

Studies on chitosan as an admixture for cement-based materials: assessment of its viscosity enhancing effect and complexing ability for heavy metals

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Abstract

Chitosans of different molecular weights were assessed as cement admixtures in order to modify the rheological properties of a fresh cement paste. Their sequestering capability with respect to several heavy and toxic metals was checked and the complexation processes were investigated by different approaches based on electrochemical measurements. The aim was to conduct research on a potentially useful polymer to be added to cementitious materials acting as a viscosity modifier as well as a heavy metal immobilising agent. Pb, Cu, Zn, Cd, Mo and Cr were used as target metals. The highest complexation affinity was found towards Zn, with stoichiometries up to 1:40 having been calculated. Chitosan was proved to act as a thickener in cement mixtures. The highest molecular weight chitosan showed the greatest effectiveness taking into account its combined role as heavy metal retainer and thickener. In addition, a clear interaction between this high molecular weight chitosan and cement particles was also demonstrated by means of zeta potential measurements.

Keywords

metal-polymer complexes, viscosity, additives, composites, electrochemistry

INTRODUCTION

The use of viscosity-enhancing admixtures (VEAs) has been shown to be efficient in improving the stability and cohesion of cement-based materials. VEAs usually increase the viscosity of the fresh cement paste, thus reducing the risk of the separation of the heterogeneous constituents of a cement-based mortar or concrete.¹ Especially when used for rendering, VEAs also prevent cement mortars from sagging. They have also been reported as anti-washout admixtures for underwater concrete placement. At the same time that they show a viscosity-enhancing behaviour, these additives might act as set-retarders, water-reducers, and water-retainers.² Regarding the chemical composition of these admixtures, polysaccharides can be quoted as some of the most widely used products.³⁻⁵ Sugars, starches, and cellulose ethers have been studied and their effect when added to cement-based materials reported.⁶

Cement materials have also shown the ability to act as effective agents towards the solidification/stabilisation of hazardous waste substances, especially heavy metals (studies on Cr(VI) and divalent Pb, Cd, Ni and Hg have been published).⁷ Cement functions as a non or less hazardous deposit for unwanted by-products and rejects. Besides low cost, availability and versatility are additional advantages for cement-based systems.⁸

Certain polymers, present in cement as typical additives (such as CMC and HEC), show a good adsorption of heavy metals and may act as effective removing agents from polluted waters and untreated sludges.^{9,10} Understanding of metal retention in polymer-cement composites requires a previous knowledge of the mechanisms involved in adsorption and fixation of those metals by the components of the material. Apart from some interaction with certain components of cement, complexation processes may be expected to occur between metallic species and the added polymer.¹¹ Voltammetric studies have shown usefulness to elucidate complexation behaviour in aqueous solutions, providing relatively simple approaches to the estimation of polymer-metal stability constant, stoichiometry of formed complex and complexing capacity of the ligand (i.e., the amount of metal that the polymer may uptake and stabilise in the matrix).¹² This set of data is very useful when determining what amount of metal can be added to the cement matrix and, at the same time, will serve in the modelling of the leaching patterns that may follow these metals when solidified/stabilised on the polymer-cement.¹³

Chitosan, the deacetylated derivative of chitin, is the second most abundant natural polysaccharide. This polymer and its derivatives have been used as biomaterials because of their biocompatibility, biodegradability, and biological activities.^{14,15} Purified qualities of chitosans have been used as additive for many biocements, dental biocements, and cements for reparation of bones.¹⁶ In these composites, chitosan has been reported i) to enhance injectability of these composites; ii) to increase setting time in a similar way to cellulose derivatives in cement-polymer systems,¹⁷ and iii) to act as a thickener - i.e. a cohesion-improving agent - in calcium phosphate cement for the repair of bones.¹⁸

Furthermore, chitosan has shown its successful role as heavy metal retainer. Some recent studies have pointed to its excellent capacity to act as an effective complexing and removing agent for heavy metals.¹⁹⁻²¹ The binding mechanism of metal ions onto chitosan is not yet fully understood; mechanisms such as adsorption, ion exchange and ion chelation have so far been proposed.^{22,23} The hydroxyl groups and amine sites in the polymeric chain are the more active binding sites for metal ions, establishing dative bonds with transition metals.²⁴

Literature is rather lacking on the behaviour of chitosan and its derivatives as cement admixtures for building purposes. The strong resemblance that chitosan bears to other polysaccharides like cellulose endorses the interest of these studies. In addition, as mentioned above, chitosan and its derivatives have shown a clear capacity for chelating heavy metals. The rationale for this work is that chitosans -or derivatives- would be potential admixtures (rheological modifiers) in order to obtain polymer-modified cements with heavy metals retaining and/or immobilizing properties.

As a preliminary study devoted to assessing the aforementioned potential use of chitosan, the present paper intends i) to test whether most toxic metals -Cu, Zn, Cd, Pb, Cr and Mo- undergo complexation with chitosan, and ii) to evaluate the behaviour in fresh state of cement mortars modified by chitosan addition.

EXPERIMENTAL

Voltammetric studies on chitosan complexing ability of heavy metals

Chitosans with different molecular weights [low molecular weight, 50-190 kDa (LMW), Ref. 448869-50G; medium molecular weight, 190-310 kDa (MMW), Ref. 448877-50G; and high molecular weight, 310-375 kDa (HMW), Ref. 419419-50G] and different deacetylation degrees (92%, 80% y 76%, respectively) used in this study are

commercial products from Sigma-Aldrich (Steinheim, Germany). The MW and DDA data were supplied by the manufacturer, and their validity was subsequently checked according to previously published procedures.^{25,26} Acetic acid and sodium acetate were purchased from Merck (Darmstadt, Germany). The Certipure standard solutions containing 1000 ppm of the heavy metals, Copper ($\text{Cu}(\text{NO}_3)_2$ in HNO_3 2-3%), Zinc ($\text{Zn}(\text{NO}_3)_2$ in HNO_3 2-3%), Cadmium ($\text{Cd}(\text{NO}_3)_2$ in HNO_3 2-3%), Lead ($\text{Pb}(\text{NO}_3)_2$ in HNO_3 2-3%), Chromium (K_2CrO_4 in H_2O) and Molybdenum ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in H_2O) were supplied by Merck. Chitosan and metal solutions were dissolved in 0.44 M acetic-0.04 M acetate buffer solution (pH = 4.0). The optimum concentration of ligand for the determinations was found to be 0.5 μM . Lower concentrations than 0.1 μM showed a very weak signal and values higher than 1 μM caused the saturation of the electrode.

