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Hydration Characteristics And Leaching Behavior of Different Mixes Of Slag Based – Geopolymer Cement In Presence Of Heavy Metals

Doaa A. Ahmed*, Shereen M. Ragai, Sara H. Abdallah

Faculty of Women for Arts, Science and Education Ain Shams University, Asmaa Fahmi St Al Golf, Nasr City, Cairo, 11566, Egypt

Abstract

Geopolymer binders are now considered to be a necessary condition for replacing Portland cement (OPC) to improve environmental and durability efficiency. Heavy metal contamination has become a very dangerous environmental issue that is becoming increasingly over time. The purpose of this work is to examine the effect of some heavy metals on the hydration characteristic of different mixes of slag-based geopolymer pastes containing some waste materials such as fly ash (FA) and cement kiln dust (CKD), and also, to study the stabilization of heavy metals on the geopolymer matrix to measure the possibility of using this method to remove it. Geopolymer synthesis by 100% slag and partial substitution of slag by 15% FA (85% slag+15%FA) and 5% CKD replacement (95% slag+5% CKD) were investigated. The mixture of liquid sodium silicate (Na_2SiO_3) and sodium hydroxide (5M NaOH) with a ratio (1:1) is used as an alkaline activator solution. Various percentages of copper ions (Cu^{2+}) or cadmium ions (Cd^{2+}) are added to the alkali -activated mixes. The results indicated that best mix for immobilization of Cu^{2+} is 100 %slag + 0.5%$CuCl_2$ and for Cd^{2+} were in case of 100% slag + 0.5%$CdCl_2$ and 95% slag + 5% CKD +0.5%$CdCl_2$. . Our study results support the use of different prepared geopolymer pastes in heavy metals solidification /stabilization up to 90 days.

Keywords: Slag,; Fly ash; Geopolymer; immobilization; heavy metal.

1. Introduction

New binders are now accepted as essential to replace Portland cement (OPC) for improved environmental and durability efficiency. The production of OPC is contributing between 5 and 7% of the current anthropogenic CO2 emissions worldwide [1]. The production process of OPC is also energy extensive. As a result, there are many researches on using supplementary cementitious materials. It has gained a lot of attention to protect the environment [2, 3]. Binders have been used also in solidification/stabilization to immobilize heavy metal-contaminated and are an effective technique according to several studies [4- 6].

Alkali activated materials or geopolymers which are materials distinguished by chains or networks of inorganic molecules. These materials are made by polymerizing alkali-activated aluminosilicate raw materials in the presence of a high pH environment. The polymerization reaction involves the formation of three-dimensional polymeric chains by Si-Al minerals to form a ring structure that consists of Si-O-Si bonds [7]. Compared to Portland cement, the resulting products, known as geopolymer cement, have better engineering properties such as compressive strength and resistance to aggressive media [8].

Low carbon dioxide output achieved by adding supplementary cementitious materials, such as fly ash or ground granulated blast-furnace slag which has a significant negative impact on health [9]. Several studies [10-12] have shown that adding fly ash (FA) to the GBFS geopolymer enhances the system's mechanical and microstructure properties. The durability of fly ash-based geopolymer pastes in the marine environment was examined [13]. The results indicated excellent resistance of the geopolymer concrete to chloride attack.

The use of cement kiln dust (CKD) with its high alkali content in the activation of geopolymer

specimens to create nonconventional cementitious binders was investigated. It was observed that CKD could provide the necessary environment to activate geopolymer materials [14]. Several studies [15-17] investigated the effect of the addition of CKD on the properties of slag geoplymer.

Heavy metal contamination has become a very dangerous global environmental issue that is becoming severe over time. Heavy metal bioaccumulation in humans and animals may be caused by high concentrations of heavy metals in soil, water, and air. The immobilization of heavy metals in geopolymers may be due to the participation of heavy metal cations in the balance of the negative charge of Al in the frameworks of unreacted zeolite, kaolin, and geopolymer phases. Immobilization using kaolin-based geopolymers has a lower cost than metakaolin-based geopolymers [18].

Different geopolymers contain metakaolin and blast furnace slag and its geopolymer's solidifying performance toward Cu^{2+}, Pb^{2+} ions were studied [19]. The results revealed that the highest compressive strength and the solidification rate above 98.5%, in the case of 50 % slag content. During the investigation of a series of geopolymeric matrices containing Cu and Pb ions. It was discovered that many factors, such as heavy metal composition and nature, can affect the immobilization behavior of heavy metals [20]. In another study, the effects of Cr(VI), Cd(II), and Pb(II) in the forms of various nitrate and chromate salts on geopolymer structures were investigated. The results stated that the addition of low levels of heavy metal salts has a little effect on the compressive strength of the geopolymeric material [21].

