Absorption and Desorption of Chromium Ions by Poly(acrylic acid) Gels

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ABSTRACT: The ability of crosslinked poly(acrylic acid) gels to retain chromium species was studied as a function of pH. Chromium retention was found to increase with pH according to two mechanisms. In the low pH range where chromium species are soluble, retention occurs via ion-binding in the whole volume of the gel. At higher pH where insoluble chromium hydroxide particles are formed, retention comes from an adsorption process at the surface of the gel. The desorption of chromium species under acidic conditions was also investigated and found to be very dependent on retention mechanism and aging time of the polymer–chromium complex. When retention occurs by ion-binding, only partial desorption was achieved at very short aging time. In contrast, a very fast desorption was observed when retention occurs via adsorption at the surface of the polymer gel. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 455–466, 1999

Key words: poly(acrylic acid); chromium ions; adsorption; desorption

INTRODUCTION

An important problem of environment is related to the decontamination of waste water polluted by heavy metals such as zinc, copper, chromium, or nickel. The processes commonly used today in industry are mainly based on hydroxide precipitation, which gives high volumes of sludge difficult to deal with.[1,2] Several more promising processes are based upon the specific interactions between ions and water swellable or soluble polymeric materials. The use of the ion–polyion interactions is quite direct since one can profit from the retention of cationic and anionic pollutants by polyelectrolyte matrix of opposite charge.

The development of polymer-based materials is parallel to a renewal of interest in the problem of the interactions between polyelectrolytes and multivalent counterions in solution. The behavior of charged polymers in the presence of monovalent counterions is at least qualitatively well understood through the Manning or Iwasa theories, which predict ionic condensation when the charge density of the polymer exceeds a critical value.[3,4] However, these theories fail to predict the various phenomena observed in the presence of multivalent cations, and due to specific interactions, such as phase separation and gelation with or without syneresis.[4–14] Some progress was recently achieved in order to rationalize these behaviors according to the polymer and counterion properties, the ionic strength and the temperature, by comparing synthetic and biological systems.[15] Theoretical approaches emerge, which are in qualitative agreement with the observations.[15–17] It turns out that most phenomena can be simply explained by equilibrium laws ruling the binding of the counterions on the polyions and by mini-

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mizing the corresponding free energy of the system. The progress made on a fundamental point of view should allow us to optimize the nature of the materials of practical interest.

The swelling and deswelling of crosslinked polyelectrolytes in the presence of complexing ions were already the subject of several works and the ability of small spherical particles of poly(acrylic acid) (PAA) gels to retain some multivalent ionic species has been demonstrated.[18,21] However, to our best knowledge, there are few systematic studies about the retention of various counterions as a function of the driving parameters (pH, ion concentration).

The goal of this article is to study the ability of PAA particles to retain chromium ions and to propose retention mechanisms. Experimental conditions leading to the highest retention at equilibrium as well as the swelling kinetics and the equilibrium swelling of the PAA particles are determined. The possibility of removing the ionic species from the gel are also discussed.

EXPERIMENTAL

Materials

The PAA particles were prepared by polymerization in reversed suspension by Elf Atochem.[22] The degree of crosslinking was controlled by addition of 0.05% of bisacrylamide.

The chromium chloride from Merck of analytical grade was used without further purification.

Methods

The electrophoretic mobility and the particle size of the chromium species were measured with a MALVERN Zeta Sizer 3 apparatus, operating at a wavelength of 633 nm. Aqueous solutions of $CrCl_3$ were prepared in 3× distilled water. After 24 h of solubilization, this solution was filtered on Dynagard filters of 0.2 μm of porosity. Then, the pH was adjusted to the desired value by addition of an aliquot of sodium hydroxide solution (1*M*), which had also been filtered.

The residual amount of chromium species in the supernatant was determined either by atomic absorption using a Varian AA 30 spectrometer or by UV spectroscopy after acidification at pH below 1 using a Shimadzu UV 240 spectrometer.

An optical Zeiss Photo Mill microscope and a scanning electronic microscope were used to study the gel swelling. The PAA gel particles which were swollen under various conditions (in the presence or in the absence of salts) were dried for 24 h at 40°C and then metallized.

