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Volcanic Scoria as Cement Replacement

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Abstract

Numerous volcanic scoria (VS) cones are found in many places of the world. Many of them have not yet been investigated, although few have been used as binders for a very long time. The use of natural pozzolans as cement replacement could be considered as a common practice in the construction industry due to the related economic, ecologic and performance benefits. This chapter highlights the advantages and disadvantages of the use of volcanic scoria as cement replacement in concrete mixes in terms of fresh and hardened concrete properties. The chemical and mineralogical composition of volcanic scoria samples collected from 36 countries is presented in this chapter, with some further analysis. The effects of using volcanic scoria as cement replacement on some paste, mortar and concrete properties, such as the setting times, the heat of hydration, the compressive strength, the water permeability and the chloride penetrability, have been studied. The improvement in resistance against the chemical attack of volcanic scoria-based cement mortar has also been highlighted. Some estimation equations depending on the data available in literature have also been derived from the analyzed data. The modification of the microstructure of VS-based cement paste has been confirmed, as well.

Keywords: volcanic scoria, blended cement, compressive strength, concrete durability, pozzolan

1. Introduction

Concrete is the most widely used construction material around the world, because of the economic and widespread availability of its constituents, its versatility, its durability and its adaptability [1]. In the year 2000, more than 1.5 billion tons of cement were produced to make, on average, nearly 1 m³ of concrete per capita [2].

Ordinary Portland cement concrete (OPC) is a composite material and its constituents are cement mixed with water, fine-grained aggregate (sand) and coarse-grained aggregate consisting of natural gravel or crushed stones [3]. Cement is a finely pulverized, dry material that by itself is not a binder but develops the binding property as a result of hydration (i.e., from chemical reactions between cement minerals and water) [4]. The considerable amount of carbon dioxide (CO_2) liberated during the production of Portland cement, the most commonly used hydraulic cement, is of a greater concern. On average, about 1 ton of CO_2 is liberated per ton of Portland cement produced [1].

The use of mineral admixtures such as pozzolans (materials containing reactive silica) in concrete is now widespread due to many economic, ecological and performance-related benefits [4, 5]. Pozzolanic material is “a siliceous or siliceous-aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of water, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties” [6]. Pozzolanic supplementary cementitious materials (SCMs) differ from hydraulic SCMs in that hydraulic SCMs can form cementitious products in water, without the presence of calcium hydroxide [6]. The term “pozzolan” comes from the town of Pozzuoli, northeast of Naples in Italy, where red pozzolanic deposits from the volcano Vesuvius were found [7].

Pozzolanic materials can be divided into natural and artificial pozzolans. Natural pozzolans could be considered the first cementing materials used for the production of artificial stones, ancient mortars and concretes, 3000 years ago [8]. For example, according to Jackson et al. [9], the binding pozzolanic mortars of 2000-year-old concretes in the monuments of imperial age Rome contained 40–50 vol. % of scoriaceous volcanic ash. The natural pozzolans may be further divided into two main groups: (1) those derived from volcanic rocks (volcanic scorias, ashes, tuffs, pumices and obsidians) and (2) others derived from rocks and earths, such as the diatomaceous earths (cherts, opaline silica), clays which have been naturally calcined by heat from flowing lava [10].

Volcanic scoria is loose, rubbly, basaltic to andesitic (40–60% SiO_2) ejecta that accumulates around Strombolian eruptive volcanic vents, eventually building up as a scoria cone, whose height may range from a few tens of meters to 300 m. The scoria clasts range widely in size, from millimeters to centimeters in size, and have a light, frothy texture, being full of vesicles (**Figure 1e**). The vesicular nature of scoria is due to the escape of volcanic gases during eruption. Sometimes these vesicles are refilled with minerals like zeolite, calcite and quartz that form from hot water-rich fluids. The scoria clasts are mainly dark gray in color, although when fresh they may be iridescent, but often the scoria oxidizes by reaction with steam escaping from the vent, when it becomes a deep reddish brown [11–13]. The most economically valuable volcanic scoria deposits are late tertiary or quaternary in age [14]. Most of the scorias are composed of glassy fragments and may contain phenocrysts. The word scoria comes from the Greek *skōria*, rust. An old name for scoria is cinder [15].

With respect to pumice, typical scoria has larger and more interconnected vesicles, is characterized by lower silica content and displays a darker, brown, reddish or black color [16]. Volcanic scoria can be utilized, other than as cement replacement, in several industrial applications including the manufacturing of lightweight concrete, as a heat-insulating material, in addition to other uses such as fillers, filter materials, absorbents and other architectural applications [17].

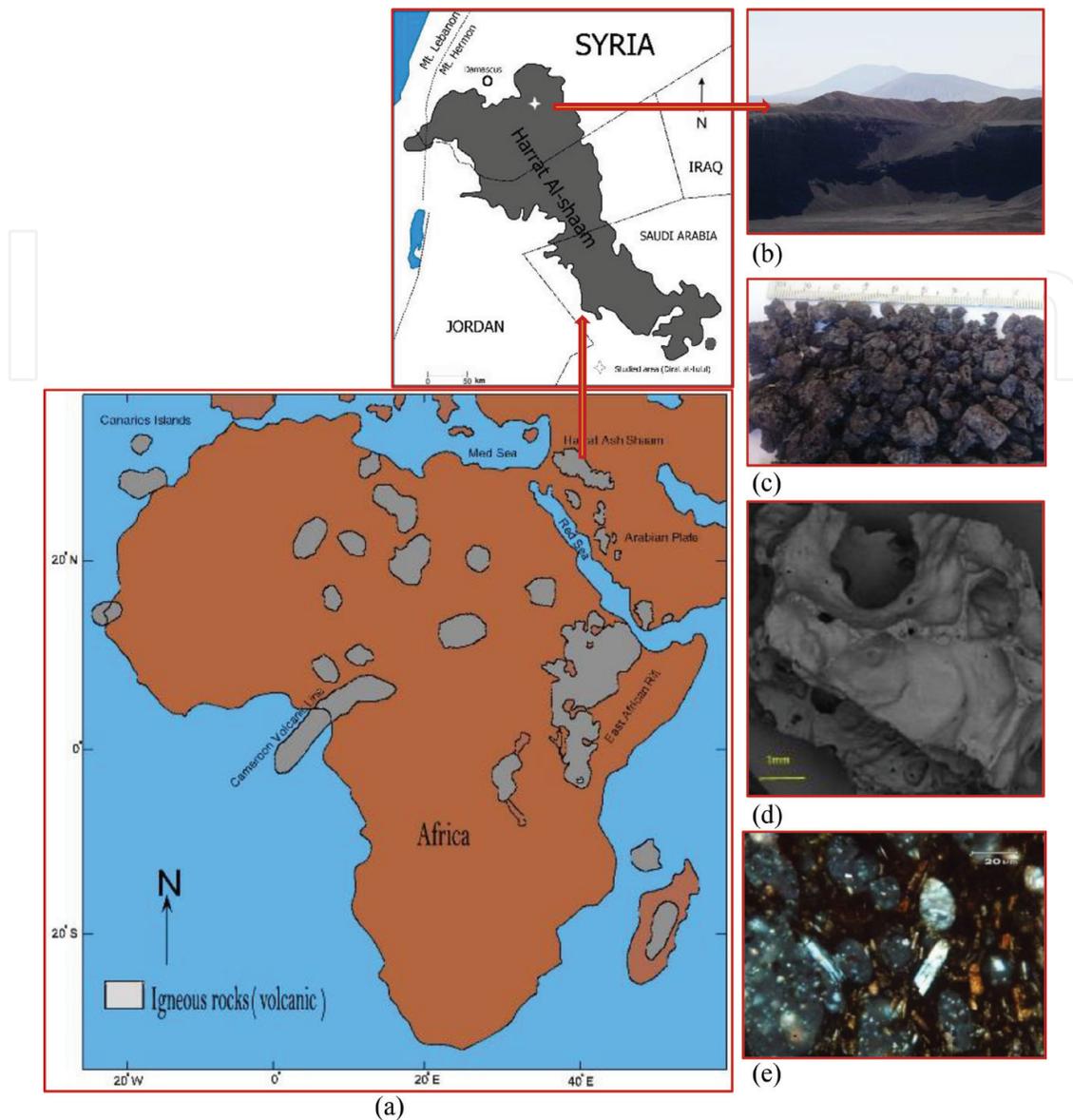


Figure 1. (a) Map of African and Arabian plate with a clearer map of Harrat al-Shaam in the upper part of the figure, (b) Photo of Syrian volcanic scoria cones, (c) Macrograph of volcanic scoria aggregates, (d) SEM of volcanic scoria particle with clear vesicles, (e) Thin section in a Syrian volcanic scoria sample.

