

The Effect of Chromium on the Chemical and Physical Properties of Industrial Sludge Based Geopolymer



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ABSTRACT

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This paper investigates the immobilization of chromium in the industrial sludge-based geopolymer. Mechanical, physical and microstructure properties were used to characterize different samples. The results show that lower heavy metals addition has less effect on the compressive strength. However, excessive addition of Cr(VI) (1.5 and 3%) causes a deterioration of geopolymer matrix with a significant drop of the compressive strength. The compressive strength shows that the use of sodium hydroxide as an alkaline activator is not suitable for chromium immobilization. The use of 1.5 and 3% amount of chromium increases the conductivity of leachates, which explains a change in the microstructure of materials. This is in agreement with the results of compressive strength. XRD patterns of all samples show an amorphous structure with less effect of chromium on the crystalline phases. SEM of the reference sample demonstrates a dense structure of binder. However, the porosity of the matrix increases with the addition of 3% Cr(VI).

1. INTRODUCTION

The geopolymers was first developed by Davidovits in 1970 [1]. The term geopolymer divided into two elements: "Geo" indicate the stability of these materials at high temperature and the term "polymer" exhibit the polymerized structure of these materials. Geopolymer is an inorganic material with amorphous three-dimensional Si-O-Al structure. It produced by the reaction of solid precursors with alkaline solutions at low temperatures, generally under 100°C [2]. The most common solid precursors used are fly ash, ground granulated blast furnace slag, kaolin, and metakaolin produced from thermal treatment (500-800°C) of koalin. The most used alkaline solutions are mixtures of NaOH, KOH, Na₂SiO₃ and K₂SiO₃ [3].

According to the International Agency for Research on Cancer, the chromium is classifying as one of the most hazardous heavy metals [4]. It is generated in several industrial processes like textile dyes, wood preservation, anti-corrosion products. Chromium hexavalent is the most dangerous type of chromium due to its carcinogen substance [5]. Thus, represents a real threat to the environment [6-8].

Therefore, the removal of chromium is one of the major challenges. One of the most appropriate methods is Immobilization in binders, which is considered as an effective method that involves both physical adsorption or encapsulation and chemical bonding of the hazardous waste into cement materials, allows its conversion into stable materials [9, 10].

Physical and chemical properties represent important factors in the immobilization process. Much research has been done on these parameters. Muhammed et al revealed that

addition of 0.3% Cr(VI) increases the strength of composite geopolymer based on Ground Granulated Blast Furnace Slag (GGBFS) and Fly Ash (FA) compared to 0.1% and 0.5% [11]. In addition, Al-Mashqbeh et al confirmed that addition of 1% Cr(VI) decreases greatly the compressive strength of metakaolin-based geopolymer from 13.3 to 7.71 MPa [12]. Chen et al indicated that the presence of 0.1% Cr(VI) had less effect on the strength of metakaolin-based geopolymer [13]. Nevertheless, Violeta Nikolić et al show that 0.5 and 1.0% concentrations of Cr(VI) had a minor effect on the compressive strength of fly ash-based geopolymer (changes up to 5%), while the addition of 2% of Cr decreases significantly the strength (5-14%) [14]. On the other hand, several works studied the mineralogical structure of geopolymer contaminated by heavy metals. Chen et al. [13], Huang [15] and Guo et al. [16], reported that XRD patterns of the geopolymer samples contaminated by chromium are almost identical with that of samples without metal. However, many searches indicate that adding of chromium causes the appearance of new crystalline phases. Paloma and Palacios [17], and Al-Mashqbeh et al. [12] reported that addition of chromium encouraged the formation of Na₂CrO₄. Moreover, Song et al. [18], and Sun et al. [19] suggested that the chromium will be in oxide form and appears in the crystalline phases of geopolymer as calcium chromate form (CaCrO₄).

The present study deals with an industrial sludge based-geopolymer. It is a solid waste generated by the treatment of wastewater from a sanitary ceramic products industry.

Accordingly, the purpose of this work is firstly to examine the influence of chromium on the mechanical properties, microstructure and phase composition of industrial sludge based-geopolymer, and then evaluate the use of industrial

sludge-based geopolymer as an eco-friendly material alternative of cement in the stabilization/solidification of the chromium. Compressive tests were performed on samples with different amount of Cr(VI). The conductivity test was conducted to reveal the blending behaviors of all samples with and without Cr(VI). The mineralogical and morphological structures were analyzed by X-ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS).