Voltammetric measurements, both differential pulse anodic stripping voltammetry (DPASV) and cathodic differential pulse voltammetry (DPV), were performed with a Metrohm 746 VA Trace Analyzer coupled with a 747 VA Stand equipped with a static mercury drop electrode (SMDE). A conventional three-electrode arrangement consisting of a glassy carbon counter electrode, an Ag/AgCl/KCl 3M reference electrode and Metrohm multimode mercury electrode were used. Before each titration, the procedure involved the transfer of the solution to the cell and purging with nitrogen for 10 min. The conditions used for each metal are specified in Table I. All the complexes were proved to be formed quasi-instantaneously, so that a minimum conditioning time (4 min.) was allowed after every spike of metal.

When the assayed metals amalgamated onto the mercury electrode, a known amount of ligand was placed in the electrochemical cell and then increasing amounts of Cu, Zn, Cd and Pb, were spiked on the solution. On the other hand, when metals did not amalgamate onto the electrode, as in the case of Cr and Mo, increasing amounts of ligand were added to a solution containing a fixed metal concentration.

Assessment of the fresh state behaviour of cement mortars modified by chitosan addition

Materials

An ordinary Portland cement (OPC) (CEM II 32,5 N, supplied by Portland S.A. Olazagutía, Spain) and a standardised siliceous aggregate (mineralogical composition as well as grain size distribution can be found in Izaguirre *et al.*²⁷) were used to prepare the mortars. The selected binder: aggregate ratio (B:Ag) was 1:3, by weight. Instead of

volume proportions, weight proportions were selected in order to avoid any imprecise measurement. The three different commercial chitosans previously reported were used as admixtures. One only additive was incorporated in each one of the remaining mortars, in order to check clearly its possible efficiency, avoiding other variables. For each chitosan, a dosage of 0.1% of the total dried mortar's weight was incorporated.

Mortars preparation

The mixer was a Proeti ETI 26.0072. 450 g of cement, 1350 g of aggregate and additive (when necessary) were blended for 90 seconds at low speed. The water was added in accordance with a 0.5 water/cement ratio, which makes it possible to achieve suitable workability, avoiding any excess of water.

Water was then added and mixed for 90 more seconds at low speed. Mortars settled for 10 minutes before being tested, to let the additive take effect. Straight afterwards, fresh state properties were determined as described below.

Fresh state properties

The consistency and water-retention capacity of the fresh state of cement mortars were determined.^{28,29} The first one was carried out by means of the flow table test. This method is based on the measurement of the spread of slurry placed into a cone-shaped mould. When the mould, filled with fresh mortar, is vertically lifted, 15 knocks of the table take place for 15s, and the slump is determined.

Water-retention capacity was determined by weighing absorbent materials placed on the fresh sample before and after 5min of contact under pressure, as reported elsewhere.²⁷

Viscosity measurements

In order to assess any rheological change, viscosities of cement pastes modified by chitosan addition were determined. To this end, a HAAKE Viscotester VT 550, with a programme of rotation speeds varying from 1.5 to 510 s⁻¹ during 5.5 minutes was used.

Particle size distribution

As reported by Chiou *et al.*³⁰, Khayat³¹, and Saric-Coric *et al.*³², fixation of water, interaction between cement particles and polymer molecules, and intertwining process between polymer chains are expected to produce agglomerates, hence particle size distribution of cement-polymer mixtures should change.

20 g of cement were added to 100 g of solutions with different amounts of chitosan in water, the resulting chitosan/cement ratios ranging from 0% to 1%. The particle size distribution of these samples was determined using a Malvern Mastersizer (Malvern Instruments, Ltd., U.K.).

Conductivity

Set retarding ability of different polysaccharides used in cement pastes has been reported to be determined by means of conductivity measurement.² A Thermo Orion 4-Star benchtop pH/conductivity meter equipped with a Dura Probe 4-electrode conductivity cell (Orion 013605MD) with a nominal cell constant of 0.55 cm^{-1} intended for a conductivity measurement range from $10 \mu\text{S cm}^{-1}$ to 200 mS cm^{-1} , was used for conductivity assays.

Different cement pastes were prepared by mixing 5 g of cement and 0.05 g of each one of the tested chitosans with 100 mL of ultrapure water previously thermostated at $25 \text{ }^\circ\text{C}$. The experiments were carried out in a reaction vessel magnetically stirred inside a water bath thermostatically adjusted at $25 \text{ }^\circ\text{C}$. The conductivity measurements were recorded each 10 minutes for 24 hours. These data were used in order to draw the conductivity curve.

Zeta potential measurements

Specific mixtures of cement, water and additive were prepared to assess the zeta potential. The determination of zeta potential of solid-liquid interface permitted us to study the adsorption of the admixture on the solid surface of binder, since it modifies this property, as stated by Papo and Piani,³³ and Zhang *et al.*^{34,35}

Following the method proposed by Zhang *et al.*^{34,35} and assayed previously³⁶ solutions with different concentrations of chitosans were prepared (percentages w/w of 0.025, 0.05, 0.1, 0.15, 0.2 and 0.25), and cement was added with a solute/liquid ratio of 0.0025. After 5 minutes of stirring, the mixtures were separated by centrifuge, and the supernatants were analysed using a Zeta Potential Analyzer ZETA PLUS (Brookhaven Instruments Corporation, New York, U.S.A.). The average of ten measurements was regarded as the zeta potential of the cement particles.

