The Effect of Hydrothermal Curing on the Efflorescence of Micro/Nanometric Size Jordanian Aluminosilicate Inorganic Polymers

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Abstract

This study investigates the possibility of reducing the efflorescence (excess or non-reactive salts) effect of inorganic polymers based on aluminosilicate materials from Jordan. This was achieved by minimizing the particle size of the raw materials, and using hydrothermal curing at 80º C, 120º C and 150º C, then comparing the results with other different curing conditions; ambient and humid. Kaolinite (K), volcanic tuff (Vt), and silica sand (Ss) raw materials were used. The raw materials were ground to the average particle sizes (d_{50}) of: <10µm, <200nm, and <100nm. Three different mixing ratios of Vt, K, and Ss were used to study their dissolution behavior and to prepare inorganic polymers. X-ray diffraction (XRD), X-ray fluorescence (XRF), and inductively coupled plasma (ICP) techniques were used to identify the mineralogical and chemical composition of the raw and processed materials. The samples of <10µm were successful to be molded and analyzed for compressive strength. The average compressive strength was about 65 Mpa under hydrothermal condition cured at 150ºC. The samples of nanometric size failed because the material in this range of size behaves and exhibits one or more nanoscale phenomena. Qualitative and quantitative measurements of efflorescence formation were also determined. The average alkali leaching was reduced from 3.14% of ambient cured samples to 0.83% of hydrothermally cured ones. This highest strength result indicates that the alkaline solution has reacted with the majority of Al^{3+} and Si^{4+} of silicates raw material.

1. Introduction

Inorganic polymers technology has been the focus of several studies for two decades and has shown potential to transform the building products industry (Cong and Cheng, 2021; Aliques-Granero et al., 2019; Al-Slaty, 2018; Lahoti et al., 2018; Lemougna et al., 2014; Duxson et al., 2007; Rowels and O'Connor, 2003; Van Jaarsveld et al., 2002; Davidovits, 1994). Some works were carried out by a Geo-Materials Research Project at the University of Jordan, which represents an international scientific collaboration between the University of Jordan, and Vrije Universiteit Brussel, to support the project entitled "Chemical Stabilization of Natural Geomaterials for Construction and Industrial Applications". The goal from this project was to produce low cost construction materials for green housing (Aldabsheh et al., 2015; Esaifan et al., 2015 and 2016; Slaty et. al., 2015; Slaty et al., 2013; Alshaaer, 2013; Rahier et al., 2011a, 2011b; Aldabsheh, 2011; Slaty, 2010). In terms of costs, the inorganic polymers-based building material has similar cost to the replaced material, in addition to their greater environmental benefits. They are characterized by a comparable compressive strength, chemical stability, and hardness. However, during the production of such material, less energy is used and fewer greenhouse gases are released. For example, for every one ton of manufactured cement, one ton of carbon dioxide is produced (Krausmann et al.,

2009; Horvath, 2004; Van Oss and Padovani, 2003; Aïtcin, 2000; Ames et al., 1994). Inorganic polymer technology has the potential to reduce emissions by 80 percent since high-Atemperature calcination is not required (Steveson and Crentsil, 2005). Aluminosilicate could be used as raw materials in the geopolymerization process (Rovnaník, 2010).

Efflorescence refers to the deposition of unreacted chemical additives on specimen surfaces after curing. It is difficult to quantify. Most of the standard methods for estimating efflorescence end up with a qualitative description of its extent on the sample. These unreacted chemicals are transported by water through the voids in partially immersed specimen. The soluble material is transported from the immersed zone to the upper dry zone and precipitates at the specimen's surface after evaporation. Overtime, this process causes degradation of the specimen's structure (Al-Slaty, 2018; Esaifan et al., 2015 and 2016; Slaty et al., 2015; Alshaaer, 2013). Efflorescence indicates an incomplete curing reaction. The present work aims on keeping the water in the reaction mixture as long as possible during the curing process to complete the setting reactions. The production of geopolymeric materials is expected to improve the mechanical and chemical properties of the products.