2. MATERIAL AND METHODS

2.1 Materials

The industrial sludge was collected from a ceramics activity. The major Chemical composition percentages of the used industrial sludge is illustrated in Table 1. The industrial sludge was calcined at 800°C for 2h. Sodium hydroxide pellets (98%). Sodium silicate, (12.85 wt% Na₂O, 32.12 wt% SiO₂ and 65 wt% H₂O, initial modulus (m(SiO₂)/ m(Na₂O)) is 2.5). Potassium Dichromate (K₂Cr₂O₇) was used as source slats for Chromium metal ions (CrVI).

Table 1. Chemical composition of industrial sludge determined by X-ray fluorescence

Oxides	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O
%	57.4	26.3	2.42	1.68	1.29
Oxides	ZrO ₂	MgO	Fe ₂ O ₃	ZnO	TiO ₂
%	0.823	0.459	0.449	0.349	0.301

2.2 Synthesis of geopolymers

Two types of sequences samples were prepared. The first one based only on sodium hydroxide as an alkaline activator (GN). The second one, was prepared from mixed NaOH

pellets dissolved in deionised water to obtain 12M and water glass solution with ratio mass 1.2 [20]. Different concentrations of chromium salt were dissolved in an appropriate amount of deionized water and mixed with the Industrial sludge. The prepared products and the alkaline solutions were mixed all together in the mechanical mixer for 10 minutes to form the geopolymer pastes. The content of heavy metal added (0.1, 0.3, 1.5, or 3% ion per mass of industrial sludge). The resulted pastes were casted and compacted into cylindrical polyethylene molds (20mm width and 40mm height), and cured at 50°C for 21h, then demoulded and sealed in plastic bags for 7 days.

The mix proportions of geopolymer samples with different chromium concentrations are listed in Table 2. The procedure of samples preparation is illustrated in Figure 1. The result geopolymers are shown in Figure 2.

2.3 Compressive strength

Compressive strength tests were performed at 7 days. Compressive strength was corresponding to the average value of three samples.

2.4 Conductivity

After 24h of aging, the conductivity test was carried out by immersing the samples in 150ml of deionized water.

2.5 Characterization

DRX analysis was used to determine the mineral properties of the geopolymer samples.

Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) were utilized to study the microstructure of the samples and the percentage of elements, respectively.

Table 2. The mix proportions used for the preparation of geopolymer samples

Mix	Reagent	Heavy metal ion (wt/%)	Concentration of NaOH (M)	S/L ratio	Na ₂ SiO ₃ /NaOH Mass ratio	Curing temperature (°C)	Time (h)
GI	-	-	12	1.7	1.2	50	21
GI-0,1Cr	K ₂ CrO ₇	0.1	12	1.7	1.2	50	21
GI-0,3Cr	K ₂ CrO ₇	0.3	12	1.7	1.2	50	21
GI-1,5Cr	K ₂ CrO ₇	1.5	12	1.7	1.2	50	21
GI-3Cr	K ₂ CrO ₇	3	12	1.7	1.2	50	21
GN	-	-	12	1.7	-	50	21
GN-0,1Cr	K ₂ CrO ₇	0.1	12	1.7	-	50	21
GN-0,3Cr	K ₂ CrO ₇	0.3	12	1.7	-	50	21
GN-1,5	K ₂ CrO ₇	1.5	12	1.7	-	50	21
GN-3	K ₂ CrO ₇	3	12	1.7	-	50	21

S/L is the weight ratio of the industrial sludge powder to the alkali-activated solution
wt/% is the weight ratio of the chromium salt to industrial sludge

