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An evaluation of hydroxyapatite-based filters for removal of heavy metal ions from aqueous solutions

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Three hydroxyapatite(HA)-based materials have been investigated with respect to their potential for removing heavy metal ions from aqueous solutions. The materials have been evaluated as both loose powders and in the form of ceramic foams. The results have shown that all three grades of HA were found to be capable of removing a number of different ionic species although the more impure grades generally yielded the best performance. It is believed that the increased impurity levels resulted in increased numbers of lattice defects which were ideal adsorption/exchange sites. 100% removal could be achieved for some ions under the correct experimental conditions. For the ceramic foam filters, the optimum filtration parameters were found to be a high surface area, long filtration times, a low pH and a high filtrate temperature. Ion adsorption was positively detected as a mechanism of ion removal. Ion exchange was not observed but could not be completely ruled out.

1. Introduction

In recent years, waste water treatment has been raised in importance due to increased concern about the environment and tighter international regulations on water pollution [1]. Toxic heavy metal ions are generally removed from industrial waste water by one of three mechanisms [2]: coagulative precipitation, reverse osmosis or ion exchange, with ion-exchange resins being favoured in many applications. Although these can provide adequate performance, it is always desirable to investigate alternatives. Hydroxyapatite (HA) has received much attention recently due to its potential for use as a bioactive bone substitute [3]. However, owing to its crystal structure and chemical composition, the material also shows a high capacity for ion exchange with heavy metal ions [4]. Although it has already been proven that HA can be applied successfully to remove certain ions from aqueous solutions in the laboratory, there have been few commercial applications as water filters. This is due in part to very high material costs. Hence, if the cost of HA could be reduced it could become more competitive with other commercially available filter materials.

1.1. Ion exchange

Ion exchangers carry an electric surplus charge which is compensated for by ions of the opposite sign, the so-called counter-ions [5]. In the case of HA these are the Ca^{2+} ions. They are free to move into solution and can be replaced by other ions. The process of reversible interchange of ions of similar charge between a liquid and a solid is universally referred to as ion exchange [6, 7] and has been found to be generally accompanied by a second process, that of ion adsorption. The exchanger must have an open crystal structure which allows ions to interchange within it.

Electrostatic forces in ion-exchange systems were studied by Helfferich as early as 1962 [8]. He found considerable concentration differences for cations and anions between the ion exchanger and the filtrate, leading to differences in potential. For HA, for example, the cation concentration is larger in the ion exchanger whilst the anion concentration is larger in the filtrate. Migration of cations into solution and anions into the filter results in an accumulation of positive charge in the filtrate and of negative charge in the ion exchanger. The first few ions which diffuse thus build up an electric potential difference between the filter and the filtrate. This so-called Donnan potential ([8] p. 134) pulls cations back into the filter and anions back into the filtrate. Hence an equilibrium is established in which the tendency of the ions to equalize existing concentration differences is balanced by the action of the electric field.

The following ion-exchange mechanism is generally believed to take place between divalent cations in the filtrate and the Ca^{2+} ions of HA [9]

$$\text{Hydroxyapatite-Ca}^{2+} + \text{M}^{2+} \rightleftharpoons \text{Hydroxyapatite-M}^{2+} + \text{Ca}^{2+} \quad (1)$$

The total number of ions in the filtrate will stay constant throughout the ion-exchange [10] process. Although the crystal structure of the hydroxyapatite will be maintained, the unit-cell dimensions are expected to change due to the differing sizes of the cations. Suzuki *et al.* [11] determined the crystal dimensions of $Ca_{3.6}Pb_{6.4}(PO_4)_6(OH)_2$ to be $a = 0.9882$ nm and $c = 0.7417$ nm in comparison with $a = 0.9418$ nm and $c = 0.6884$ nm for pure HA. Thus a change in lattice parameters can be an indication of ion exchange having taken place. The surface charge on the HA will not change for ion exchange with divalent cations, because the same number of Ca^{2+} ions are released into the filtrate as divalent cations are built into the HA lattice. However, it has been suggested that Ca^{2+} release can be measured to monitor the ion-exchange capacity [12]. If the Ca^{2+}/exchangeable ion ratio is close to 1, most ions have been exchanged into the HA lattice. If the ratio is much less than 1 and the ions can no longer be detected in the filtrate, they have to have been adsorbed on to the surface of the HA. This adsorption will produce a positive charge on the surface, causing the electrostatic repulsion between HA particles to increase. This will be directly reflected in the dispersion properties of HA powders and their zeta potential, as revealed by Saleeb and de Bruyn [13].

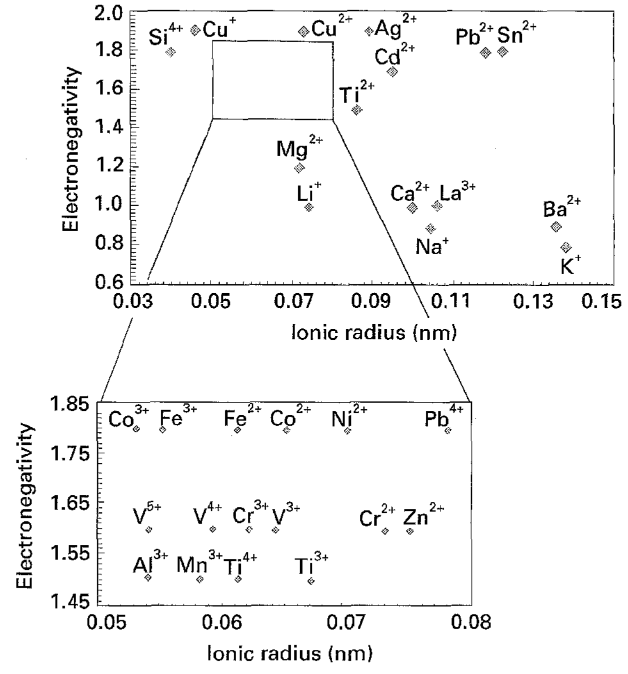

Figure 1 Ionic radius versus electronegativity of various ions.

1.1.1. Conditions for ion exchange in HA

Two conditions have to be fulfilled by the ion which is to be exchanged. Firstly its ionic radius has to be similar to that of Ca^{2+} so that it fits into the lattice structure of HA without deforming it significantly. Saleeb and de Bruyn [13] stated the following general rule for apatites; two ionic species may only exchange if their ionic radii do not differ in size by more than 15%, which limits the ionic radius to 0.085–0.115 nm. This hypothesis contradicted the findings of many authors who claimed that ion exchange had taken place between ions outside this range and the Ca^{2+} ion of HA. Secondly, the electronegativity values have to be large to allow easy replacement as indicated by Suzuki *et al.* [14].