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2. Materials and Methods

Two reactive Jordanian aluminosilicate materials (kaolinite; K, volcanic tuff; Vt) and filler material (silica sand, Ss) from Jordan were used. Kaolinite belongs to Ordovician-Silurian Hiswa Deposit, 280-300 km south of Amman. A volcanic tuff sample was taken from Pleistocene Harrat Ash-Shaam, Tell Hassan NE-Jordan (between Azraq and Safawi area). The silica sand sample was collected from the Late Cambrian-Early Ordovician Disi Sandstone Formation, Ram Group SW-Jordan (70 km north of Aqaba) (Barjous, 1995; Ala'li, 2001 and 2004).

A sequential X-ray spectrometer Phillips PW2400 housed at Faculty of Earth Sciences, University of Barcelona was used to determine the chemical composition of raw materials. X-ray diffraction (XRD) analysis was used to identify the crystalline phases of the representative portions of the raw material as well as the activated samples by using Bragg-Brentano PANAnalytical X'Pert Diffractometer system (Cu Kα1 radiation, using 45 kV and 40 mA).

Starting raw materials are ground using different ball mills to the average particle sizes (d_{50}) of: <10µm, <200nm, and <100nm. The particle size distribution was measured by Beckman Coulter LS230 Laser Diffraction Particle Size Analyzer and Laser Particle ANALYSETTE 22 Nano Tec plus for micro and nano-sized particles, respectively.

To determine the optimal ratio in terms of the leached Al and Si, the dissolution properties of the dry binder made from three mixed raw materials in different ratios; (100:75:25), (100:50:50) and (100:25:75) of (K:Vt:Ss) were studied. This was accomplished by mixing 5g of starting raw materials with 200 ml of 10M NaOH solution for 168 h. The liquid portion was collected by centrifuging at 10000 rpm for 10 min, and the extent of leaching Al^{3+} and Si^{4+} was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES)

Three raw materials, alkali solution (NaOH) and reaction media (H_2O) were used for the fabrication of the inorganic polymers specimens. Sodium hydroxide (NaOH (98 %)) was used as an alkali activator. Three mixing ratios are used to fabricate inorganic polymers pastes and molds as shown in Table (1). The dimensions of the used mold are 3cm*0.5cm*5cm.

Table 1. Mixing ratios of the prepared inorganic polymers.

Ratio	Kaolin	Volcanic tuff	Silica sand	NaOH	H_2O
R1	100	75	25	16	22
R2	100	50	50	16	22
R3	100	25	75	16	22

Compressive strength and efflorescence formation of inorganic polymer samples were examined after curing under different conditions (ambient, humid, hydrothermal at (80ºC, 120ºC and 150ºC)). Quantitative (extent of alkali leaching) and qualitative measurements were used to describe the efflorescence effect.

Mechanical tests were performed using a universal testing machine tension-compression-fatigue model MTS Bionix 358 (MTS, USA). A 25kN load cell equipped with a PC connection and a software package Test Star II model control. 1mm/sec is used. Most of the standard methods for estimating efflorescence (extent of alkali leaching) end up with a qualitative description of its extent. In this study, a simple "percentage coverage" quantitative method was used to estimate any efflorescence. It was calculated by measuring the weight of empty can before and after drying.

3. Results and Discussion

The chemical and mineralogical composition are illustrated in Table (2). XRF results show that SiO_2 and Al_2O_3 are the main components of kaolinite and volcanic tuff raw materials; SiO_2 content represents s about 51.38% and 45.85% respectively. SiO_2 is the only oxide in the silica sand sample (99.13%). Al_2O_3 content is 25.68 % in kaolinite and is about 14.23% in volcanic tuff.