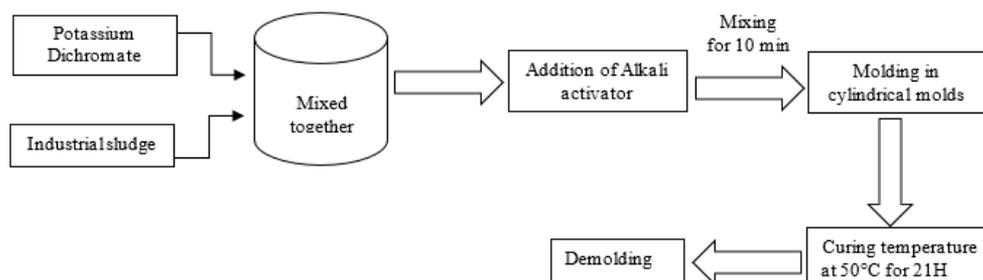


Figure 1. The procedure of sample preparation

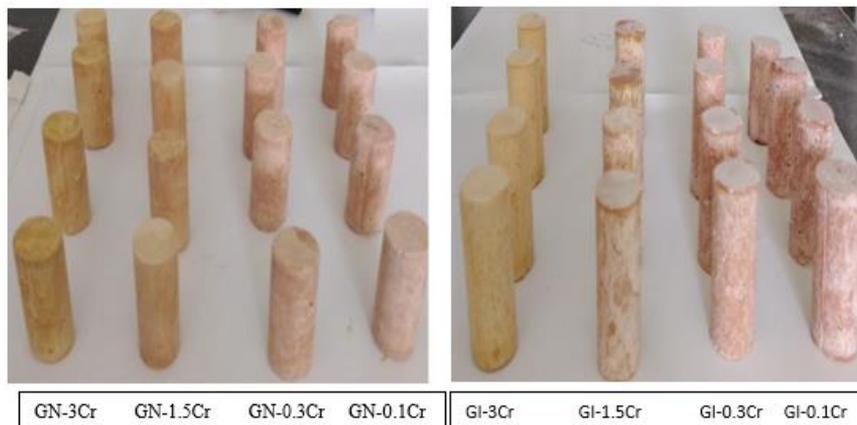


Figure 2. Industrial sludge based-geopolymer made with different percentages of chromium

3. RESULTS AND DISCUSSION

3.1 Compressive strength

Figure 3 shows the compressive strength of the prepared geopolymers without and with chromium.

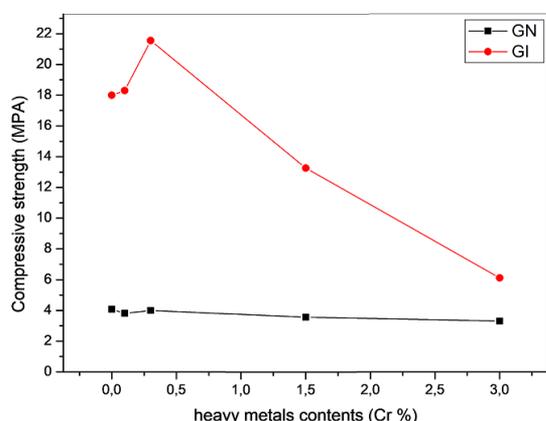


Figure 3. Effect of chromium concentration on compressive strength

It can be seen that the reference samples of geopolymers without chromium show a strength about 18 MPa and 4.1 MPa for GI and GN, respectively. The geopolymers prepared with sodium silicate reveal higher compressive strength than those prepared with NaOH, due to the greater gel aluminosilicate formation during geopolymerization process [21, 22]. It can be seen that compressive strength of all samples prepared with sodium hydroxide are lower than 5 MPa satisfactory for landfill stabilized materials, which indicates the limitation of chromium immobilization in the geopolymer matrix.

On the other hand, the presence of lower content of chromium (0.1%Cr) shows a less effect on the strength, and then increases to 21.5 Mpa with 0.3%Cr addition for GI sample, this may indicate the best inclusion of this chromium amount in the matrix network. However, the excessive amount of chromium (1.5 and 3 wt.%) causes a drop in the compressive strength from 18 Mpa to 13.25 Mpa for GI-1,5Cr, and to 6.11Mpa for GI-3Cr.

These relative changes of strength could be related to the variation of pores volume. Various researches indicated that the porosity of the matrix affected by addition of heavy metals.

The lower concentration of heavy metals reduces the porosity of the matrix [23, 24]. However, an excessive amount in these metals contributes to grow of pores volume [25]. Hence, causes a drop of the compressive strength values.

3.2 The effect of chromium on the conductivity of leachates

The Conductivity of the resulted solution of the samples without and with heavy metals immersed in 150ml are illustrated in Figure 4.

The Conductivity tests were used to determine the effect of chromium on the leaching of ions K^+ , Na^+ , Mg^{2+} , soluble silicates, and soluble aluminates out of the matrix. It can be seen that the conductivity increases with the increase of the contact time, which confirm the leaching of those ions in deionized water, and then remained stable after 7h. This might be attributed to the leaching limitation of the matrix.