The aim of this study is to investigate a new suitable method to stabilize heavy metals using supplementary cementitious materials or geopolymer binders. Also, study the effect of different heavy metals concentrations in the hydration characteristics of different geopolymer pastes. The solidification/stabilization of copper and cadmium with different geopolymer pastes containing 100% slag, 15% fly ash +85% slag and 5% CKD + 95 % slag were studied. According to our investigation, the alkali-activated materials give a high immobilization efficiency toward copper and cadmium ions (with different concentrations 0.5 and 1 wt). On the other

hand, The addition of heavy metals has a retardation effect on hydration properties of geopolymer pastes. Also the addition of different waste materials such as fly ash and cement kiln dust has different effects on the hydration characteristic and leaching behavior of alkali activated slag. Our findings support the use of geopolymers in heavy metal solidification/stabilization for up to 90 days. Compared to previous studies, we were able to compare the leaching behavior of three different geopolymer pastes towards different heavy metals concentrations at variable hydration time in the same way from studying the effect of this metals on hydration characteristic of geopolymer pastes.

2. Experimental
2.1. Materials:

Ground Granulated blast furnace slag (GGBFS) supplied by the Egyptian iron and steel company, Helwan. Cement kiln by-pass dust (CKD) was provided by El- Nahda Cement Factory, Qena, Egypt. Fly ash (FA) provided from Sika Egypt Company El- Obour, Egypt, for construction chemicals. These materials are the source of silica and alumina that used for the synthesis of geopolymer specimens. The chemical composition of starting raw materials obtained from X-ray fluorescence (XRF) analysis is present in Table (1).

Table1: The chemical composition of starting raw materials (L.O.I= loss on ignition)

Oxides	Slag	Fly ash	Cement klint dust
SiO_2	34.10	63.20	14.16
Al_2O_3	12.40	26.34	3.98
Fe_2O_3	0.77	5.10	3.42
CaO	42.30	2.20	53.87
MgO	6.50	0.10	0.86
SO_3	0.90	0.15	3.68
K_2O	0.35	0.76	6.62
Na_2O	0.26	0.44	3.01
Cl^-	0.08	0	7.43
L.O. I	1.50	2.3	2.80
Total	**99.08**	**100.59**	**99.8**

The NaOH pellets supplied from the EL-Goumhoria chemical company, Cairo, Egypt with a purity of 99%. Liquid sodium silicate (LSS) supplied from silica Egypt Company, Burg Al-Arab, Alexandria, Egypt. As an alkaline activator, a mixture of liquid sodium silicate Na_2SiO_3 and sodium hydroxide NaOH used to make geopolymer cement. The

chemical analysis of sodium silicate liquid is 32.8 wt % SiO_2, 11.7 wt %Na_2O and H_2O 55.5 mass%, and silicate modulus SiO/Na_2O equal 2.8

2.2 Geopolymer synthesis
2.2.1. Preparation of alkaline activator (AA)

The alkaline activator solution was a combination of sodium hydroxide and liquid sodium silicate, which was required for geo-polymerization. The NaOH concentration is 5 M, which is obtained by dissolving NaOH pellets in distilled water and allowing them to cool at room temperature. A fixed proportion of (1:1) liquid sodium silicate and sodium hydroxide solution were mixed until a clear gel was observed.

2.2.2. Preparation of specimens

The mixture proportions of prepared samples were signified in Table (2). Geopolymer pastes were synthesized by mixing raw materials of each mix with the alkaline activator solution until a homogeneous paste was made. Two ratios of $CuCl_2$ and $CdCl_2$ were used: 0.5 and 1.0% by mass of solid. After mixing, the fresh pastes were cast into a cubic mold with a dimension of 25x25x25 mm3. The mold was vibrated to remove the entire air bubbles and then left undisturbed in humidity (100% R.H.). under room temperature for 24 hours. After this period, the cubes are demolded and divided into two sets one of them cured under tap water in a plastic container until the required time of testing 3, 7, 28 and 90, days of curing, and the other was used for leaching measurement in a static mode at the time intervals 28 and 90 days. To determine the leachability, 3 cubes of each mixture have been separately cured in 100 ml distilled water in a sealed plastic bottle. At the end of curing, the leachate solution was used to check the concentration of the leached ions by Atomic Absorption Spectrophotometer (Savant AA-GBC Scientific Equipment, Australia). So, the cubes were removed from their curing condition and confirmed to the compressive strength, combined water content, and total porosity measurements. The hydration reaction was stopped by taking the resulted crushed specimens and stirred with a stopping solution of alcohol/acetone (1:1) to avoid further hydration followed by drying of the crushed specimens for 24 hours at 50°C, then kept for analysis [22].

2.3. Methods of investigation

1.The phase characteristics are investigated by using X-ray diffraction analysis (XRD). The XRD is carried out with a Ni- filtered diffractometer (Empyrean diffractometer, Holland) and Cu-Kα radiation of wavelength □= 1.5418 Ao and pixel detector operating at the following condition; voltage 40 kV and current 40 mA.