RESULTS AND DISCUSSION

Voltammetric studies on chitosan complexing ability of heavy metals

Electrochemical study of Pb, Cd and Zn

The electrochemical approach consisted of the titration of a given amount of chitosan (acting as complexing ligand) with increasing amounts of added standard metals. All three metals are able to amalgamate -upon reduction at suitable electrode potential- on the mercury working electrode. Subsequent scanning of the potential in the positive going sense forces the reoxidation of the metal, giving rise to a current that is monitored in the Differential Pulse mode. Depending on the previous situation of the metal in solution (either free or chitosan-bound), the amount of metal to be deposited on the mercury electrode and subsequently reoxidized will differ. Thus, if chitosan is in excess of the stoichiometry of the possible complex with a given metal, most of the metal added to the chitosan-containing solution will be stabilized by the ligand (chitosan) and it will amalgamate on the mercury electrode to a much lesser extent with respect to the amount of deposit that would be achieved when free. This results in diverse patterns when current vs. metal concentration are plotted. In general, two linear portions are obtained: a first one with a lower slope, corresponding to the anodic stripping current measured for the respective metal when complexed by the chitosan in solution, and a second steeper branch indicative of free metal in solution, that is to say, when in excess of the stoichiometric ratio of the chitosan-metal complex. The break in this type of graph allows the stoichiometry to be estimated and the population of chitosan acting as ligand to be calculated.

The background electrolyte has to be carefully selected in order to ensure that it does not play any competitive complexing role with respect to the main ligand under observation. An acetic acid/acetate buffer solution of pH 4 was used, guaranteeing, on one hand, the prevalence of ionic state of metals³⁷ and, on the other hand, the absence of any significant complexing activity towards the metals, as previously reported.³⁸ Besides, at this pH protonation of the amino groups (and the consequent reduction of the complexation capacity) is prevented, which could not be ensured with lower pH values. Finally, in this buffered solution the precipitation of both chitosan and metal hydroxides is precluded.

Stripping voltammograms were recorded for Pb, Cd and Zn when accumulated on the mercury electrode at the optimal potentials. Titration data were obtained for all of them by plotting their respective stripping peak currents vs. increasing concentrations of the

added metals as shown in Fig. 1. In all instances, the voltammograms showed a constant potential peak at -379, -560 and -840 mV for Pb, Cd and Zn, respectively, the height of which increased with increasing metal concentrations. A surprising feature observed was the fact that the Zn stripping peak in presence of chitosan showed, in the first place, a marked decrease in its intensity compared to that of the free metal and, in the second place, a displacement of its peak potential towards less negative values (from -960 mV to -840 mV in presence of chitosan).

Stoichiometries were calculated from titration data collected for the three assayed molecular weights of chitosan and three different concentrations (0.1, 0.5 and 1 μM) of a fixed molecular weight chitosan (MMW), as presented in Table II.

As can be seen, the higher the molecular weight of chitosan, the larger the binding capacity observed for Pb and Zn. On the other hand, the highest complexation capacities were found for both Zn and Pb when more diluted chitosan solutions were assayed, irrespective of the MW of the chitosan studied. It is also noteworthy that whatever the MW of chitosan, the coordination of Zn is always larger than that of Pb.

These results can be explained bearing in mind the structure of chitosan. A higher molecular weight implies a larger number of available amino groups to bind the metals, which explains the first assertion. As for the second, dilution of chitosan implies a corresponding diminishing of the aggregation of the polymer and the steric hindrances, so that metals can be easily placed between sheets of the polymer. Furthermore, the breaking of stabilizing hydrogen bonds within the structure of the diluted chitosan contributes to this trend. Finally, ionic radii of both Zn and Pb differ significantly (0.74 and 1.20 Å, respectively) so that inclusion of Zn into the polymer is sterically more favourable. Moreover, the complex of the polymer with this metal seems to have a different geometry to the binding with the other two metals.³⁹

Linearization algorithms of titration data are usually employed to estimate affinity constants of complexes, such as those developed by Buffle⁴⁰ and Ruzic.⁴¹ For simple 1:1 stoichiometries, both Scatchard⁴² and Langmuir⁴³ algorithms are straightforward, allowing the disclosure of differently behaving ligands. Experimental data of Pb and Zn were processed according to Scatchard and Langmuir in spite of the fact that the stoichiometry of the complexes is far from 1:1.

Equations [1] and [2] are obtained from these mathematical treatments:

$$\frac{[ML]}{[M']} = K' L_T - K' [ML] \quad [1]$$

$$\frac{[M']}{[ML]} = \frac{[M']}{L_T} + \frac{1}{K' L_T} \quad [2]$$

where $[M']$ is the free metal concentration, $[ML]$ is the complexed metal concentration obtained by subtracting $[M']$ from the total metal concentration $[M_T]$; L_T is the total ligand concentration as calculated from these expressions and K' is the conditional stability constant derived from the slope and from the ordinate respective plots. Equation [1] is commonly known as the Scatchard equation. The Langmuir linearization (equation [2]), also called Ruzic/van den Berg linearization method, usually gives rise to a linear relationship when the ratio $[M']/[ML]$ is plotted against $[M']$. The slope is equal to $1/L_T$ and the intercept yields $1/K' L_T$.

Surprisingly, both metals adjust well to these theoretical patterns. Although calculations of total available chitosan cannot properly resemble the real amount of ligand present in the electrochemical cell, the data obtained corroborate the above described trends. The calculated effective concentration of chitosan in every instance increases with its ability to link the metal (stoichiometry) and a linear tendency ($R^2 = 0.9905$ and 0.9175 for Pb and Zn respectively) is observed. Even when using the Scatchard algorithm, a single straight line was always achieved, indicating the existence of a unique type of complex with these two metals.