The Donnan potential attracts counter-ions into the ion exchanger and thus balances their tendency to diffuse out into the filtrate. The force with which the potential acts on an ion is proportional to its ionic charge [8]. Hence the higher the charge on the counter-ion the more strongly it will be attracted to the filter.

The ionic radii of various cations and their corresponding electronegativity values are shown in Fig. 1, which should give a first indication of which ions can exchange for Ca^{2+} of HA.

1.2. Ion adsorption

There are two types of adsorption, physical and chemical. During the former, ions of opposite charge compared with the particle surface are attracted towards the particle surface. No electrons are exchanged between the adsorbed molecules and the adsorbent surface and only intermolecular forces are involved [15]. In chemisorption, on the other hand, electron transfer and sharing of electrons has been suggested by Rosen [16] to take place between the adsorbate and the adsorbent.

1.2.1. Ion adsorption on HA

Attia and Fuerstenau [17] showed that HA acquires a surface charge when brought into contact with water by three mechanisms:

(i) the preferential dissolution of some lattice ions into the solution. A number of researchers (Hyakuna *et al.* [18], Vereecke and Lemaître [19] and Gramain *et al.* [20]) have shown that the dissolution molar ratio of Ca/P was not necessarily always equal to 1.67, but there are also authors who were in favour of a simultaneous dissolution of Ca^{2+} and P^{5+}, for example, Attia and Fuerstenau [17];

(ii) the presence of surface groupings which can ionize or adsorb H^+ and OH^- ions;

(iii) the adsorption of specific ionic species present in solution.

Adsorption of ions in solution can thus take place either via hydrogen bonding between H^+ adsorbed on the HA surface and the ion in solution, or directly on to the HA surface, where dislocations or defects of the HA lattice form ideal adsorption sites [21]. Shimabayashi *et al.* [22] reported the highest adsorption values for ions of similar ionic radius to that of the Ca^{2+} ion of the HA, because these ions are assumed to fit adsorption sites formed by Ca^{2+} defects on the HA surface.

2. Experimental procedure

2.1. Production of HA filters

Three different grades of HA-based powder (Jesse Shirley and Son, Stoke-on-Trent, UK) were used to produce ceramic foam bodies. The purest grade was a white powder coded H. The other two grades were grey–brown powders and designated M/L, and the latter representing the lowest purity. This powder had a residual water content of approximately 12%. Upon drying this caused the powder to cake and form pellets which had to be broken up either mechanically or by using ultrasonic dispersion before the powder could be used. The Ca/P ratio was 1.67 for the H and M powders and 1.66 for the L grade.

The required amount of HA powder was added to a specific volume of deionized water and subsequently a known amount of Decon 75 (a general purpose surfactant added to deagglomerate the powder and encourage the foaming of the slip; Decon Laboratories Ltd, Sussex, UK) added under constant stirring at 1200 r.p.m. for 1 min. The slip was then transferred to an ultrasonic unit where the powder was dispersed for 2 min. (This procedure was only used to deagglomerate powder particles if the purity of the final product was not crucial.The tip of the ultrasonic probe was subject to wear during use and this introduced metal impurities into the slip.) The optimum settings were found to be an amplitude of 24 μm at a frequency of 20 kHz. The slip was then stirred with a high-speed stirrer at 1200 r.p.m. By this means, remaining agglomerates were broken down, the slip was further homogenized, and air bubbles were simultaneously introduced. After 2 min stirring, the maximum foam volume was reached and the bubble size was homogenous. The foamed slip was then transferred into boxes made of filter paper for drying before sintering at temperatures in the range 1000–1350 °C for 90 min. Further information on the powders and the foaming process route may be found elsewhere [23].

Disc-shaped filters, 33 mm in diameter, were produced by machining the sintered foams with a diamond-tipped core drill. The filters were then rinsed with distilled water to remove any loose powder and other impurities and then dried.

Unsintered powder was also used as filter material to compare the effectiveness of the sintered filters with unsintered powder. In these cases the same mass of powder as ceramic filter material was used in each individual experiment. All three filter grades had an approximate surface area of 1 $m^2 g^{-1}$, whilst the powder had a surface area of approximately 9 $m^2 g^{-1}$.

2.2. Ion filtration

Two types of heavy metal ion-containing solutions were used to determine the filtration characteristics of the ceramic and powder filters.

1. Standards used for atomic absorption spectroscopy (AAS). Each of the solutions contained 1000 $mg\,l^{-1}$ (± 0.5%) of the metal ion. The metal was dissolved in approximately 1 M nitric acid, with the exception of titanium which was dissolved in 2 M hydrochloric acid, and lanthanum which was supplied as 10% $LaCl_3$ solution. The pH of these solutions was generally very acidic (see Table I). This was a disadvantage because the acid could dissolve the filter if the solution was used in very high concentrations. The standard solutions were diluted to the concentrations required for individual experiments.

TABLE I pH of various AAS standard solutions (all concentration 1000 $mg\,l^{-1}$) used for ion filtration

AAS solution	pH
Fe	0.8
Al	0.8
Pb	0.8
Cr	0.8
Ni	0.9
Cu	0.8
Co	0.9
Mg	0.8
Zn	0.9
Si	12.3
La	1.6
V	0.8
Ti	0.6
Na	0.8
K	0.8
Ca	0.8

2. Less acidic solutions were obtained when nitrates of the metal ions were used which were dissolved in deionized water to make up standard solutions of various concentrations.

Two different filtration methods were used. The first, a column method involving only the ceramic filters, involved simply pouring the filtrate through the filter contained in a Pyrex filter holder with O-ring seals at both top and bottom. The residence time depended on the structure of the ceramic foams and its thickness, but was typically about 10 s.

The second approach, a batch method, enabled a direct comparison of powder and ceramic filter effectiveness. The filters were completely immersed individually in the filtrate for a fixed time period after which the ceramic filters were removed and dried whilst the powder filters were retrieved using filter paper and dried.

Initial experiments focused on determining which ions could be removed from aqueous solution by HA filters. Subsequently, a matrix of experiments was performed to evaluate the influence of a number of parameters on filter effectiveness. A distinction was drawn between (a) characteristics of the filter material, such as surface area, grade and sintering temperature, and (b) characteristics of the filtrate, such as ionic species present, ion concentration, filtrate pH and temperature. Filtration time was also examined in this section. Filter effectiveness was determined by measuring the concentrations of the heavy metal ions in solution before and after filtration using atomic absorption spectrometry.