2.The Fourier Transform Infrared Spectroscopy (FTIR) measurements are carried out on infrared spectrophotometer (Perkin Elmer-1430 infrared spectrophotometer, USA) using potassium bromide (KBr) pellets, about 2mg of the sample was ground with 20-fold of KBr (dried in an oven before its use) and then pressed in the form of a disc, to test the shifting of functional groups. The wavenumber of infrared spectra was ranging from (400 to 4000 cm-1).

3.Determining the immobilization percent of the different heavy metal's ions in the used hardened geopolymer pastes as follows,

x (grams in 100 ml) =Concentration (ppm)$X10^{-4}$
Original Wt. of metal ion = wt. of cube X percent used of the ions/ 100
Leaching % = (x/original wt. of metal ion) 100
Immobilization = 100 –Leaching %

4.The water for normal consistency is determined according to ASTM C187 [23].

5. The compressive strength of all set pastes is measured. A manual compression testing machine (D550-control type, Milano Italy) with a measuring range of 0 to 55 KN.

6. Chemical combined water content [Wn] is calculated from the relation:

$$Wn\% = [(w1 – w2) / (w2)] \times 100 \quad ---- (1)$$

Where, w1: The weight of the sample before ignition, w2: The weight of the sample after ignition at 900C°.

7. Total porosity tests are carried out by determining the weight of samples of hardened pastes suspended in water, W2, and those in air, W1 and then dried at 100o C for about 24 hours and weight in the air, W3. The total porosity percentage of (P %) calculated according to the following equation [24]:

$$P \% = [(W1-W3)/ (W1-W2)] \times 100, \quad ------- (2$$

Table 2: Description and composition of the various mixtures.

Mix Abb.	GGBFS	FA	CKD	Metal% Cu+2	Metal% Cd+2	W/S Ratio (%)
S	100 %	----	----	----	----	22.00
S1	100 %	----	----	0.5%	---	24.00
S2	100 %	-----	----	1%	---	32.50
S3	100%	----	----	----	0.5%	23.75
S4	100%		----	----	1%	25.00
SF	85 %	15 %	----	----	---	22.60
SF1	85%	15 %	----	0.5 %	----	30.00
SF2	85%	15 %	----	1 %	-----	31.25
SF3	85%	15%	----	----	0.5%	25.00
SF4	85%	15%	----	----	1%	28.70
SC	95%	---	5%	----		23.75
SC1	95%	---	5%	0.5%		25.00
SC2	95%	---	5%	1%		27.00
SC3	95%	---	5%	----	0.5%	27.00
SC4	95%	---	5%	----	1%	30.00

Table(3): Compressive strength of activated slag pastes ,activated slag /Fly ash and slag/CKD pastes containing various ratios of copper and cadmium chloride at different hydration ages.

Mixes / Curing time (Days)	Compressive strength (kg/cm^2) in case of CuCl$_2$								
	S	**S1**	**S2**	**SF**	**SF1**	**SF2**	**SC**	**SC1**	**SC2**
3	353	236	176	385	266	222	311	176	166
7	441	365	270	500	390	311	399	299	266
28	711	695	666	800	755	703	660	530	440
90	883	839	735	972	880	790	795	670	580

Compressive strength (kg/cm^2) in case of CdCl$_2$						
Time (days)	**S3**	**S4**	**SF3**	**SF4**	**SC3**	**SC4**
3	235	182	309	280	298	178
7	365	230	397	360	356	321
28	700	680	760	710	628	540
90	842	740	890	810	720	618

Table (4): Total porosity of activated slag pastes, activated slag /Fly ash and slag/CKD pastes containing various ratios of copper and cadmium chloride at different hydration ages

Mixes / Curing time (days)	Combined water content % in case of CuCl$_2$								
	S	S1	S2	SF	SF1	SF2	SC	SC1	SC2
3	6.50	6.00	5.30	6.72	6.25	6.12	6.40	6.00	5.70
7	8.10	7.40	7.00	9.50	8.22	7.67	8.60	8.00	7.00
28	10.50	9.76	8.66	11.58	10.00	9.70	11.28	9.20	8.50
90	12.50	11.20	10.88	12.73	11.40	11.01	12.30	10.85	10.07
Combined water content % in case of CdCl$_2$									
Time (days)	S3		S4		SF3		SF4	SC3	SC4
3	6.10		5.37		6.35		6.25	6.10	5.90
7	7.50		7.10		8.50		7.70	7.80	7.36
28	9.42		8.70		10.32		9.83	10.01	8.60
90	11.4		11.15		11.50		11.30	10.95	10.20

Table (5): Combined water of activated slag pastes, activated slag /Fly pastes, and slag/CKD containing various ratios of copper and cadmium chloride at different hydration ages.