As for Cd (Fig. 1b) its behaviour differs from that of Pb and Zn; chitosan ability to complex Cd is lower (see Table II) and either chitosan concentration or MW influences the stoichiometry variations to a much lesser extent.

Electrochemical study of Cu

Copper is, amongst the heavy metals, the most troublesome to determine voltammetrically due to its low solubility in mercury, the coincidence of its stripping peak potential with the potential interval in which many organic species are adsorbed on the mercury electrode and the presence of a pre-wave.⁴⁴

The assayed concentrations of both ligand and metal were lower than those used for the previous metals in order to avoid the saturation of the electrode. Experiments were carried out in the presence of the fixed $0.05 \mu\text{M}$ chitosan and stripping voltammograms were recorded for increasing Cu concentrations.

The peaks obtained in this case were difficult to evaluate due to their broadening, showing a pre-wave that is not observed in free metal solutions. For this reason, the correction of the base line is critical to obtain reliable results. It is also worth mentioning that the peak potential of the metal in presence of chitosan suffers a displacement towards more positive potentials (ca. 38 mV) in comparison with the peak potential of free Cu, confirming that the complexation occurs.

An interesting aspect inferred from the titration curve (Fig. 1d) is that this binding seems to be independent of the molecular weight of chitosan, as the concentration of metal that saturates the ligand is almost the same no matter what the chitosan characteristics are. It has been previously reported that Cu (as well as Zn) interacts differently with chitosan from other metals³⁹ and a square-planar or tetrahedral geometry has been previously proposed for the complex.⁴⁵ According to our results, an inter-layer binding mechanism is proposed as the main retention factor of Cu by chitosan, so that cavity between the sheets of the polymer would be more relevant than length of the chains.

Electrochemical study of Mo and Cr

Since both Mo and Cr do not amalgamate on Hg electrodes, their complexation by chitosan was followed-up in a more traditional way, consisting of the monitoring of their reduction peak upon increasing concentrations of ligand (chitosan). Each metal showed a diverse pattern so that attention has been focused on either peak intensity or peak potential for Mo and Cr, respectively. It must be taken into account that, unlike the previous metals, Mo and Cr were added to the solutions as anionic forms, as reported in the experimental section.

Mo peak intensity decreased regularly as chitosan concentration in cell increased up to a point at which the peak intensity remained constant upon addition of chitosan (Fig. 2a). Mo peak potential did not suffer any displacement in the presence of chitosan. As has been reported in the literature, different Mo chemical species co-exist in solution at the selected pH.⁴⁶ Besides, we have, in this case, detected that complexation of Mo by the background electrolyte takes place to a certain extent, giving rise to non-linear responses of Mo peak intensities vs. Mo concentration in acetate buffer. Nevertheless, when chitosan is present in the solution, it turns out to be the most important complexing agent, displacing the acetate, as proved by the fact that Mo peak intensity signal decreases linearly in the presence of increasing concentrations of chitosan.

Furthermore, this effect is more pronounced as the molecular weight of chitosan increases. The indent of Fig. 2a shows the linear trend of this latter effect.

On the other hand, Cr reduction peak potential was more negative when in the presence of chitosan. This displacement was more acute once the added chitosan was enough to fully bind the initial Cr in solution. The degree of displacement is related to the strength of the retention of the metal.

Experiments carried out at different polymer MW showed that the higher the molecular weight, the larger the retention of Cr as measured in terms of peak potential displacement, as shown in Fig. 2b.

Since electrochemical approaches were different for these two metals with respect to the one used before -for Zn, Cd, Pb and Cu- absolute numerical figures cannot be compared for the two groups of metals; however, from breaks in the linear portions of the respective titration curves obtained for both Mo and Cr (Fig. 2) it can be concluded that chitosan is able to retain 7-fold more Cr than Mo.

As has been emphasized before, as the polymer chain increases, there is a greater number of linking groups available for the retention of the metals within the three-dimensional structure of the acting ligand. This fact is consistent with a predominant intra-chain linkage of both metal atoms rather than the binding between the sheets formed by the different chitosan chains.⁴⁷

Different models have been previously proposed to elucidate the chitosan-metal linkages. One of them is the 'bridge model' in which the metallic ion is coordinated with several nitrogen atoms from the same or different chains of chitosan.⁴⁸ The other model proposed is called the 'pendant model', which considers that the metal is bound to an amino group of the chain as a pendant (Fig. 3).⁴⁵ For this reason, depending on the characteristics of the metal, some metal ions could bind only a helical loop of polymer, while others might correlate with several helical loops.³⁹ In our case, all the metals under study seem to bind with several polymer chains as the stoichiometry is always superior to 1:1.

Assessment of the fresh state behaviour of cement mortars modified by chitosan addition

Table III shows the slump determined through the flow table test. As can be seen, the chitosan addition increases the viscosity of the fresh cement mortars, giving rise to a drop in fluidity. Taking into account the slump value of the control mortar (OPC

without admixture), LMW chitosan led to a reduction of 9.7% in terms of fluidity; medium and high molecular weight chitosans caused a decrease of 17.4% and 20.3%, respectively. It might be expected that the addition of a higher molecular weight polymer resulted in a greater thickening effect, owing to the higher possibility of entanglement between polymer chains.⁴⁹ The obtained results confirmed the expectations.