Although there are numerous studies on using natural pozzolan as cement replacement, few works on studying volcanic scoria were reported in the literature. The present chapter highlights some characteristics of volcanic scoria and their effects on performance-related properties of paste, mortar and concrete. The importance of this chapter is to encourage countries having ample sources of volcanic scoria cones to further investigate the possibility of using it as cement replacement and thus making a greener concrete.

2. Chemical and mineralogical composition of volcanic scoria

The chemical composition of volcanic scoria varies within wide ranges and depends on its sources. Various scoria cones are abundant in many parts of the world, such as Syria, Turkey,

Source	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	LOI	SO ₃	R ₁	R ₂	Detected phases	Ref.
Algeria	45.9– 47.2	16.6– 18.9	8.4– 10.6	9.0– 10.8	2.8–4.4	0.2–1.5	0.8– 4.3	4.1	n.a.	3.9– 5.8	0.4–1.0	63–66.1	72.4– 76.1	Gl, Ca, Pl, Py, Qz, Co, Hm, Ac, Ax, Mm, Il	[18–21]
Argentina	47.6	15.4	10.0	10.8	9.8	1.3	3.4	1.4	0.5	n.a.	n.a.	63.0	73.0	Gl, Ol, Pl, CPy, Op	[22]
Armenia	53.6	19.6	7.5		13	4		n.a.	n.a.	n.a.	n.a.	73.2	80.7	n.a.	[23]
Cameroon	41.4– 46.9	15.0– 16.2	12.8– 14.5	7.9– 10.5	5.3–8.7	0.9–1.6	2.2– 4.5	2.1– 3.4	0.4– 0.6	0–9.3	0.01	56.8– 62.3	69.7– 75.9	Gl, Pl, CPy, Py, Ol, Qz, Hm, Mg, An, Ma, Mc, SCAS	[24–30]
Canada	45.7– 54.3	12.7– 16.0	11.3– 12.2	7.1– 8.7	4.1– 12.5	1.2–1.9	3.2– 4.0	1.6– 2.2	0.74	0.43	n.a.	58.4– 70.3	70.6– 81.6	Gl, Pl, Ol, CPy	[31, 32]
Chile	46.4	18.5	12.9	6.5	3.0	1.1	3.5	1.8	0.4	6.4	n.a.	64.9	77.8	Gl, CPy, Pl, Mn, Kn	[33]
China	45.1	14.7	12.4	9.3	9.2	1.8	3.6	2.0	1.8	1.5	n.a.	59.8	72.1	Gl, Ol, Mn, Pl, Py	[34]
Congo	46.7	15.3	13.4	11.3	8.1	3.3	2.1	3.5	0.3	n.a.	n.a.	62.0	75.1	Gl, Ol, CPy, Pl, Mn, Le	[35]
Costa Rica	53.3	19.7	8.1	9.8	5.0	0.6	2.9	0.7	0.2	n.a.	n.a.	72.9	81.1	Gl, CPy, Pl, Ho	[36]
Ethiopia	47.2– 49.0	16.1– 16.5	12.4– 13.7	8.2– 10.8	5.4–6.2	0.6–0.9	3.0– 3.3	2.4	0.5	0.7	n.a.	63.7– 65.1	76.1– 78.8	n.a.	[37, 38]
France	45.1– 56.8	15.2– 17.7	7.0–8.2	7.8– 12.6	3.7–8.8	0.9–1.8	3.2– 3.6	0.7– 3.0		n.a.	n.a.	60.3– 74.5	68.5– 81.5	Gl, CPy, Py, Pl, Ol, Mn, Am,	[39, 40]
Germany	45.5– 47.9	6.4– 15.4	7.4– 14.8	8.2– 23.7	6.5– 12.6	0.03– 0.5	0.6– 1.2	3.0– 3.1	1.2	6.05	n.a.	51.9– 63.3	59.2– 78.1	Gl, Ol, Pl, CPy, Py, Am, Mi	[41, 42]
Indonesia	55.1– 56.7	18.0– 18.5	8.2–8.8	8.1– 9.2	3.7	0.8–1.4	2.9– 3.1	0.6– 0.8	0.2	0.0– 0.3	n.a.	73.6– 74.7	82.4– 82.9	Gl, Pl, Py, CPy, Mn	[43, 44]
Iran	48.0– 48.3	12.3– 16.4	9.4– 11.4	9.6– 9.8	4.4–7.7	1.3–2.7	3.3– 5.6	1.8– 2.6	1.1– 1.6	1.1	n.a.	60.3– 64.7	69.7– 76.1	Gl, Py, Ol, Mn, CPy	[45, 46]
Italy	50.6	19.7	9.1	6.2	3.8	2.3	0.7	1.0	0.3	7.2	n.a.	70.3	79.3	n.a.	[47]
Japan	54.3	15.6	13.7	9.5	3.9	0.5	2.0	1.2	0.1	n.a.	n.a.	70.0	83.7	Gl, Ol, CPy, Pl	[48]
Jordan	41.7	10.6	8.9	12.8	6.3	1.4	1.1	2.3	0.4	n.a.	n.a.	52.3	61.2	n.a.	[49]
Madagascar	44.6	13.0	12.5	12.1	9.6	1.3	2.4	2.3	0.7	n.a.	0.02	57.7	70.2	Gl, Pl, Mn, CPy, Ol	[50]
Mexico	54.2– 56.0	15.5– 18.0	7.1– 14.7	7.1– 7.7	5.3–9.5	0.9–1.1	3.4– 4.8	0.8– 1.0	0.2– 0.3	0.01	n.a.	69.7– 73.9	81.0– 84.5	Gl, Pl, Ol, Py, CPy	[51, 52]

Source	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	LOI	SO ₃	R ₁	R ₂	Detected phases	Ref.
New Zealand	46.3– 47.3	11.5– 13.7	10.8– 13.0	8.4– 9.4	9.2– 16.7	0.8–1.3	2.9– 3.3	2.8	0.6	n.a.	n.a.	58.8– 59.9	69.6– 73.0	Gl, Ol, CPy, Pl, Fe-Ti oxides	[53, 54]
Nicaragua	56.4	18.0	7.8	7.3	2.2	1.2	3.0	0.8	0.6	n.a.	n.a.	74.5	82.3	Gl, Pl, Ol, CPy, Mn	[55]
Papua New Guinea	47.5	14	3.5	6.5	5	5.0		n.a.	n.a.	1.4	0.02	61.5	65.0	n.a.	[56]
Peru	57.4	17.9	6.2	4.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	75.3	81.5	n.a.	[57]
Philippines	53.2	18.5	8.9	8.5	4.4	0.95	3.4	0.7	0.3	0.2	n.a.	71.7	80.6	n.a.	[58]
Romania	46.1	18.8	9.9	10.4	7.2	1.7	3.2	1.6	1.1	n.a.	n.a.	64.9	74.8	n.a.	[59]
Russia	52.6	14.4	9.7	8.0	4.2	2.1	3.7	1.5	0.5	n.a.	n.a.	70.0	79.7	Gl, Ol, Py, Pl	[60]
Saudi Arabia	42.0– 46.5	13.1– 16.6	11.1– 15.8	7.8– 10.0	2.5– 11.4	0.6–1.5	0.2– 3.5	2.1– 2.8	0.3– 0.6	0.9– 4.9	0.02– 0.27	58.0– 61.2	69.4– 74.4	Gl, Pl, Ol, CPy, Py, Qz	[61–65]
Southern Pacific Ocean	43.9	10.8	12.6	13.1	12.9	1.5	1.4	3.1	0.5	n.a.	n.a.	54.7	67.3	n.a.	[66]
South Africa	47.3	15.7	13.1	8.7	5.5	1.0	4.2	3.7	0.7	n.a.	n.a.	62.9	76.0	Gl, Ol, CPy, Pl	[67]
Spain	44.3– 46.3	14.2– 17.1	10.0– 12.2	8.8– 9.5	4.5–9.0	1.7–2.1	2.7– 4.9	2.4– 3.3	0.7– 1.3	n.a.	n.a.	59.2– 63.4	70.9– 73.4	Gl, Ol, CPy, Mn, Pl, Le	[68–70]
Syria	44.9– 46.5	13.0– 17.0	8.6– 11.4	9.4– 10.1	8.9–9.1	0.8–1.8	2.1– 2.8	0.9	n.a.	0.4– 2.6	0.01– 0.27	59.5– 61.9	70.5– 70.9	Gl, Ol, Pl, Ca, CPy, Fu	[71, 72]
Tanzania	40.0	13.0	13.9	9.6	4.6	n.a.	n.a.	n.a.	n.a.	10.8	n.a.	53	66.9	n.a.	[73]
Taiwan	51.5	18.8	11.1	10.0	4.7	0.4	2.8	0.9	0.1	1.4	n.a.	n.a.	n.a.	Gl, Ol, Pl, Py	[74]
Turkey	54.9– 55.6	16.9– 17.7	6.6– 10.3	6.5– 8.1	2.0–5.1	1.2–1.9	2.2– 3.5	1.1– 2.6	0.3– 0.4	0.3– 0.9	0.29	71.8– 73.2	79.8– 82.2	Gl, Pl, Py, CPy, Qz, Ho,	[75–77]
USA	48.0	16.7	11.8	8.6	5.9	1.8	3.5	2.0	1.2	n.a.	n.a.	64.8	76.6	Gl, Ol, Pl	[78]
Yemen	48.5	16.5	12.2	8.6	5.7	1.0	3.6	1.9	0.4	1.8	n.a.	65.1	77.3	n.a.	[79]

LOI: Loss On Ignition; n.a.: Not available.