The potentiometric measurements were performed with a pH meter, Metrohm 605, using a combined glass microelectrode. The PAA gels were available under their sodium salt form. In order to obtain their potentiometric titration curve, they were transformed in PAA by addition of a large excess of HCl, followed by a careful rinsing and drying at 90°C for 12 h. They were then equilibrated in 25 mL of pure water at a concentration corresponding to $10^{-2}M$ of carboxylic functions.

PROPERTIES OF CHROMIUM SOLUTIONS

Polyion–counterion interactions depend on the nature of the ionic species formed after dissolution of the salt in water. These species and their relative proportions vary with the pH and the concentration. The easiest method to determine the amount of free ionic species in equilibrium with the polymeric materials is the UV-visible spectroscopy which requires knowing the spectroscopic properties of the aqueous salt solutions.

Distribution of the Ionic Species

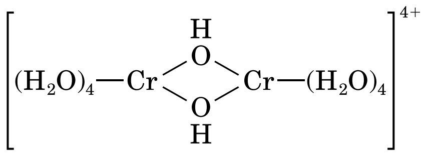
The distribution and the nature of the ionic species in aqueous $CrCl_3$ solutions are governed by different reactions and equilibria: (1) fast hydrolysis reactions associated with the following equilibria:

$$H_2O + M(OH)_p(H_2O)_{k-p}^{(m-p)+} \rightleftarrows H^+ + M(OH)_{p+1}(H_2O)_{k-p-1}^{(m-p-1)+} \quad (1)$$

with constants $K_{m,p}$, m is the maximum charge of the metallic ion, k the hydration number equal to 6 for chromium. (2) solubility limit

$$m(OH)^- + M(H_2O)_6^{m+} \rightleftarrows M(OH)_m(H_2O)_{6-m} \quad (2)$$

with a solubility product $K_S = 10^{-30}$ (mol^{-4}). (3) Slow reactions of olation giving rise to the formation of hydrolytic oligomers and polymers. These polynuclear compounds consist of a number of metal ions with hydration molecules connected by "ol" bridges. For example, the tetravalent binuclear species of chromium is



which can be formed either by reaction of $Cr(H_2O)_6^{3+}$ and $Cr(OH)_2(H_2O)_4^+$ with elimination of two water molecules or by reaction of two $Cr(OH)(H_2O)_5^{2+}$. The general formula of these polynuclear species is $[M_y(OH)_x(H_2O)_{6y-x}]^{(3y-x)+}$ and their formation is associated with a constant $K_{y,x}$.

Ionic species of chromium with polymerization degree up to 100 have been identified.[23] The structure and properties of the oligomers are well described. They are characterized by a slow rate of formation and dissociation.[23–25] However, the equilibrium and rate constants are not well known and for long aging time of chromium chloride solutions, the exact distribution of the mono and polynuclear species is difficult to calculate. We have used, in most cases, freshly prepared solutions. It is important to keep in mind that the charge of the dimer, trimer and tetramer is 4, 5, and 6, respectively.

Figure 1 gives the solubility limit of $CrCl_3$ and shows the distribution of the mononuclear ionic species ($Cr(H_2O)_6^{3+}$, $Cr(OH)(H_2O)_5^{2+}$, and $Cr(OH)_2(H_2O)_4^+$) in fresh solutions. The pH of the solutions and consequently the fractions of trivalent or bivalent species decrease when the chromium concentration increases (Fig. 1).

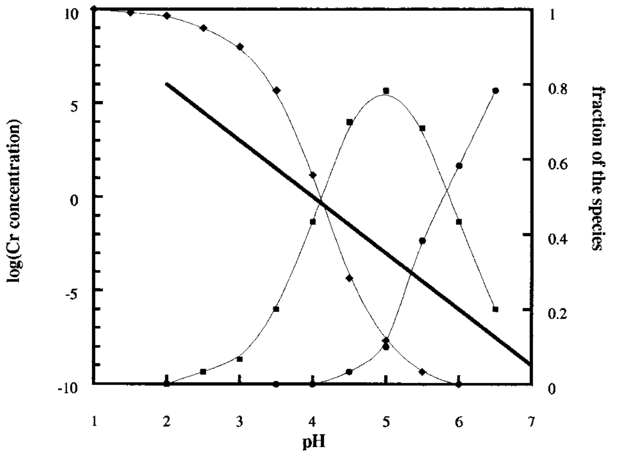


Figure 1 Solubility limit of $CrCl_3$ (▬) and distribution of the mononuclear species in a freshly prepared solution: $Cr(H_2O)_6^{3+}$ (◆), $Cr(OH)(H_2O)_5^{2+}$ (■), $Cr(OH)_2(H_2O)_4^+$ (●).