2.2.1. Evaluation of filter characteristics

Various masses of the powder and ceramic filters were immersed in 30 ml of 84 $mg\,l^{-1}$ Pb^{2+} solution for 10 min in order to evaluate the influence of filter material grade, sintering temperature and surface area on ion removal. It should be noted that the surface area of any given ceramic filter was proportional to its mass. This, in turn, varied according to the thickness of the filter plate from which it was taken. Hence, a reduction in the total number of exchange or adsorption sites in the filter – or a reduction in the amount of ions removed – was expected with decreasing filter mass.

2.2.2. Evaluation of filtrate characteristics

Ceramic filters made from each grade of HA and weighing between 3 and 6 g were immersed in 30 ml of a range of filtrates containing different ions for periods of 1 and 24 h. In addition, L grade ceramic filters were immersed in 30 ml of 9.7 $\mathrm{mg\,l^{-1}}$ Pb^{2+} AAS solution for a range of times between 5 min and 24 h. The latter experiment was repeated with the mass of the filters being reduced to 1 g and the concentration of the Pb^{2+} solution increased to 79.3 $\mathrm{mg\,l^{-1}}$. By this means the relative ratio of Pb^{2+} concentration to filter mass was increased significantly.

To investigate filtrate concentration, ceramic filters made from each grade of HA and weighing 5 g were immersed in 30 ml Pb^{2+} ion solution having concentrations of 10 and 1000 $\mathrm{mg\,l^{-1}}$ for periods of 1 h. The effect of filtrate pH was studied by immersing ceramic filters made from each grade of HA and weighing between 3 and 6 g for 1 h in nitric acid of controlled pH and containing no ionic additions. The mass of the filters used directly matched the masses used in the 1 h filtrations described above. This permitted the influence of pH on Ca^{2+} dissolution to be determined which was required for analysis of the ion removal mechanism.

L grade filters were immersed in a range of solutions at different temperatures for 1 h to investigate the effect of filtrate temperature. Filter mass varied between 3.4 and 3.9 g but was kept constant for each ion tested as a function of temperature. The filtration time for the Pb^{2+} and Cr^{3+} ion-containing filtrates was set at 10 min, because it was known that 100% removal could be obtained in 1 h even at 20 °C.

2.2.3. Selectivity

Selectivity measurements were carried out to determine the preference of HA for specific ions by filtering solutions containing three different types of ions. The concentrations of each ion species in the filtrate had to be very similar to minimize the influence of varying initial concentration. It was also important to select the ionic species so that they did not influence each other during analysis by AAS. This limited the species which could be combined in any given filtrate.

Specific experiments involved using L ceramic filters with a mass of 4.3 g to filter 30 ml of each of three different filtrates for 1 h. The first filtrate contained 3.1–3.2 $\mathrm{mg\,l^{-1}}$ Co^{2+}, Cr^{3+} and Pb^{2+} ions, the second the same quantities of Co^{2+}, Fe^{3+} and Pb^{2+} ions, and the third Al^{3+}, Cu^{2+} and Ni^{2+} ions. For the latter, the ion concentrations were 30.0–30.7 $\mathrm{mg\,l^{-1}}$ except for the Ni^{2+} ions, which was lower at 6.3 $\mathrm{mg\,l^{-1}}$, due to the specifications for the AAS measurement.

2.2.4. Regeneration

The possibility of cleaning the filters after use is a potentially very important aspect from an environmental point of view because it would make them reusable. The experimental approach was the same for all ionic species investigated and is described below for the case of the Cr^{3+} ions.

Three L ceramic filters of 1.5 g weight were used to filter 40 ml of a 98 $\mathrm{mg\,l^{-1}}$ Cr^{3+} nitrate solution for 1 h. The concentration of Cr^{3+} ions after filtering was measured to determine the ion uptake of the filter. The filters were then left in 40 ml deionized water for 1 h to wash off any loosely adsorbed ions. The concentration of these ions in the water was also measured.

The three filters were then immersed in 80 ml of one of three different solutions, each with a pH of 2.3. The first solution was a 100 $\mathrm{mg\,l^{-1}}$ Na^{+} AAS standard solution, the second was a 100 $\mathrm{mg\,l^{-1}}$ Ca^{2+} AAS standard solution, and the third 0.1 M nitric acid. In each case, after 1 h the filters were removed and the Cr^{3+} ion concentration in the filtrate measured. The higher the Cr^{3+} ion concentration in the filtrate, the more successful was the recharge.

2.2.5. Determination of the ion-removal mechanism

The ion-removal mechanism was determined by a combination of examining the ratios of heavy metal ion uptake to Ca^{2+} ion release and by characterizing the filters before and after use. Techniques used included energy dispersive X-ray analysis (EDX), lattice parameter measurement via X-ray diffraction (XRD), and zeta potential measurement.

3. Results

Table II divides the full range of ions examined into two groupings, those that could be at least partially removed from solution and those that were not affected by any of the filtration processes described above.

TABLE II Classification of heavy metal ions in terms of success for removal by HA filters

Ions removed by filtration	Ions not removed by filtration
Cr^{3+}	Ca^{2+}
Co^{2+}	K^{+}
Ni^{2+}	Na^{+}
Al^{3+}	Ti^{2+}
Cu^{2+}	V^{5+}
Pb^{2+}	La^{3+}
Fe^{3+}	Mg^{2+}
	Zn^{2+}
	Si^{4+}

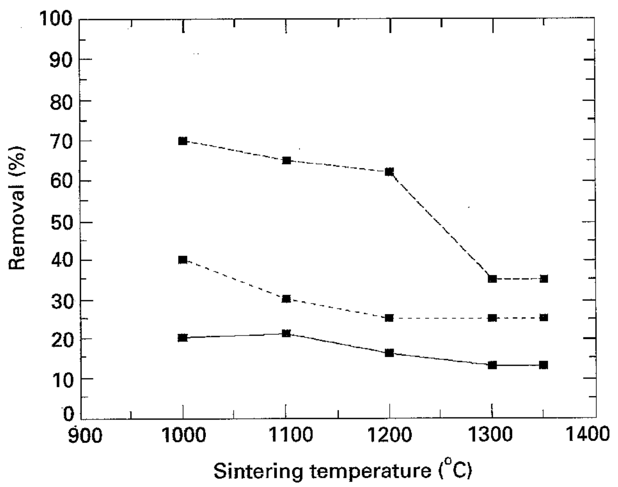

Figure 2 Effectiveness of 1 g ceramic filters, sintered at different temperatures, in removing Pb^{2+} ions from 30 ml of a 10 mg/l Pb^{2+} filtrate after 1 h. (——) H grade, (- - -) M grade, (— — —) L grade.