Gl: Glass; Pl: Plagioclase; Ol: Olivine; Py: Pyroxene; CPy: Clinopyroxene; Mu: Muscovite; Qz: Quartz; Ma: Managocalcite; An: Anatase; Mc: Microcline, SCAS: Sodium calcium aluminum silicate; Co: Cordierite; Ac: Analcime; Ax: Axinite; Mn: Magnetite; Ca: Calcite; Hm: Hematite; Il: Illite; Mm: Montmorillonite; Ho: Hornblende; Mg: Maghemite; Fu: Fugasite; Am: Amphibole; OP: Opaque minerals; Mi: Mica; Kn: Kaolinite; Le: Leucite

Table 1. Chemical composition of some different scoria samples quarried from 36 countries.

Saudi Arabia, Cameroon, Ethiopia, Jordan, Libya, Algeria, Spain and others [18–79]. Harrat Al-Shaam volcanic field, for example (**Figure 1a**), is a basaltic province, extends widely at the Arabian plate (over 50,000 km²), covers the south of Syria, northeast of Jordan, north of Saudi Arabia and contains hundreds of volcanic scoria cones [80, 81]. The chemical analysis of some volcanic scoria reported for 36 countries [18–79] is presented in **Table 1**.

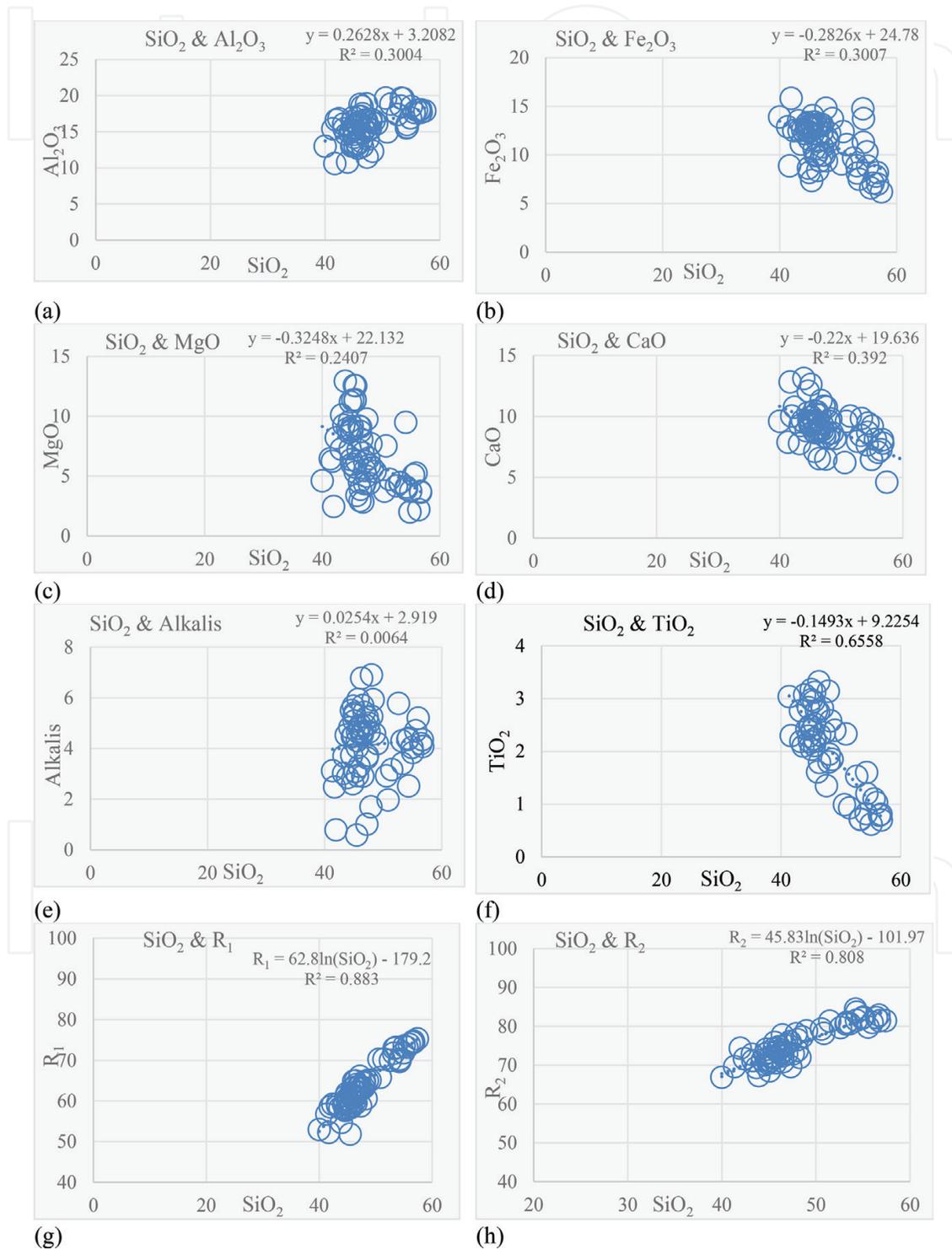


Figure 2. Different oxides versus silica content in the volcanic scoria (R₁: sum of SiO₂ and Al₂O₃; R₂: sum of SiO₂, Al₂O₃ and Fe₂O₃) [18–79].

Table 1 shows that most of the volcanic scoria samples are relatively rich in silica (40–60%) and alumina (10–20%). The next oxides are iron (5–16%), calcium (5–13%) and magnesium (2–13%) oxides. The alkali content is not high but may vary between 1 and 7%. Loss on ignition is generally low but may reach 10% in some pozzolans. Harker variation diagrams (**Figure 2**), using SiO_2 , show a general increase of Al_2O_3 and alkalis with increasing SiO_2 . However, the elements such as Fe_2O_3 , MgO , CaO and TiO_2 display inverse relationships with SiO_2 . The author attempted to derive an equation in order to estimate R_1 (sum of SiO_2 , Al_2O_3 and Fe_2O_3) and R_2 (sum of SiO_2 , Al_2O_3 and Fe_2O_3) from the knowledge of SiO_2 content (**Figure 2**).

The mineralogical composition of volcanic scoria also varies depending upon their sources. Owing to their formation process, volcanic scoria consists of crystalline and noncrystalline particles as glassy particles. The most detected minerals are plagioclase, olivine, pyroxene and clinopyroxene.

3. Reactivity of volcanic scoria

Volcanic scoria as a pozzolanic material has high silica (SiO_2) and alumina (Al_2O_3) content with a glassy/amorphous structure for reactivity with lime or cement [82]. Reactive silica content can react with portlandite (CH) liberated from the hydration of C_3S and C_2S in cement. This reaction forms additional calcium silicate hydrates (C-S-H). The principal reaction is.



The composition of C-S-H is not very different from that formed in regular hydration, although generally the C/S molar ratio is slightly lower [83]. Analogously to reactive silica, reactive alumina present in volcanic scoria can react with CH to form calcium aluminate hydrates (C-A-H) [83]. This reaction which is frequently called the pozzolanic reaction is slow, portlandite consuming and very efficient in filling up capillary spaces [4]. It depends on several factors, such as the glassy phase content in volcanic scoria and the fineness of volcanic scoria.

3.1. Glassy phase in volcanic scoria

ASTM designation C618 (2012) [84] requires that for a material to be accepted as a natural pozzolan, the sum of SiO_2 , Al_2O_3 and Fe_2O_3 should have a minimum value of 70% and the strength activity index should exceed 75% of the control mortar's compressive strength at either 7 or 28 days. The strength activity index (SAI) gives an indication of the reactivity of volcanic scoria by comparing the compressive strength of mortar cubes made with 80 wt.% cement and 20 wt.% volcanic scoria to the compressive strength of the control mortar cubes made with only cement. In addition, EN 197-1(2000) [85] requires a reactive silica content of more than 25% for volcanic scoria to be accepted as natural pozzolan.