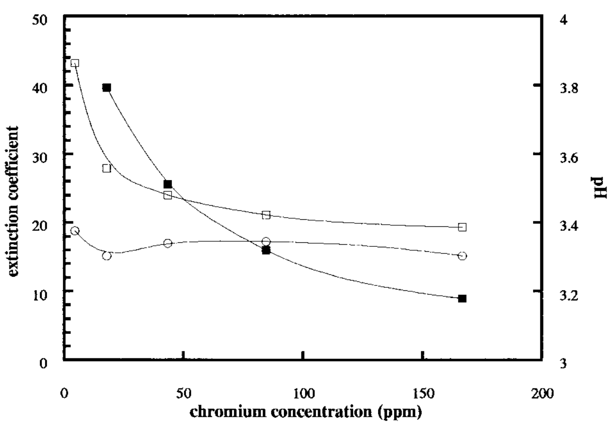


Figure 2 Concentration dependences of the extinction coefficients of $CrCl_3$ solutions at $\lambda = 415$ nm (□), $\lambda = 580$ nm (○), and pH (■).

Spectroscopic Properties of the Chromium Solutions

The UV-visible spectra of the aqueous solutions of $CrCl_3$ are characterized by three absorption maxima at $\lambda = 580$, 415, and 265 nm. At 415 nm, the extinction coefficient ε decreases when the concentration of chromium increases (see Fig. 2), while ε remains approximately constant at $\lambda = 580$ nm. Such a behavior is not surprising since in aqueous solutions of variable concentration at their own pH, the distribution of ionic species is different. When the concentration decreases, the nature of the chromium ion ligands is changed. The hydration molecules are replaced by hydroxyl groups of higher binding strength, resulting in an increase of the extinction coefficient. Finally, as seen from the comparison of atomic absorption and UV spectroscopy measurements, whatever the initial pH of the chromium solution (even if it corresponded to the insolubility range), it was possible to determine the Cr amount by measurements at 575 nm after lowering the pH to 1. Under such conditions, the extinction coefficient is 12.6 $mol^{-1}\ L^{-1}\ cm^{-1}$.

Size and Charge of the Chromium Hydroxide Particles

Since the formation of chromium hydroxide occurs at relatively low concentration and pH (see Fig. 1), it was important to verify whether the chromium hydroxide particles are completely uncharged or partially charged, as demonstrated for aluminum hydroxide.[9] For this purpose, we used a Zeta Sizer, which provides the electrophoretic mobility μ_e of the particles and their average charge Q_e; it allowed us also to determine the average hydrodynamic radius R_H and the polydispersity index PI. For freshly prepared solutions of $CrCl_3$, the following results were obtained at pH 6.1 and for a chromium concentration, $5\ 10^{-3} M$.

$$R_H = 78 \text{ nm} \qquad \mu_e = 2.6\ 10^{-4} \text{ cm}^2 \text{ s}^{-1} V^{-1}$$
$$\text{PI} = 0.24 \qquad Q_e = 5.72\ 10^{-17} \text{ C}$$

The value of PI indicates a rather broad distribution of the particle size but we have no direct information about their shape. Even if the value of Q_e which was however calculated assuming a spherical shape is an approximation, it can be concluded that the hydroxide particles maintain a residual positive charge even for pH much higher than the solubility limit. One can roughly estimate from the above value of Q_e that 3% of the chromium atoms carry one charge.

We have investigated the variations of the size and charge of $Cr(OH)_3$ with the aging time of the solution. The electrophoretic mobility of the particles for 6 days of aging is 3.1×10^{-4} cm^2 s^{-1} V^{-1} while the size remained unchanged, which means that the average charge increases. The inverse effect has been observed for the aluminum hydroxide.[9] In the case of $CrCl_3$ solutions, the initial pH was 6.1 but it decreased down to 5.7 after 6 days. This favors the formation of oligomeric species of higher charge to the detriment of the hydroxide.

