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ASSESSMENT OF THE EFFECT OF PH VALUES ON THE COMPLEXING ABILITY OF TWO ETHERIFIED DERIVATIVES OF CHITOSAN WITH A VIEW TO IMPROVING RETENTION OF HEAVY METALS INTO CEMENT MORTARS

J.M. Fernández, E. Lasheras-Zubiate, B. Bessarda, I. Navarro-Blasco, J.I. Álvarez
Departamento de Química y Edafología, Universidad de Navarra,
Irunlarrea, 1. 31008 Pamplona, Spain
[a] Département Chimie, IUT A de Lille, France
jmfdez@unav.es

Removal of heavy metals from polluted aqueous systems (industrial and waste waters) may be accomplished by complexing and sequestering them into inert matrices. A suitable matrix can be cement mortars, owing to the fact that they have the capability of immobilise and stabilise the complexes, reducing heavy metal leaching. The complexing ligand has to be properly chosen so that it presents high affinity for the metal and a good performance of the formed complex in the largely alkaline medium of the cement mortar. Our research interest is focused on chitosans and its derivatives as a model ligand that fulfills both demands. The complexing ability of unmodified chitosans for several target heavy metals has been checked in acetated buffer (pH = 4) [1]. In this contribution we will take advantage of the fact that some etherified chitosans are soluble in alkaline pH mimicking the cement mortar conditions. Retention of Zn and Pb in alkaline media by the etherified chitosans will be related to the heavy metal concentrations found in the leaching coming from polymer modified mortars.

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[1] M. Lasheras-Zubiate, I. Navarro-Blasco, J.M. Fernández "Distinct complexing trends of chitosan with toxic metals". Euchis 2009 - 9th International Conference of the European Chitin Society, Venice, 2009

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J.M. Fernández, M. Lasheras-Zubiate, B. Bessard[a], I. Navarro-Blasco, J.I. Álvarez

Departamento de Química y Edafología, Universidad de Navarra, Irunlarrea, 1. 31008 Pamplona, Spain

[a] Département Chimie, IUT A de Lille, France

jmfdez@unav.es

Universidad de Navarra

INTRODUCTION

Immobilization of heavy metals by cement has been reported to be effective for some metals and some wastes. Given that cement alone is not always useful, the development of new and cheaper stabilizing agents is of great interest [1]. However, some heavy metals have been shown to be detrimental for some fresh-state cement properties. For example, Pb and Zn compounds cause a retardation of the setting process of the cement owing to their interaction with calcium silicate hydrates (CSH) and calcium sulfoaluminate hydrates, such as ettringite and monosulfate [2]. Polymer molecules like chitosan and its derivatives have shown ability to complex different heavy metals. The use of such polymeric additives in cement-based materials would be interesting in order to improve the solidification/stabilization (S/S) of the heavy metals as well as to minimize or even overcome the drawbacks of the contaminants on the rheological properties of the cement matrices.

An in-depth knowledge of the way of interaction between heavy metals and chitosan derivative (CD) polymers out of and within the cement matrix would be useful to assess the effectiveness of these polymers improving the S/S processes of heavy metals in cement-based systems.

This work is aimed to study the complexing capability of heavy metals by a chitosan derivative at an alkaline medium and, eventually, to elucidate whether the addition of this polymer improves the S/S of Cr(VI) and Pb(II) in cement mortars dodging the negative effects on the properties of the fresh cement mixtures.

MATERIALS AND METHODS

An ordinary Portland Cement CEM II 32,5 N was used as binding material. The aggregate was of siliceous nature, standardized and supplied by Eduardo Torroja Institute. The selected binder: aggregate ratio (B:Ag) was 1:3, by volume. Water was added in a ratio of 0.55 water/cement. Consistency, through the flow table test, water-retention capacity and setting time were determined.

RESULTS AND DISCUSSION

Figure 1 shows no complexation between CD and the heavy metals tested.

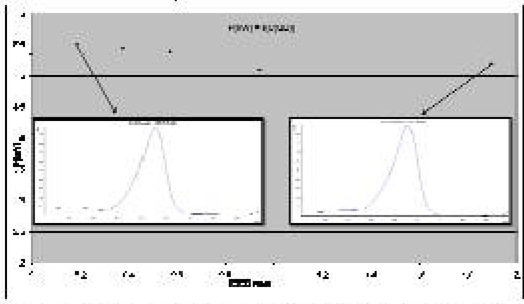

Figure 1 : Voltammetric assessment of Zn complexation with CD in alkaline media

Some modifications in the fresh state mixtures were found when heavy metals were added to the cement mortar. The addition of lead gave rise to an outstanding delay in the setting time compared with the control mortar, while chromium shortened it. The water retention capacity of the samples was hardly modified.

