴ = 10.54
		Ca ⁺² = 73.85	Ca ⁺² = 151.3	Ca ⁺² = 139.5	Ca ⁺² = 134.4
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	7	Al ⁺³ = 2379	Al ⁺³ = 1649	Al ⁺³ = 1766	Al ⁺³ = 1135
		Si ⁺⁴ = 14.67	Si ⁺⁴ = 16.67	Si ⁺⁴ = 12.48	Si ⁺⁴ = 11.85
		Ca ⁺² = 0	Ca ⁺² = 8513	Ca ⁺² = 0.308	Ca ⁺² = 5085
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	10.5	Al ⁺³ = 0.730	Al ⁺³ = 0.680	Al ⁺³ = 1777	Al ⁺³ = 1429
		Si ⁺⁴ = 26.43	Si ⁺⁴ = 27.24	Si ⁺⁴ = 21.15	Si ⁺⁴ = 20.01
		Ca ⁺² = 1895	Ca ⁺² = 31.4	Ca ⁺² = 0.072	Ca ⁺² = 0.840
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
7	3.6	Al ⁺³ = 0.657	Al ⁺³ = 0.480	Al ⁺³ = 0.601	Al ⁺³ = 0.659
		Si ⁺⁴ = 16.01	Si ⁺⁴ = 24.84	Si ⁺⁴ = 23.33	Si ⁺⁴ = 14.58
		Ca ⁺² = 97.10	Ca ⁺² = 192.2	Ca ⁺² = 164.2	Ca ⁺² = 155.9
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	7	Al ⁺³ = 1660	Al ⁺³ = 1471	Al ⁺³ = 1836	Al ⁺³ = 1323
		Si ⁺⁴ = 26.81	Si ⁺⁴ = 24.90	Si ⁺⁴ = 24.14	Si ⁺⁴ = 13.73
		Ca ⁺² = 0	Ca ⁺² = 0.172	Ca ⁺² = 0.980	Ca ⁺² = 0.162
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	10.5	Al ⁺³ = 0.514	Al ⁺³ = 0.522	Al ⁺³ = 1226	Al ⁺³ = 1188
		Si ⁺⁴ = 36.17	Si ⁺⁴ = 39.24	Si ⁺⁴ = 35.65	Si ⁺⁴ = 35.21

Table 5 (continued)

Days	pH	0% Scrap tire	20% Scrap tire	40% Scrap tire	60% Scrap tire
9	3.6	Ca ⁺² = 0.867	Ca ⁺² = 9604	Ca ⁺² = 0	Ca ⁺² = 0
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
		Fe ⁺³ = 0	Fe ⁺³ = 0	Fe ⁺³ = 0	Fe ⁺³ = 0
		Al ⁺³ = 2184	Al ⁺³ = 0.547	Al ⁺³ = 0.632	Al ⁺³ = 0.763
	7	Si ⁺⁴ = 22.27	Si ⁺⁴ = 27.53	Si ⁺⁴ = 26.29	Si ⁺⁴ = 17.74
		Ca ⁺² = 104.7	Ca ⁺² = 217.4	Ca ⁺² = 193.3	Ca ⁺² = 174.8
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
		Fe ⁺³ = 0	Fe ⁺³ = 0	Fe ⁺³ = 0	Fe ⁺³ = 0
	10.5	Al ⁺³ = 1214	Al ⁺³ = 0.919	Al ⁺³ = 1256	Al ⁺³ = 1258
		Si ⁺⁴ = 25.23	Si ⁺⁴ = 34.81	Si ⁺⁴ = 34.72	Si ⁺⁴ = 20.70
		Ca ⁺² = 0.180	Ca ⁺² = 0	Ca ⁺² = 0	Ca ⁺² = 0.427
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
12	3.6	Al ⁺³ = 0.606	Al ⁺³ = 0.568	Al ⁺³ = 0.911	Al ⁺³ = 0.531
		Si ⁺⁴ = 20.07	Si ⁺⁴ = 29.53	Si ⁺⁴ = 29.99	Si ⁺⁴ = 19.57
		Ca ⁺² = 107.1	Ca ⁺² = 220.2	Ca ⁺² = 213.7	Ca ⁺² = 190.1
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	7	Al ⁺³ = 0.761	Al ⁺³ = 0.695	Al ⁺³ = 0.815	Al ⁺³ = 1308
		Si ⁺⁴ = 29.62	Si ⁺⁴ = 40.47	Si ⁺⁴ = 42.87	Si ⁺⁴ = 32.89
		Ca ⁺² = 3279	Ca ⁺² = 2939	Ca ⁺² = 0.347	Ca ⁺² = 2433
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
	10.5	Al ⁺³ = 0.528	Al ⁺³ = 0.524	Al ⁺³ = 0.480	Al ⁺³ = 0.502
		Si ⁺⁴ = 44.25	Si ⁺⁴ = 58.11	Si ⁺⁴ = 43.06	Si ⁺⁴ = 60.70
		Ca ⁺² = 1550	Ca ⁺² = 4639	Ca ⁺² = 0.003	Ca ⁺² = 0
		Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0	Mg ⁺² = 0
		Fe ⁺³ = 0	Fe ⁺³ = 0		