PAA PARTICLES

Potentiometric Titration

It is well known that the constant K_a of polyacids dissociation,

$$\text{R—COOH} \rightleftarrows \text{R} - \text{COO}^- + \text{H}^+ \qquad (3)$$

is not a constant like that of monomeric weak acids, but depends strongly on various parameters[26] such as the charge density and the concentration of the polymer as well as the ionic strength of the solution. In the case of a linear polyacid in aqueous solution, its pK_a is related to an electrostatic interaction term ΔG_e:

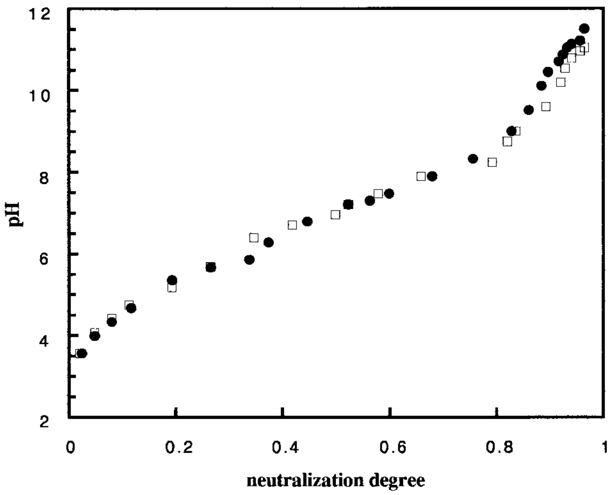


Figure 3 Potentiometric titrations of PAA particles (□) and linear PAA (●).

$$pK_a = pK_o + 0.434\ \frac{\Delta G_e}{kT} \qquad (1)$$

Mandel[27] has proposed to express pK_a as a polynome in α, the ionization degree of the acid groups. There are few data on the potentiometric titration of PAA gels. It was important, however, for the present article to control the α values as a function of pH.

A commercial sample of linear PAA (mol wt = 4×10^6) was studied under the same conditions for comparison. Figure 3 shows that the potentiometric curves can be superimposed. Nevertheless, the time required for the stabilization of the pH values after each addition of titrant aliquot is much longer for the gel particles (10 min) than for the linear PAA (10 s), as expected because of the slow diffusion of the titrant in the gels.

Size of the Particles in the Dried and Swollen States

Photo 1 shows the electronic micrographs of PAA particles which had been swollen in distilled water at 1 g/L beforehand, then dried and metallized. They are spherical, their surface is smooth, and their average radius is $\sim 50\ \mu$m.

The swelling of a particle in pure water was followed by optical microscopy. A maximum complete swelling is obtained in 3 min. An increase of the radius by a factor of 7 compared to the dried state is observed at pH 4. Under these conditions the volume fraction of the polymer in the particle is < 0.002.

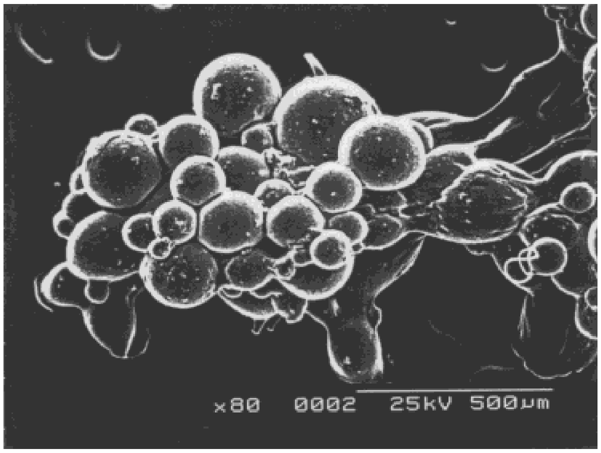


Photo 1 Electronic microscopy: PAA particles dried and metalled after swelling in water.

RETENTION OF THE CHROMIUM SPECIES

Due to the complexity of the systems, a perfect control of the method used to mix the PAA particles with the salt solutions was needed. Not only the absorption kinetics and the swelling and deswelling of the particles were found to vary with the method used, but also the chromium retention at equilibrium.

Several mixing methods were examined: (1) dried particles of PAA are added to the salt solutions. In this case, the pH stabilizes after a given time at intermediate values between the pH of the salt solution (low pH) and that of the PAA suspension (neutral pH) (method i). (2) Dried particles are added in the salt solutions whose pH was adjusted beforehand. The pH also increases to reach an equilibrium but with smaller increments (method ii). (3) PAA particles are first swollen in water at the same pH as the salt solution, and after filtration they are then added to the salt solution. In this case, very small changes of pH are observed (method iii).