Apparent viscosity measurements performed on cement pastes (1:1 water/cement ratio) modified by the addition of the chitosan polymer fit in with the flow table test results (Fig. 4 shows the apparent viscosity values of cement pastes with chitosan additions as a function of an increasing shear rate). Cement pastes with HMW chitosan showed the highest apparent viscosity at low shear rates. All the tested polymers conferred a shear-thinning behaviour on the cement pastes, which has been reported to be very useful for many practical functions (such as rendering, grouts, and shotcrete). A relatively large viscosity was determined at low shear rates but it showed a reduction when great stress was applied. Actually, materials of pseudoplastic nature are supposed to resist sedimentation and sagging at rest but can be easily mixed, pumped and sprayed (during a “wet-mix” or “dry-mix” process).⁵⁰ The fall in viscosity when the stress is applied can be explained because linkages between polymer and cement particles may break, and linear chains of the polymer could align with the flow direction. When the stress slows down, a recoagulation process could take place.⁵¹

In order to understand the fluidity decrease, the insolubility of the chitosan in alkaline pH (a pH of 12.12 was obtained from a solution of 5% w/w of the binding material), as well as in calcium-rich systems, must also be taken into account.⁵² This high sensitivity towards alkaline pH and free Ca^{2+} ions of polysaccharide molecules has been previously reported by Goycoolea *et al.*⁵³ and Knaus and Bauer-Heim⁵⁴, respectively. To a certain extent, chitosans might precipitate in such alkaline and calcium ion rich matrices, giving rise to an entanglement between different polymer chains, thus increasing the viscosity. A cross-linking phenomenon owing to the interaction with calcium ions could also be responsible for a viscosity rise.¹⁸ In addition, OH and NH_2 groups would undergo ionization under alkaline conditions, becoming the negatively charged O^- and NH^- groups. Given that LMW chitosan showed the largest degree of deacetylation, this polymer presented the highest number of negatively charged groups. As a consequence, its charge density should be larger and responsible for the appearance of electrostatic

repulsions between chains of the polymer, which inhibited intermolecular association and hence reduced viscosity.³⁴

To sum up, both the lower molecular weight of the LMW chitosan and the appearance of electrostatic repulsions between chains in this polymer could be responsible for its lower fluidity reduction. Based on these considerations, a similar trend in terms of fluidity can be proved with respect to DDA for MMW and HMW chitosans. The lower the DDA and the higher the MW, the larger the viscosity of the cement solutions was.

Water retention ability of these samples (Table III) was also assessed. All the modified samples retained larger percentages of mixed water than the control mortar. These data can be related to the DDA. The higher the deacetylation degree in chitosan, the larger was the water retention value. A polymer molecule with a high DDA shows a greater number of hydrophilic substituents ($-NH_2$ groups), being capable of binding water molecules by hydrogen bonds.⁵⁵ Therefore, owing to its high DDA, samples with LMW showed a slightly high ability of water retention.

Particle size distribution measurements carried out in cement-polymer mixtures confirmed that chitosan addition shifted the distribution of the largest particles towards larger sizes (Fig. 5 depicts, as an example, the particle size distribution of cement pastes with different MMW chitosan dosages). The bimodal distribution of the plain cement mixture contrasted with the trimodal and sometimes even tetramodal distribution of the cement-polymer mixtures. All the samples showed a maximum around $0.27\ \mu\text{m}$, which did not present further modifications. The plain cement mixture showed other maximum at around $12\ \mu\text{m}$. Samples with chitosan presented other relevant population at around $26\ \mu\text{m}$ (sometimes depicted as a shoulder). The ratio of particles with sizes bigger than $30\ \mu\text{m}$ was larger for chitosan-added samples. Finally, a population above $100\ \mu\text{m}$ can be also observed (with an average value ca. $200\ \mu\text{m}$). Polymer entanglement could be responsible for these displacements towards larger sizes and for the appearance of the largest populations, thus suggesting that a certain kind of interaction with cement particles takes place. In general, a dosage-dependence could be proved: the larger the dosage, the greater the displacement of the particle population towards larger sizes, as it can be seen in Fig. 5 that collects data from MMW chitosan samples.

Set-retarding ability has been reported to be one of the roles played by some of the polysaccharides used as cement admixtures.² The setting process evolution has been assessed by means of conductometric curves in cement suspensions, according to the

works by Peschard *et al.*² and Pourchez *et al.*³ The conductometric curve of a cement suspension presents different steps, the portlandite precipitation time, shown by an electrical conductivity drop, being the most useful marker in order to assess the hydration delay. In Fig. 6 the conductometric curves of cement suspensions can be seen (conductivity of the cement suspensions as a function of the time): one as control sample, without chitosan addition, and the others with the addition of the three different chitosans tested. There is no change either in the dissolution rate of the cement particles or in the nucleation rate of CSH (belonging to the first part of the curves). However, the conductivity drop (portlandite precipitation) shows outstanding differences, involving hydration delays as different chitosans were added to the cement suspensions. Results indicate that chitosans exert a set-retarding action in cement suspensions. As far as the interaction mechanisms are concerned, the reported insolubility of chitosans in alkaline pH suggests some kind of adsorption between precipitants and anhydrous cement particles, hydrates or crystal lattices rather than water unavailability, because the water retention differences do not fully justify such a long delay in the hydration time.² The particle size distribution further reinforces this assumption on the interaction mechanism (Fig. 5).

With the aim of assessing the interaction between chitosan molecules and cement particles, zeta potential measurements were obtained for increasing quantities of admixture (Fig. 7). The net-surface charge for cement suspensions without chitosan was negative. This matches previous results, which stated that the zeta potential of early hydration of ordinary Portland cement suspensions is dominated by the negative zeta potential of the ettringite.⁵⁶

LMW chitosan does not modify the zeta potential of the cement particles at most dosages. This fact suggests that there is no adsorption of the polymer (owing to the alkaline pH, a negatively charged polyelectrolyte) on the cement particles. Only the highest dosage of polymer shifts the zeta potential towards more negative values, showing a certain degree of interaction. These experimental results agree with the poorer set-retarding capability of LMW chitosan (Fig. 6). They also point to the adsorption on cement particles as the mechanism for the set-retarding effect.

