Interaction of carboxymethylchitosan and heavy metals in cement media

M. Lasheras-Zubiate, I. Navarro-Blasco, J.I. Álvarez*, J.M. Fernández

Department of Chemistry and Soil Sciences, University of Navarra, Irunlarrea, 1, 31008 Pamplona, Spain

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ABSTRACT

The performance of an etherified chitosan, carboxymethylchitosan (CMCH), when added to cement mortars doped with heavy metals, was assessed. In the presence of heavy metals (Cr, Pb, Zn) strong modifications of the fresh-state properties were evaluated. The addition of the polymer was seen to be useful in minimising some of these modifications, as those related to the setting time. A competitive mechanism for adsorption between the oxoanionic form of the metals and the carboxylate groups of the chitosan derivative was established. Studies on the metal chelating ability of the polymer and leaching from the hardened specimens showed scarce complexation under alkaline conditions, pointing to physical entrapment based on metal adsorption. However, significant chelation of metals was proved at near-neutral pH, suggesting the potential usefulness of the polymer as an agent for removing heavy metals from polluted waters and subsequently immobilizing them in cement mortars. Leaching tests carried out on polymer–metal complex-bearing samples showed a reduction in the amount of released Pb and Zn.

1. Introduction

Cement mortars have usually been used to block the pernicious effects of hazardous wastes (e.g. heavy metals) by immobilizing them [1,2]. As a result of the chemical properties of the cement, the solidification/stabilization (S/S) processes may involve both physical entrapment (adsorption) and/or chemical binding (complexation) of the contaminant to the cement matrix. It has been reported that Pb, Cr and Zn compounds modify the hydration and rheological properties of the cement owing to their interaction with different cement phases [3,4]. The reported changes in fresh-state properties of the cement mortars can be detrimental to their usefulness and applicability. In addition, their long-term stability can be jeopardized, thus increasing the leaching of heavy metals.

Some polymeric additives can be added to cement mortars in order to modify their properties, improving their heavy metal retention ability and minimizing, or even overcoming, the negative effect of those metals in fresh-state properties [4]. Other admixtures such as sugar derivatives have been shown to add flexibility to the handling of cement-treated metal waste, by modifying the fresh-state properties of the cement mortar [5]. In a previous study, chitosan molecules have been reported to complex several heavy metals efficiently [6]. However, as a consequence of the insolubility of the chitosan at the alkaline pH of the cement matrices, its incorporation in the cement mortars led to slight changes in

the fresh-state mixtures. In this paper, the role of a water-soluble carboxymethylchitosan (CMCH) derivative is addressed. The introduction of some functional hydrophilic groups (carboxylic) in the polymer chain leads to a solubility increase at alkaline pH, justifying of the potential of this derivative with a view to its use in cement systems.

The aim of the current research is to investigate the effects of the addition of CMCH on fresh-state properties and leachability for heavy metal doped-cement mortars. The selected metals were Pb(II), Cr(VI) and Zn(II), as they have been identified as priority metallic pollutants and they have been shown to have an influence on the fresh-state properties of cement-based mortars [5,7–9]. The polymer's ability to chelate heavy metals as a way of removing them from waste waters and subsequently retaining them in cement mortars was also studied.

2. Experimental

2.1. Materials

An ordinary Portland cement (OPC) (CEM II 32,5N, supplied by Portland S.A. Olazagutía, Spain) and a siliceous aggregate were used to prepare the mortars. Material characterization and grain size distribution of the aggregate are reported elsewhere [10].

The tested polymer was a carboxymethylchitosan derivative, which was purchased from Heppe Medical (Ref. 40002). The characterization of the CMCH polymer showed a molecular weight of 51 kDa and a deacetylation degree of 99%. These data were obtained according to methods based on viscosity measurements and first
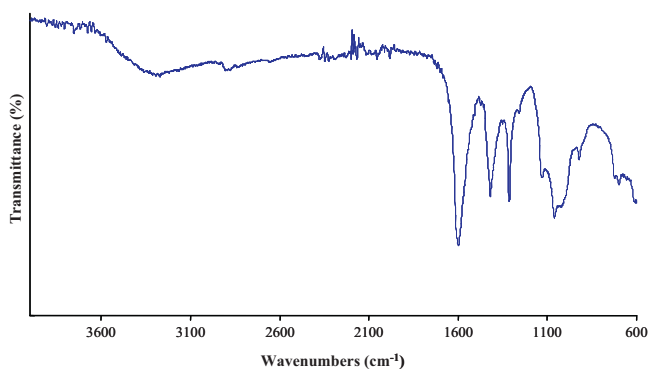
Fig. 1. FTIR spectrum of the assayed carboxymethylchitosan (CMCH).

derivative ultraviolet spectrophotometry, respectively [11,12]. The derivative is a N,O-carboxymethylchitosan, with a degree of substitution (DS) of 0.9 according to the data from the supplier. DS can be determined by the molar ratio of carboxymethyl acid groups to monosaccharide units, as follows: DS_{abs} = mol of $-CH_2COOH$ groups/mol of monosaccharide unit [13]. In Fig. 1, FTIR results of the polymer show the occurrence of an intense band at $1588\,cm^{-1}$ and a moderate band at $1411\,cm^{-1}$, which, in accordance with previously published results, were attributed to the symmetric and asymmetric axial deformations of COO, respectively [14,15]. These facts confirmed the introduction of the carboxymethyl groups to the polymer chain.

When necessary, the heavy metal load was made from $Zn(NO_3)_2$, $Pb(NO_3)_2$ (Merck, Darmstadt, Germany) and $K_2Cr_2O_7$ (Panreac, Barcelona, Spain).