In each case, we either kept constant the concentration of the PAA particles (typically 1 g/L) and increased the salt concentration or added successive amounts of particles to a salt solution of a given concentration.

Degree of Retention at Equilibrium

For this study, we consider separately the behaviors observed when the initial pH of the salt solutions is lower or higher than the solubility limit of chromium (see Fig. 1).

Table I Final pH of $CrCl_3$ Solutions of Various Initial pH and Chromium Concentrations and in Contact with 1 g/L of PAA Particles as a Function of the Initial pH

Chromium Concentration (ppm)	16	48	167
Initial pH			
1	1.2	1.3	2
2	2	3.9	3.2
3	3.6	4.5	3.7
4	6.9	5.6	5.9

Inside the Solubility Range

Table I shows the shift of pH observed with method (ii) at different concentrations of chromium (C_{si}) and 1 g/L of PAA particles. As expected, when method (iii) is used this shift is negligible. In Figure 4, we compare the variation of the percentage of residual chromium (with respect to its initial concentration) R_{Cr} versus pH as obtained by using methods (ii) and (iii), for a polymer concentration of 1 g/L. R_{Cr} decreases when pH increases for each chromium concentration. This is qualitatively consistent with the increase of the concentration of dissociated carboxylate groups, and as explained below can be un-

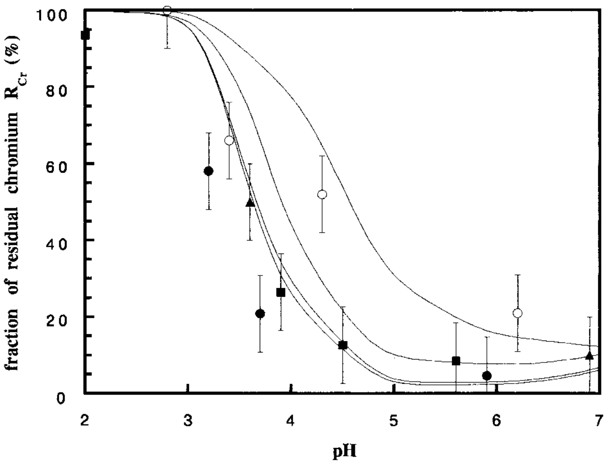


Figure 4 Variation of the fraction of residual chromium versus pH for 1 g/L of PAA particles; (method ii): initial chromium concentration C_{si} = 167 ppm (●), 48 ppm (■), 16 ppm (▲); (method iii) C_{si} = 520 ppm (○). The lines correspond to the values calculated as described in the Discussion for C_{si} = 16, 48, 167, and 520 ppm, from the bottom to the top.

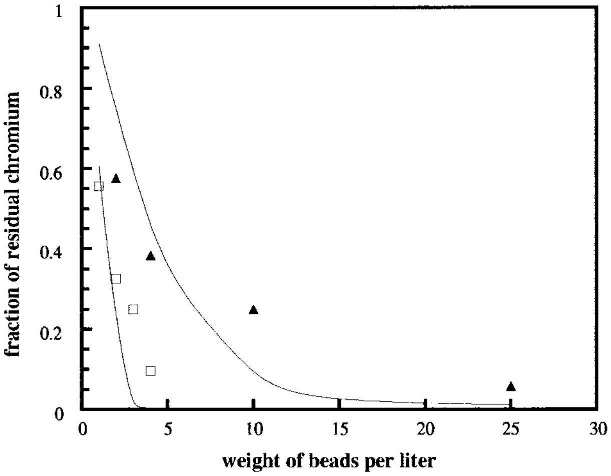


Figure 5 Variation of the fraction of residual chromium versus the amount of PAA particles; constant pH = 3.4 (method ii) (▲); 4.5 < pH < 5.4 (method i) (□). The lines correspond to the values calculated as described in the Discussion.

derstood in terms of simple equilibria between these groups and the various soluble chromium species. In Figure 5, we represent the variations of R_{Cr} for a given initial concentration of chromium (520 ppm, 0.01*M*) and different concentrations of particles, for two different experiments. In the first one, the pH was adjusted at 3.4 by using method (iii) while in the second one, the equilibrium pH varies from 4.3 to 5.4, the mixture being prepared according to method (i). This result confirms that the increase of pH favors the chromium absorption, as known for other cations.[19] From the measurements performed with method (ii), we can determine the minimum pH which yields a residual chromium concentration lower than that allowed by the international laws (3 ppm) as a function of the initial salt concentration, C_{si}, for 1 g/L of particles. We find 4, 4.5, and 5.5 for C_{si} = 16, 47, and 167 ppm, respectively. Under the same experimental conditions, this limit may be reached for a pH of ~ 6.3 when C_{si} is equal to 520 ppm.