The X-ray diffractogram of an unreacted sample of representative kaolinite sample confirmed the presence of kaolinite and quartz. The identified minerals in kaolinite sample are the same that obtained by Awwad et al. (2009). Muscovite and hematite are present as traces. The volcanic tuff sample consists essentially of plagioclase and diopside. Forsterite is also detected. The identified minerals in volcanic tuff sample are the same that obtained by Sarireh et al. (2021). The main dominant mineral in the silica sand sample is quartz.

Table 2. Mineralogical and chemical composition of raw material (Aldabsheh et al., 2018) and activated inorganic polymers.

	Identified minerals (using XRD)		Chemical composition (XRF)	
	Raw material	Activated Inorganic polymers	SiO_2%	Al_2O_3%
Kaolinite	Kaolinite, quartz, muscovite, hematite	Thermonatrite, natrite, sodalite, Na-Al-silicate hydrates phases (SAS)	51.38	25.68
Volcanic tuff	Plagioclase, diopside, forsterite		45.85	14.23
Silica sand	Quartz		99.13	-

The particle size distributions of the three raw materials are illustrated in Figure (1a) for d_{50}<10µm and Figure (1b) for d_{50} 100-200 nm.
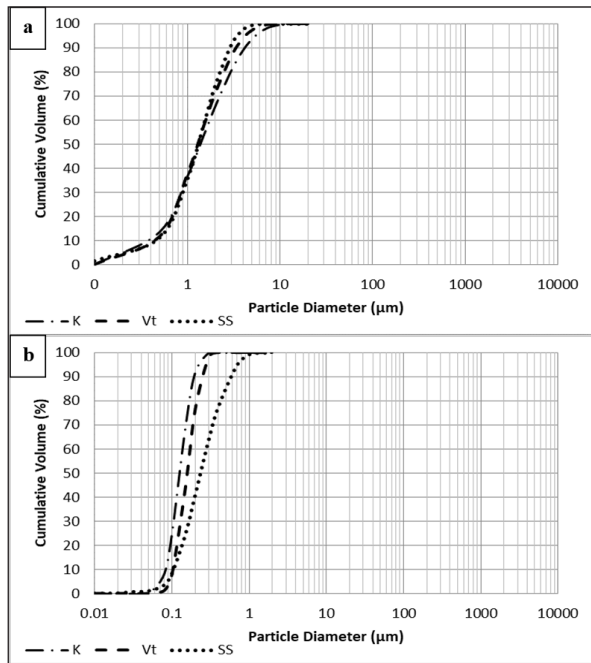
Figure 1. The particle size distributions of kaolinite (K), volcanic tuff (Vt), and silica sand (Ss). a: $d_{50}<10$ µm, b: d_{50}100-200 nm.

Figure (2) shows the leached Al^{3+} and Si^{4+} (w/w %) of treated mixed materials at different ratios with different particle sizes in 10 M NaOH for 168 h. In general, the leaching of Si^{4+} and Al^{3+} has significantly increased when particle size has decreased to less than 100 nm. This is because smaller particle sizes have stronger electrostatic attractive forces and a larger surface area, which can speed up a reaction (Ginebra et al., 2004). This finding consistent with the results obtained from a previous study done by Aldabsheh et. al. (2018) that investigated the dissolution of each raw material alone. As shown in Figures (2a and b), R3 of (100:25:75) of (K:Vt:Ss) is the best mixing ratio in terms of leached Si^{4+} (51.79%) and Al^{4+} (86.28%) for the particle size <100nm
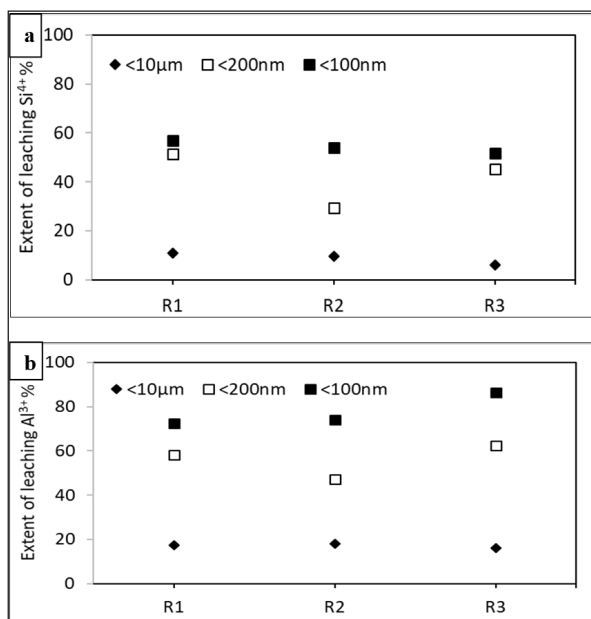