2.2. Mortar preparation

Cement, aggregate, additive and heavy metal (these last compounds only when necessary) were blended for 5 min with a solid mixer (Lleal S.A.). Then, water was added and mixed for 90 s at low speed, in a Proeti mixer. Mortars settled for 10 min before the tests. The binder:aggregate ratio was 1:3 by weight. In order to compare the effect of the addition of the polymer to the mortar, all the samples were prepared with the same water:cement ratio, 0.55. The additive was added at 0.4% of the cement weight while the heavy metal was incorporated in 1% with respect to cement.

2.3. Tests

2.3.1. Fresh state properties of the mortars

The following standardised tests were used: the flow table test in order to measure consistency [16], water retention capacity [17] and setting time [18].

2.3.2. Cement solutions

Specific mixtures of cement, heavy metal, water and additive were prepared to assess the zeta potential. Following the method proposed by Zhang et al. [19,20] and assayed previously [21], solutions with different concentrations of CMCH (from 0.025 to 0.60 wt.%) were prepared. Cement was added with a solute/liquid ratio of 0.0025 and heavy metal (Zn, Pb or Cr) was added at a 1% metal/cement ratio. After 20 min of stirring, the mixtures were separated by centrifuging, and the supernatants were analyzed using a Zeta Potential Analyzer ZETA PLUS (Brookhaven Instruments Corporation, New York, U.S.A.). Reported values are the average of twenty measurements.

For particle size distribution (PSD) measurements, 20 g of cement were added to 100 g of solutions with different amounts of CMCH in water, the resulting CMCH/cement ratios ranging from

0% to 1%. A 1% (metal/cement) load of Zn, Pb or Cr was, in each case, added to the solutions. PSD of these samples was determined using a Mastersizer (Malvern Instruments, U.K.).

Optical microscopy and TEM examinations were carried out in order to assess the above-mentioned measurements. For optical microscopy, the solutions prepared were similar to those of PSD (20 g of cement in 100 g of solution) with CMCH/cement ratio of 1%. The images were taken with an optical Olympus CH40 microscope, with Color view-soft imaging systems camera. TEM images were obtained from a solution of 5 g/L of cement with a 1% of CMCH. One drop of this suspension was disposed on a copper grid and subsequent measurements were carried out with and without contrast (phosphotungstic acid) in a LIBRA 120 energy-filtering TEM (Zeiss) operated at 80 kV.

2.3.3. Chelating behaviour in solutions

The carboxymethylchitosan derivative and metal solutions were dissolved at different pHs (13, 11, 8.25 and 7). Either $0.1\,M\,HAc/NaAc$ or $0.1\,M\,Na_2HPO_4/H_3PO_4$ were used for pH = 7.00 whereas $0.1\,M\,NH_4Cl/NH_3$ buffer solutions were prepared for pH 8.25. Certipur standard solutions containing 1000 ppm of the heavy metals Zn(II) ($Zn(NO_3)_2$ in HNO_3 2–3%) and Pb(II) ($Pb(NO_3)_2$ in HNO_3 2–3%) and Cr(VI) (K_2CrO_4 in H_2O) were purchased from Merck (Darmstadt, Germany).

Voltammetric measurements were performed with a Metrohm 746 VA Trace Analyzer coupled with a 747 VA Stand. A three-electrode arrangement consisting of a glassy carbon counter electrode, an Ag/AgCl/KCl 3 M reference electrode and mercury electrode were used. All the complexes were proved to be formed quasi-instantaneously, so that a minimum conditioning time (60 s) was allowed after every spike of metal. A known amount of ligand was placed in the electrochemical cell and then increasing amounts of Zn and Pb, respectively, were spiked on the different solutions.

Metals were accumulated onto the mercury electrode by applying a sufficiently negative potential (ca. 300 mV with respect to the respective anodic stripping peaks) for 60 s, followed by a resting time of 30 s. Measurements were made on the differential pulse mode (DPV) with a pulse amplitude of 50 mV throughout and a scan rate of $20\,mV\,s^{-1}$.

Dynamic light scattering measurements were done by means of a Dynapro (model MS/X) photonic correlation spectrometer equipped with a 248 multi-tau correlation channel and a Peltier thermostat unit. Laser source wavelength was 825.2 nm. Detector was orthogonal to the source and autocorrelation intensity software was included in the Dynamics^{TM} package. Cells of 1 cm pathway were employed and hydrodynamic radii were calculated from diffusion coefficients according to the Stokes–Einstein equation.

2.3.4. Leaching tests of heavy metals in CMCH-modified cement mortars

Fresh mixtures prepared according to Section 2.2 were afterwards moulded and cured for 28 days [22]. Cylindrical test pieces of 40 mm × 37 mm were placed in sealable 110 mm × 110 mm × 110 mm methacrylate tanks.

The determination of the leaching of inorganic components of mortars was carried out following the Tank Test [23]. This test involves placing a complete sample in a leaching fluid (demineralized neutral pH water) and replenishing the leachate at specified times.

After the period indicated, all the eluate was drained off and filtered with a nylon membrane of 0.45 μm of pore size (CHMLAB Group, Barcelona). A fixed volume of 10 mL of each sample was stored with nitric acid sub-boiling for further analysis of the concentration of the leached components. Afterwards, the tank was filled again with the same quantity of water (1 L) and the proce-

Table 1
Experimental parameters for Zn and Pb quantification by electrothermal atomic absorption spectrometry.

Instrumental parameters	Zn	Pb
Wavelength (nm)	213.9	283.3
Slit width (nm)	0.7	0.7
Lamp current (mA)	4	10
Sample – modif. vol. (μL)	15 – 5	15 – 5
Measurement mode	Peak area	Peak area
Source lamp	Hollow cathode	Hollow cathode
Background correction	Zeeman	Zeeman

Temperature programme

Step	Temperature (°C)		Ramp (s)		Hold (s)		Argon (mL min^{-1})		Read on
	Zn	Pb	Zn	Pb	Zn	Pb	Zn	Pb	
Drying	130	130	15	20	40	50	250	250	–
Charring	600	850	15	20	35	35	250	250	–
Atomization	1700	1600	0	0	5	5	250	0	Yes
Cleaning	2400	2500	1	2	3	5	250	250	–

dure was repeated. The eluates were collected at eight different times (0.25, 1, 2.25, 4, 9, 16, 36 and 64 days).