than the concentration in the basic medium because of the precipitation of CSH and CASH. The necessary Ca²⁺ ions for these precipitations were supplied from the Ca(OH)₂ of the solid cement part of the brick to reach equilibrium with the cation charge in the solution (Berube et al., 2004).

3.2. Effect of aging on the solubility of metal ions

Aging tests were performed by immersing the brick samples into the test solution after the pH adjustments and leaving them for previously fixed time intervals. As clearly observed in Fig. 3, the Ca²⁺ ions were substantially dissolved from the brick structure in the first days and subsequently slightly slowed down in the acidic medium because there was initially more available Ca(OH)₂, CSH, and CASH to be dissolved on the surface for corrosion by acid attacks; then, this surface was gradually consumed, which caused dissolution to occur in the lower part of the corroded region. These dissolution reactions of the bricks with acid increased the pH of the solution in the corroded layer from the value of the attacking acid at the brick surface to the pH of the equilibrium state, which was approximately 10.8, and resulted in more porosity in different parts of the structure and produced more calcium ions from the dissolution of soluble solid hydration products and Ca(OH)₂. In addition to the acidic-corrosion reaction, when calcium was removed from the structure, the porosity significantly increased and enhanced the transport of ions in the corroded layer via diffusion.

In an alkaline medium, the solubility of calcium decreased because CSH, CASH and ASR products precipitated in the presence of calcium, as suggested by Berube et al. (2004). The solubility of silicon increased with time because of the diffusion process, as shown in Fig. 3(b), (d), (f) and (h) (Zaman et al., 2003; Broekmans and Jansen, 1998).