3.2. Fineness of volcanic scoria

An increase in fineness that exposes more surface area of the volcanic scoria may accelerate the early pozzolanic reactivity [86, 87]. The specific surface area of volcanic scoria, which is the area

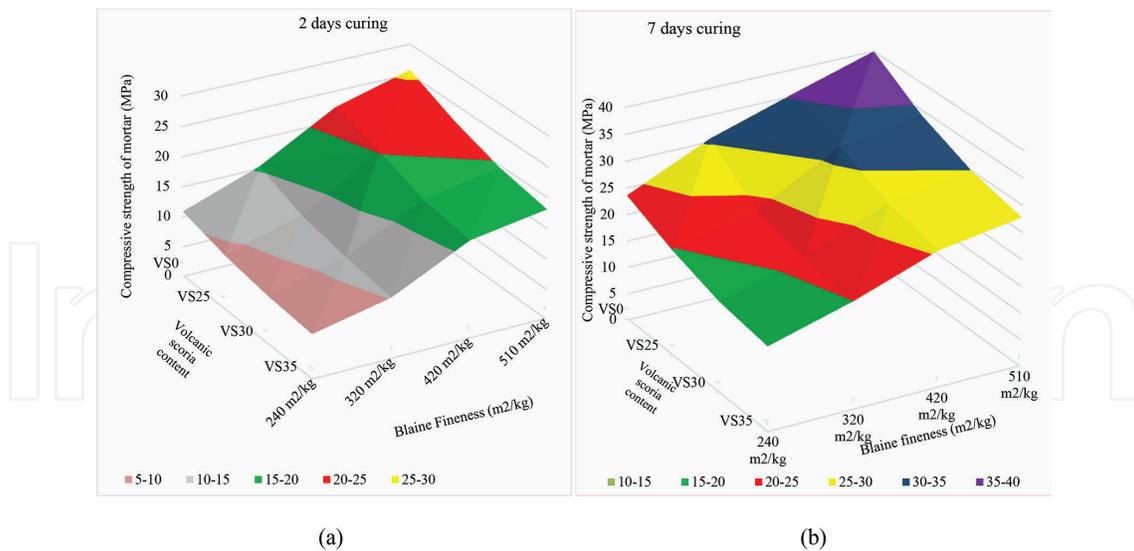


Figure 3. Effect of fineness on compressive strength of VS-based cement mortars cured for 2 (a) and 7 (b) days [89].

of a unit mass, is measurable by different techniques. The most common is the Blaine-specific surface area technique, which measures the resistance of compacted particles to an air flow. A laser particle size analyzer can also be used for the determination of the specific surface area of volcanic scoria [88, 89]. Al-Swaidani et al. [89] reported an increase of about 145% in the early compressive strength when the Blaine fineness of 2-day-cured volcanic scoria (VS)-based cement increased from 240 to 510 m²/kg at replacement levels ranging from 25 to 35% by mass, as shown in **Figure 3**. The authors also concluded that an increase of about 5 MPa can be expected for every 1000 cm²/g increase in Blaine fineness for VS-based binder mortars at all curing times [89]. Similar results were obtained by other researchers [90, 91]. This reactivity enhancement was explained by the effect of grinding which breaks the vitreous body, decreases the particle size and increases dissolution rate and solubility of volcanic scoria, which will accelerate pozzolanic reaction rate and the strength development of mortar containing volcanic scoria [89, 90, 92].

4. Properties of VS-based cement paste

4.1. Setting times

Most of the studied scoria samples showed an increase, ranging from slight to significant, in setting times of the VS-based cement paste with the increase in volcanic scoria content. This can be explained by the reduction of hydration heat on the binder system with the presence of VS [91]. A significant relationship ($R^2 \approx 0.9$) between initial and final setting times was obtained by the author depending on data collected from other papers [20, 62, 71, 72, 75, 79, 89, 91], as clearly shown in **Figure 4**. So, knowing initial setting time, the final setting time of the VS-based cement paste can be predicted by using the equation shown in **Figure 4**. It is worth to note that among all the investigated volcanic scoria compiled with the standard requirements in terms of the initial setting time, most of them met the requirements in terms of final setting times (i.e., initial setting time ≥ 45 min and final setting time ≤ 420 min), according to ASTM C595 [93].

4.2. Heat of hydration

The hydration of cement paste is accompanied by the liberation of heat that raises the temperature of the concrete mix. Because of the slower pozzolanic reaction, the partial replacement of cement by volcanic action results in a release of heat over a longer period of time enabling the heat to dissipate and the overall concrete temperature to remain lower. This is of great importance in mass concrete where cooling, following a large temperature rise, can lead to cracking. As shown in **Figure 5**, a volcanic scoria from Syria reduced the heat of hydration [94]. Similar results were also reported by Alhozaimy et al. [95] who concluded that the heat of hydration of VS-based cement pastes liberated in the first 72 h was, on average, 85% of the control mix.

4.3. Microstructure

The presence of volcanic scoria leads to the disappearance of portlandite crystals and the appearance of the condensed type of C-S-H crystals, as shown in **Figure 6**. This type of condensed C-S-H results from the interaction of pozzolanic material with portlandite. Condensed

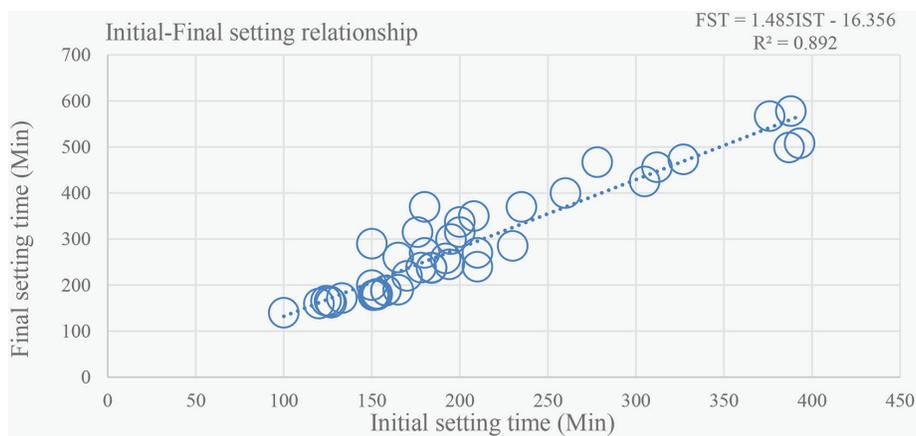


Figure 4. Relationship between initial and final setting times.

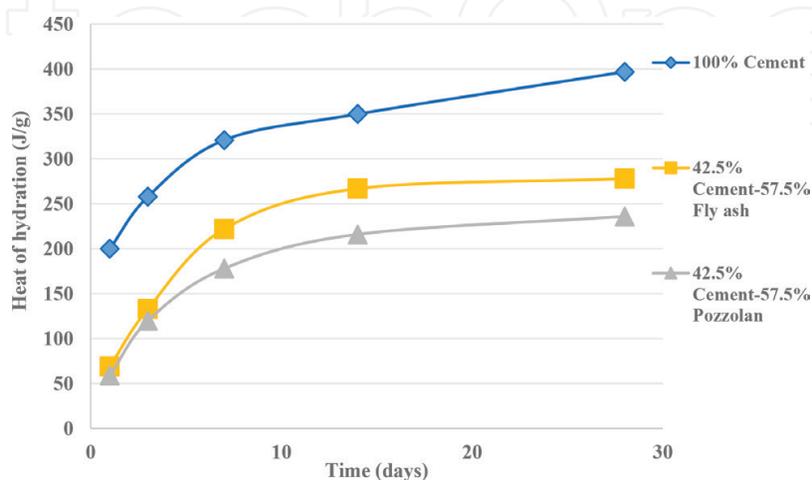


Figure 5. Influence of different SCMs on the heat of hydration of the mixtures [94].