The concentration of the leached Cr, Zn and Pb was measured by atomic absorption spectrometry (Perkin-Elmer AAnalyst 800).

Chromium measurements were performed at 357.9 nm, using a hollow cathode lamp operated at 25 mA and bandwidths of 0.7 nm. An air/acetylene flame with a 10.0/2.0 mL min^{-1} flow ratio was used.

Transversely heated graphite tubes with end caps supplied by Perkin-Elmer were used for zinc and lead determinations. Integrated absorbance peak areas were measured by using single element hollow lamps. Argon was used as the inert gas, the flow rate being 250 mL min^{-1} during all stages except atomisation, when the flow was stopped exclusively for lead. The instrumental settings and temperature programme of the spectrometer were optimised as summarized in Table 1.

Pore structure of the hardened specimens was assessed by mercury intrusion porosimetry. A Micromeritics AutoPore IV 9500 with a range of pressure between 0.0015 and 207 MPa was used.

Additionally, in order to assess the effectiveness of a previous complexation, the leachability of a series of mortars prepared with a previous reaction of the metal and polymer in solution was studied. These mortars were obtained as follows: solutions of 1% (metal/cement ratio) of each metal (Zn and Pb, in this case) were prepared and the pH was adjusted to 7.00 or 8.25 with a solution of NH_4Cl/NH_3. The criterion for pH selection was to set a pH value as high as possible (keeping, to a certain extent, similarity to the alkaline matrix of the cement) but allowing a certain degree of complexation to take place. This fact depends on the metal speciation, i.e. the chemical form of the heavy metal that can be complexed. As CMCH at neutral or alkaline pH deprotonates giving rise to carboxylate groups, cationic forms of heavy metal would be able to

be retained by the polymer. In this sense, pH 7 turns out to be the limit for the appearance of Pb^{2+}, as from this pH onwards it starts to precipitate as $Pb(OH)_2$ and cannot be chelated. On the other hand, pH 8.25 is the limit for the Zn^{2+} presence.

Then, the CMCH powder was added to the solutions. This mixture was kept under magnetic agitation for 24 hours to guarantee the dissolution and the complexation of the components. The resulting solution was added to the solid components of the mortar (as mixing water) and mixed as indicated in Section 2.2. Leaching tests were also carried out as described above.

3. Results and discussion

3.1. Fresh-state behaviour of CMCH-modified mortars

Fig. 2 shows the slump results of cement mortars modified by loading the target heavy metals with and without the addition of CMCH. The addition of either Pb or Cr caused, if any, very little changes in the slump (a fluidity reduction of around 6% for Cr and around 3% of flowability increase when Pb was added by comparison with the plain cement mortar). Nonetheless, the addition of Zn was highly detrimental for the consistency behaviour of the mortars, because it gave rise to a notably heterogeneous mixture, which in fact was disaggregated, hindering the right measurement of the slump.

The addition of CMCH involved a strong fluidity reduction for the plain cement mortar (48% reduction in fluidity). The heavy metal bearing mortars also showed a slump reduction, but to a lesser extent than the plain mortar (4.5% for Cr-loaded mortar and 9% for Pb-loaded mortar). It is thus evident that the presence of the heavy metals thwarted the effect of the polymer addition on the consistency of the fresh mixture.
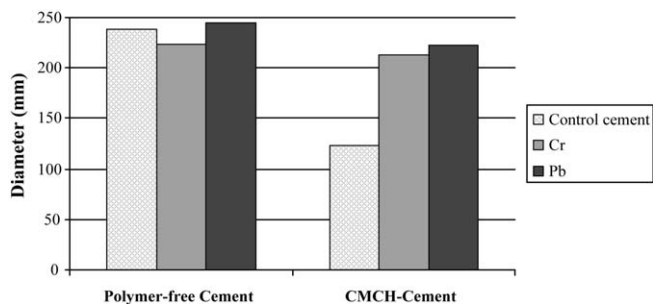
Fig. 2. Effect of the addition of different heavy metals on the consistency – slump values – of polymer-free and CMCH-modified fresh cement mortars.
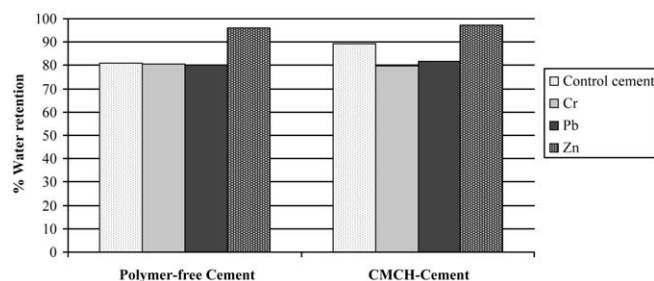
Fig. 3. Effect of the addition of different heavy metals on the water retention ability of polymer-free and CMCH-modified fresh cement mortars.
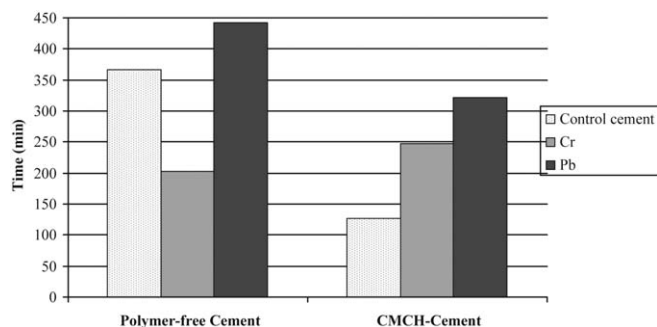
Fig. 4. Influence of the heavy metal addition on the setting time of polymer-free and CMCH-modified fresh cement mortars.
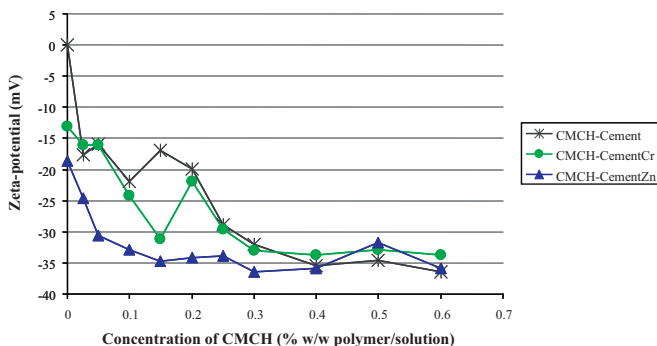