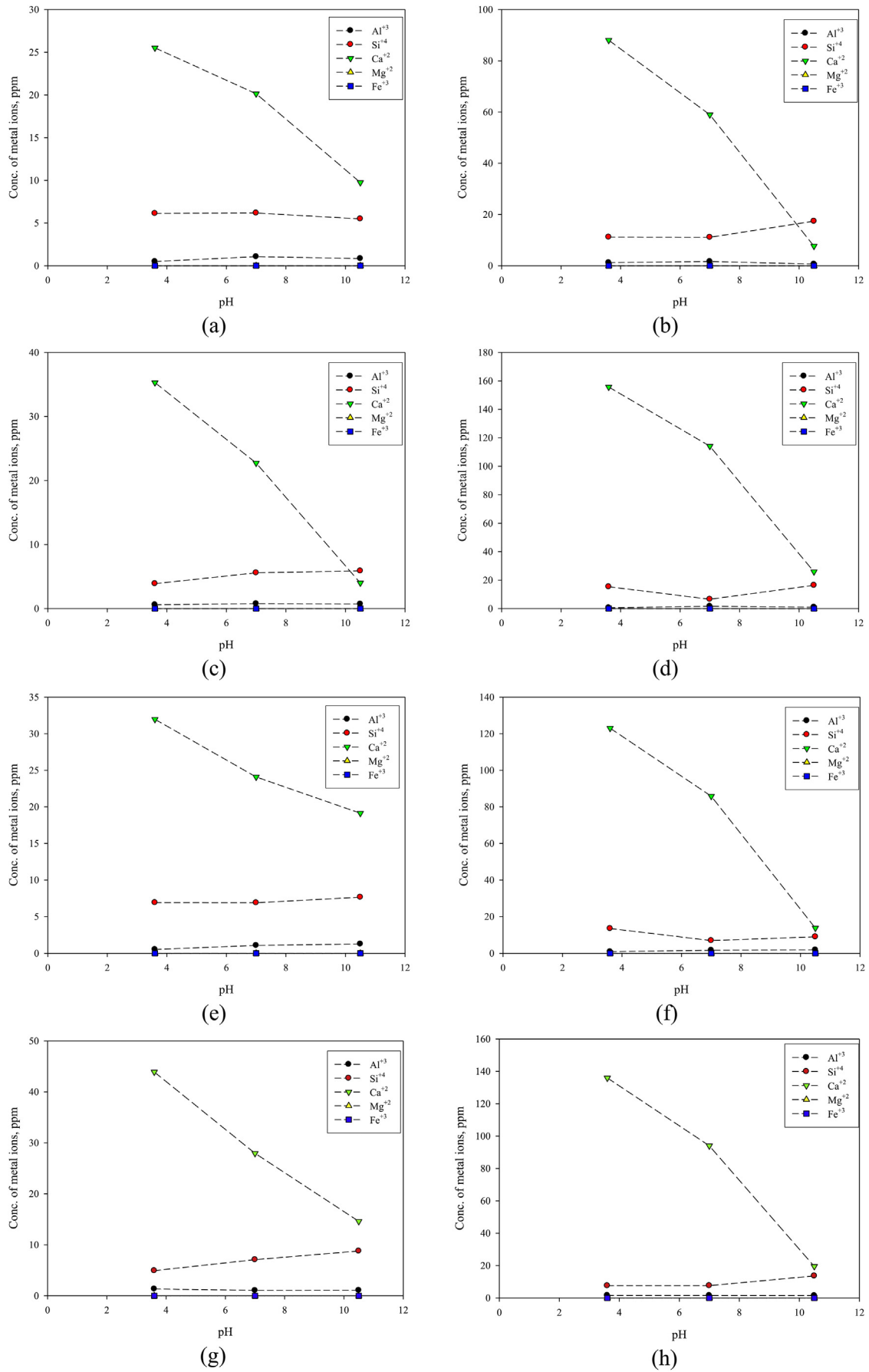


Fig. 2. Effects of pH on the solubility of metal ions from the scrap tire-concrete structure. (a) %Scrap tire = 0, Day = 0; (b) %Scrap tire = 0, Day = 2; (c) %Scrap tire = 20, Day = 0; (d) %Scrap tire = 20, Day = 2; (e) %Scrap tire = 40, Day = 0; (f) %Scrap tire = 40, Day = 2; (g) %Scrap tire = 60, Day = 0; (h) %Scrap tire = 60, Day = 2.