Mixes / Curing time (days)	Total Porosity% in case of CuCl$_2$								
	S	S1	S2	SF	SF1	SF2	SC	SC1	SC2
3	29.70	30.52	31.34	29.65	30.42	30.98	31.05	32.60	32.79
7	27.01	29.40	30.00	26.86	27.90	29.70	29.18	30.00	31.34
28	24.50	25.70	26.80	23.00	24.3	25.00	26.45	27.70	28.80
90	20.00	23.35	24.47	19.80	23.40	23.96	22.86	23.92	24.52
Total Porosity% in case of CdCl$_2$									
Time (days)	S3		S4		SF3		SF4	SC3	SC4
3	30.40		31.45		30.10		30.21	31.80	32.50
7	28.70		31.10		27.80		29.44	29.93	31.17
28	25.50		26.70		24.20		24.95	27.20	28.18
90	23.85		24.32		21.72		23.50	23.53	24.10

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Table (6): Leaching percent of different geopolymer mixes containing various ratios of Copper and Cadmium chloride (0.5% and 1%) at different hydration ages (28 and 90 days).

Mixes	Time (days)	0.5% Cu^{2+}			Mixes	1% Cu^{2+}		
		Leaching percent %	Leaching mg/l	Immobilization%		Leaching percent %	Leaching mg/l	Immobilization%
S1	28	0.1	0.0055	99.994	S2	0.43	0.012	99.988
	90	0.14	0.0076	99.992		0.65	0.0187	99.981
SF1	28	0.26	0.0150	99.985	SF2	0.45	0.0123	99.986
	90	0.30	0.0171	99.982		0.45	0.0123	99.986
SC1	28	0.19	0.0109	99.989	SC2	1.24	0.037	99.963
	90	0.39	0.0215	99.978		1.60	0.0449	99.955
		0.5% Cd^{2+}				1% Cd^{2+}		
S3	28	0.01	0.00058	99.999	S4	1.60	0.0458	99.954
	90	0.02	0.0011	99.998		2.50	0.0697	99.930
SF3	28	0.05	0.0027	99.997	SF4	0.10	0.00278	99.997
	90	0.24	0.0138	99.986		0.34	0.00893	99.991
SC3	28	0.01	0.00054	99.999	SC4	0.12	0.00336	99.996
	90	0.02	0.0011	99.998		0.20	0.0057	99.994

3. Result and discussion:

3.1. Compressive strength:

The compressive strength values of the hardened activated slag pastes in the absence and presence of two different percentages (0.5 and 1% by weight) of each copper and cadmium ion (S, S1, S2, S3 and S4) are listed in Table (3). Results of the compressive strength demonstrated a continual increase with increasing hydration ages up to 90 days. This is attributed to the higher rate of hydration as well as the formation of more hydration products such as sodium and calcium aluminum silicate hydrate. It can be noticed that the presence of Cu^{2+} and Cd^{2+}ions reduces the values of compressive strength. This reduction in the values of compressive strength can be attributed to the retarding effect of both ions. An additional increase in copper and cadmium ions concentrations has resulted in an evident strength drop of hardened pastes signifying heavy metals have a retardation effect on the activation process [19].

According to Table.(3), we can notice that with the addition of fly ash to hardened activated slag (SF), the compressive strength rises with hydration time up to 90 days due to the higher rate of hydration as well as the formation of more hydration products. The addition of heavy metals (SF1, SF2, SF3 and SF4) will result in an evident strength reduction of hydrated pastes, indicating the retardation effect of heavy metals ions. While the proportion of Cu^{2+} or Cd^{2+} rises, a reduction in compressive strength values can be detected. Heavy metal ions inhibited the growth of the network of silicon aluminum skeletons and reduced the gel structure of the system. This could be the principal cause of the decrease in compressive strength [20].

By the addition of cement kiln dust to activated slag (SC, SC1 and SC2), as the ratio of Cu^{2+} ions increases, the retardation effect increases. From Table (3) we can also notice that the values of compressive strength in the presence of Cd^{2+} ions (SC 3 and SC4)

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is lowering than those in absence of Cd^{2+} (SC) at all hydration ages. This may be attributed to the reaction between heavy metal ions and hydroxide ion, and formation of hydroxyl complex ion during geopolymerizations process [25]. . *Wang et al. (2018)* [19] suggested that the formation of hydroxyl complex leads to the decrease of alkalinity and increase of viscosity of the system. Heavy metal complex ions formed can also interfere with the condensation reaction of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons, thus hindering the growth of silicon and aluminum network skeletons and reducing the gel structure of the system, resulting in a decrease in the compressive strength of geopolymer.

3.2. Total porosity (P %) :

The total porosity of hardened activated slag, slag/ fly ash, and slag/CKD specimens containing different ratios of copper and cadmium chloride 0, 0.5, and 1% are listed in Table (4). It can be noticed that the total porosity decreases with hydration ages up to 90 days for all specimens. This may be attributed to the continual activation and creation of hydration products that precipitated in some of the open pores. For slag pastes that contain different concentration of copper and cadmium ions (S1, S2, S3, and S4), we can notice that by increasing the concentration of heavy metals the porosity increases. These are attributed to the retardation effect of the metal ions toward geopolymer hydration and these ions precipitated as insoluble hydroxide salt causes pores in the hydration product network.

