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Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers

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ABSTRACT

The present work investigated the efficiency and mechanism of immobilization of Pb(II), Cu(II), Cd(II) and Cr(III) metal solutions in kaolin/zeolite based geopolymers. Leaching of heavy metals from the geopolymeric matrix into different aggressive solutions was studied by measuring the amount of metal, pH and conductivity of leachates. The effect of heavy metal concentrations, pressing pressure that employed through preparing geopolymer, and aging time on the geopolymer resistance toward leaching was also studied. The mechanical strength, XRD, XRF and SEM of geopolymers containing heavy metals were investigated. The results indicated that heavy metals could be effectively immobilized in kaolin/zeolite based geopolymers with a release of safe metal ions like Na^+ and K^+. The immobilization of heavy metals in geopolymer may be due to 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 lower cost than metakaolin-based geopolymers. The kaoline-based geopolymerization process is of much lower energy cost than metakaolin-based one.

1. Introduction

The term “geopolymer” is used to describe a family of synthetic alkali aluminosilicate material (Duxon et al., 2007). Geopolymers are produced by the reaction of solid aluminosilicate (metakaolin or fly ash) with a highly concentrated aqueous alkali hydroxide or silicate solution (Duxon et al., 2007). The structure of geopolymers consists of a polymeric Si–O–Al framework, similar to that found in zeolites. The main difference to zeolite structure is observed through X-ray diffraction techniques, which reveals an amorphous microstructure. Geopolymers are sometimes also referred to as alkali-activated aluminosilicate binders (Luna et al., 2007) that have a high compressive strength, low shrinkage, acid resistance, fire resistance and low thermal conductivity (Duxon et al., 2007).

Geopolymerization is thought to occur through dissolution, migration and polymerization of Al and Si precursor species (from metakaolin or fly ash) as well as surface reaction on surface of undissolved particles (Luna et al., 2007). In the geopolymer framework, aluminum is four coordinated to oxygen atoms, therefore, a negative charge is created and the presence of cations such as Na^+, K^+, Li^+, Ca^{2+}, and NH_4^+ is essential to balance the negative charge of Al (Rahier et al., 2007).

Heavy metals are significant components of many industrial and residual wastes, and preventing their release into the ecosystem is of great interest. There are also many areas worldwide where soils have become contaminated with heavy metals, and the treatment of these soils to prevent mobility of contaminants is becoming very essential (Zhang et al., 2008).

Solidification/stabilization is a process that involves the mixing of a waste with a binder to reduce the contaminant leachability by both physical (adsorption or encapsulation) and chemical (fixation) means to convert the hazardous waste into an environmentally acceptable waste form for land disposal or construction use (Shi and Fernandez-Jimenez, 2006). Solidification/ stabilization of heavy metals using geopolymers have been investigated over a number of years (van Jaarsveld et al., 1999; Lee and van Deventer, 2002; Phair et al., 2004; Shi and Fernandez-Jimenez, 2006; Zhang et al., 2008; Sun et al., 2014). Metakaolin and fly ash based geopolymer matrix provided a satisfactory binder for the immobilization of a number of toxic heavy metals because of their low permeability, resistance to acid and chloride attack, and durability (Zhang et al., 2008). It is worth to mention that the leachability of contaminants from stabilized metal geopolymer wastes is lower than that from hardened Portland cement stabilized wastes (Shi and Fernandez-Jimenez, 2006).

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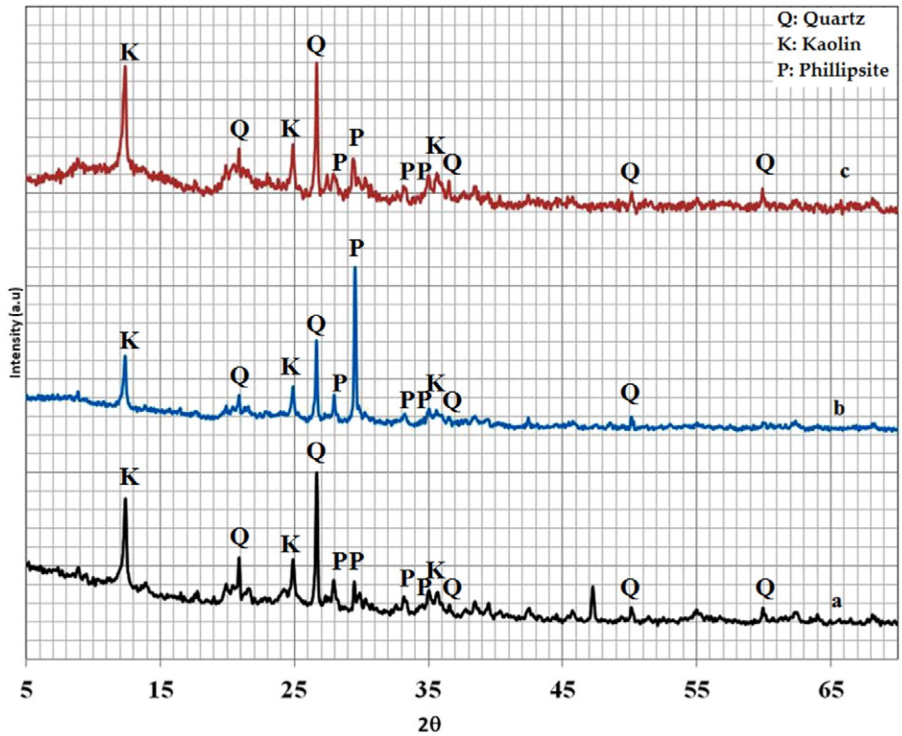