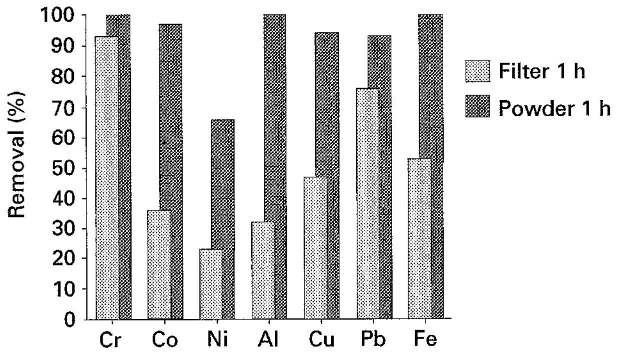

Figure 3 Comparison of removal effectiveness of equal masses of H grade powder and ceramic filters (filtrate volume 30 ml, filtration time 1 h).

3.1. Evaluation of filter characteristics

Fig. 2 shows that Pb^{2+} removal for all grades decreased with increasing sintering temperature and an increasing purity of the filter material. The purest material, H grade, removed the least Pb^{2+} from the filtrate. However, as will be seen later in Figs 6 and 7, the latter was not the case for all of the ions examined. H grade filters were the most effective of the three in removing Co^{2+}, Ni^{2+} and Fe^{3+}, while the less pure L grades, particularly L, were more effective at removing Cr^{3+}, Al^{3+} and Cu^{2+}, as well as the Pb^{2+}.

Figs 3 and 4 show the ion-removal properties of equal weights of H grade powder and ceramic filters for the full range of removable ions. As expected, owing to its higher surface area, the powder was found to be much more effective at removing heavy metal ions from solution, particularly at the shorter filtration time. The results shown in Fig. 5 show the effect of increasing filter mass (and hence surface area) on the removal of Pb^{2+} ions. Only 3.5 g powder was sufficient to remove all the ions within the limits of measurement error, whilst 6 g ceramic filter only removed approximately 40%.

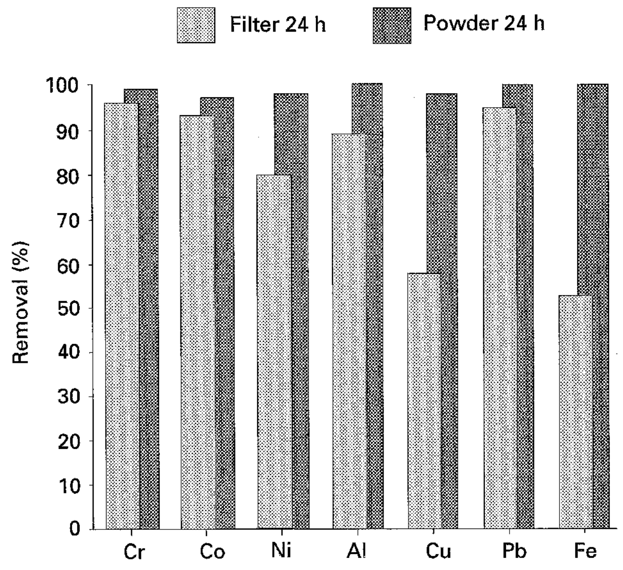

Figure 4 Comparison of removal effectiveness of equal masses of H grade powder and ceramic filters (filtrate volume 30 ml, filtration time 24 h).

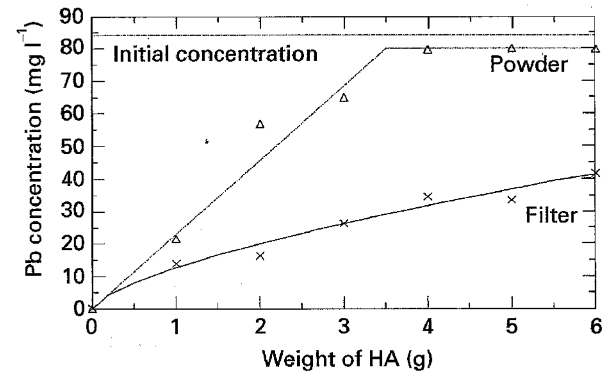

Figure 5 Ion removal from a 30 ml solution of 84 mgl^{-1} Pb^{2+} by various masses of H grade powder and ceramic filters after a filtration time of 10 min.

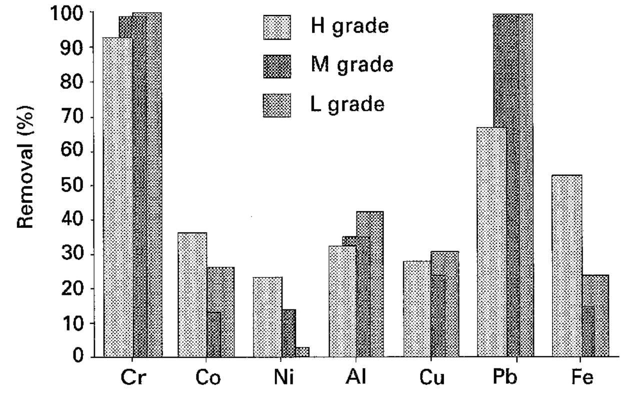

Figure 6 Ion removal (%) results for ceramic filters of all grades, 1 h filtration time, 30 ml filtrate volume.

3.2. Evaluation of filtrate characteristics

3.2.1. Influence of filtration time

Figs 6 and 7 show the removal efficiency of all three filter grades for all the ions removable from solution over 1 and 24 h, respectively. More detailed results for the removal of Pb^{2+} ions by L grade ceramic filters are presented in Fig. 8. As expected, ion removal is

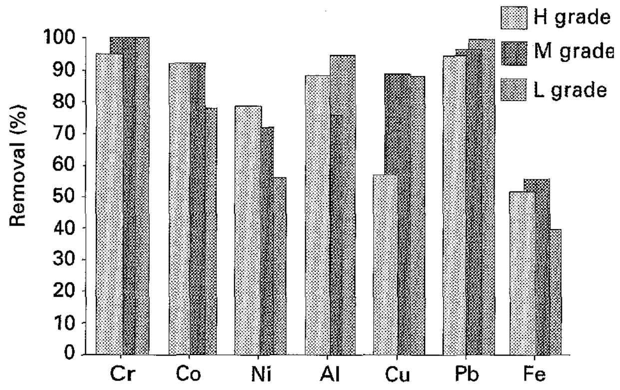

Figure 7 Ion removal (%) results for ceramic filters of all grades, 24 h filtration time, 30 ml filtrate volume.