Figure 2. Extent of leached Si^{4+} and Al^{4+} (w/w %) of three-mixed dry binder of raw materials at different ratios. a: Si^{4+}, b: Al^{3+}. R: ratio.

Mineralogical characterization by XRD of solid residues of activated inorganic polymer confirms the formation of new sodium-aluminum-silicate hydrates phases (SAS), thermonatrite, natrite and sodalite because of alkaline activation of the raw materials (Figure 3).
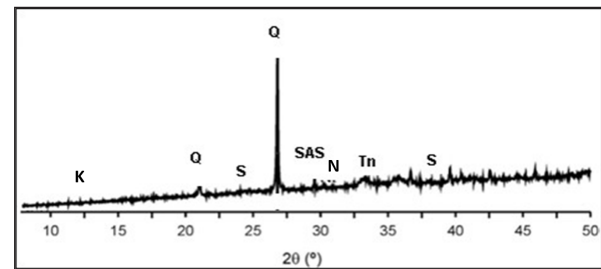

Figure 3. The XRD spectrum of the activated inorganic polymer specimens. (Q: Quartz, K: Kaolinite, S: Sodalite, SAS: Na-Al-silicate hydrate phases, Tn: Thermonatrite, N: Natrite).

The samples less than 10 µm were successful in molding and measuring their mechanical strength and efflorescence. The samples smaller than 200 nm and 100 nm fail because the material behaves and demonstrates one or more nanoscale phenomena/properties in this size range.

The compressive strength values (MPa) of samples ($d_{50}<10$ µm) prepared from the three ratios (R1, R2, and R3), cured at ambient (Figure 4a) and humid conditions (Figure 4b) are plotted vs. extent of alkali leaching (%). The Highest compressive strength (37.0 MPa) under ambient conditions is for samples prepared by using mixing ratio R2 of (100:50:50) of (K:Vt:Ss) (Figure 4b). In addition, these samples have the lowest efflorescence (3.14%), suggesting that the alkaline solution reacted with most the Al^{3+} and Si^{4+} in the samples. A compressive strength of 32 MPa is obtained from a previous study of the same raw material (kaolinite and silica sand) for a mixture cured at 80 °C for 24 h (Slaty et al., 2010). The authors did not use volcanic tuff in preparing the inorganic polymer samples. The particle size of the starting powder raw material had a particle size distribution between 90 and 250µm.

The results plotted in Figure (4b) indicate that under the humid conditions; the samples with highest compressive strength- (26.19 MPa) have the lowest efflorescence (4.59%)
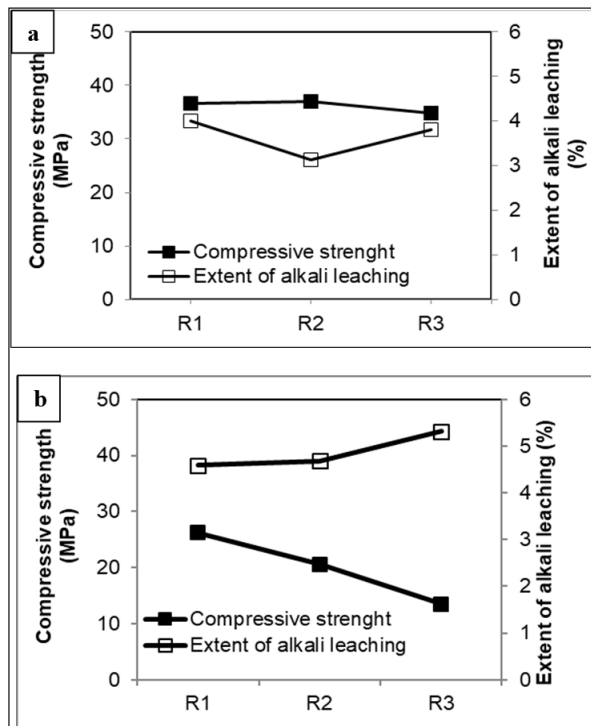
Figure 4. Compressive strength and extent of alkali leaching of samples cured at (a) ambient, (b) humid. R: ratio.