Fig. 5. Influence of heavy metals on the zeta potential trend for the metal-free cement solution, 1 wt.% Cr/cement solution and 1 wt.% Zn/cement solution, under increasing CMCH concentrations.

From the results of the water retention ability (Fig. 3), it can be concluded that chromium and lead did not modify this property when added to a plain cement mortar. However, the zinc addition clearly increased the retained water (almost 20% increase compared to the plain mortar).

When CMCH was added to the plain mortar, the water retention capability of the fresh mixture was increased by 10%. No significant changes were found when CMCH was incorporated in heavy metal loaded mortars. Once again, the presence of the metals spoilt the polymer effect.

Measurements of the setting time showed the most important changes in fresh-state performance of the mortars (Fig. 4). Chromium gave rise to a setting time reduction of 45% in comparison with the plain mortar, whereas the addition of lead caused a delay in the setting time of 75 min. Owing to the aforementioned

effect of the Zn on the mortar's consistency, setting time results could not be properly determined in the presence of this metal, so the results are not shown.

The effect of the CMCH polymer on these samples was noteworthy: it caused a strong decrease in the setting time in plain cement mortars (the setting process was accelerated by 65%). On the other hand, CMCH lessened the effect of heavy metal addition in the mortar setting time either by delaying the setting time for chromium-samples or by reducing it for lead-samples. In the latter case, the setting time was reduced by as much as 120 minutes. These experimental findings suggest the effectiveness of CMCH addition in overcoming the strong modifications in setting time produced by the incorporation of either Cr or Pb in cement-based mortars. Therefore, this experimental evidence takes on practical relevance for the handling of metal-bearing cement mortars.

3.2. Cement solutions

The previous results prompted us to make zeta potential measurements that provide information on the net-surface charge for cement particles in the cement suspensions. Fig. 5 shows that the presence of the polymer, which, at such an alkaline pH, would be a negatively charged polyelectrolyte owing to its functional carboxylate groups, shifts the zeta potential values of the cement particle surfaces towards more negative figures.

This implies an interaction between the polymer and the positively charged cement particles, giving rise to adsorption on the surface of the particles. Fig. 6a depicts simulation of the adsorption of carboxylate groups of the CMCH onto the cement surface. This finding is supported by previous work reporting adsorption onto cement particle surfaces for carboxylate substituted polymers [24,25]. The adsorbed polymer molecules could then link different cement particles (Fig. 6b) through the multiple carboxylate moieties, giving rise to large agglomerates of cement particles and, therefore, to a fluidity reduction as proved by the slump reduction.

However, when negative ions were added (chromate, CrO_4^{2-}), they might compete with polymer molecules for the binding sites on the surface of the positively charged cement particles, leading to an increase in "free" polymer molecules. Since CrO_4^{2-} ions might be adsorbed on the cement particles, zeta potential values were expected to remain negative, as Fig. 5 confirms: when 0% of polymer was incorporated, zeta potential turned out to be negative as a result of the adsorption of chromate ions on the cement particles. In the presence of increasing polymer amounts, zeta potential values followed a similar trend to that of the metal-free samples.