The addition of fly ash or CKD to slag pastes in the absence and presence of Cu^{2+} or Cd^{2+} ions were affected on the values of total porosity, according to Table (4). As we notice, the addition of FA to the activated slag geopolymer (SF, SF1, SF2, SF3 and SF4) decrease the values of total porosity for all systems. But the addition of CKD to the geopolymer pastes increased the total porosity values. From Table (4), it was observed that the retardation effect of metal ions on the hydration of geopolymer pastes, may be attributed to the precipitate of heavy metal ions as insoluble hydroxide forms which cause pores in the hydration materials and increase the porosity of geopolymer matrix.

3.3. Combined water content (Wn %) :

Chemically combined water contents of the activated slag, 85%alkali activated slag +15% Fly ash, and 95% slag+5%CKD containing different Cu^{+2}

or Cd^{+2} concentrations of 0, 0.5 and 1 wt % are reported in Table (5). It was found that the chemical combined water contents Wn % increased for all mixes with hydration time. The increase in (%Wn) with hydration age is attributed to the progress of hydration of hardened activated slag [26]. The main hydration products are calcium silicate hydrate (CSH) and calcium aluminum silicate hydrate (CASH).

The addition of copper and cadmium ions marks a decrease in the values of combined water content Wn%, reflecting the retarded effect of heavy metals on the rate of hydration product formation [27]. As the ratio of Cu^{2+} or Cd^{2+} ions increase the values of Wn % decrease which confirmed the retardation effect of heavy metal on the activation process. This may be due to the reaction of heavy metal with silicate and hydroxyl groups in the $NaOH/Na_2SiO_3$ activator which preventing the alkali-silica reaction and hinders the formation of hydration product [28].

3.4. Leaching percent % :

The results of the leaching percent of activated slag, slag/fly ash, and slag/CKD including 0.5 and 1 % $CuCl_2$ are shown in Table (6). The degree of immobilization of copper ions in alkali hardened pastes is thought very highly. This indicates the high efficiency of alkali-activated aluminosilicate materials in the immobilization of copper ions, converting hazardous slag to user-and environmentally friendly building materials. This can be caused by the low solubility product of its hydroxide besides the high ability of adsorption of these impurities on the surface of hydration products of the geopolymer, mainly CSH and CASH phases [29]. Hardened activated slag mixes demonstrated copper ions concentration (mg/l) in leachate below the limit of toxicity (1 mg/l). The leaching results of alkali-activated slag containing 0.5

and 1% cadmium ions (S3 and S4) are reported in Table (6). The results showed that the cadmium ions concentration (mg/l) in leachate is slightly high than the limit of toxicity (0.01 mg/l) according to the Egyptian Environmental law1994 [30]. On the other hand, the lower Cd^{2+} ions concentration (mg/l) in leachate compared to the initial concentrations of 1% Cd^{2+} (10000mg/l) demonstrates the high efficiency of alkali-activated aluminosilicate materials toward the heavy metal immobilization.

The effect of the addition of 15% FA to alkali-activated slag on the values of leaching percent of both metal ions (SF1, SF2, SF3, and SF4) was shown

in Table (6). It can be noticed that all the examined FA-alkali activated pastes demonstrated very low values of leached percent of copper and cadmium ions which show a high degree of immobilization toward both ions up to 90 days. The activation process producing

hydration products that could stabilize and solidify heavy metals [28].

According to Table (6) alkali activated (5% CKD/ slag) mixes show also a higher degree of immobilization of Cu^{2+} and Cd^{2+} ions in hardened pastes up to 90 days. This can be attributed to the low solubility product of heavy metals hydroxide as well as the high ability of the adsorption of copper and cadmium ions on the surface of hydration products [29]. As we noticed that, most alkali-activated geopolymer pastes (Slag, 15% FA/ Slag, 5%CKD /Slag) showed a higher degree of immobilization for Cd^{2+} compare to Cu^{2+} ions. The leached cadmium ion range in ppm is from (0.01-0.20) mg/l. This can relate to as the ionic radius increases the efficiency of stabilization and immobilization of heavy metals increased too (ionic radius in pm 109 Cd^{2+} > 87 Cu^{2+}) [31]. The highest value of the degree of immobilization showed for mix SC3 after 90 days (99.998%). The mechanisms of immobilization of different heavy metals in geopolymer matrices could be physical encapsulation or chemical bonding or it is a combination of the two mechanisms [29]