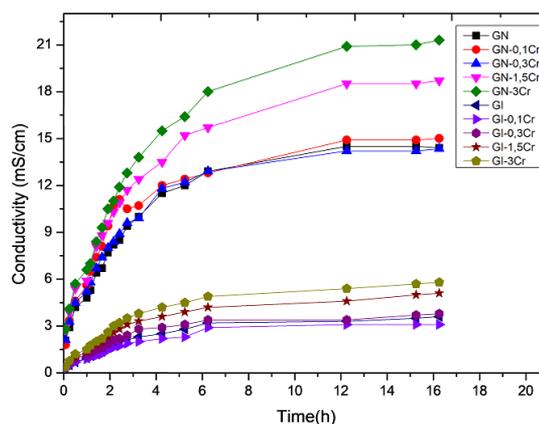


Figure 4. The effect of chromium concentrations with time on the conductivity

Furthermore, the change of conductivity was not detected with the addition of low concentrations of the chromium hexavalent (0.1 and 0.3%Cr), which indicates less influence on gel structure of the samples. This result is in agreement with the study of El fellah et al, about the Hg(II) addition [26]. Moreover, El-Eswed et al, indicated a high stabilization of conductivity with the addition of 0.5% Th(IV) and 0.5% U(VI) in metakaolin-based geopolymers [27], and 200ppm of Cr(III) in kaolin/zeolite-based geopolymers [28]. By contrast, the addition of 1.5% of chromium increases significantly the conductivity of the resulted solution compared to the sample

without heavy metals. This high leachability of ions resulted from a high charge of excess amount of chromium, which is difficult to balance the negative charge of Al tetrahedral in the matrix. This result was consistent with the compressive strength tests (paragraph 3.1).

3.3 X-ray diffraction analysis (XRD)

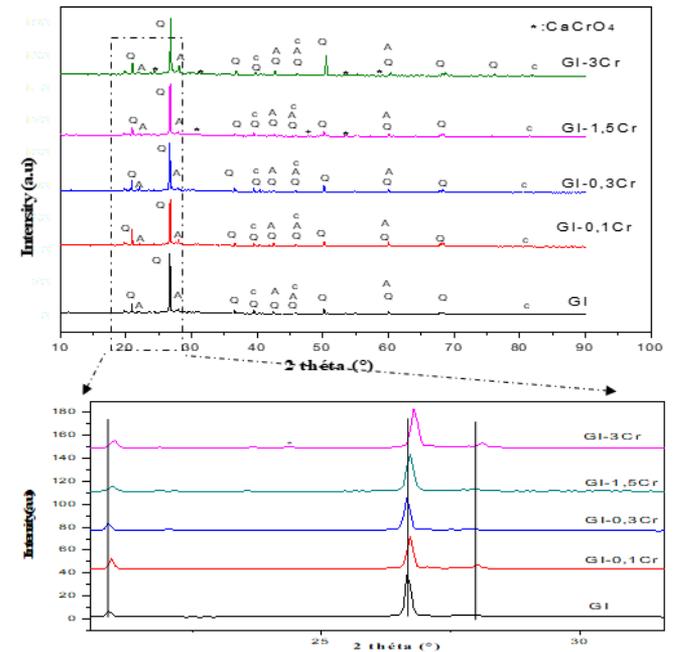
The XRD patterns of industrial sludge-based geopolymers without and with chromium are shown in Figure 5. The geopolymers structure consists mainly of amorphous phases. Additionally, crystalline structures were presented in quartz and albite peaks, as well as calcite due to the carbonatation reaction [29].

The intensity of quartz peaks decreased in all samples after geopolymerization process. In addition, same peaks of albite and calcite were detected. With the addition of a low amount of chromium in the industrial sludge, no new crystalline phases were observed. By contrast, the XRD peaks intensity of crystalline phases were strengthened with the addition of 3w% of Cr (VI), which decreases the compressive strength (paragraph 3.1). In addition, the position of peaks was shifted to a high angle with an increase of Cr(VI) amount. This change indicates the notable effect of Cr (VI) on geopolymerization process. Moreover, the chromium will be in oxide form and appears in the crystalline phases as calcium chromate form (CaCrO_4), which showed the encapsulation of Cr in the geopolymer gel.

3.4 Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS)

Figure 6 and 7 demonstrate the SEM micrographs and EDS analysis of the reference sample and with 3% of chromium.