It is noteworthy that zeta potential measurements for Zn and Cr follow the same pattern. This is a confirmation that most Zn is,
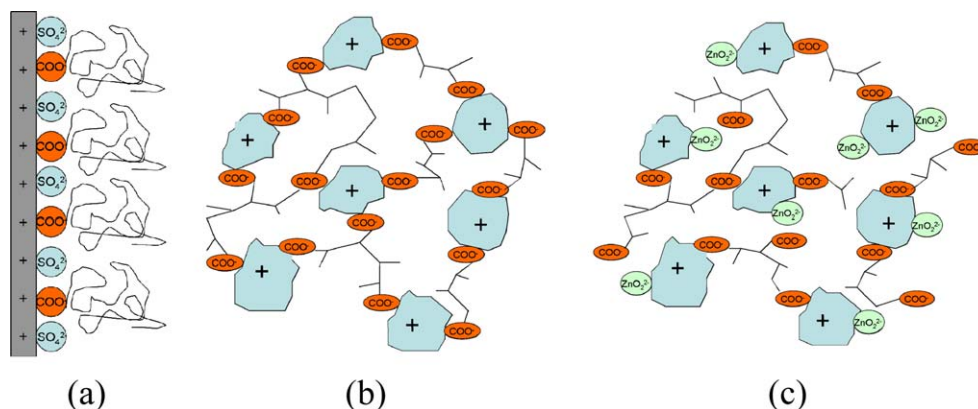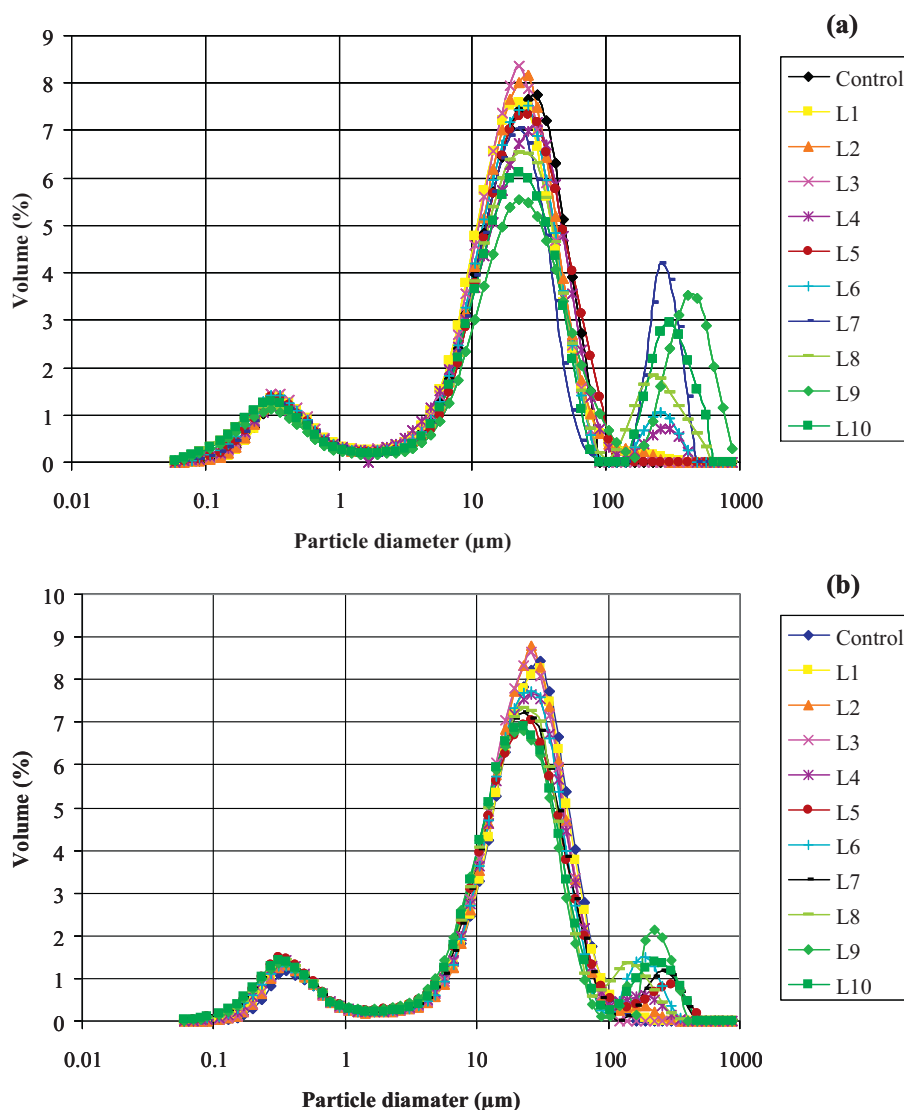

Fig. 6. Schematic representation of (a) the adsorption of CMCH to the positively charged surface of the cement particles; (b) interlinking of cement particles with CMCH; and (c) example of a competitive adsorption of the negatively charged oxoanions (e.g. zincates in this case).

Fig. 7. Effect of the heavy metal presence on the particle size distribution in cement solutions for increasing CMCH concentrations (control: 0% CMCH; L1–L10: 0.1–1.0% CMCH). (a) Metal-free cement solution; (b) 1 wt.% Pb-bearing cement solution.
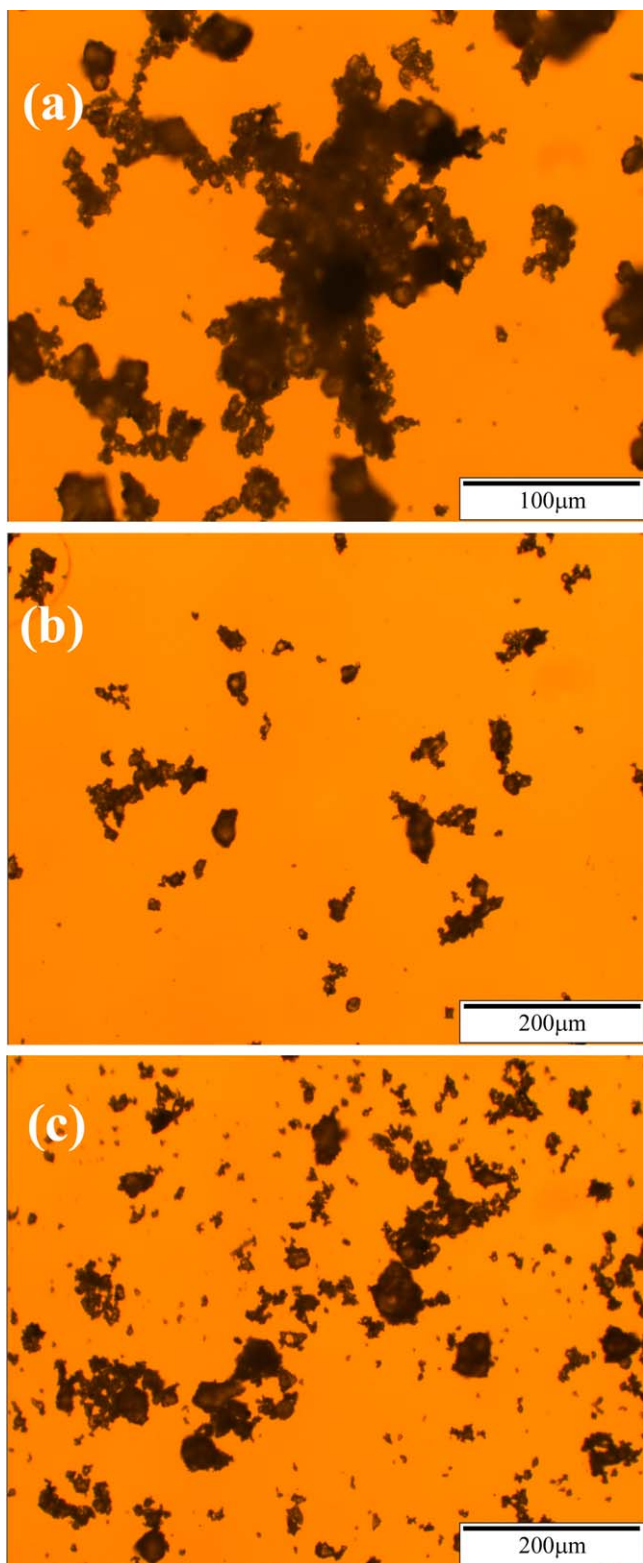
under the alkaline conditions of the solution, present in the anionic form (i.e. ZnO_2^{2-}) and its competitive adsorption onto the cement particles yields a flaky consistency to the metal-loaded cement. This preference for adsorption onto the cement has previously been described elsewhere [26], although the authors claimed Zn to be in the cationic form linked in some way to the silicates of the cement phases. From the experiments carried out in this research and within the experimental limits of the present study, we conclude that Zn is rather acting in the anionic form and it competes with CMCH for the cement particles (Fig. 6c). This competition for the available binding sites on the cement particles justifies the attenuation of the effect of the CMCH in fresh-state properties observed in the presence of the assayed heavy metals.