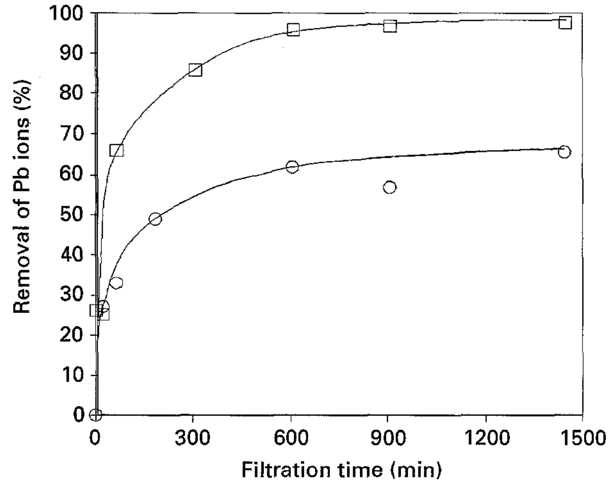

Figure 8 Pb^{2+} ion removal versus filtration time for L grade filters using 30 ml filtrate with an initial Pb^{2+} concentration of (□) 9.7 $mg\,l^{-1}$ (5.7 g filters), and (○) 79.3 $mg\,l^{-1}$ (1 g filters).

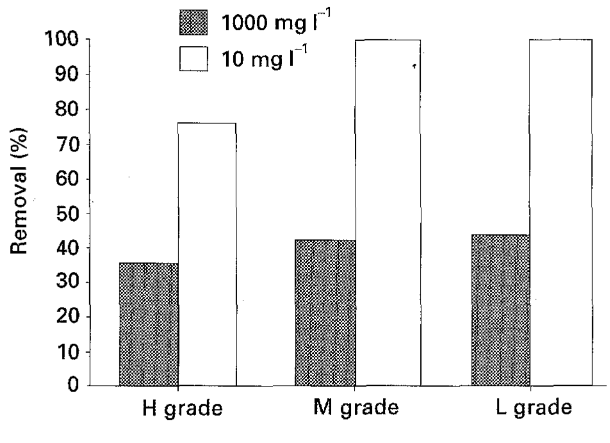

Figure 9 Comparison of filtration effectiveness for all filter grades at different initial Pb^{2+} concentrations; 5 g filters, 30 ml filtrate, 1 h filtration time.

TABLE III Ca^{2+} ion release of the filters as a function of filtrate pH. Results correspond to the 1 h ion filtration tests (see Fig. 6). Ions in parentheses refer to the equivalent filtration test

pH	Filter mass (g)	Ca^{2+} ion release after 1 h ($mol\,l^{-1}$)		
		H grade	M grade	L grade
0.7	3.4(Cu^{2+})	0.02545	0.03393	0.02375
0.7	3.2(Al^{3+})	0.02396	0.03194	0.02375
1.0	5.0	0.03493	0.04590	0.03293
1.5	3.5(Ni^{2+})	0.01477	0.01188	0.00849
1.7	3.9(Pb^{2+})	0.01168	0.00681	0.00487
1.8	3.9(Co^{2+})	0.01128	0.00642	0.00389
1.8	3.3(Fe^{3+})	0.00897	0.00560	0.00339
1.9	5.0(Cr^{3+})	0.01317	0.00689	0.00494
2.0	5.0	0.01347	0.00399	0.00299
3.0	5.0	0.00699	0.00070	0.00040

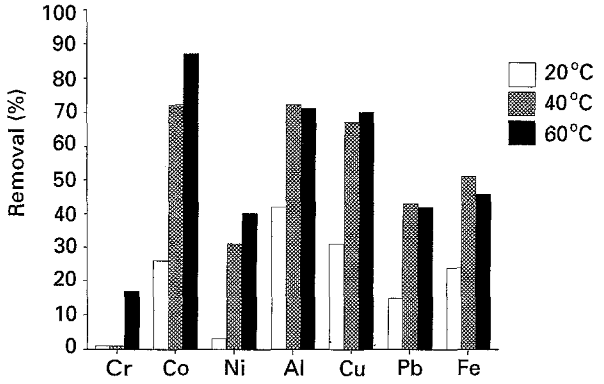

Figure 10 Ion removal (%) for various ions from 30 ml filtrate at various temperatures after 1 h (Cr^{3+} and Pb^{2+} 10 min) by L grade filters.

initially very rapid but decreases as a function of time. Evidence was found for Fe^{3+} saturation with all filter grades and Cu^{2+} with the H grade.

3.2.2. Influence of initial filtrate concentration

Evidence for the effect of initial concentration has already been seen in Fig. 8. Fig. 9 shows that the same behaviour was found for all filter grades. An increase in the filtrate concentration decreases the removal rate although it should be remembered that the absolute number of ions removed is greater.

3.2.3. Influence of pH of the filtrate

It should be noted that in all cases the quantity of Ca^{2+} ions increased after filtration, even when no heavy metal ion removal had occurred. This was due to the acidity of the filtrates which chemically attacked the HA. Table III shows the increasing Ca^{2+} ion release values in moles per litre for each grade of ceramic filter as a function of pH. To ensure that the results corresponded to the ion filtration tests presented in Fig. 6, the same filter masses were used in each individual experiment. It can be observed that with increasing solution pH, the Ca^{2+} ion release per gram of filter decreased.

3.2.4. Temperature of the filtrate

Fig. 10 shows the influence of temperature on the removal efficiency of L grade filters. The removal level increased for all ions when the filtrate temperature was increased from 20 °C to 40 °C. However, increasing the temperature to 60 °C only

TABLE IV Selectivity results using 4.3 g L grade ceramic filter and 30 ml of filtrate containing Cr^{3+}, Co^{2+} and Pb^{2+} ions

Filtrate 1	Cr^{3+}	Co^{2+}	Pb^{2+}
Initial concentration ($mg\,l^{-1}$)	3.1	3.1	3.2
Concentration after filtration ($mg\,l^{-1}$)	2.5	2.4	1.8
Ion removal ($mg\,l^{-1}$)	0.6	0.7	1.4
Removal (%)	19	23	43

TABLE V Selectivity results using 4.3 g L grade ceramic filter and 30 ml of filtrate containing Pb^{2+}, Co^{2+} and Fe^{2+} ions

Filtrate 2	Pb^{2+}	Co^{2+}	Fe^{3+}
Initial concentration ($mg\,l^{-1}$)	3.2	3.1	3.2
Concentration after filtration ($mg\,l^{-1}$)	1.8	2.4	1.6
Ion removal ($mg\,l^{-1}$)	1.4	0.7	1.6
Removal (%)	43	23	50

TABLE VI Selectivity results using 4.3 g L grade ceramic filter and 30 ml of filtrate containing Ni^{2+}, Al^{3+} and Cu^{2+} ions

Filtrate 3	Ni^{3+}	Al^{3+}	Cu^{2+}
Initial concentration ($mg\,l^{-1}$)	6.3	30.0	30.7
Concentration after filtration ($mg\,l^{-1}$)	6.3	25.0	24.8
Ion removal ($mg\,l^{-1}$)	0	5.0	5.9
Removal (%)	0	17	19

significantly increased the percentage removal further in the case of the Cr^{3+}, Co^{2+} and Ni^{2+} filtrates.