In Figure 6, we report the variations of the ratio $X = [\mathrm{Cr}]_b/[\mathrm{COO}]_t$ as a function of pH for various experiments. $[\mathrm{Cr}]_b$ is the molar concentration of absorbed chromium and $[\mathrm{COO}]_t$ is the total molar concentration of carboxylate groups. In the simplest hypothesis where only the mononuclear species are considered, one may write that the system is governed by equilibria of the type:

$$\mathrm{Cr(OH)}_p(\mathrm{H_2O})_{6-p}^{(m-p)+} + (m-p)\mathrm{COO}^- \rightleftarrows \mathrm{Cr(OH)}_p(\mathrm{H_2O})_{6-p}\mathrm{COO}_{(m-p)} \quad (4)$$

One should expect the formation of complexes with a number of chromium per carboxylate varying from $\frac{1}{3}$ to 1 when pH increases, by considering the distribution of the mononuclear species shown in Figure 1. By assuming that the chromium binding induces a complete shift of the ionization equilibrium of the carboxylate groups, we can evaluate the value of X. For pH between 6 and 7 where only monovalent chromium species are present, the maximum values of X (all chromium-bound) calculated with these assumptions are 0.03, 0.09, 0.31, and 0.98 for C_{si} = 16, 48, 167, and 520 ppm, respectively. These values must be compared with the experimental ones: 0.04, 0.08, 0.32, and 1, and a reasonable agreement with both sets of values is obtained. It must be pointed out that if small amounts of oligomeric chromium ions (degree of oligomerization N_o) are present, the ratio X is expected to be < 1 since their charge is equal to $(N_o + 2)$. At very low pH, the X values are expected to be 3 times lower than at higher pH since the trivalent chromium species are preponderant. The experiment leads to X values significantly lower, which indicates that the binding

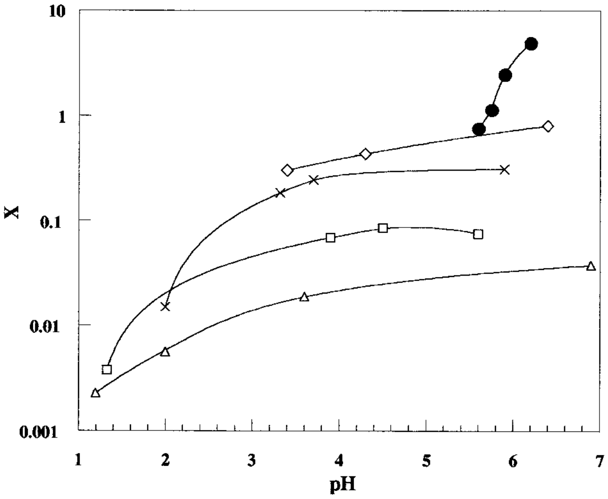


Figure 6 Variation of the ratio $X = [\mathrm{Cr}]_b/[\mathrm{COO}]_t$ in the particles after equilibrium versus pH for 1 g/L of PAA particles; the pH is that at equilibrium. −pH < solubility limit (method ii) (same experiments as in Table 2), C_{si} = 167 ppm (×), 48 ppm (□), 16 ppm (△); (method iii); C_{si} = 520 ppm (◇). −pH > solubility limit (method ii) C_{si} = 240 ppm (●) (in this last case, the pH is the initial one of the salt solution).

constant of chromium is not high enough with respect to K_a and that carboxylic acid functions remain present. The results obtained by adjusting pH at values lower than the solubility limit seem qualitatively reasonable when taking into account the properties of the compounds already described. We will try to give a more quantitative description of the phenomenon in the Discussion.