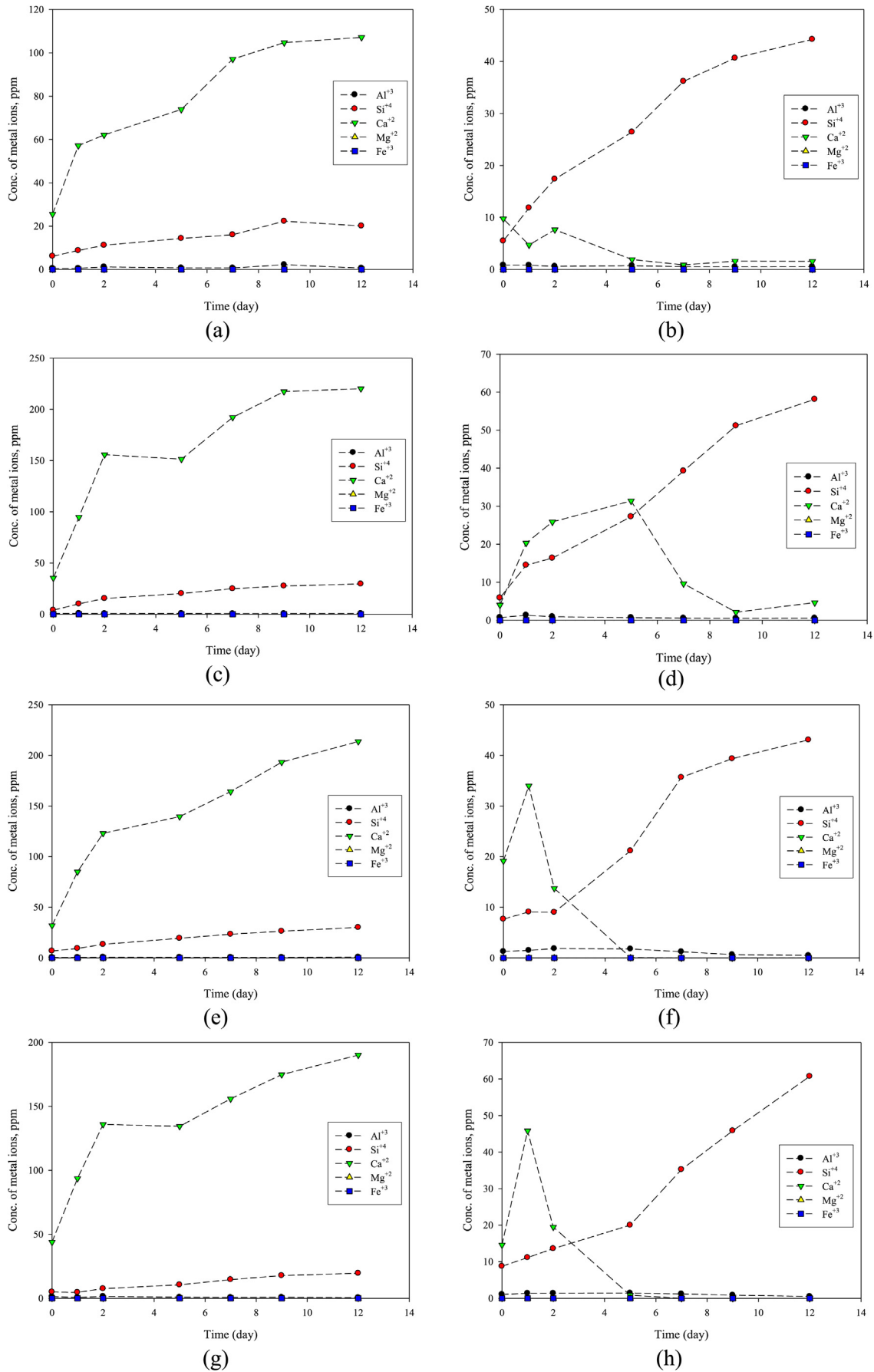


Fig. 3. Effects of aging on the solubility of metal ions from the scrap tire-concrete structure. (a) %Scrap tire = 0, pH = 3.6; (b) %Scrap tire = 0, pH = 10.5; (c) %Scrap tire = 20, pH = 3.6; (d) %Scrap tire = 20, pH = 10.5; (e) %Scrap tire = 40, pH = 3.6; (f) %Scrap tire = 40, pH = 10.5; (g) %Scrap tire = 60, pH = 3.6; (h) %Scrap tire = 60, pH = 10.5.

3.3. Effect of the scrap tire amount on the solubility of metal ions

The increase in the scrap tire content increased the surface area and porosity on and in the brick structure, which resulted in the release of more Ca^{2+} , and Si^{4+} ions. This situation increased the contact surface with the acid and diffusion, which increased the solubility, as shown in Fig. 4. In the acidic medium, low scrap tire content caused a denser corrosion layer on the brick surface compared to the others, which led to a decrease in corrosion. However, at alkaline pH values, the brick samples dissolved via diffusion, and more silicon appeared mostly because of this process. A small amount of calcium was present in the solution because the CSH, CASH and ASR products precipitated.

4. Summary and conclusion

In this study, the solubility of metal ions (Al^{3+} , Si^{4+} , Mg^{2+} , Ca^{2+} , Fe^{3+}) from the new concrete-scrap tire mixture structures was investigated under different experimental conditions. The main conclusions and observations are briefly indicated below:

- The addition of sulfuric acid dissolved CSH, CASH and ASR products and calcium hydroxide of the new concrete-scrap tire mixture structures via a naturalization reaction, which released more soluble metal ions, particularly calcium, in the solution.
- The porosity significantly increased because calcium was removed from the new concrete-scrap tire mixture structure over time; thus, the diffusion of other metal ions was enhanced.