The average compressive strength of samples prepared by using R2 and cured under hydrothermal conditions at 80ºC, 120ºC and 150ºC are 52.1, 59.5, 65.2MPa, respectively are shown in Figure (5). A significant aspect here is keeping the water inside the materials to enable the reaction process to continue. The extent of alkali leaching measurements matches with the compressive strength values. The measurements decrease with the increase of compressive strength values. A low quantity of efflorescent material is observed on the sample surfaces represented by a thin layer of efflorescent material covering an external surface of inorganic polymer specimens (Figure 6). No signs of change in length or weight are noted in the hand specimens and no erosion and cracks are observed (Figure 6).
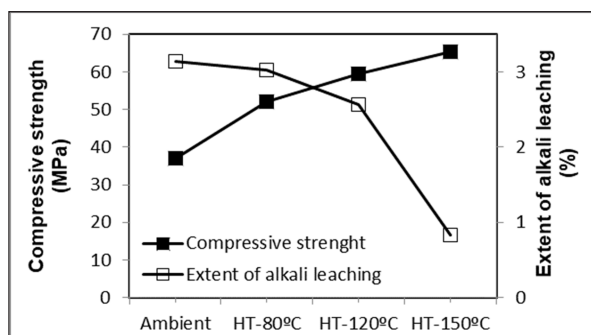

Figure 5. Compressive strength and extent of alkali leaching of samples cured under hydrothermal (HT) conditions at 80°C, 120°C and 150°C.
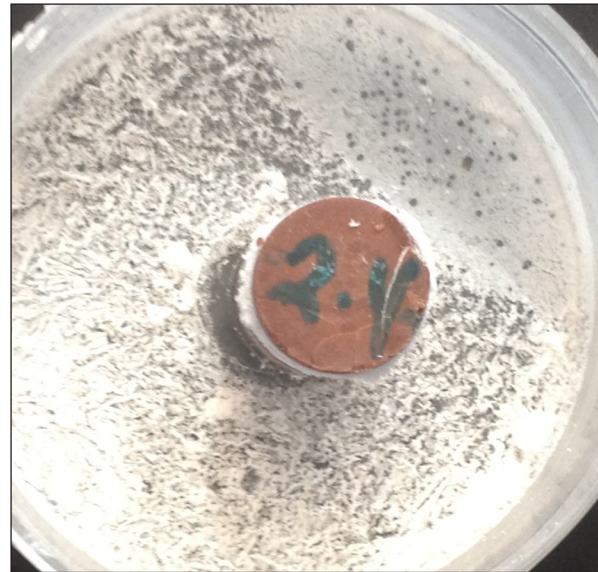

Figure 6. Extent of alkali leaching (efflorescence) observed in the samples.

4. Conclusions

The ability to produce reliable inorganic polymers binder is achieved with enhanced properties by minimizing the particle size, adding a suitable amount of volcanic tuff, or by using different curing conditions to drive the alkaline reaction with more Al^{3+} and Si^{4+} from the aluminosilicate phases. The results also confirm the effectiveness of reducing particle size and using hydrothermal curing on the extent of leaching (efflorescence effect). Samples of nanometric particle size (<200nm, and <100nm) failed to exhibit one or more nanoscale phenomena/property.

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