3.6. The XRD analysis:

The X-ray diffraction (XRD) patterns of $NaOH/Na_2SiO_3$ activated slag containing 0, 0.5, and 1 wt % of Cu^{2+} and Cd^{2+} ions at different hydration ages (28 and 90 days) are shown in Fig (1). The XRD patterns of specimens of pastes suggest the presence of a major phase of calcium silicate hydrates and sodium/calcium aluminosilicate gel which increased the compressive power, the peak appears at 2Θ =25-35 [32]. It was found that the calcite phase overlaps with CSH as a hydration product. The formation of calcite is induced by the interaction between (OH⁻) for alkaline activator and Ca^{2+} for the source material of specimen to create calcium hydroxide $Ca(OH)_2$ which later reacts with CO_2 in the atmosphere. Pastes sintering (denser microstructure) was noted in the creation of a good resolved crystalline peak attached to Gehlenite ($Ca_2Al_2SiO_7$) [d- values = 3.066, 2.84, 2.74,1.91,1.81,1.76],Zoisite Ca₂Al₃(SiO₄)(Si₂O₇)O(OH) [d values = 2.693, 2.874, 4.03, 8.09, 2.019, 1.601,

5.01], and wollastonite ($CaSiO_3$). These phases are dehydrated types of strength-giving phases like calcium silicate hydrate (CSH) and calcium aluminum silicate hydrate (CASH).
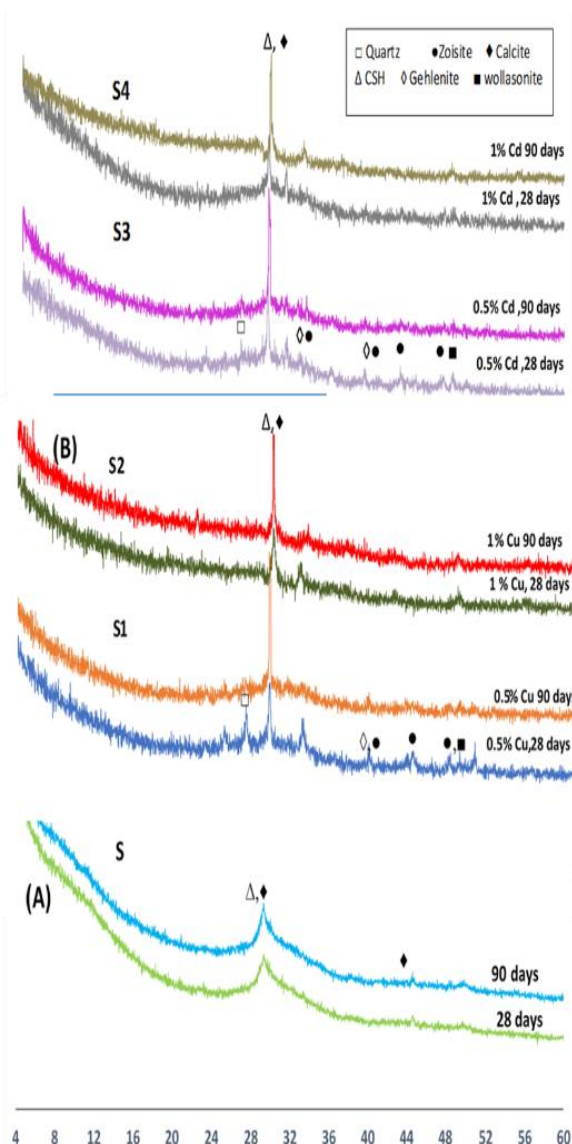

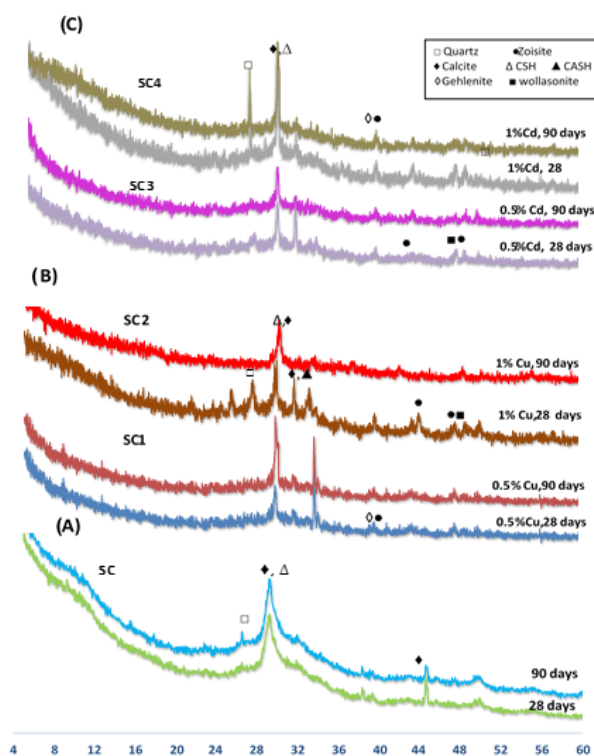**Fig. (1):** X.R.D of A) hardened activated slag (S), B) hardened activated slag containing 0.5and 1% CuCl2 (S1,S2), C) hardened activated slag containing 0.5 and 1% CdCl2 (S3, S4) at different hydration ages.