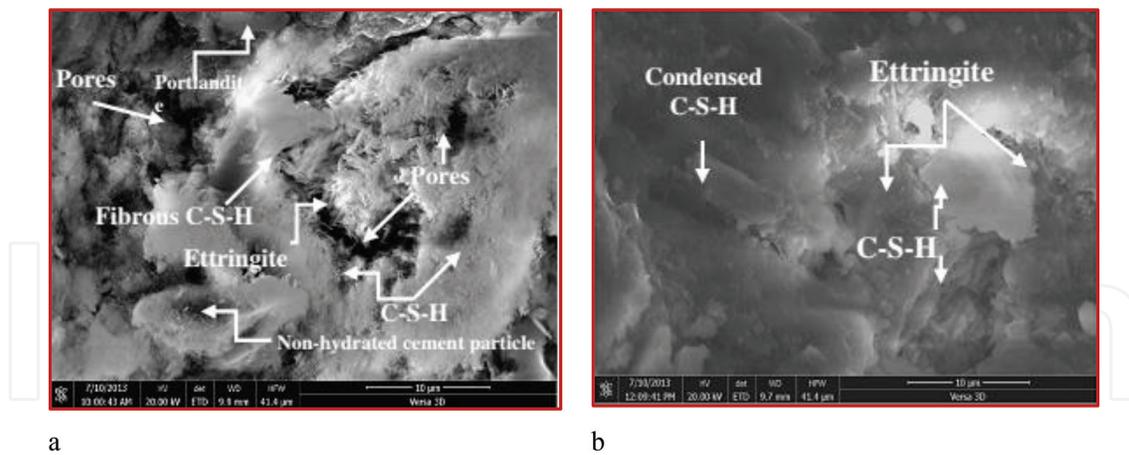


Figure 6. SEM of (a) control cement paste; (b) 20% VS-based cement paste [63].

C-S-H fills the micropores, reduces the porosity and consequently improves the impermeability and the compressive strength. The enhancement in the microstructure in the mixtures with volcanic scoria can be attributed to the formation of additional C-S-H, which generally fills in the pores, creates denser hydration products and accordingly reduces the permeability [63]. Similar observations were also reported in the literature [71, 72].

5. Properties of VS-based cement mortar/concrete

5.1. Compressive and flexural strength

All the results reported in the literature [18–20, 30, 56, 62, 63, 71, 72, 75, 79, 89, 91, 96, 97] show that the compressive strength of VS-based cement mortars/concretes increases with the curing age and decreases with the replacement level of volcanic scoria content (**Figure 7**). This reduction in the compressive strength is attributed mainly to slower pozzolanic activity at room temperature of volcanic scoria as natural pozzolan [71, 83]. This ascertainment is explained by the interaction between the reactive silica which is in the glassy portion of the addition and the $\text{Ca}(\text{OH})_2$ released by the hydration of the cement. It has also been noted that the mortars containing volcanic scorias exhibit compressive strength comparable to those of the control mortar starting from the period of 90 days.

The author attempted to derive an equation in order to reasonably estimate the relative compressive strength of VS-based mortars. This prediction equation could be written as follows:

$$\text{RCS} = (0.176 \ln t - 1.343) \text{VS} + 1.01 \quad (R^2=0.81) \quad (2)$$

where RCS is the relative compressive strength, t is the curing age (day) and VS is the volcanic scoria content (%). This prediction equation having a relatively high coefficient of determination ($R^2 = 0.81$) was obtained through the regression analysis of literature data (**Figure 8**). The variants in the equation are the curing age and the volcanic scoria content. So, knowing the

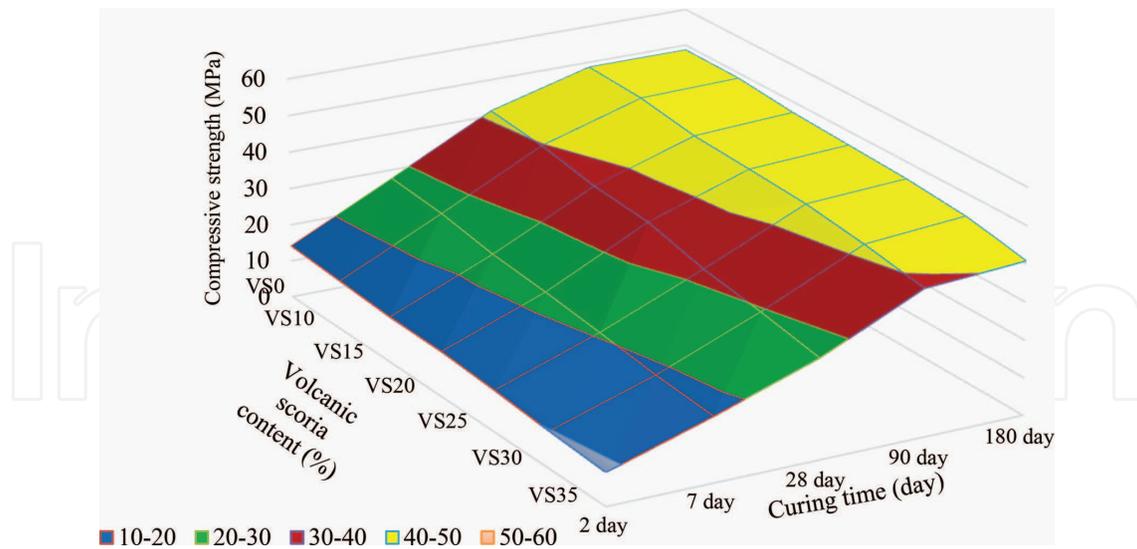


Figure 7. Compressive strength of VS-based cement concrete at different curing times [98].

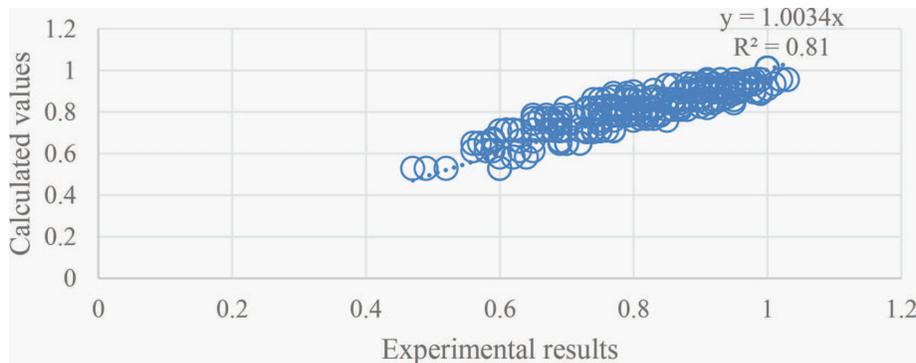


Figure 8. Experimental results versus calculated values for relative compressive strength of volcanic scoria cement-based mortars.

curing age and the volcanic scoria content and the compressive strength of the control sample (i.e., without volcanic scoria), the compressive strength of VS-based cement and mortar could be reasonably estimated.

It is worth to mention that, in contrast to previous literature, studying the effect of total alkali content (Na_2O and K_2O) and K_2O on the compressive strength of VS-based cement mortars did not give definite correlations (**Figure 9**).

A similar behavior was observed by many researchers in terms of flexural tensile strength of VS-based cement mortars. An attempt to predict the flexural strength based on the compressive strength, with a reasonable coefficient of determination ($R^2 = 0.83$), is clearly shown in **Figure 10**.

5.2. Drying shrinkage

Drying shrinkage represents the strain caused by the loss of water from the hardened material. The shrinkage is believed to originate in the C-S-H and its associated porosity [83].