The surface charge of cement particles with MMW chitosan showed more negative values, proving that adsorption of this chitosan on cement particles took place. This interaction could be useful to explain the delay in the setting process when MMW chitosan was added. Further studies will be necessary to elucidate where the adsorption

takes place: stern or diffuse double layer, and to decide the kind of phases that interact: silicates (C_3S , CSH), CH (calcium hydroxide), or aluminate phases (C_3A , ettringite, monosulfate).⁵⁶

Finally, HMW chitosan led to a charge inversion of the zeta potential (high positive values), suggesting a very diverse interaction between cement particles and this chitosan. The strong flocculation ability of this chitosan could give rise to the formation of agglomerates of cement particles and polymer molecules (as proved by particle size distribution measurements). As a hypothesis, these agglomerates should be negatively charged, taking into account both the net-surface charge of the cement particles and the ionized negatively charged groups of the chitosan chains, the agglomerates being sheltered by a layer of positive counterions (calcium ions). As a result, the zeta potential turned out to be positive and the hydration of cement particles inside such agglomerates was hindered. This approach confirms the most effective thickening behaviour observed for HMW chitosan, together with both its set-retarding ability and its lower water retention.

CONCLUSIONS

In the present study, a natural biodegradable polymer, chitosan, was tested as a heavy metal retainer and a viscosity-enhancing admixture with the aim of investigating its usefulness as an addition to cement-based materials.

With regard to chitosan's ability to retain heavy metals, voltammetric techniques have been shown to be suitable for this study. This polymer proves to be an effective ligand with all the six assayed metals. For all of them - Pb, Cd, Mo, Cu, Zn and Cr-, it can be said that not only adsorption but also complexation actually takes place in acetate buffer (pH=4) with chitosans of different MW.

The length of the chains of the polymer, together with the assayed concentration, have been seen to play a key role in the chitosan binding activity with Zn and Pb as well as Cr and Mo.

A predominant intra-chain linkage is proposed in all instances except for Cd and Cu, which response seem more independent of the chitosan characteristics (molecular weight and concentration) for which an inter-layer binding mechanism fits better.

Regarding the viscosity modifying role of the chitosan, it has been proved to increase viscosity in fresh mortars while retaining more water than plain cement. Owing to the greater probability of entanglement between chains of the polymer as well as a cross-

linking phenomenon in a calcium-rich system and a low degree of deacetylation, the HMW polymer was responsible for the greatest thickening effect. The degree of deacetylation of the polymer could also be connected to the slight differences in water-retention ability.

The rise of these properties is enough to prove the capability of the chitosan as a modifier of the rheological behaviour of cement-based materials. Furthermore, the hydration delay assessed by means of conductometric curves suggests a set-retarding role of the chitosan in cement mortars, the HMW chitosan being the polymer with the greatest retarding ability. The mechanism for this set-retarding action has been related to an interaction of the chitosan with cement particles according to the zeta potential measurements.

Among the assayed chitosans, both voltammetric studies and rheological tests have shown that the HMW chitosan has the best effectiveness as a complexing agent for Zn, Pb and Cr, and also the best thickening behaviour in cement-based materials. These combined methodologies allow us to conclude that high molecular chitosan derivatives will be most appropriate for the final aim of this research.

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Table I. Electrochemical conditions used for the different metals.

<i>Parameters</i>	<i>Pb</i>	<i>Cd</i>	<i>Mo</i>	<i>Cu</i>	<i>Zn</i>	<i>Cr</i>
<i>Type</i>	DPASV	DPASV	DPV	DPASV	DPASV	DPV
<i>Drop size</i>	9	9	9	9	9	9
<i>Pruge time (s)</i>	300	300	300	300	300	300
<i>Conditioning time (s)</i>	120	120	120	120	120	120
<i>Rotation speed (rpm)</i>	2000	2000	2000	2000	2000	2000
<i>Accumulation potential (E, mV)</i>	-600	-900	-	-300	-1200	-
<i>Accumulation time (s)</i>	60	60	-	60	60	-
<i>Equilibration time (s)</i>	20	20	-	20	20	-
<i>Initial potential (mV)</i>	-600	-900	150	-300	-1200	-200
<i>Final potential (mV)</i>	0	-200	-1200	150	-700	-1200
<i>Pulse amplitude (mV)</i>	100	100	25	100	100	25
<i>Scan speed (mV s⁻¹)</i>	20	12	40	12	12	40

Table II. Influence of chitosan molecular weight and chitosan dilution on the number of metal nuclei complexed by each chitosan molecule.

<i>Element</i>	<i>LMW</i> <i>0.5 μM</i>	<i>MMW</i>			<i>HMW</i> <i>0.5 μM</i>
		<i>0.1 μM</i>	<i>0.5 μM</i>	<i>1.0 μM</i>	
<i>Zn</i>	10	40	20	10	40
<i>Pb</i>	6	24	12	6	16
<i>Cd</i>	6	-	8	6	10

Table III. Slump and water retention of cement pastes with chitosan additions.

<i>Cement pastes</i>	<i>Slump (mm)</i>	<i>Water retention (%)</i>
<i>Control group</i>	190.0	81.1
<i>CEM + LMW</i>	171.5	85.2
<i>CEM + MMW</i>	157.0	84.6
<i>CEM + HMW</i>	151.5	83.5

Figure 1. Titration curves for increasing concentrations of Pb (a), Cd (b), Zn (c) in 0.5 μM chitosan, and Cu (d) in 0.05 μM chitosan solution.

Figure 2. Effect of increasing concentrations of chitosan on the peak intensity of Mo 10^{-4} M (a) and on peak potential displacement for Cr $3.4 \cdot 10^{-4}$ M (b).

Figure 3. Pendant (a) and bridge (b) models according to Guibal⁴⁸ and Rhazi *et al.*⁴⁵

Figure 4. Apparent viscosity of cement pastes with chitosan additions vs. increasing shear rate.

Figure 5. Particle size distribution of cement pastes with different medium molecular weight chitosan dosages (w/w percentages chitosan/cement).

