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Encapsulation, solid-phases identification and leaching of toxic metals in cement systems modified by natural biodegradable polymers

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HIGHLIGHTS

- Speciation of Zn, Pb and Cr has been studied in chitosan-modified cement mortars.
- Metal retention mechanisms have been clarified by newly identified crystalline forms.
- Native chitosan induced and stabilized newly characterized Pb (IV) species.
- Dietrichite is responsible for the Zn immobilization in the polymer-modified mortar.
- Leaching of Zn decreased by 24% in the presence of low molecular weight chitosan.

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ABSTRACT

Cement mortars loaded with Cr, Pb and Zn were modified by polymeric admixtures [chitosans with low (LMWCH), medium (MMWCH) and high (HMWCH) molecular weight and hydroxypropylchitosan (HPCH)]. The influence of the simultaneous presence of the heavy metal and the polymeric additive on the fresh properties (consistency, water retention and setting time) and on the compressive strength of the mortars was assessed. Leaching patterns as well as properties of the cement mortars were related to the heavy metals-bearing solid phases. Chitosan admixtures lessened the effect of the addition of Cr and Pb on the setting time. In all instances, chitosans improved the compressive strength of the Zn-bearing mortars yielding values as high as 15 N mm^{-2}. A newly reported Zn phase, dietrichite ($ZnAl_2(SO_4)_4{\cdot}22H_2O$) was identified under the presence of LMWCH: it was responsible for an improvement by 24% in Zn retention. Lead-bearing silicates, such as plumalsite ($Pb_4Al_2(SiO_3)_7$), were also identified by XRD confirming that Pb was mainly retained as a part of the silicate network after Ca ion exchange. Also, the presence of polymer induced the appearance and stabilization of some Pb(IV) species. Finally, diverse chromate species were identified and related to the larger leaching values of Cr(VI).

1. Introduction

The use of Portland cement (OPC) to immobilize hazardous wastes has become widespread because of their availability, versatility and low cost [1]. In particular, the immobilization of heavy metals by solidification/stabilization (S/S) is an effective method to reduce their hazard to the environment [2–4]. The incorporation of the waste into the hydrated cement system takes place through different mechanisms [5–7], encapsulation being one of the most important.

The contaminants included in the cement can, eventually, be transferred from this stabilized matrix to a liquid medium such as water or other solutions, this process being known as leaching. Both field and laboratory leaching studies are relevant to obtain information about the chemical speciation and the mobility of contaminants in the S/S process evidencing the associated potential risks [5,8].

The hydration of cement mortars is influenced by the presence of heavy metals. Some of the rheological properties may be also jeopardized [9,10]. Hardened state properties, such as compressive strength, can also undergo alteration upon addition of toxic metals. Zinc, for example, has been reported to strongly delay OPC hydration and to reduce the compressive strength [11], such as in the case of S/S of toxic ashes [12]. The literature abounds with proposed mechanisms to explain the effect of the heavy metals addition on the setting time of OPC mortars [10,13–16]. Changes in the fresh state properties and long-term stability of the cement mortars can have deleterious effects on the applicability and usefulness of cement mortars loaded with heavy metals. In order to minimize these adverse effects on the properties of the cement, mineral admixtures such as zeolites, metakaolin, bagasse ash, clinoptilolite

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[17–19] and polymeric admixtures, such as polycarboxylate ethers, naphthalene-based superplasticizers, latexes and acrylic polymers can be added to the cement mortars [8,13,20–22].

One of this type of admixtures is chitosan, a natural biopolymer structurally analogous to some well-known cement cellulosic additives. Chitosans show remarkable complexing abilities for heavy metals [23] and they have been proved to modify some of the cement properties [24–26]. In this case, noticeable results were obtained even when incorporated in a very low amount (i.e. 0.4 wt.% by cement) [26]. Although long-term biodegradation performance could be considered a hypothetical drawback, its influence on the cement mortar would be minimum given the scarce amount of the polymer in the total weight of the mortar.

The objective of the present paper is to bring information on the immobilization of Cr, Pb and Zn by cement mortars modified by the addition of an unexplored range of natural chitosan biopolymers. Fresh and hardened state properties of the metal-loaded mortars were also assessed with the aim of shedding light on the observed changes as a function of the added polymer. Identification of the chemical forms in the solid state of the retained metals was also carried out to gain understanding of the immobilization process of heavy metals in cement when polymeric additives were simultaneously present. The metals selected for this study were Pb(II), Cr(VI) and Zn(II), identified as priority metallic pollutants [13,23,27–29].