Outside the Solubility Range

If we use method (ii), starting from a turbid and colored $CrCl_3$ solution, (pH 6 at $C_{si} = 260$ ppm) and add dried PAA particles, for the first 10 min of contact the particles swell and appear very colored while the supernatant becomes uncolored and transparent. Despite the fact that the main species of chromium at such pH is, theoretically, the uncharged hydroxide, there is a strong interaction with the PAA particles. This can be explained through our previous electrophoresis measurements which indicate the presence of residual positive charges on the hydroxide particles. Thus, the percentage of residual chromium, R_{Cr}, in the supernatant is low and after 1 h of contact, with a freshly prepared $CrCl_3$ solution, stabilizes at $< 8\%$. Moreover, we studied the influence of the aging time t_v of the salt solution before mixing with the PAA particles. For t_v equal to 50 min, 44 h, and 13 days, the values of R_{Cr} were 8, 5, and 3%. This result is consistent with the previous observation of an increase of the particle charge with the aging time. Since aging is also accompanied by a decrease of pH, this does not necessarily mean that the retention should increase at constant pH. To elucidate this point, we prepared different $CrCl_3$ solutions outside the solubility range of the same C_{si} but of different pH and with different amounts of PAA particles. The mixtures were stirred for 1 h. In all the cases the particles settle rapidly but with or without absorbed hydroxide particles, depending on the experimental conditions. Table II summarizes these observations. The pH above which settling occurs is a decreasing function of the PAA concentration, and the settling is very sensitive to the pH.

Table II Settling (+) or no Settling (−) of PAA Particles with Adsorbed Chromium from a Solution of $CrCl_3$ (260 ppm) at Different pH in the Presence of Various Amounts of PAA Particles

PAA Particles (g/L)	pH = 5.6	pH = 5.75	pH = 5.9	pH = 6.2
0.05				−
0.1			−	+
0.2	−	−	+	+
0.3			+	
0.4	−	+	+	
0.5			+	
0.6	+	+		
0.8	+	+		

Figure 6 shows that parameter X is much higher for 1 g/L of polymer than that would be obtained for a same salt concentration at lower pH. This clearly demonstrates the importance of the initial state of the salt solutions and of the method of preparation of the mixtures. The high value of X is not really surprising, since the interactions occur between particles and hydroxide particles of high degree of aggregation number. A rough evaluation using the results of the electrophoresis measurements should indicate that at pH ~ 6 the neutralization of the particles by the chromium hydroxide may occur for 15 chromium atoms per ionized carboxylate function. This is approximately three times the experimental value of 4.9 observed for pH = 6.2.

SWELLING OF PAA PARTICLES IN THE PRESENCE OF CHROMIUM SALTS

The swelling of a PAA particle was followed by optical microscopy when immersed in a drop of a $CrCl_3$ solution (123 ppm or $2.4 \times 10^{-3}M$) at two different pH, below and above the solubility limit. Under these conditions, the approximate concentration of PAA is 0.02 g/L ($\sim 2 \times 10^{-4}$ mol/L) which corresponds to a large excess of chromium ions with respect to the carboxylate groups. The variation with time of the ratio V_t/V_i (where V_t is the volume of particle at time t and V_i is the initial volume of the dried particle) are reported in Figure 7. The behaviors obtained for pH 4 and pH 6 are very different. While in the first case the volume passes through a maximum and decreases slightly all the way to its equilibrium value, in the second case it increases continuously and stabilizes for a ratio equal to 300. In pure water the ratio reaches a value of $\sim$ 380. We reported in the same figure the results obtained with a solution of copper chloride at the same concentration as that of $CrCl_3$ and at pH 4. The swelling and deswelling kinetics differ significantly from that observed with chromium. In the

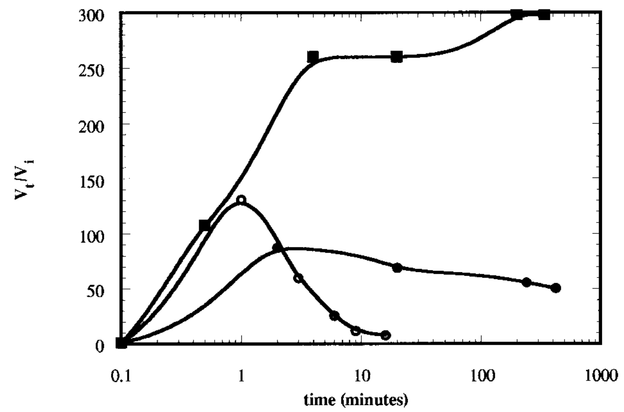


Figure 7 Swelling of a PAA bead expressed as V_t/V_i (see text) as a function of time in a $CrCl_3$ solution (123 ppm) at initial pH 4 (●) and pH 6 (■) and in a solution of $CuCl_2$ of the same molar concentration (○).