Fig. 7a shows PSD in cement solutions with different amounts of CMCH. The addition of CMCH gave rise to a flocculant effect that can be observed through the growing quantity of large agglomerates ranging between 250 and 450 μm as a function of the polymer dosage. As explained above, this effect arose as a result of the linking between polymer molecules and cement particles. The negatively charged functional groups of the polymer molecules, acting as anchoring groups, can be adsorbed onto positively charged cement particles (such as ettringite) causing a negative measurement of

the surface potential in the compact Stern layer [27]. The formation of the agglomerates was evidenced by the optical microscopy and TEM observations of the cement solutions (Figs. 8a and 9, respectively). Large agglomerates of cement particles can be observed in these photographs, confirming the previous assumptions on the action mechanism of the polymer.
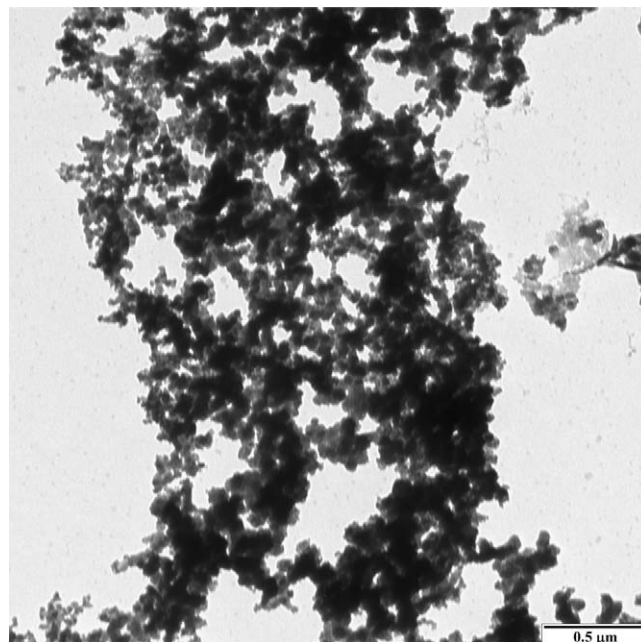
However, the addition of a 1 wt.% of lead, zinc and chromium exerted an influence on the performance of the polymer, decreasing the amount of large agglomerates of cement particles, as exemplified in Fig. 7b (in the case of Pb). This behaviour is in agreement with the previous zeta potential data. The addition of the heavy metals involved a competitive blockage of the binding sites on the cement particles, thus preventing some polymer molecules from adsorbing on the surface of these particles. Accordingly, the size of the agglomerates was reduced. The competition between heavy metals and CMCH for binding on cement particles rendered the flocculation less marked. Optical microscopy photographs allowed us to see a lower degree of flocculation between cement particles when different heavy metals were added compared to the samples without heavy metals (Fig. 8b and c).

Further experiments were set up in order to see whether the adsorption pattern prevails over any other mechanism such as com-

Fig. 8. Images of (a) metal-free, (b) Cr-bearing and (c) Pb-bearing CMCH-cement solutions.

Fig. 9. TEM micrograph of a cement particle agglomerate in the presence of CMCH.

extent owing to the proportional scarce ratio of metals in their original cationic form.

These studies were also performed in less alkaline media or even in neutral solutions, in order to check if the assayed CMCH polymer would be of value in chelating heavy metals from slightly alkaline or neutral waste waters, so that they could afterwards be incorporated and immobilized into a cement mortar. Besides, this research would be interesting in order to explore a potential use of CMCH as admixture for cement with near-neutral pH, such as some phosphate-modified calcium aluminate cement [28].

The marked influence exerted by the different CMCH assayed concentrations on the electrochemical response of the metal matched a typical complexing behaviour at pH 7.00 and pH 8.25. Maximum chelating effect (up to 12 mol of metal per MW of the CMCH) was obtained for the minimum polymer assayed concentration (0.05 μM). This chelation ability decreased as the CMCH concentration was increased: complexation was reduced by half for a 1 μM CMCH concentration.

This behaviour can be ascribed to intertwining of polymer chains among themselves when in relatively high concentrations leaving less binding positions available for the metals. At lower CMCH concentrations, metals could be allocated in an interlayer arrangement so that an overall larger stoichiometry results.

Dynamic light scattering studies have been devised as to support this explanation. The aim of the experiments was to check whether any substantial difference in either particle size or diffusion coefficient could be found for solutions containing the metal–CMCH complex with respect to a blank solution. The solution containing just the CMCH polymer gave rise to a scatter pattern in which a polymer agglomerate was detected with a theoretically estimated hydrodynamic radius of 0.126 nm and a diffusion coefficient value of 1.94×10^{-5} cm^2 s^{-1}. The same solution with an excess of metal (Zn as a model) showed a different scattering profile in which a signal responsible for the 99.8% of the polymer agglomerate mass has a larger radius (1.107 nm) and a significantly decreased diffusion coefficient (2.22×10^{-6} cm^2 s^{-1}). This finding supports the hypothesis of a folded-like structure being formed between the CMCH and Zn [29,30].