The incorporation of a CD turned out to be effective in reducing the fluidity and in shortening the setting time (Fig. 2). Regarding the behaviour of these polymer modified mortars when lead and chromium were also added, the polymer lessens the effect of these metals on the setting time by shortening the setting time of samples with lead and increasing the setting time of samples with chromium. In addition, the fluidity of the fresh mixtures was also well-balanced.

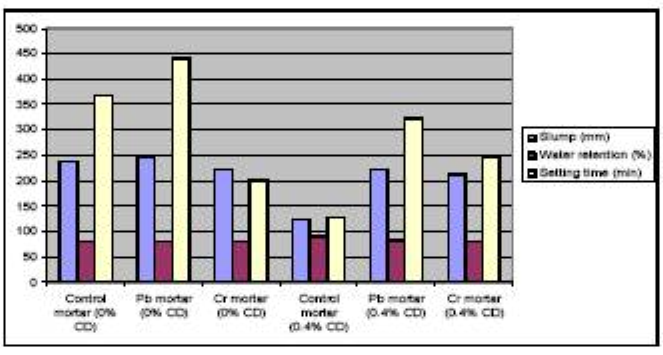

Figure 2. Fresh state properties of cement mortars with or without Pb or Cr and CD

Figure 3 shows the particle size distribution (PSD) in solution of cement with different amounts of CD. The flocculant effect of the CD addition can be observed through the growing quantity of large agglomerates ranging between 250 and 450 mm as function of the polymer dosage. However, the addition of both lead and chromium resulted in a "plasticizing" action, reducing the amount of large agglomerates of cement particles, as can be observed exemplified in Figure 3b (in the case of Pb).

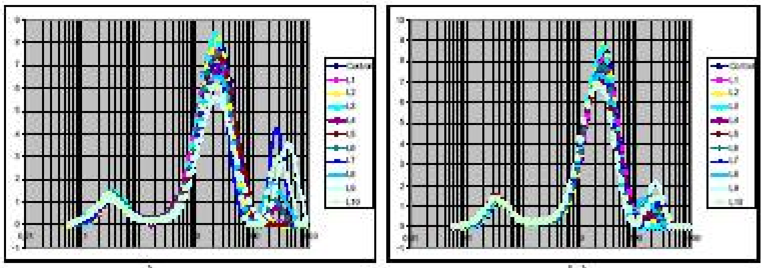

Figure 3. Particle size distribution of the cement solutions with increasing dosages of CD (0% for control sample): a) in the absence of heavy metal; b) containing Pb.

Zeta potential measurements give an impression of the net-surface charge for cement particles in cement suspensions. Results in Fig. 4 show that the presence of the polymer, which, at such alkaline pH, would be a negatively charged polyelectrolyte owing to its functional groups, shifts the potential zeta values towards more negative figures. This fact may suggest that the polymer interacts with cement particles, giving rise to an adsorption on the surface of the particles (some of them with a positive double layer) [3]. The molecules of the polymer could then link different cement particles, producing a thickening effect, as proved by the slump results and PSD. However, when negative ions are added (chromate, CrO_4^{2-}), they can compete with polymer molecules for the binding sites on the surface of the cement particles, leading to an increase of "free" polymer molecules. These "free" polymer molecules do not cause agglomeration of the cement particles, as can be observed in results of the slump and PSD. Nevertheless, since some CrO_4^{2-} ions may be adsorbed on the cement particles, zeta potential values should be kept negative, as Figure 4 confirms: when 0% of polymer was incorporated, zeta potential turned out to be negative as a result of, probably, the adsorption of chromate ions on the cement particles. Negative values of the zeta potential similar to those of the metal-free samples were obtained when polymer was added.

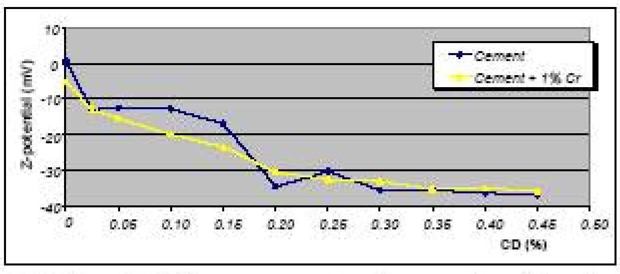

Figure 4. Zeta potential measurements of cement particles in the presence of increasing CD concentrations.

CONCLUSIONS

Disadvantages arising from loading cement-based mortars with heavy metals are minimized by adding a chitosan derivative. In fact, the addition of the CD balances out the drawbacks of the metal presence: several improvements were observed with respect to setting time and fluidity of the fresh mixtures (slump values). This positive performance is accompanied by a negligible increase in leaching measurements in the case of lead, whereas a significant increase was observed in the case chromium.

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