3.3. Selectivity

Ion-removal results for the selectivity experiments are given in Tables IV–VI. From these it can be seen that the overall selectivity of the L grade filters was:

$$Fe^{3+} > Pb^{2+} > Co^{2+} > Cr^{3+}$$

$$Al^{3+} > Cu^{2+} > Ni^{2+}$$

A simple comparison of the removal levels obtained in other experiments when only one counter-ion species was present in the solution resulted in the following approximate ranking:

$$Pb^{2+} = Cr^{3+} > Co^{2+} > Al^{3+} > Cu^{2+} > Ni^{2+} > Fe^{3+}$$

The effect of possible interactions between different ion species is neglected in this ranking.

The major variation between the two rankings can be seen to be the position of Fe^{3+}. It is preferably removed when two other kinds of ions were present, but its removal level was rather low when it was the only heavy metal ion in the filtrate.

3.4. Regeneration

The results of the experiments are given in Table VII. The results show that, in general, it is not possible to recharge HA filters. Although high recharge values were obtained in specific cases, such as Co^{2+} with Na^+ and H^+, these results are deceptive, because only very small fractions of the Co^{2+} ions had been removed from the filtrate in the first place.

TABLE VII Recharge percentages for L grade filters using Ca^{2+}, Na^+ and H^+ nitrate solutions

Ion previously filtered	Recharging nitrate solutions		
	Ca^{2+} (%)	Na^+ (%)	H^+ (%)
Cr^{3+}	0	20	20
Co^{2+}	0	100	100
Ni^{2+}	25	25	25
Al^{3+}	0	0	0
Cu^{2+}	66	33	33
Pb^{2+}	11	11	4
Fe^{3+}	4	4	4

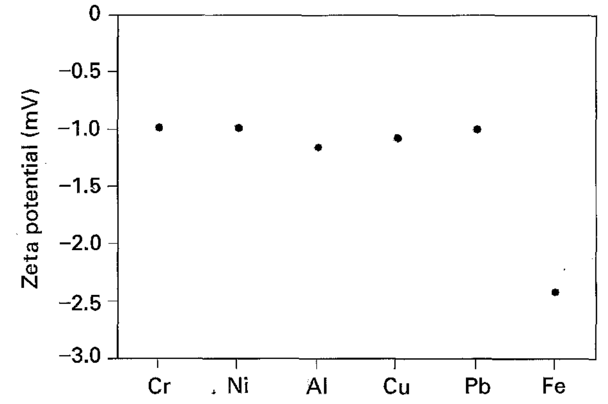

Figure 11 Zeta potential of H grade powder samples after use as filters for 30 ml of various ion-containing solutions for 1 h (original zeta potential −10.2 mV).

3.5. Determination of the ion-removal mechanism

XRD analysis failed to detect a change in lattice parameters within measurement error (0.7%) due to the substitution of the Ca^{2+} ion with ions of different sizes for the used filters compared with unused filters. EDX measurements were also unsuccessful in detecting the location of the heavy metal ions in the filter after use.

The results of the zeta potential measurements are shown in Fig. 11. They show that ion filtration increased the zeta potential significantly in the case of all ions from −10.2 to $\leqslant -2.5$ mV (with a measuring inaccuracy of about 20%).

The amount of Ca^{2+} released during filtration ($[Ca]_{measured}$) can be taken as a further indicator for ion exchange or ion adsorption. If ion exchange was the exclusive mechanism of ion removal, every mole of heavy metal ion taken up by the filter must have caused the release of 1 mol Ca^{2+} ions into the filtrate. This fraction of the Ca^{2+} release is named $[Ca]_{ion\ exchange}$. However, Ca^{2+} ions will also be released due to the dissolution of the HA in the highly acidic solutions used, this quantity is named $[Ca]_{pH}$. Thus, if ion exchange was the only mechanism for ion removal from the filtrate then:

$$[Ca]_{measured} = [Ca]_{ion\ exchange} + [Ca]_{pH} \quad (2)$$

or

$$\frac{[Ca]_{measured}}{[Ca]_{pH} + [Ca]_{ion\ exchange}} = 1 \quad (3)$$

TABLE VIII Ca^{2+} release from H grade filters after a filtration time of 1 h, filtration volume 30 ml

Ion solutions	Cr^{3+}	Co^{2+}	Ni^{2+}	Al^{3+}	Cu^{2+}	Pb^{2+}	Fe^{3+}
Filter mass (g)	4.8	3.9	3.7	3.2	3.4	3.9	3.1
$[\mathrm{Ca}]_{\mathrm{measured}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	1746	2495	5189	449	39920	6113	6986
$[\mathrm{Ca}]_{\mathrm{pH}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	13170	11280	14770	23960	25450	11680	8970
$[\mathrm{Ca}]_{\mathrm{ion\ exchange}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	165	58	75	2532	326	31	90
Ratio (from Equation 3)	0.12	0.22	0.35	0.02	1.55	0.52	0.77

TABLE IX Ca^{2+} release from M grade filters after a filtration time of 1 h, filtration volume 30 ml

Ion solutions	Cr^{3+}	Co^{2+}	Ni^{2+}	Al^{3+}	Cu^{2+}	Pb^{2+}	Fe^{3+}
Filter mass (g)	4.6	3.9	3.4	3.2	3.4	3.9	3.4
$[\mathrm{Ca}]_{\mathrm{measured}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	2250	1750	6390	420	44910	3990	2500
$[\mathrm{Ca}]_{\mathrm{pH}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	6890	6420	11880	31940	33930	6810	5600
$[\mathrm{Ca}]_{\mathrm{ion\ exchange}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	180	20	30	2740	260	50	10
Ratio (from Equation 3)	0.32	0.27	0.54	0.01	1.31	0.58	0.45

TABLE X Ca^{2+} release from L grade filters after a filtration time of 1 h, filtration volume 30 ml

Ion solutions	Cr^{3+}	Co^{2+}	Ni^{2+}	Al^{3+}	Cu^{2+}	Pb^{2+}	Fe^{3+}
Filter mass (g)	5.5	3.9	3.4	3.4	3.4	3.9	3.4
$[\mathrm{Ca}]_{\mathrm{measured}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	3740	3490	9180	420	56140	3190	4500
$[\mathrm{Ca}]_{\mathrm{pH}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	4940	3890	8490	23750	23750	4870	3390
$[\mathrm{Ca}]_{\mathrm{ion\ exchange}}$ ($10^{-6}\,\mathrm{mol\,l^{-1}}$)	180	40	10	1420	370	50	30
Ratio (from Equation 3)	0.73	0.89	1.08	0.02	2.33	0.65	1.32

If this ratio was < 1, then some adsorption must have taken place. A ratio of > 1 should not occur, in theory.