According to Figures (2 and 3), the addition of FA or CKD to slag in the absence and presence of the two heavy metals with two concentrations is un affected on the type of hydration products formed.

According to Figure (3), the crystalline peaks of Quartz (d= 3.34 A^o) that were observed are attributed to the unreacted silica from raw materials and mullite ($2Al_2O_3SiO_2$) peak attached for fly ash. Also, it was increasing in the intensity of hydration products characteristic peaks by the addition of CKD to slag-geopolymer systems (Figure 3-a). This can be attributed to that the high alkaline content of CKD serves as an effective accelerator which increases the dissolution of blast furnace slag particles and subsequently the binder phase formation. From the XRD patterns, there is a decrease in the intensity of the characteristic peaks of CSH with an increase in the amount of copper and cadmium ions added for all pastes. This can be attributed to the interaction of heavy metals with geopolymer matrix which has a negative impact on its hydration reaction.

Fig. (2): X.R.D of A) hardened activated FA/slag (SF), B) hardened activated FA/slag containing 0.5and 1% CuCl2 (SF1, SF2), C) hardened activated FA/slag containing 0.5 and 1% CdCl2 (SF3, SF4) , at different hydration ages

3.7. Fourier transform infrared spectroscopy (FTIR)

The FTIR of geopolymer specimen containing alkali-activated slag, slag /Fly ash, and slag/CKD in the absence and presence of two ratios 0.5 and 1% of

CuCl$_2$ and CdCl$_2$ after 90 days of hydration are shown in Figures 4 and 5. The spectrum shows that the absorption band related to stretching vibration mode of the O-H group at (3449-3460) cm-1 and bending vibration mode of H-O-H at 1641-1649 cm-1 appeared. The band at 1450 and 875 cm-1 is due to
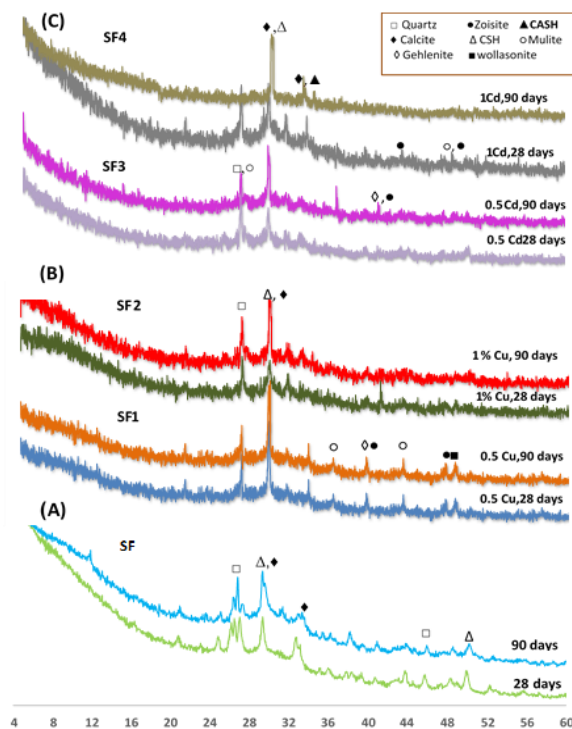

Fig. (3): X.R.D of A) hardened activated CKD/slag (SC), B) hardened activated CKD/slag containing 0.5and 1% CuCl2 (SC1, SC2), C) hardened activated CKD/slag containing 0.5 and 1% CdCl2 (SC3, SC4), at different hydration age

the carbonation process, namely stretching vibration of C-O bond in CO$_3$ groups. We can notice also, the asymmetric stretching vibration band of Si-O-T (Si or Al), at 1011 cm-1 is shifted around 1000 cm-1 for geopolymer mixes. This change can result from the geopolymerization process and formation of aluminosilicates gels CSH and CASH in a geopolymer [33]. The shift toward the low wavenumber may be attributed to the partial replacement of SiO_4 tetrahedron by AlO_4^- tetrahedron, resulting in a change in the local chemical environment of the Si-O bond. This agreement with the lower in shift band at about 712-711 cm-1 and 673-647 cm-1 which related to the symmetric stretching vibration of Si-O-Si and Si-O-Al and bending vibration mode of Si-O-Si at about 449-451 cm-1 related to Quartz. In the presence of heavy metals, the main band at 1000 cm-1 shifted to