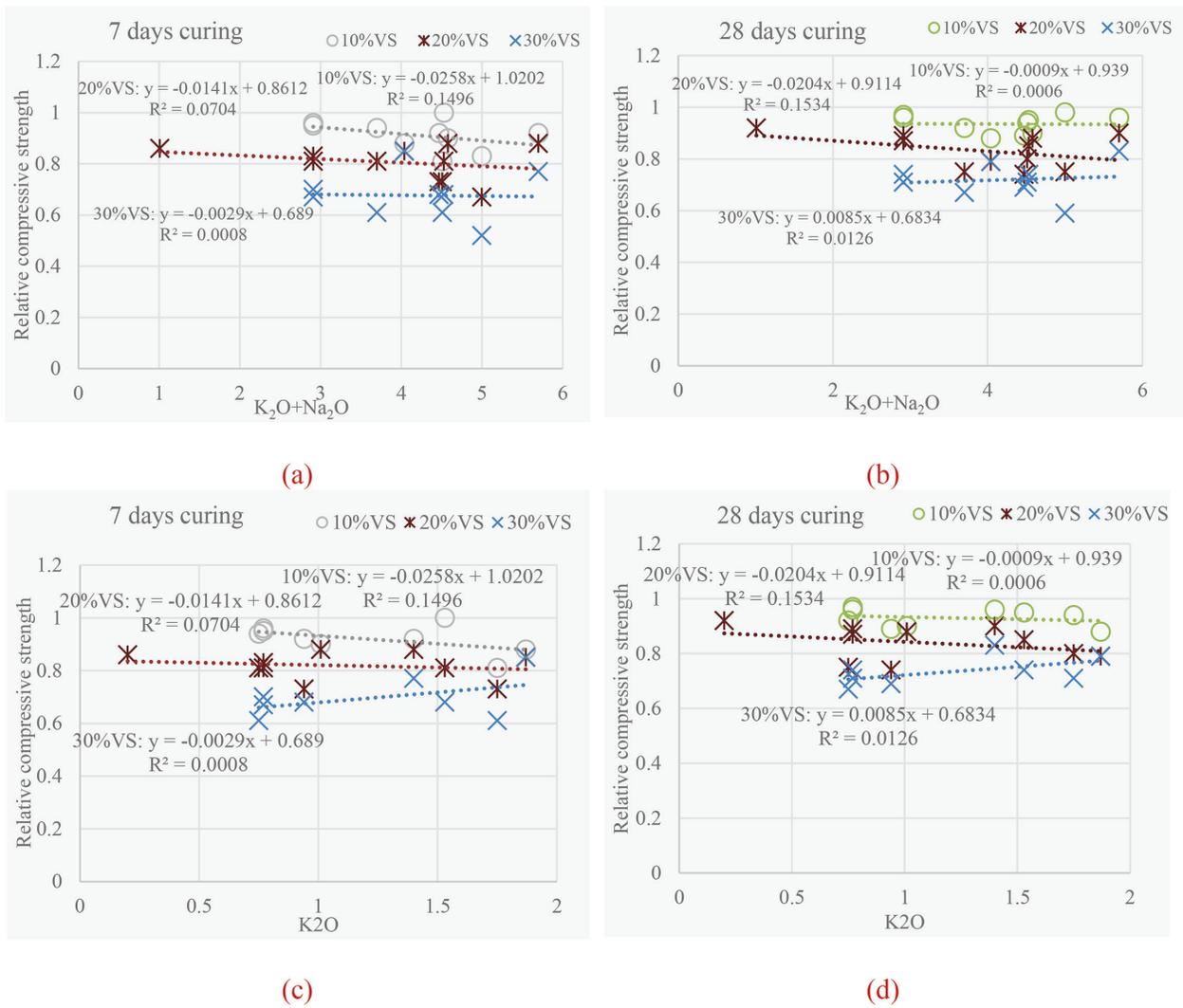


Figure 9. Effect of total alkali content (a and b) and K_2O content (c and d) on compressive strength of VS-based cement mortars at 7 and 28 days curing.

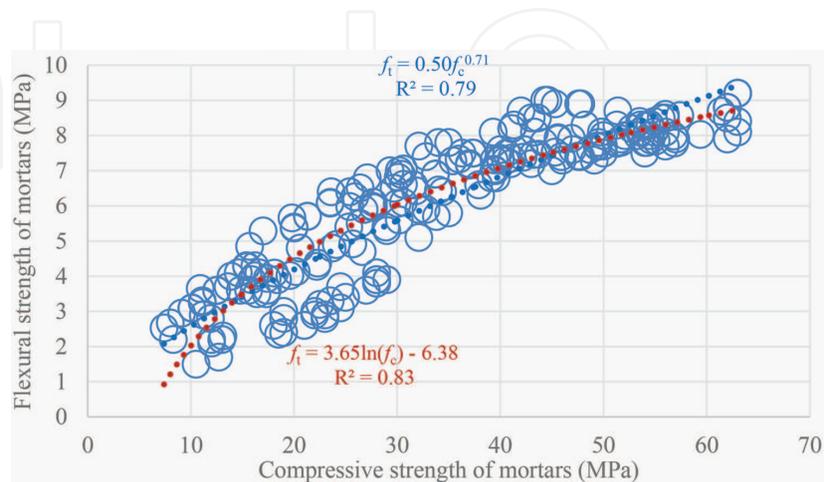


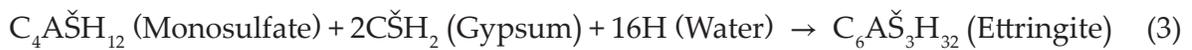
Figure 10. Relationship between compressive and flexural strengths of VS-based cement mortars.

The increase of drying shrinkage with the cement replacement level [99] might be due to: (1) the pozzolanic reaction, generating an additional CSH, resulting in the decrease in spacing of CSH particles; (2) the transportation of large pores into fine pores (pore size refinement) increasing capillary tension [99–103]; (3) the higher water demand of scoria-based cements [99, 102]; (4) the porous microstructure of scoria [104] (**Figure 1d**). However, this increase was lower than the maximum 0.03% allowed by ASTM C618 (**Figure 11**) [99].

Figure 11 shows the results of drying shrinkage of VS-based cement mortars.

5.3. Sulfate attack

The sulfate attack on the cement mortar is a complex process involving the hydration products produced by Portland cement. The damage caused by sulfate attack may involve cracking and expansion of mortar as a whole, as well as softening and disintegration of cement paste [83]. Cements with a high C₃A content will be subject to sulfoaluminate corrosion in which ettringite is formed, as displayed in Eq. (3) [83, 105].



This type of corrosion is initiated by the reaction between sulfate ions and calcium hydroxide (CH):



This reaction can be described as gypsum corrosion. Both reactions are accompanied by an expansion in solid volume causing internal stresses and ultimately lead to cracking [83].

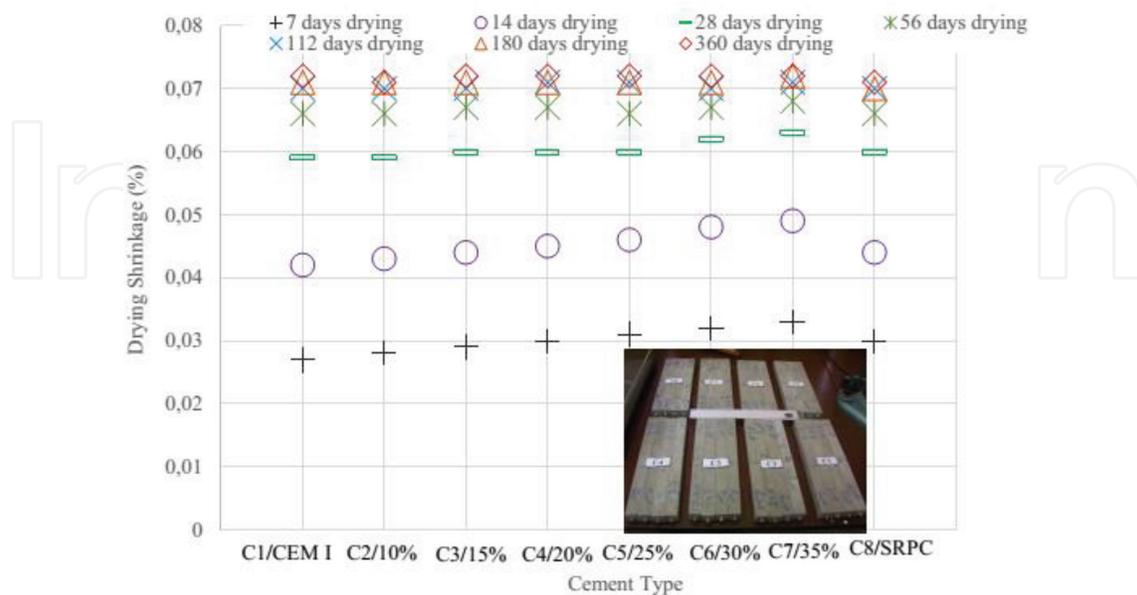


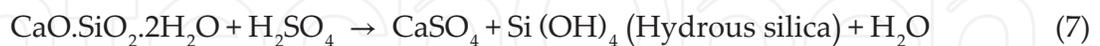
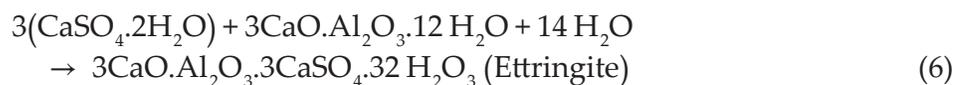
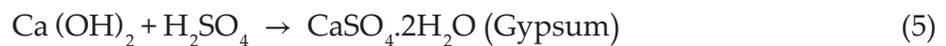
Figure 11. Drying shrinkage values of prismatic mortar specimens [99].

The beneficial effects of using volcanic scoria on the sulfate resistance of mortar as reported by many authors [5], **Figure 12**, may be ascribed to a number of mechanisms [5, 106–108], including:

- reduced permeability,
- dilution of the C_3A phases and CH (both participants in reactions with sulfates) as a result of the partial replacement of Portland cement,
- consumption of CH by pozzolanic reaction and
- alteration of hydrated aluminate phases, making them more resistant, for example, the presence of reactive silica may favor the formation of strätlingite (C-A-S-H).