Tables VIII–X show the Ca^{2+} concentration after filtration ($[\mathrm{Ca}]_{\mathrm{measured}}$), the Ca^{2+} release due to the high acidity of the filtrate ($[\mathrm{Ca}]_{\mathrm{pH}}$), as determined from Table III, and the $[\mathrm{Ca}]_{\mathrm{ion\ exchange}}$ values determined from the number of moles of heavy metal ions removed from solution assuming that the only mechanism was ion exchange. From these values the ratio in Equation 3 is calculated for each grade of filter.

4. Discussion

4.1. Filter characteristics

4.1.1. Surface area of filter

The porous ceramic filters were found to have a much lower filtration effectiveness than the powder filters due principally to their lower surface area. Similarly, ceramic filter effectiveness decreased with increasing sintering temperature as reported previously by Yoshida and Kataoka [24].

4.1.2. Grade of filter

In general, the lower the purity of the HA the higher is the fraction of lattice defects which will be present due to the presence of impurity ions in the lattice. These defects will form ideal sites for ion exchange or adsorption due to the lower energy required for the processes to occur, compared with the ideal crystal structure. This theory would account for the superior ability of the M and, particularly, L grades in removing Cr^{3+}, Al^{3+}, Cu^{2+} and Pb^{2+} ions from solution when compared to the H grade. It is also a very satisfying result from an economic point of view because the cost of the lower purity grades was much lower than that for the purer HA. However, this cannot be the complete story, because the H grade filters were the most effective of the three in removing Co^{2+}, Ni^{2+} and Fe^{3+} ions. Further work is required to understand the relationship between grade and ion-removal capability.

4.2. Filtrate characteristics

4.2.1. Filtration time

This is an important factor for consideration for commercial applications of HA as a water filter; short filtration times are necessary to make the process economical. In agreement with previous researchers [11], it was found that the ion-removal rate decreased with an increasing filtration time. This occurred because the concentration of the heavy metal ions in the filtrate was reduced and hence the average diffusion distances of the ions in the bulk of the solution towards the surface of HA became longer. In addition, as the surface exchange or adsorption sites became exhausted, the ions had to move deeper into the filter. The removal rate would be expected to decrease to zero when the equilibrium concentration was reached, or when the filtrate was completely deprived of heavy metal ions.

Given that removal effectiveness decreases as filtration progressed, it is important to determine the minimum filtration time that will still yield a relatively high removal level. Consideration of the results indicates that for the experiments performed in this work, a filtration time of 1 h is a good compromise between length of filtration time and level of ion removal.

4.2.2. Filtrate concentration

In agreement with other researchers [4, 8], it was noted that an increased initial filtrate concentration decreased the *relative* removal efficiency of the filter. This can be explained by the tendency of a system to minimize concentration differences. With a lower filtrate concentration the concentration difference of cations between the filter and the solution was increased at a fixed cation concentration of the filter. This encouraged more counter-ions in the filter to diffuse into solution. Hence the Donnan potential was increased. The ion adsorption/exchange process was therefore encouraged and the removal level increased. Despite this, it should be noted that the *absolute* amount of ions removed was still larger in the highly concentrated solutions, because the average diffusion paths of ions from the bulk of the solution to the adsorption/exchange sites on the HA were shorter.

4.2.3. Filtrate pH

The results indicate that the lower the filtrate pH the larger the dissolution tendency of the HA and hence the greater the Ca^{2+} release. This was found to be favourable for the application of HA as filter material because counter-ions from the filtrate were encouraged to diffuse into the HA lattice due to an increased Donnan potential, in agreement with previous work [11]. The Ca^{2+} vacancies generated in the HA lattice also offered ideal adsorption or exchange sites.

4.2.4. Filtrate temperature

Ion-removal effectiveness was found to increase for all types of ions if the filtrate temperature was increased from 20 °C to 40 °C, in line with previous research [12]. This can be explained by the greater diffusion rates at elevated temperatures. Hence the time required for the ions to diffuse to the exchange/adsorption sites was reduced.

4.3. Selectivity

It was difficult to determine accurate selectivity values for all the ionic species examined because the initial concentrations in the filtrates were restricted by the method of analysis, here AAS. Because different initial concentrations yielded different removal levels, as previously discussed, the results obtained from filtration tests with only a single type of heavy metal ion present should only be taken as a trend. Nevertheless, the removal levels obtained in Fig. 6 enables the following ranking after a filtration time of 1 h to be determined:

$$Cr^{3+} > Pb^{2+} > Fe^{3+} > Al^{3+} > Co^{2+} > Cu^{2+} > Ni^{2+}$$

It should be noted that after 24 h, the position of Fe^{3+} had changed to that of least preferred ion (see Fig. 7) due to possible saturation effects. The above ranking is in approximate agreement with previous work [4, 12]. The following explanations are offered for the selectivity behaviour of the filters.

Cr^{3+} is one of the least suitable ions for ion exchange or adsorption from the aspect of ionic radius and electronegativity. Hence it is speculated that it might have been strongly attracted due to its trivalence. The ionic radius of Pb^{2+} was the closest to that of Ca^{2+} of all the ions which were successfully filtered. Thus it would fit best into Ca^{2+} vacancies. Pb^{2+} also exhibited a high electronegativity which increased the attraction towards the filter surface due to the Donnan potential. Al^{3+} showed the same parameters as the Cr^{3+}, a very small ionic radius and electronegativity, but again it was a trivalent ion and might have thus been strongly attracted due to the Donnan potential developed. Co^{2+}, Cu^{2+} and Ni^{2+} displayed ionic radii and electronegativity values which were similar but differed from those of Ca^{2+}, reducing their suitability for filtration. Cu^{2+} had a slightly higher electronegativity and an ionic radius closer to Ca^{2+} than the other two. Hence it would have been expected to have shown higher removal levels. Copper-complex formation in the filtrate might be a possible explanation for the low removal level as also observed by Shimabayashi *et al.* [22]. It was impossible to explain the behaviour of the Fe^{3+} over the filtration times used purely in terms of its electronegativity and ionic radius. Again, complex formation on the HA surface may have occurred. Bonner *et al.* [25] have reported an increased tendency of complex formation for transition metals.