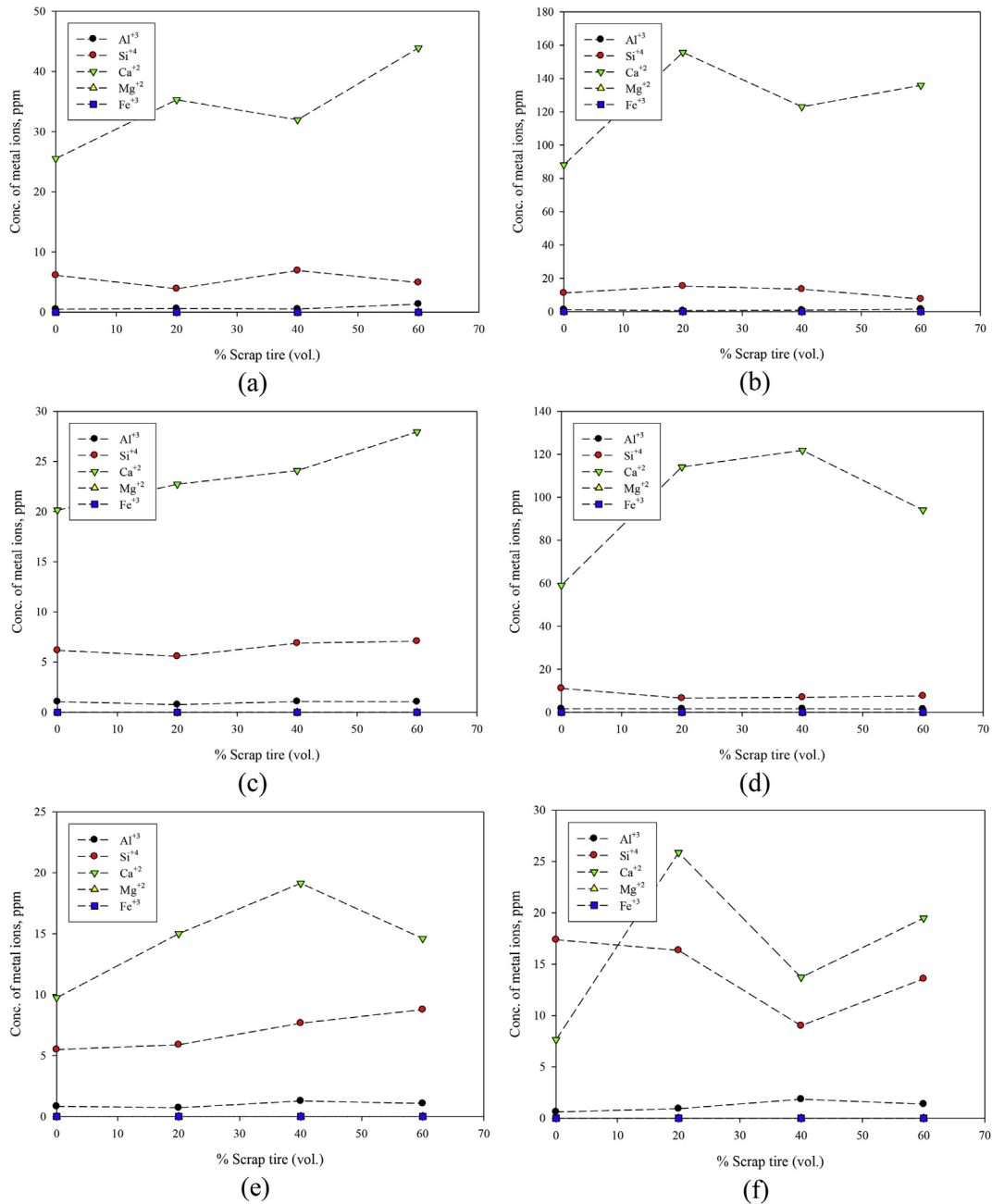


Fig. 4. Effects of the amount of scrap tires on the solubility of metal ions from the scrap tire-concrete structure. (a) pH = 3.6, Day = 0; (b) pH = 3.6, Day = 2; (c) pH = 7, Day = 0; (d) pH = 7, Day = 2; (e) pH = 10.5, Day = 0; (f) pH = 10.5, Day = 2.

- The addition of sodium hydroxide significantly decreased the solubility of calcium because of the precipitation of CSH, CASH and ASR products.
- The aging test showed that calcium was substantially dissolved from the new concrete-scrap tire mixture structures during the first days and subsequently slightly slowed down in the acidic medium because the corrosion surface was gradually consumed, which caused dissolution to occur in the lower part of the corroded region with time.
- The increase in the percentage of scrap tires caused an increase in surface area of the porous regions, which led to a higher dissolution of metal ions.

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