Journal of Hazardous Materials 260 (2013) 89–103

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Solidification/stabilization of toxic metals in calcium aluminate cement matrices

I. Navarro-Blasco, A. Duran, R. Sirera, J.M. Fernández, J.I. Alvarez*

Inorganic Materials & Environment (MIMED), School of Sciences, University of Navarra, Irunlarrea, 1, 31008 Pamplona, Spain

HIGHLIGHTS

- Reliable encapsulation and effective sorption of Pb, Zn and Cu on CAC was proved.
- Cu and Pb were fully retained in the CAC mortar, while Zn was retained in 99.99%.
- A maximum sorption capacity ca. 60 mg/g CAC was attained for Cu.
- Three different PSD patterns were established as a function of XRD phase assemblage.
- Some metal-loaded mortars achieved suitable mechanical strengths for landfilling.

ARTICLE INFO

Article history:
Received 6 February 2013
Received in revised form 24 April 2013
Accepted 27 April 2013
Available online 4 May 2013

Keywords:
Metal
Cement
Sorption
Leaching
Strength

ABSTRACT

The ability of calcium aluminate cement (CAC) to encapsulate toxic metals (Pb, Zn and Cu) was assessed under two curing conditions. Changes in the consistency and in the setting time were found upon the addition of the nitrates of the target metals. Both Pb and Cu caused a delay in CAC hydration, while Zn accelerated the stiffening of the mortar. Compressive strengths of the metal-doped mortars, when initially cured at 60 °C/100% RH, were comparable with that of the free-metal mortar. Three different pore size distribution patterns were identified and related to the compounds identified by XRD and SEM. Sorbent capacities of CAC for the toxic metals were excellent: a total uptake was achieved for up to 3 wt.% loading of the three metals. In this way, CAC mortars were perfectly able to encapsulate the toxic metals, allowing the use of CAC for waste management as proved by the leaching tests.

1. Introduction

Heavy metal bearing waste normally needs solidification/stabilization (S/S) processes to reduce contaminant leaching prior to landfill disposal. Cement is the most adaptable binder currently available for this immobilization. A growing number of papers have dealt with this subject, mainly using ordinary Portland cement (OPC), some of its phases or OPC modified by calcium aluminate, calcium sulphate, and/or admixtures [1–7], occasionally forming new phases with the metallic cations. In addition, Qian and co-workers have extensively studied the S/S processes of toxic metals in fly ash-calcium sulfoaluminate cement, Friedel's salt or fly ashes [8–10].

Calcium aluminate cement (CAC) is an alternative construction material to OPC. This type of cement is especially employed in the production of fire-resistant materials and in cases in which concreting in temperatures below zero or a fast increase in strength is required [11]. Different calcium aluminate compounds, such as CA, CA_2 and $C_{12}A_7$, exist, the reactivity increasing when CaO content rises. CAC reaction with water usually leads to the formation of metastable hexagonal phases, CAH_{10} and C_2AH_8 and amorphous aluminium hydroxide, which is followed by the formation of the stable cubic phases C_3AH_6 and AH_3 at higher temperature and in the presence of humidity. This process is associated with an increase in porosity -owing to a contraction in the volume of solids- and a subsequent decrease in strength [12,13].

Recently CACs have been reported to show potential advantages when used to encapsulate certain toxic and radioactive wastes [14], owing to their high early strength, chemical attack resistance and abrasion endurance [15]. Interaction between CACs and alkaline and alkaline-earth metal chlorides has been reported focusing on the hydration chemistry and on the setting behaviour [16–18]. Results were recognized to be unclear and sometimes opposite to those obtained with OPC. The effect of counter-ions (sulphates, chlorides or nitrates) cannot be disregarded [19]. Only a few studies dealing with the effect of some transition metal chlorides and

* Corresponding author. Tel.: +34 948425600; fax: +34 948425740.
E-mail addresses: jalvarez@unav.es, mimed@unav.es (J.I. Alvarez).

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http://dx.doi.org/10.1016/j.jhazmat.2013.04.048