Figure 6. Effect of the different chitosans on cement hydration.

Figure 7. Zeta potential of the cement particles for different molecular weight chitosans vs. polymer concentration.

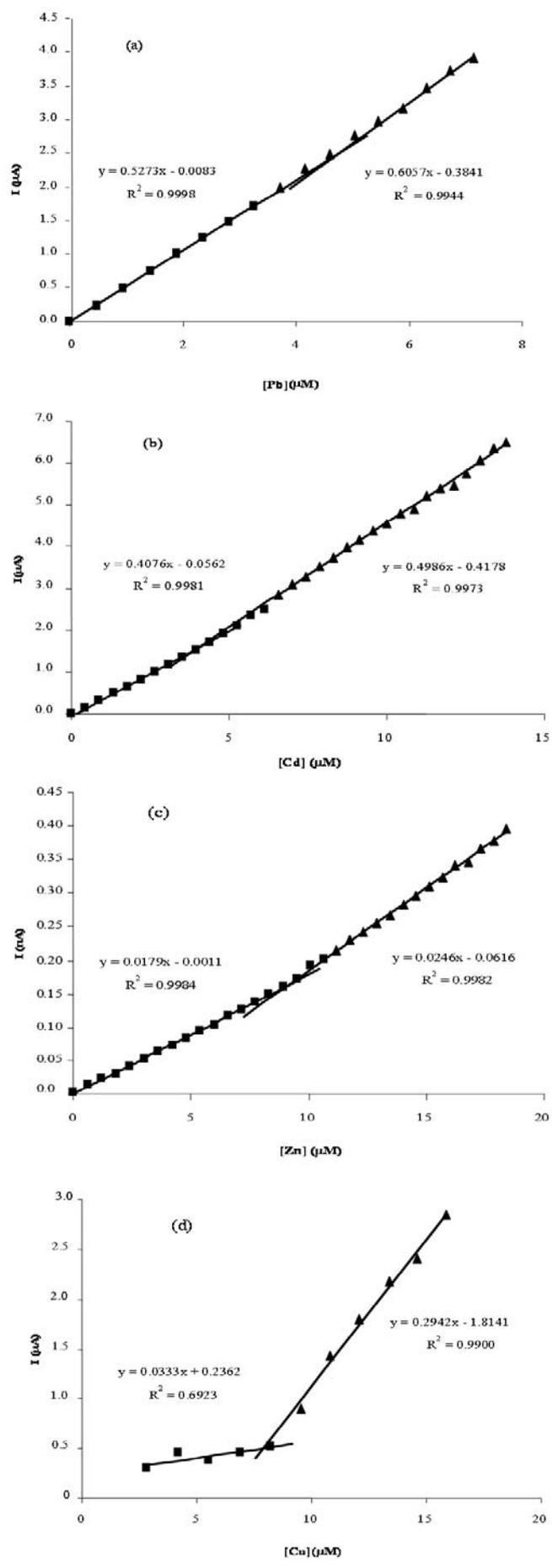
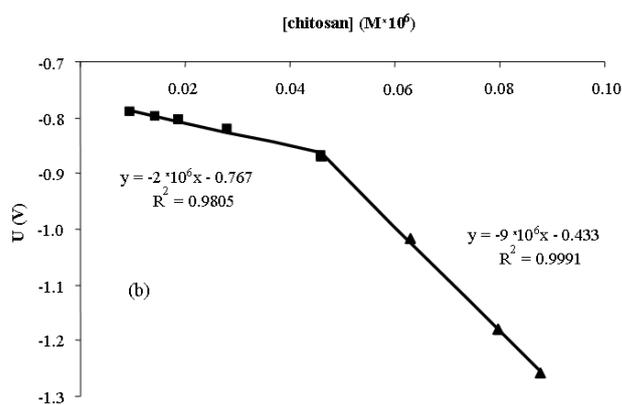
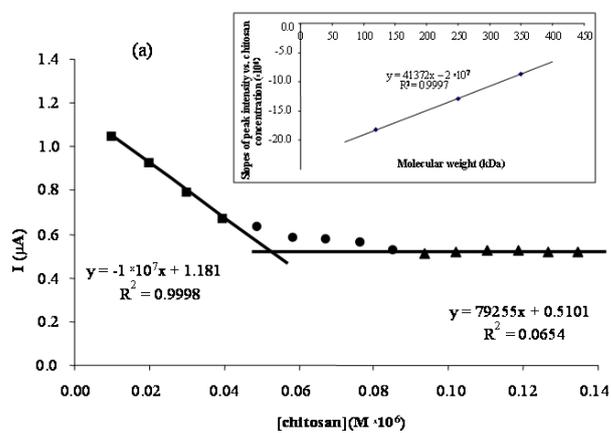