Figure 6 revealed the existence of a large part of amorphous phases combined with some crystalline structures. The image exhibited in Figure 6(a), (b) reveals a dense matrix, due to the high degree of geopolymerization, consequently, greater amount of aluminosilicate gel with the stronger interconnection of Si-O-Al and/or Si-O-Si bonds. The spherical voids show the evaporation process of excessive water content during geopolymerization [30, 31].



A: Albite; Q: Quartz; C: calcite.

Figure 5. The XRD patterns of calcined industrial sludge based-geopolymer with and without heavy metal

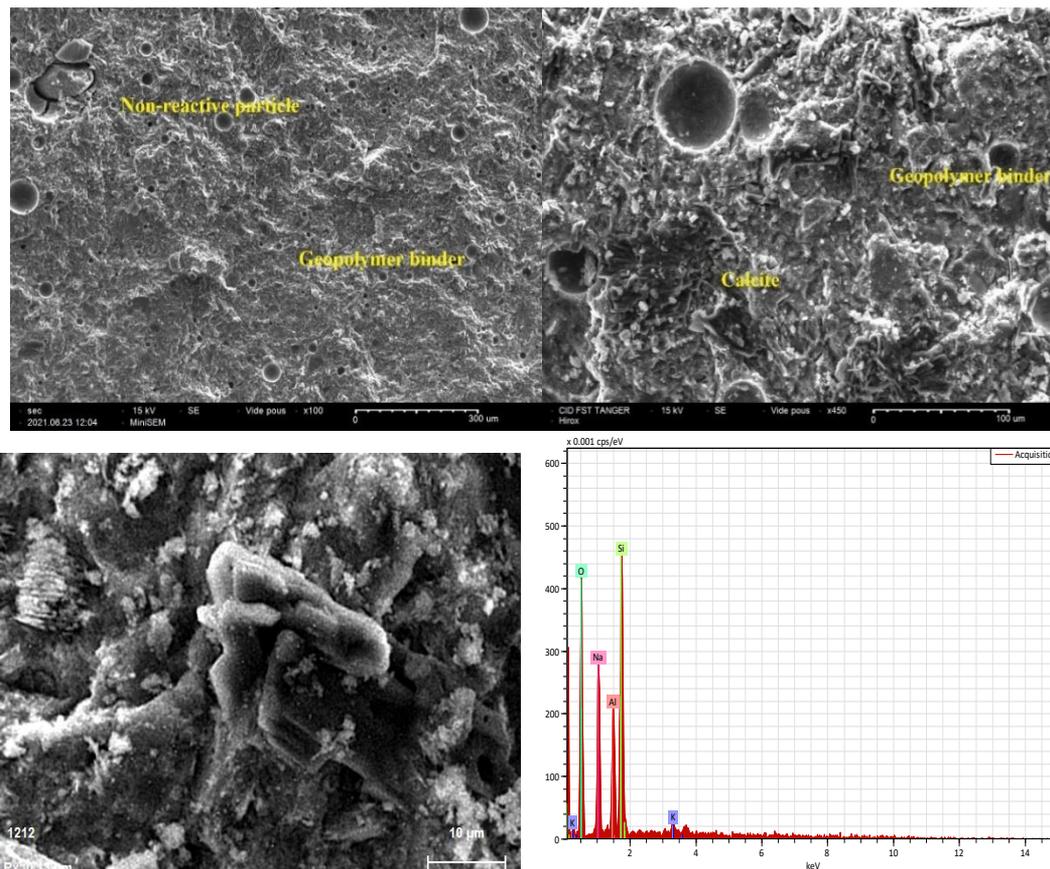


Figure 6. SEM and EDS analysis of the reference sample (GI)