5.4. Acidic attack

Sulfuric acid, among other aggressive acids such as HCl, HNO_3 and CH_3COOH , is very damaging to mortar as it combines an acid attack and a sulfate attack [109]. At the first stage, deterioration of $Ca(OH)_2$ results in an expansive gypsum formation. The gypsum then reacts with C_3A in the aqueous environment and forms a more expansive product called ettringite. These very expansive compounds cause internal pressure in the mortar, which leads to the formation of cracks [110] and the transformation of the mortar into a mushy or a noncohesive mass [111]. Sulfuric acid may also cause the decalcification of calcium silicate hydrates C-S-H and will ultimately transform the C-S-H into amorphous hydrous silica. The following equations express these reactions [110]:



The white gypsum, which covers the surface of mortar, can potentially lead to the blocking of pores on the surface, leading to a slower rate of attack initially. However, this effect lasts only temporarily [112].

The better performance of VS-based cement mortars in terms of the acid attack, as shown in **Figure 13** [99], can be due to the pozzolanic reaction [5, 113, 114]. This reaction between scoria and calcium hydroxide liberated during the hydration of cement [5, 114] leads to a refinement of the pore structure resulting in a highly impermeable matrix [5, 113]. The pozzolanic reaction also fixes $Ca(OH)_2$, which is usually the most vulnerable product of the hydration of cement insofar as the acid attack is concerned [115]. In the study by al-Swaidani and Aliyan [5],

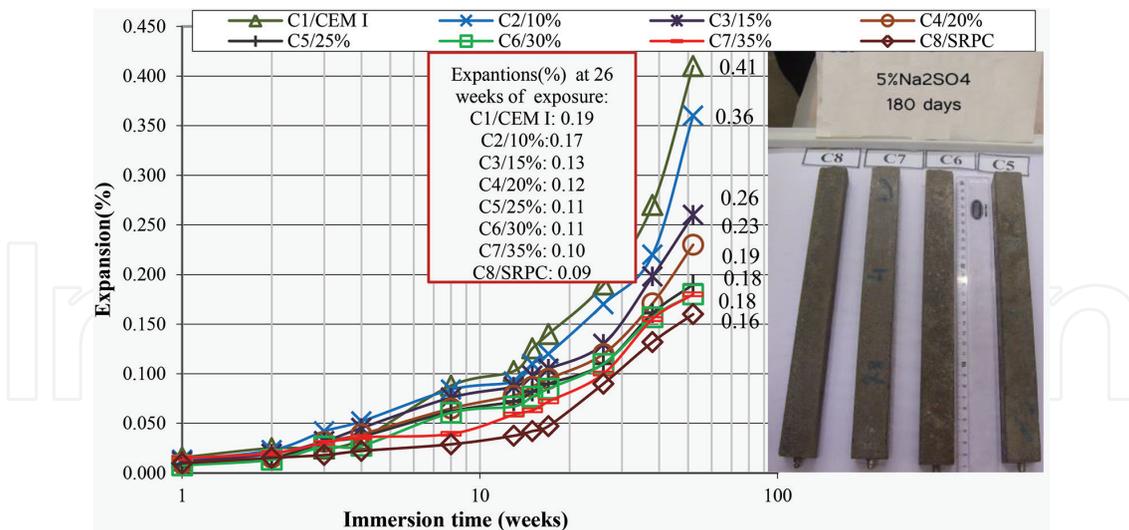


Figure 12. Length changes over time of prismatic mortars immersed in 5% Na₂SO₄ [5].

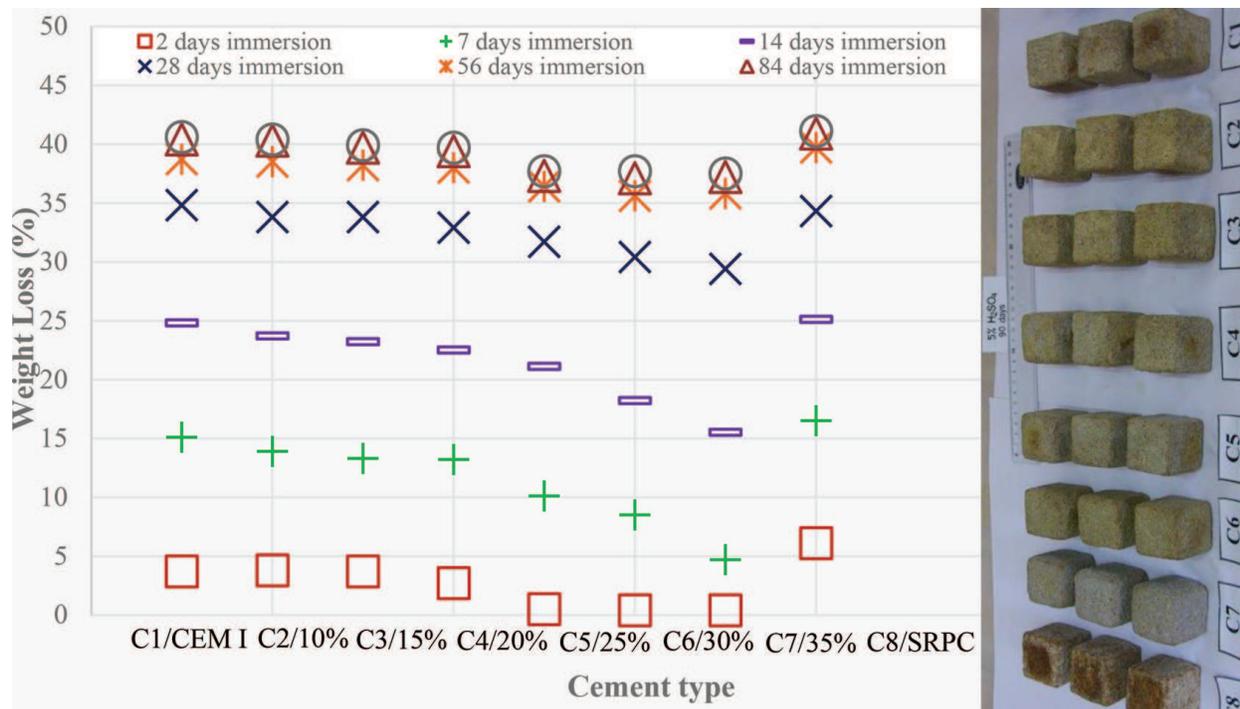


Figure 13. Weight losses over time of 90 days-cured mortars exposed to 5% H₂SO₄ [99].

the number of days needed to register a 10% loss in weight was considered in their evaluation. As shown in **Table 2**, the 10% weight loss was obtained with 35% VS-based cement mortars up to 6.2 and 6.70 days of exposure to sulfuric acid and 4.6 and 5.2 days of exposure to hydrochloric acid at 28 and 90 days curing, respectively. In addition, none of the mixtures containing 25% volcanic scoria and more lost 10% weight even after 100 days of exposure to nitric and acetic acids.

Cement type	Number of days to register 10% weight loss							
	5% H ₂ SO ₄		10% HCl		5% HNO ₃		10% CH ₃ COOH	
	28 days curing	90 days curing	28 days curing	90 days curing	28 days curing	90 days curing	28 days curing	90 days curing
C1/CEMI	3.5	3.5	3.7	3.2	22.5	25.9	NR	NR
C2/10%	3.7	3.7	3.7	3.1	25.4	22.8	NR	NR
C3/15%	3.8	3.8	3.8	3.6	55.5	48.9	NR	NR
C4/20%	4.0	4.1	3.9	3.7	79.1	97.3	NR	NR
C5/25%	4.7	5.1	4.1	4.3	NR	NR	NR	NR
C6/30%	5.2	5.8	4.4	4.9	NR	NR	NR	NR
C7/35%	6.2	6.7	4.6	5.2	NR	NR	NR	NR
C8/SRPC	3.0	3.0	3.2	2.9	20.1	18.8	NR	NR

NR 10% weight loss was not reached.

Table 2. Number of days needed to register a 10% weight loss of mortar cubes [5].

5.5. Permeability

Permeability of concrete to water is closely related to the durability of concrete. Permeability is the rate at which aggressive agents penetrate through concrete [115].

5.5.1. Water permeability

Water penetration depth can be considered as an indication of permeable and impermeable concrete [115]. A depth of less than 50 mm classifies the concrete as impermeable and a depth of less than 30 mm as impermeable under aggressive conditions [115]. The water penetration depth test results for concretes containing VS-based cement concretes show their lower permeability when compared with plain Portland cement, particularly at late ages (**Figure 14**) [98].