In the case of filtrates containing three types of ions (see Tables IV–VI) the valence of the ions did not seem to have been the major factor in deciding which ions were removed from solution most effectively. Trivalent ions were not preferred in two out of three filtrates. Rather it appears that the electronegativity of the ions played an important role in the decision as to which ions were preferentially removed from the filtrates. If the ions showed the same electronegativity value then the valence of the ions became the determining factor. It should be noted, however, that these conclusions are only based on a small number of experiments because permutations were restricted by the requirements for AAS.

4.4. Regeneration

None of the solutions examined was found to be capable of recharging the filters significantly. The evidence which was found is debatable because only very small quantities of ions were detected in the regeneration fluid and thus the potential for measurement error was high. The low regeneration ability indicates very strongly that ion removal by HA is an irreversible process.

4.5. Ion-removal mechanism

Initially it was assumed that ion exchange was the only operational mechanism for HA because it features strongly in all the literature (see, for example, [11, 26] and ion removal by adsorption remains unaddressed. During experimentation, however, it became increasingly apparent that ion adsorption was responsible for at least part of the filtration capability of HA. From a practical point of view it matters little whether the uptake of ions is achieved by ion exchange or adsorption, but in this work an attempt has been made to find out which process took place or whether it was a combination of both.

Ion exchange is a stoichiometric process. Every ion that is removed from the filtrate is replaced by another ion from the filter. In adsorption, on the other hand, the ions are taken up by the filter without being replaced by another species. This distinction seems clear cut. However, it is difficult to apply it in practice, because most ion-exchange processes are accompanied by adsorption.

If the heavy metal ions were exchanged with the Ca^{2+} ions in the HA lattice the spacings between the lattice planes would have to expand to make room for a bigger ion or would have to contract if a smaller ion than Ca^{2+} was incorporated. Although XRD is a very sensitive means of determining cell parameters, no significant change in the a and c lattice parameters were noted after ion filtration. This might have been due to insufficient ion removal from solution. A similar lack of proof was forthcoming from the EDX analyses. Again, possibly due to insufficient ion removal from solution and the resolution limits of the technique, EDX failed to detect the presence of heavy metal ions in the structure of the HA after filtration. Hence ion exchange could not be ruled out by these results, but no positive indication of the process could be provided either.

Zeta potential measurements were more informative. If the positively charged heavy metal ions were adsorbed on to the surface of the HA then, for all ions, the surface charge would be expected to increase (or become less negative). If the ions were being exchanged into the lattice then the zeta potential would increase for exchange of Ca^{2+} with trivalent cations but would remain unchanged for the divalent cations. The zeta potential of the pure H grade before filtration was −10.2 mV. After filtration the zeta potential was less negative in the case of all ions. Hence the results of Fig. 11 can be taken as a clear indication of ion adsorption having been present with no evidence for ion exchange.

Yamashita *et al.* [27] reported the only successful exchange of trivalent cations in apatite material to date. They used calcium oxyhydroxyapatite where the positive surplus charge of the trivalent ions was balanced by the missing hydrogen atom. Thus no evidence has been found anywhere in the literature of ion exchange with HA using ions of mismatching charges. This would support the view that the trivalent cations (Cr^{3+}, Al^{3+} and Fe^{3+}) were removed purely by an adsorption process.

It was observed for all ionic species except Cu^{2+} that the ratio of the Ca^{2+} concentration in the filtrates after filtration, $[Ca]_{measured}$, to the Ca^{2+} release measured in the reference system where the pH of the solution was the same but heavy metal ions where absent, $[Ca]_{pH}$, was significantly less than 1. This is a clear indication of ion adsorption having taken place. It is believed that the heavy metal ions reduce the dissolution tendency of the HA by the formation of a protective layer that acts as a shield against the acid attack.

In the case of the Cu^{2+} filtration there are several possible explanations of the high $[Ca]_{measured}$ values. Firstly, it is known that the presence of Cu^{2+} in the filtrate interferes with the measurement of Ca^{2+} by AAS. Secondly, a (Cu/Ca) complex might have been formed in the filtrate. The free Ca^{2+} ion concentration would therefore be reduced, encouraging further dissolution of Ca^{2+}. Thirdly, a copper-complex might have formed on the surface of the HA as reported by Shimabayashi *et al.* [22].

5. Conclusions

1. All grades of HA were found to be capable of removing Al^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+} and Pb^{2+} ions from solution. The ion-removal level depended on experimental conditions, but virtually 100% ion removal could be achieved in most cases under the correct conditions.

2. For filtrates containing a single ionic species, the selectivity of the filters appears to be $Cr^{3+} > Pb^{2+} > Fe^{3+} > Al^{3+} > Co^{2+} > Cu^{2+} > Ni^{2+}$. There is some uncertainty over the position of Fe^{3+} in this series, because it appeared to reach a saturation limit, possibly due to complex formation.

3. In the case of filtrates containing three types of ions, the electronegativity of the ions appears to have played an important role in the decision as to which ions were preferentially removed from the filtrates. If the ions showed the same electronegativity value then the valence of the ions became the determining factor.

4. In order to achieve maximum ion removal levels the filtration parameters required were found to be:

(a) use of impure rather than pure grades of HA. It is believed that increased impurity levels resulted in increased numbers of lattice defects which are ideal adsorption/exchange sites;

(b) a high surface area. In this respect the powders were superior to the ceramic filters and for the latter a low sintering temperature was preferable;

(c) long filtration times. Because removal rate decreases with increasing filtration time, a suitable compromise was found to be a period of 1 h;

(d) a low pH. This encouraged initial dissolution of the HA which resulted in an increased removal level. It is believed that the HA was protected from continued acid attack by the adsorption of the heavy metal ions on the material's surface;

(e) a high filtrate temperature. With increasing temperature the diffusion rate of the ions increases, leading to higher ion-removal levels.

5. Regeneration of the filters was not found to occur using sodium, calcium or hydrogen ion-based nitrate solutions.

6. Ion adsorption was positively detected as a mechanism of ion removal. Ion exchange was not observed but could not be completely ruled out.

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