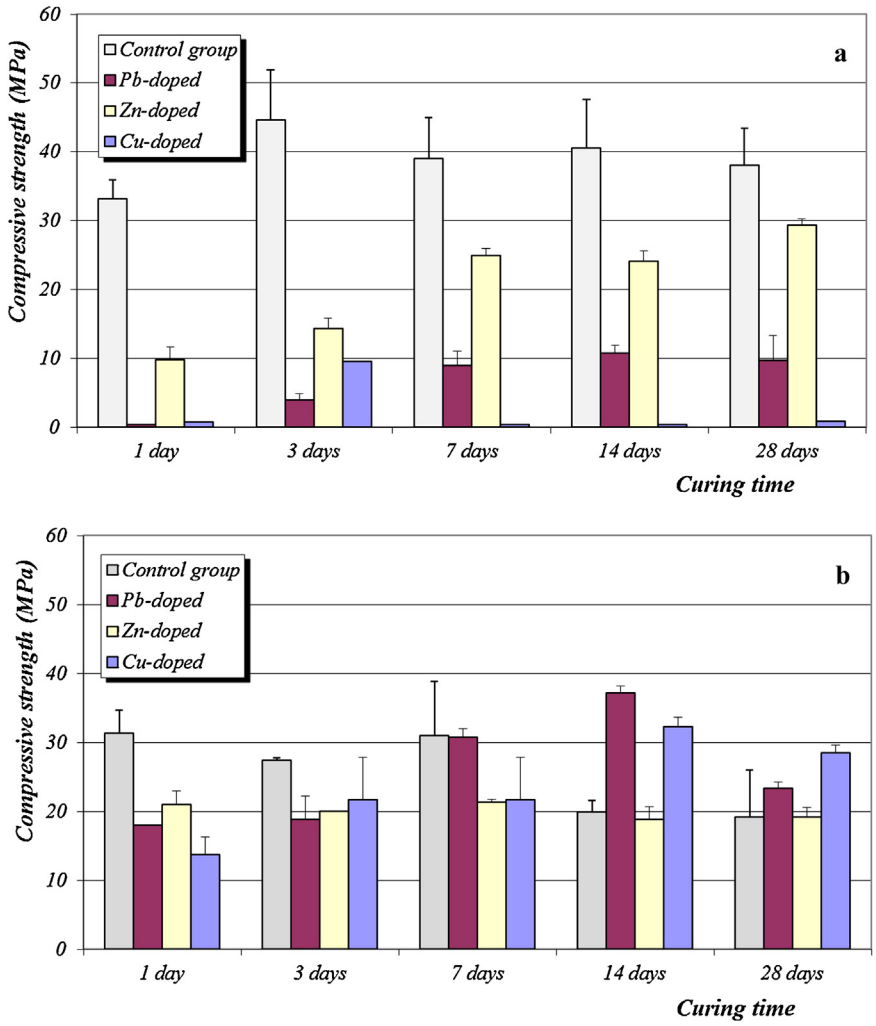

Fig. 1. Compressive strengths: (a) condition 1; (b) condition 2.

sulphates on CAC have so far been reported [15,20]. However, the performance of CAC when toxic metal nitrates are added has scarcely been researched. In addition, the effectiveness of CAC in the stabilization of hazardous waste containing soluble toxic metals remains to be ascertained. Both issues are addressed in the current paper. The effect of Pb, Zn and Cu nitrates on the fresh and hardened state properties of the CAC matrices is discussed. To this end, two sets of CAC samples, cured under two different environmental conditions – the second one selected in order to favour the formation of stable phases – were assayed and later studied on different days. The phase assemblage of the modified CAC mortars was also analyzed by XRD and related to the microstructure of the mortars and their compressive strengths. Both adsorption isotherms of the metals on CAC and leaching tests were carried out in order to ascertain the effectiveness of these CAC matrices in S/S processes of toxic metals.

2. Material and methods

2.1. Materials

A CAC (Ciments Molins) was used as the binding phase. Its XRD analysis showed CA as the main mineralogical phase (ICDD 01-070-0134), together with amounts of $C_{12}A_7$, mayenite, (ICDD 09-0413), C_5A_3 (ICDD 01-1057), C_3A (ICDD 01-1060) and C_4AF (ICDD 30-0226). The average wt.% composition was: Al_2O_3 41%, CaO 38%, Fe_2O_3 17%, SiO_2 3%, SO_3 0.1%, $Na_2O + K_2O$ 0.1%. The aggregate was a standard siliceous sand (99 wt.% of SiO_2), evenly graded, with particle diameter ranging from 0.05 to 2 mm.

Soluble $Pb(NO_3)_2$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$ (Merck) were chosen for the metal load (1 wt.% metal/cement).

2.2. Sample preparation

Cement and aggregate (1:3 ratio by weight) were blended for 5 min in a mixer. Afterwards, the mixing water (0.4 water/cement ratio) was added and mixed for 90 s. When required, one of the selected metal salts was dissolved in the mixing water. Four different batches of samples were prepared: a plain CAC mortar (control group) and three batches of samples modified upon the addition of, respectively, Pb, Zn and Cu.

According to the procedures described below, fresh state properties were evaluated. For the assessment of the hardened state characteristics, cylindrical (5 cm height and 3.5 cm diameter) PVC moulds were filled with the fresh mixture. Specimens were cured until the test day. For each batch of samples, two different curing conditions were chosen:

- Curing 1: 20 °C and 95% RH [21] over the whole curing period.
- Curing 2: 60 °C and 100% RH [22] for 24 h. Once this period was completed, temperature and RH were shifted towards 20 °C and 95% RH.