These results, showing complexation of the expected cationic form of either Zn(II) or Pb(II) by the polymer, allowed us to explore

plexation. The distinct electrochemical responses of metals in the presence of several previously fixed concentrations of CMCH (0.05, 0.1, 0.5 and 1 μM) were monitored and served as indicators of the occurrence of a complexation pattern [6]. When the assayed pH was strongly alkaline (pH 11–13, resembling the cement media), results showed that complexation proceeded to a very limited
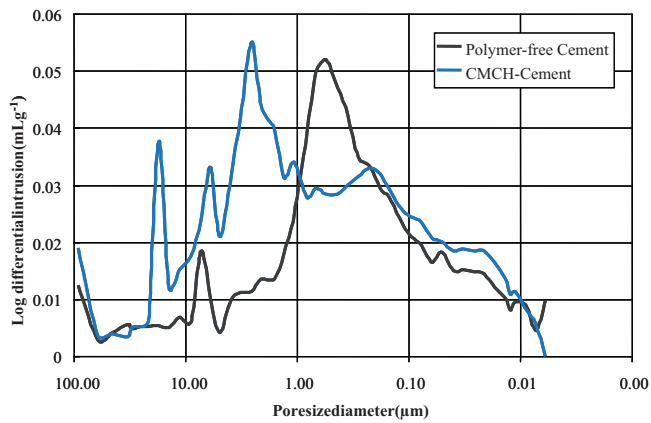
Fig. 10. Pore size distribution of polymer-free and CMCH-modified 28-day hardened mortars.

the leachability of these metals once they have been complexed by the polymer either at pH 7.00 or at pH 8.25 and incorporated into cement mortars, as described below. This study did not include Cr(VI), due to the fact that it remained as chromate.

3.3. Leaching tests of heavy metals in CMCH-modified cement mortars

Real specimens of cement mortars aged for 56 days were subjected to leaching tests, in order to assess the effectiveness of the CMCH as a metal retainer. However, it is necessary to state the experimental limits of the study, because it was addressed only in mortars with one water/cement ratio (0.55). Experimental results showed that the presence of heavy metals in the leachate increased when CMCH was added to the mortar. The accumulated values of the eluates up to testing day 64 showed that CMCH-free mortars leached 3778, 37 and 7 mg m^{-2} (mass of metal/test-probe surface area ratio) of Cr, Pb and Zn, respectively, whereas 5709, 47 and 11 mg m^{-2} of those metals were released in CMC-modified mortars. These results are in agreement with previous data reporting great immobilization in hydrated cementitious matrices for Pb and Zn, ranging from 99.82 to 99.99%. Cr is an exception and it has been reported to be immobilized in lower degree (from 85.97 to 93.33%) [31]. Owing to the large retention ability of cement matrices, the released amounts of both Pb and Zn were well below the upper limit of the regulatory norm (400 and 800 mg m^{-2}, respectively) [32], as it has been also reported in a previous work [33]. However, chromium exceeded the top value indicated in that norm (120 mg m^{-2}). These results are in line with those showing the absence of complexation phenomena at high alkaline pH between CMCH and the metals. However, when the results are confronted with the accepted criteria for waste to be used for landfills, in the case of monolithic waste [34], only the cumulative leached concentrations of Zn met the limit (100 mg m^{-2}), while the cumulative leached concentrations for Pb and Cr exceeded the limits (20 and 25 mg m^{-2}, respectively). The mechanism of the metal retention into the mortar matrix turns out to be largely a physical entrapment (adsorption), as proved by the experimental measurements (Section 3.2). The decrease of the available adsorption sites for the metal contributed to the increased metal release. Besides, CMCH was seen strongly to reduce the fluidity of the mortar as well as its degree of compactness in the fresh-state. As a consequence, larger porosity values were measured for the hardened material also contributing to the release of heavy metals in a higher ratio. Mercury intrusion porosimetry measurements showed a net porosity increase of hardened mortars prepared with CMCH-modified cement, specially for the large-size pores (Fig. 10). Further tests with a range of differ-
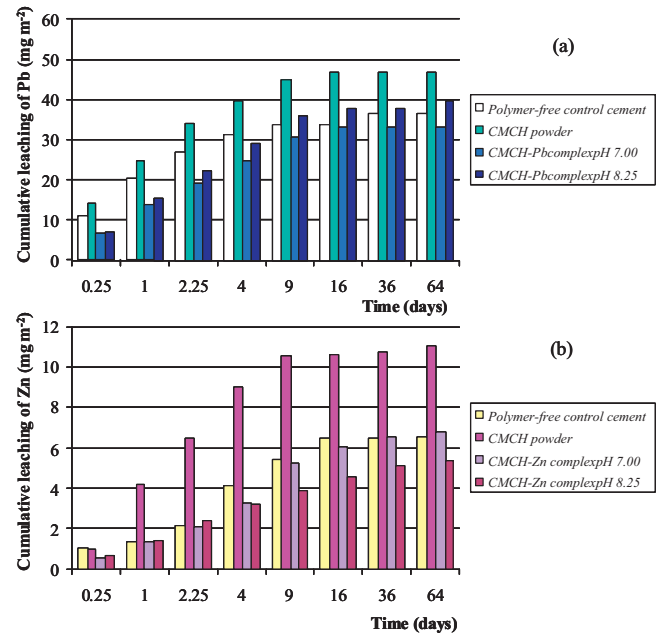

Fig. 11. Accumulated leachability results for (a) Pb and (b) Zn, in: polymer-free cement mortars; mortars modified by the addition of powdered CMCH; and mortars with metals and CMCH incorporated as a previously formed complex at either pH 7.00 or pH 8.25.

ent water/cement ratios will be necessary in order to minimize the final porosity of the hardened mortar to assess the validity of the CMCH addition comprehensively in terms of leaching.