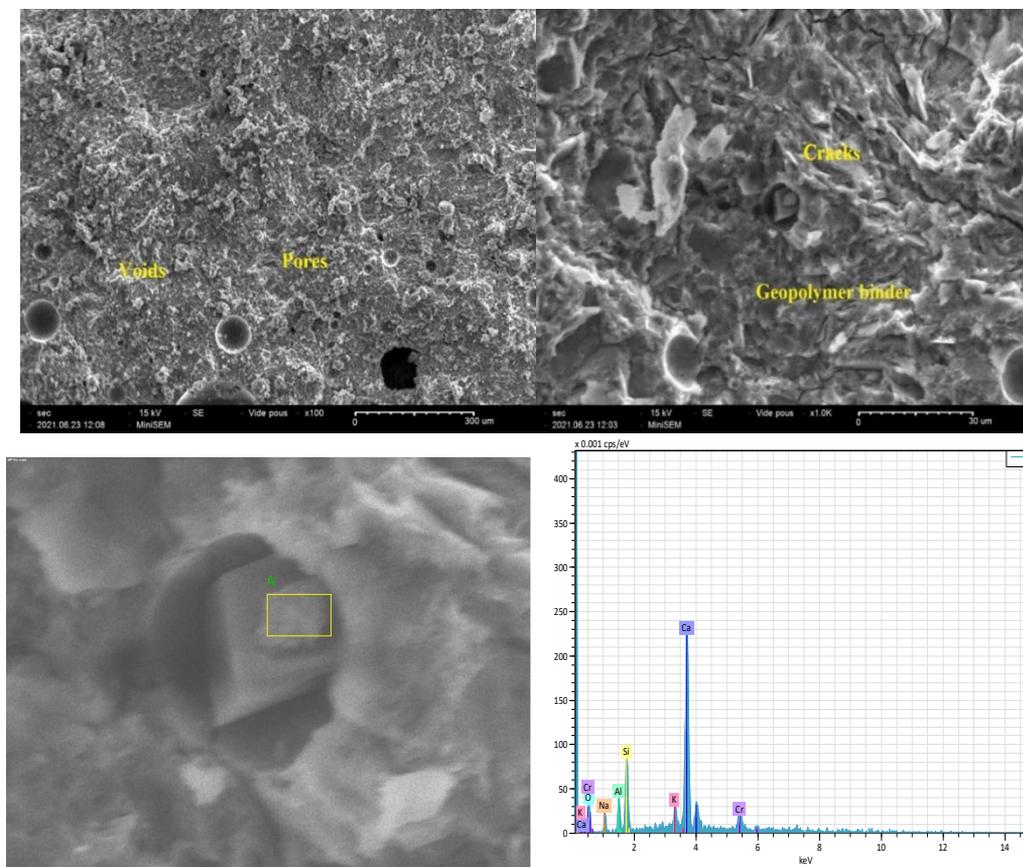


Figure 7. SEM and EDS analysis of industrial sludge based geopolymer (GN_{3Cr})

Figure 7 revealed the effect of a 3% amount of Cr(VI) on the morphology of the prepared geopolymers. A high content of Cr(VI) in the samples decreases the compactness of the matrix, due to the formation of the large pores and cracks (Figure 7a,b), which lead to the decrease of compressive strength. Huang et al. found that the porosity of alkali-activated blast furnace slag (BFS) and fly ash (FA) based cementitious increases with the addition of chromite [15].

EDS analysis of the reference sample indicates that the main elemental composition of the geopolymer is O, Si, Al, Na, which revealed the formation of sodium based aluminosilicate gel (N-A-S-H gel) as amorphous product [32-34]. Consequently, these results were consistent with the compressive strength result. The high value of compressive strength is due to the high degree of geopolymerization with the appearance of N-A-S-H bonds.

Moreover, Cr(VI) traces were displayed in the Figure 7-EDS, which shows the inclusion of this metal in the amorphous phase.

4. CONCLUSIONS

The influence of Cr(VI) on the physical properties and microstructure of industrial sludge based-geopolymers was investigated in the present study. The compressive strength and conductivity tests of the samples were evaluated. DRX, SEM, and EDS analysis were used to characterize the microstructure of different samples. The findings indicated the following:

The compressive strength increased first from 0% to 0.3%, and then decreased significantly as the chromium Cr(VI) content increased from 0.3 to 3 by weight%.

After 24 hours of aging, the conductivity of the result solution was not affected by the chromium amount increased from 0 to 0.3%. However, an important increase of the conductivity was observed for the samples with 1.5% and 3% of chromium.

The DRX analysis revealed that the reaction products of industrial sludge and alkaline activators are mainly amorphous materials. In addition, a lower amount of chromium ions was solidified in an amorphous structure. Moreover, an excessive amount of chromium causes an increase in crystalline phases, which decreases the degree of the geopolymerization reaction and consequently a decrease of chromium immobilization strength.

The SEM-EDS analysis showed a high porosity of samples with 3% of Cr(VI) compared to that without heavy metals, and EDS revealed that chromium stabilized in the geopolymer matrix.

For the future, an evaluation of leaching test of chromium for samples prepared with sodium silicate in different mediums will be needed.

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