2. Experimental

2.1. Materials

Different molecular weights (MW) chitosans (LMWCH: 210 kDa; MMWCH: 470 kDa; HMWCH: 835 kDa) were used (Sigma–Aldrich). The synthesis of HPCH (119 kDa), was done according to Peng et al. [30]. Basic structures of the chitosan and the etherified derivative are shown in Fig. 1. The degree of substitution (DS) for HPCH was seen to be 11.24 by elemental analysis. The amount of residual chloride was also determined by potentiometric titration, resulting in 320 ppm. Taking into account the admixture dosage of 0.4% by cement weight, a negligible amount of chloride (<2 ppm) was calculated to be incorporated by the polymer.

An OPC (CEM II32.5 N) and a standardized siliceous aggregate supplied by Instituto Eduardo Torroja (Spain), with a constant particle size distribution [31], were used to prepare the mortars.

The heavy metal load (1% of heavy metal/cement) consisted of $Zn(NO_3)_2$, $Pb(NO_3)_2$ (Merck) and $K_2Cr_2O_7$ (Panreac). Nitrate salts were chosen because of their solubility [32].

2.2. Mortar preparation

Cement, aggregate and chitosan (when necessary) were blended for 5 min with a mixer. Water was then added and mixed for 90 s at low speed. When required, one of the selected metal salts was dissolved in the mixing water in the aforementioned percentage. The binder:aggregate ratio (B:Ag) was 1:3, by weight, and the selected water:cement ratio was 0.55:1. These ratios yielded a control mortar with a good workability. Chitosans were added at a dosage of 0.4% of the cement weight and only one additive was added to each mortar to unequivocally evaluate their individual effect. Fresh mixtures were moulded in 40 mm × 40 mm × 160 mm casts and cured 28 days according to a norm [33] to evaluate the hardened state properties. Three specimens were prepared for each one of the mortar compositions, a total of 54 cement test pieces being assayed. Statistical significance of data was guaranteed by the adequate number (2–6) of replicates and/or instrumental measurements for the different assays.

2.3. Tests

2.3.1. Mortar properties

For the fresh state, several properties were studied: consistency through the flow table test, by measuring the slump of the mortar after 15 strokes on a specific compacting table [34]; water-retention capacity, determined by weighting absorbent materials placed on the fresh sample before and after 5 min of contact under pressure [35]; and setting time, obtained from a specific device provided with a bradawl, which pushed the fresh sample until the strength exerted to introduce it into the sample was larger than 15 N [36].

In hardened specimens, compression strength tests were executed on a Proeti ETI 26.0052 at a loading rate of 50 N s^{-1}. Pore size distributions were obtained by mercury intrusion porosimetry (MIP) using a Micromeritics AutoPoreIV9500 with a pressure ranging between 0.0015 and 207 MPa.

2.3.2. Identification of the heavy metals compounds in the solid state

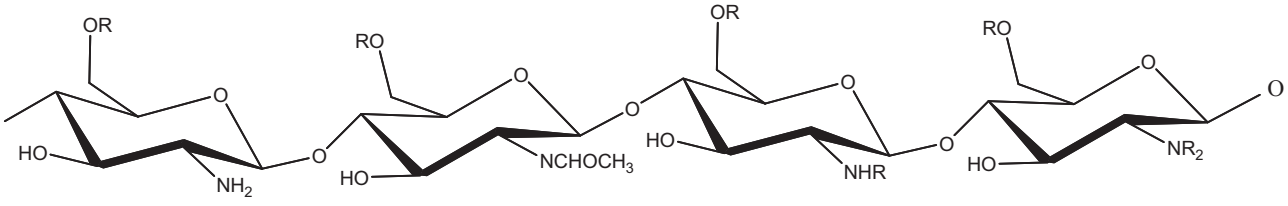
The mineralogical phases were determined by X-ray diffraction (XRD) in a Bruker D8Advance diffractometer (Karlsruhe, Germany), with a Cu $K_{\alpha 1}$ radiation and 0.02° 2θ increment and 1 s $step^{-1}$, from 2° to 90° 2θ.

Scanning Electron Microscopy (SEM), Backscatter Scanning Electron (BSE) and Electron Dispersion Analysis of X-ray (EDS) (HITACHI, S-4800) were used for microscopic observations, local composition and mapping of the metals distribution.

X-ray fluorescence (XRF) was coupled with an optical microscope to collect additional data on the chemical composition of selected areas of the samples.

2.3.3. Leaching tests

A semi-dynamic Tank Test [37] already described [24] was used. Test pieces (40 mm × 37 mm cylinders) were prepared by duplicate, moulded and cured as explained in Section 2.2. A total of 36 cement blocks were analysed and the results were the average of three instrumental measurements.



For native chitosan: R = -H

For HPCH derivative: R = -H, -(CH_2 $_3$OH

Fig. 1. Basic structures of chitosan and the etherified derivative (HPCH).