Fig. 1

Fig. 2



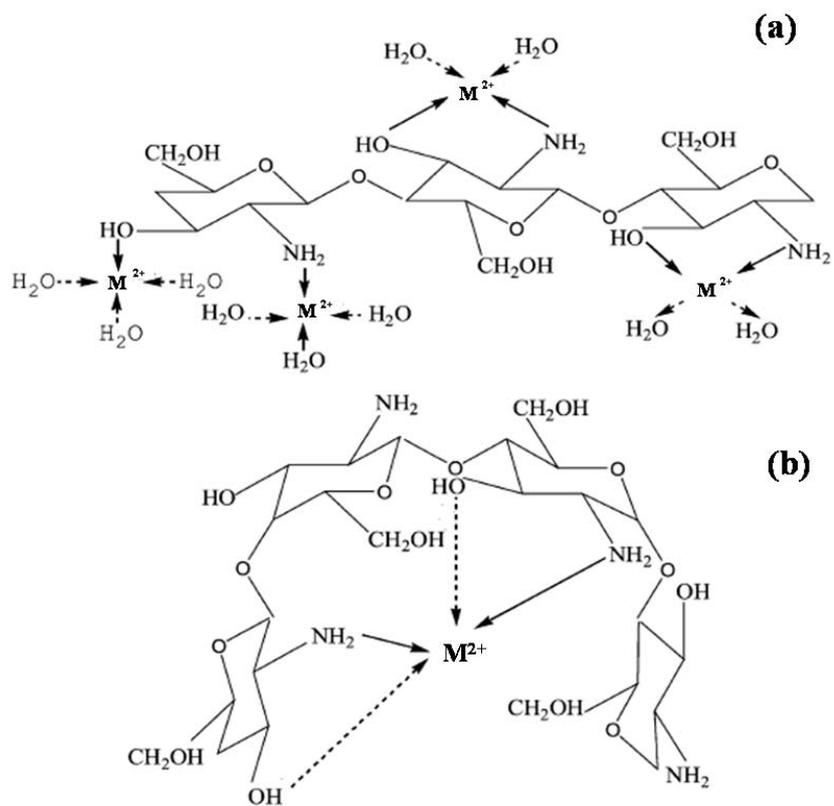


Fig.3

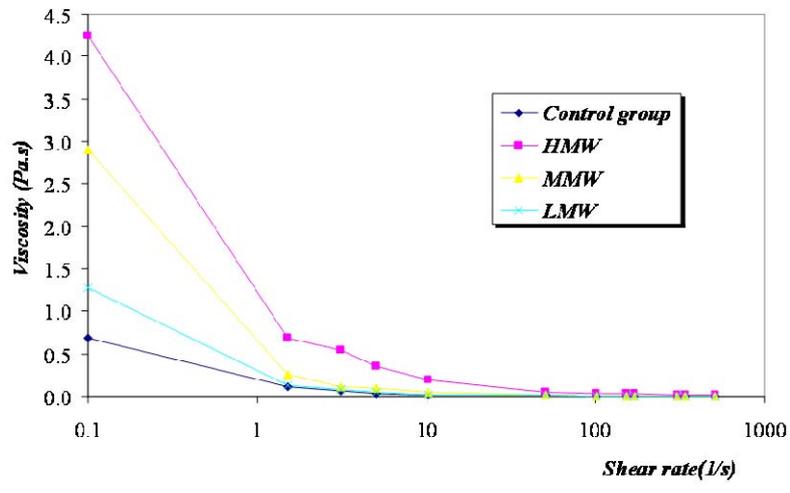


Fig. 4

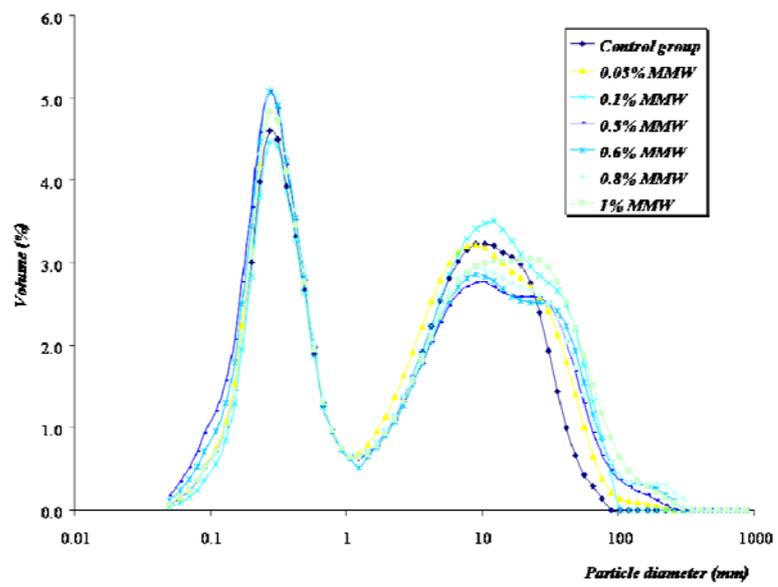


Fig. 5

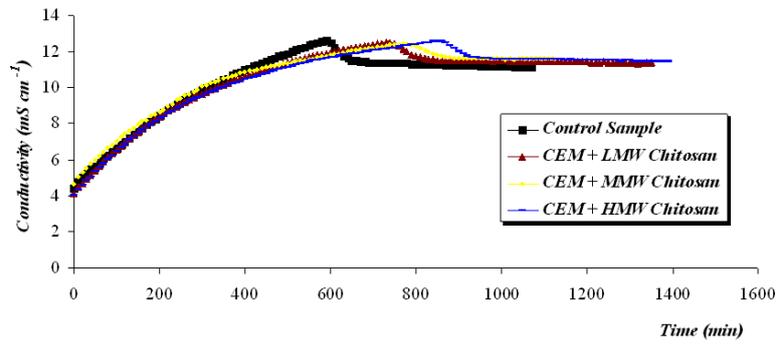


Fig. 6

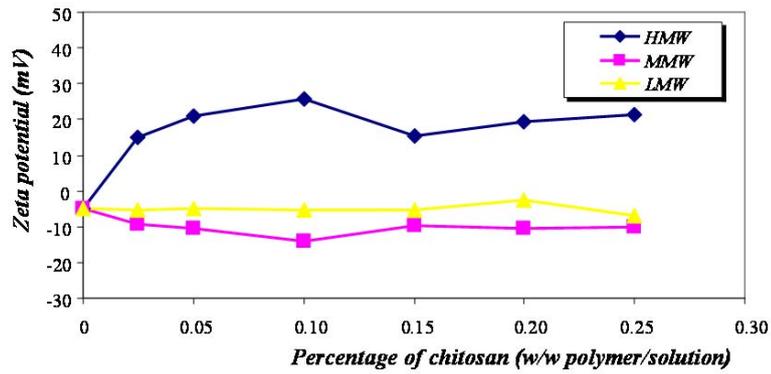


Fig. 7