Fig. 1. XRD patterns of a) GWSM, b) SPbG (200 ppm) and c) SPbG (1000 ppm). The XRD was recorded for discs leached with distilled water for 24 h at 25 °C. Assignments were made according to Yousef et al. (2009) and Duxon et al. (2007).

In the work of Zhang et al. (2008), Pb(II) and Cd(II) were effectively immobilized in fly ash-based geopolymer. It was found that fly-ash based geopolymers could effectively immobilize lead because it is precipitated as a highly insoluble silicate (Pb_3SiO_5). However, Cr(VI) could be leached out due to the formation of a highly soluble Na_2CrO_4 (Shi and Fernandez-Jimenez, 2006). The incorporation of metal contaminants in the geopolymer matrix takes place either through physical means (charge balancing of Al in framework) or covalent bonds (where the metal is bonded to the silicate chain or hydroxide links) (van Jaarsveld and van Deventer, 1999). In general, it was thought that metal cations are being immobilized through the combination of chemical and physical encapsulation (van Jaarsveld and van Deventer, 1999).

The present work deals with geopolymers based on local Jordanian resources, namely kaolin and zeolitic (phillipsite) tuff. This type of geopolymer was prepared and investigated in previous works by the research group of the present article (Yousef et al., 2009, 2012; El-Eswed et al., 2009, 2012). Kaolin/zeolite based geopolymers were prepared from 1:1 mass ratio of the two materials by a reaction with an alkali solution at 80 °C. It has been demonstrated that these geopolymers have good mechanical strength (18 MPa) and high adsorption capacity toward Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) ranges from 0.3 to 0.5 mmol metal/g geopolymer.

The process used in the present work in preparation of kaolin/zeolite based geopolymers is of much lower energy and cost than that used in preparation of most popular metakaolin based geopolymers (Yousef et al., 2009, 2012; El-Eswed et al., 2009, 2012). The latter involves calcinations of kaolin at 600 °C and complete dissolution of metakaolin which requires very large amount of sodium hydroxide and sodium silicate (Cioffi et al., 2003). The XRD and SEM study of kaolin/zeolite based geopolymers indicated incomplete dissolution of kaolin by the effect of basic solution employed in geopolymer synthesis. The phillipsite (zeolite) remains prominent in the geopolymer products (El-Eswed et al., 2012).

Although metakaolin is more reactive than kaolin in the geopolymerization process, an interesting finding by van Jaarsveld et al. (1999) was that kaolin based geopolymers have higher compressive strength and higher surface area (51.4 MPa, 16.4 m^2/g) than the corresponding metakaolin based geopolymers (28.1 MPa, 12.1 m^2/g). Similarly, Phair et al. (2004) reported that kaolin-based geopolymers have higher compressive strength (32.7 MPa) than metakaolin (26.8 MPa) and fly ash (7.7 MPa) based geopolymers. This confirms that the mechanism of geopolymerization may be a combination of dissolution–migration–polymerization as well as (of equal importance) surface solid state reactions. Thus, kaolin based geopolymers are good candidates for stabilization of heavy metals although they do not involve complete dissolution of aluminosilicate source.

The important characteristics of kaolin/zeolite based geopolymers that attracted the attention to use them as a host phase for heavy metal waste are: i) The porous zeolite and geopolymer zeolite-like components which has the ability to exhibit high cation exchange with heavy metal cations. ii) The low energy of the geopolymerization process. iii) The low cost of the starting materials: local Jordanian kaolin and zeolitic tuff. iv) The satisfactory mechanical properties of kaolin/zeolite based geopolymers.

Accordingly, the aim of the present work is to study the efficiency of kaolin/zeolite based geopolymers in solidification/stabilization of heavy metal solutions, i.e., Pb(II), Cu(II), Cd(II), and Cr(III).

2. Experimental

2.1. Preparation and characterization of stabilized metal geopolymers (SMG)

2.1.1. Materials

Jordanian kaolin was obtained from El-Hiswa deposit, which is located in the south of Jordan about 45 km to the east of Al-Quweira town. Preparation of the Jordanian kaolin samples involved crushing (using Jaw crusher RETCH-BB1A) of an oven dried clay (at 105 °C) to a grain size less than 425 mm. The purity of kaolin was found to be 60 wt.%, and about 40 wt.% of quartz using Maud program (beta version 2.52,