However, when Zn and Pb were previously sequestrated by the polymer from solutions of pH values of 7 and 8.25 and subsequently incorporated in the cement mortars, the leachability of these metals was improved when compared with results obtained for the polymer–absent metal-bearing cement mortar. Fresh-state properties of the cement mortars prepared in this way did not show any significant alteration with respect to the data obtained from mortars prepared by powdered CMCH addition, as discussed in section 3.1. Fig. 11 shows the accumulated leachability results for Pb and Zn, in: (a) polymer-absent cement mortars; (b) mortars modified by the addition of CMCH in powder (as reported above); and in mortars in which metals were incorporated in their polymer-complexed form both at pH 7.00 (c) and 8.25 (d).

The leachability of lead was clearly reduced when considering the accumulated results after 54 h (2.25 days) if the metal was incorporated in the polymer-complex form. Compared to the immobilizing ability of the plain cement mortar, the addition of the CMCH–Pb complex reduced the Pb leachability in a 28.6% (pH 7.00) or in a 17% (pH 8.25). The differential between the polymer-free cement and the CMCH–Pb complex underwent a slight reduction at day 9. The CMCH–Pb complex within the cement matrix remained stable from day 16 onwards. In Fig. 11, an increasing trend for lead leaching from plain cement can be observed, while a plateau has already been reached at day 16 for the lead leaching from the polymer-metal complex cement. As an evidence, 36-day measurements of the lead released from the pH 7.00 polymer-complex cement showed a reduction of ca. 10% in the leachate compared to the plain cement mortar, thus showing the effectiveness of the complexation process with the CMCH polymer.

As far as the leachability of Zn is concerned, encouraging leaching values were obtained for samples prepared from pH 8.25 CMCH–Zn solutions. Day-64 results showed an 18.5% reduction of the Zn released in comparison with the plain cement mortar, thus revealing the benefits of using CMCH for chelating heavy metals and their subsequent treatment by cement-based S/S.

Differences observed between Zn and Pb as a function of the pH in which the chelation took place may be related to (i) the degree of ionization of the carboxylic functionalities in the polymer chain and (ii) the relative concentration of the metal species. In fact, these two factors are dependent on the pH of the solution: a higher pH value results in a higher ratio of ionized carboxylic groups, i.e. carboxylates, which are able to chelate cationic forms of the metals. On the other hand, pH exerts – at the same time – a strong influence over the speciation of the metals. At pH 7, the majority of the Zn appears as Zn^{2+}, while at pH 8 small percentages of $Zn(OH)^+$ and $Zn(OH)_2$ have also been reported [35]. This last species of Zn cannot be complexed by the carboxylate groups of the polymer. In the case of lead, the higher precipitation of $Pb(OH)_2$ from pH 7 onwards hinders its complexation and removal from the solution. Therefore, the amount of lead released turned out to be larger from samples prepared with polymer–metal complex at pH 8.25, because, although the number of chelating groups of the polymer was higher, the concentration of the cationic form Pb^{2+} able to be chelated was as a matter of fact lower. This trend was inverted for Zn: the higher concentration of the cationic form Zn^{2+} in comparison with Pb^{2+} at pH 8.25, together with a large number of carboxylate groups of the polymer, resulted in a greater complexation of the Zn, improving its immobilization in cement mortars.

Owing to the large metal retention ability of hydrated cement matrices, the release of Pb and Zn, at the assayed concentrations of heavy metals (1% metal/cement), previously complexed or not, is within the limits of the Dutch Soil Quality Regulation [32]. In addition, cumulative leached concentrations of Zn after 64 days also met the more demanding requirements of the Landfill (England and Wales) regulations ($100\,\mathrm{mg\,m^{-2}}$), but none of the studied options complied with the limits for Pb ($20\,\mathrm{mg\,m^{-2}}$) [34]. However, these experimental findings open a route for larger improvements in metal retention by studying the most suitable parameter involved (optimum pH for complexation, larger metal load and even different polymer concentrations).

4. Conclusions

Addition of CMCH to the cement mortars caused significant changes in the fresh-state properties of the mortars: fluidity decrease and setting time reduction. Incorporation of target heavy metals (Zn, Cr or Pb) hindered the effect of the polymer. Strong modifications in setting time caused by the presence of either Cr or Pb may be overcome by the use of CMCH.

Both the polymer through its anchoring groups (carboxylate functionalities) and the oxoanionic form of the target metals have been proved to adsorb onto positively charged cement particles. In the case of the polymer, this adsorption was responsible for the flocculation and setting time reduction. A competitive mechanism between the polymer and the heavy metals has been proposed in order to explain the reduced effect of the polymer when metals were included.

Studies on the chelating role of the polymer towards heavy metals showed that when the assayed pHs resembled cement media (alkaline pH from 11 to 13), complexation proceeded to a very limited extent owing to the proportional scarce ratio of metals in their original cationic form, pointing to the physical entrapment as the main mechanism of immobilizing heavy metals in CMCH polymer-cement mortars. Studies focusing on the ability of the CMCH in sequestrating metals from polluted waste waters with slightly alkaline o near-neutral pHs showed real complexation (up to 12 mol of metal per MW of the CMCH which was obtained at low polymer concentrations).

Leachability of metals from powdered CMCH-containing cement mortars increased with respect to plain cement mortars, in accordance with the observed higher porosity of the hardened specimens. On the other hand, an improvement in the immobilization of Pb and Zn in the cementitious matrices was achieved by previously complexing the metals in near-neutral pH solutions by CMCH. After 64 days, the cumulative amount of Pb released decreased by 10% with respect to plain cement, whereas the total amount of Zn in the leachates dropped by 18.5%.

These results encourage us to undertake further studies in order to sequestrate toxic heavy metals from polluted waste waters and immobilize them in cements with different compositions.

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