5.5.2. Chloride penetrability

Although chloride ions in concrete do not directly cause severe damage to the concrete, they contribute to the corrosion of steel bars embedded in concrete that is considered as the factor causing most premature deterioration of reinforced concrete (RC) structures worldwide, especially in the marine environments. Therefore, the study of chloride penetrability is important for evaluating reinforcing steel corrosion in RC structures. This has prompted the search for economic methods of extending the service life of structures. One of these methods was the use of pozzolan such as volcanic scoria [5].

The improvement in resistance of volcanic scoria-based cement concretes to chloride penetration which was frequently noted in the literature may be related to their refined pore structure and their reduced electrical conductivity [71]. This refinement in pore structure is due to the

secondary-contributing pozzolanic reaction that makes the microstructure of concrete denser [71]. **Figure 15** clearly shows such improvement with the increase of volcanic scoria content and curing age.

Analyzing the results of chloride penetrability gathered from different works [19, 62, 63, 98, 116, 117], an estimation equation with strong correlation ($R^2 \approx 0.86$) can be derived (**Figure 16**). The estimation equation is.

$$RCP = (-0.3 \ln t - 0.68) \times VS + 1.06 \quad (8)$$

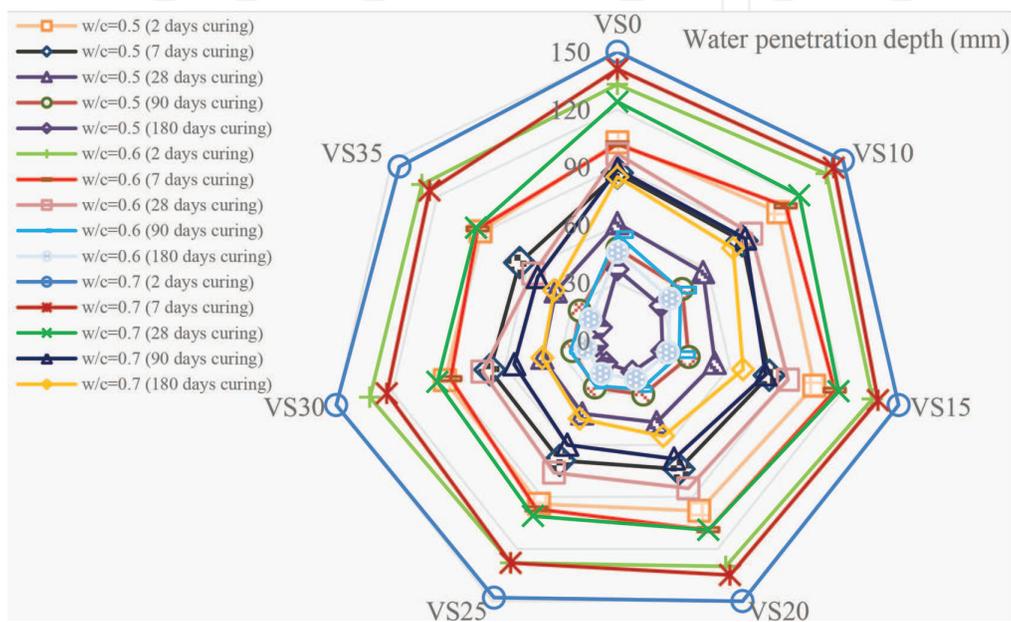


Figure 14. Water penetration depths of VS-based cement concretes prepared with different w/c ratios and cured for different ages [98].

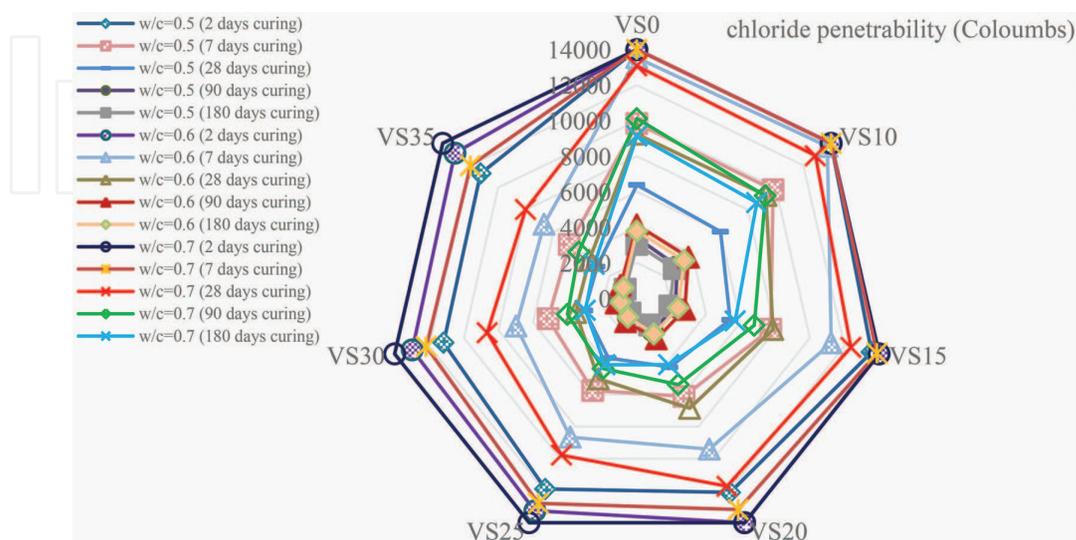


Figure 15. Chloride ion penetrability of VS-based cement concretes as reported by al-Swaidani [98].

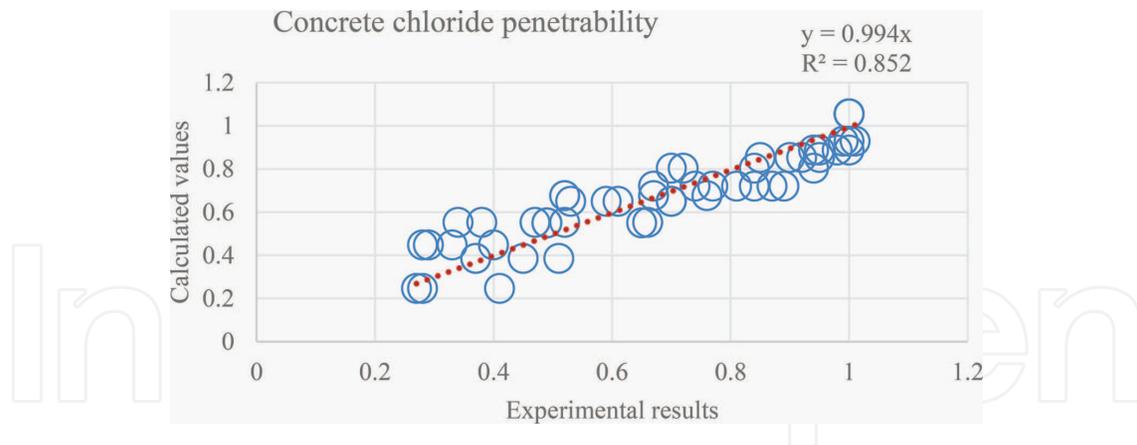


Figure 16. Experimental results versus calculated values of chloride penetrability.

where, RCP is relative chloride penetrability, t is curing age and VS is volcanic scoria content (% by mass). So, the chloride penetrability of VS-based cement concrete can be predicted from knowledge of curing time and volcanic scoria content.

6. Conclusion

- Volcanic scoria has been used in construction since ancient times in pozzolan-lime concrete providing durable structures that survived over 2000 years.
- The SiO_2 content for all sources are within the range of 40–60%; Al_2O_3 and Fe_2O_3 are within the ranges from 10 to 20% and from 5 to 16%, respectively.
- Incorporation of volcanic scoria in concrete has significant effects on the properties of concrete, particularly durability-related properties.
- The chloride permeability of VS-based cement concrete demonstrated better performance as compared to plain concrete, especially at the curing age of 28 days and longer.
- The wide availability of volcanic scoria in many countries, its low cost and the drive toward more sustainable construction have resulted in renewed interest in volcanic scoria as natural pozzolan for concrete. Historically, various types of volcanic scoria were successfully used in dams and aqueducts, where the strength demand is not high but the durability and thermal cracking control are of major concerns.
- Estimation equations for predicting the investigated concrete properties (i.e., compressive strength, water penetration depth and chloride penetration) incorporating the effect of curing time and the replacement level of volcanic scoria were derived. These equations permit the concrete properties of VS-based cement concretes to be predicted with a relatively high degree of accuracy ($R^2 \geq 0.8$).
- Investigating the volcanic scoria cones that have not been yet invested is highly recommended. In addition, making more sustainable and durable concrete using volcanic scoria is highly encouraged.

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