a lower wavenumber. It is more likely that it was related to the increase in the non-bridging oxygen. This might have been related to the formation of a connection between geopolymeric frameworks (cross-linking) by heavy metals cations. Also, the change observed in the range 710-650 related to pseudo lattice vibration (of over tetrahedral fragment of structure), ion-exchange of Na+ cation by heavy metals cation [33]. The results of FTIR demonstrated that the immobilization of copper and cadmium ions in geopolymer matrices could be through formation of chemical bonding between them.
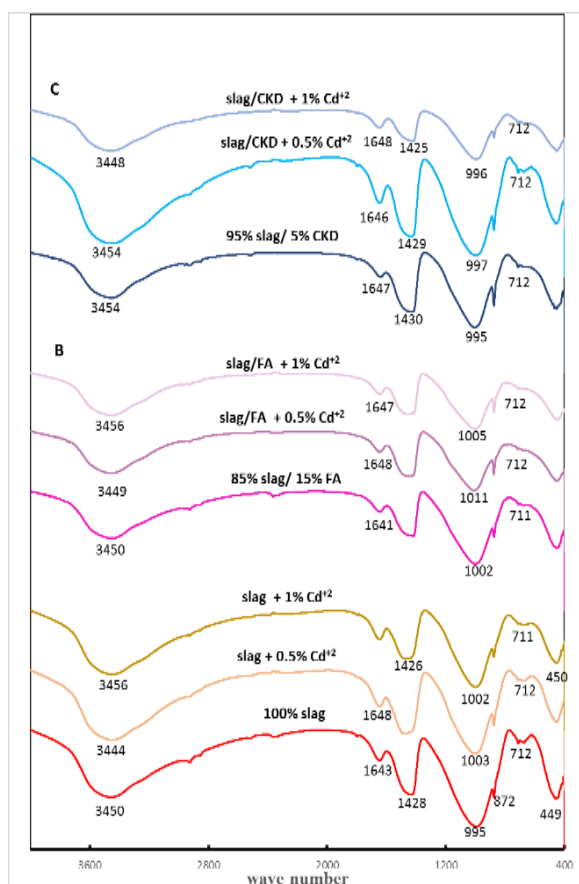
Fig. (4): IR spectra of mixes containing a) slag, b) slag/FA , c) slag/CKD in absence and presence of different concentration of copper chloride after 90 days of hydration
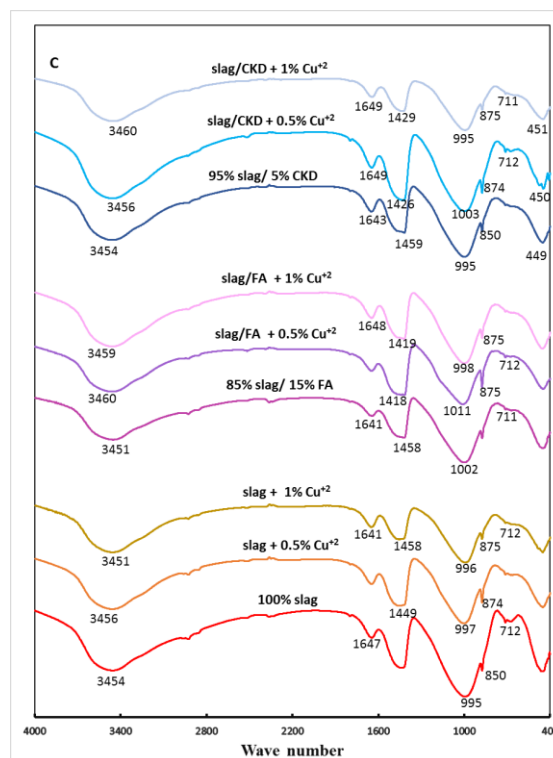

Fig. (5): IR spectra of mixes containing a) slag, b) slag/FA , c) slag/CKD in absence and presence of different concentration of cadmium chloride after 90 days of hydration.

4. Conclusions

The main examination that could be concluded from this paper can be summarized as follow:

- The used heavy metal salts caused a retarding effect for the hydration of the investigated geopolymer mixes, and this retardation increase by increase heavy metal concentration.
- The presence of fly ash for all mixes improved their hydration character but unaffected on leaching behavior. On the other hand an improvement in leaching of cadmium ions by geopolymer mixes has been observed by addition of 5% CKD.
- All alkali-activated mixes demonstrated copper ion concentration (mg/l) in leachate below the limit of toxicity (1 mg/l) while cadmium ions concentration (0.01 – 2.5 mg/l) in leachate slightly higher than the limit of toxicity (0.01 mg/l) according to the Egyptian Environmental law1994. On the other hand, the concentration of cadmium ions still very low (0.01 -2.5 mg/l) compared to the initial concentration (10000 mg/l).
- The best mixes for immobilization of heavy metals were S3 (100 % slag +0.5%CdCl$_2$) and

SC3(95%slag +5%CKD+0.5% Cd^{2+}) and the degree of immobilization is 99.998%.

- The leaching test results prove the high efficiency of alkali-activated aluminosilicate materials in heavy metal immobilization, resulting in the conversion of dangerous slag into user- and environmentally safe building material
- The XRD and FTIR analysis support that the chemical combination is the type of stabilization of copper and cadmium ions with geopolymer matrix.
- From all pervious results the copper and cadmium ions might be taken into the geopolymer network and possibly bound into the structure for charge balancing roles.

5. Conflict of Interest

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