case of copper, after a first phase of swelling (for ~ 1 min), the volume of the particle decreases and tends toward a value approximately twice as high as that of the dried particle. Since at pH 4 copper is mainly present in aqueous solutions under the form of bivalent ions $Cu(H_2O)_6^{2+}$, one expects that PAA particles contain mainly complexes of the type $COO_2Cu(H_2O)_6$ and undissociated carboxylic groups. As a consequence, their charge goes down to zero, resulting in a low swelling at equilibrium. The observed volume increase corresponds to the additional volume of the hydrated bound copper ions, which suggests that the ion binding occurs with an almost complete syneresis effect.

In the case of chromium, Figure 1 shows that at pH 4, half of the chromium is under the form $Cr(H_2O)_6^{3+}$ and the other half under the form $Cr(OH)(H_2O)_5^{2+}$. With such a large excess of chromium, a complete neutralization of the carboxylate groups and an almost complete deswelling of the particles were also expected. The experiments show that the particles remain partially expanded and this may be attributed to differences in the mechanism of complexation which modifies the diffusion of the ionic species inside the gel. In this respect, it must be pointed out that copper ions generally induce phase separation and chain collapse with polycarboxylic acids (at least for synthetic polymers), while addition of chromium salts can provoke gelation without a syneresis effect.

The behavior of the particles in the presence of $CrCl_3$ at an initial pH higher than the solubility limit is completely different. While the amount of chromium absorbed is much higher at this pH than at lower pH, the particles keep almost the same degree of swelling as in pure water. The presence of a dark layer at the surface of the particles was observed by optical microscopy. This suggests that a large fraction of the chromium is adsorbed at the surface of the particle and does not penetrate inside.

In order to confirm these different behaviors, we have observed by electronic microscopy the particles after contact in pure water (Photo 1), and $CrCl_3$ solutions at pH 4, 8, and 6. (Photo 2). The aspect of the particles after adsorption of hydroxide at pH 6 clearly suggests the presence of particles at the surface. These investigations confirm the conclusions drawn from the optical microscopy observations.

DESORPTION OF THE CHROMIUM SPECIES

From a practical point of view, it is important to know whether the materials used to eliminate pollutant ions can be easily regenerated and consequently whether they are able to release the ions. We have examined three possibilities in order to obtain this regeneration. The first one was based on the fact that negatively charged chromium species such as $Cr(OH)_4(H_2O)_2^-$ are formed in basic aqueous solutions of $CrCl_3$ at $pH > 8$. One could hope that an increase of pH would progressively induce a chromium release by electrostatic repulsion from the particles. The particles with chromium absorbed at equilibrium were put in solutions of sodium hydroxide (1*M*); no release was observed after several days.

Then, we put the particles in a solution of EDTA whose complexation constant with chromium is known to be very high. We had observed that if a strongly complexating molecule such as citrate is present in the chromium solution in equilibrium with the PAA particles, no adsorption of chromium by the particles occurred. However, no desorption of chromium was observed after 14 h. The binding of the ionic species appears irreversible, at least at time scales of practical interest. This will be confirmed below.

The third method we examined consists of adding an excess of chlorhydric acid in order to shift the ionization equilibrium of the PAA and eliminate the electrostatic interactions responsible for the chromium binding. The results are presented below and again, we must distinguish the cases of pH lower or higher than the solubility limit.

Inside the Solubility Range

Inside the solubility range we have to consider (1) the contact time t_a between the particles and the $CrCl_3$ solution (adsorption time), and (2) the contact time t_r during which the particles remain in the HCl solution (release time).

After time t_a, the degree of retention is determined as described above and the pH of the solutions containing PAA particles is lowered down to 1 by adding HCl. After a time t_r, the supernatant of these solutions is filtered on a 0.2 μm filter and the residual chromium concentration is determined by UV spectroscopy. The results are given in Figure 8(a) for an initial chromium concentration of 260 ppm and a pH of 3.3. The degree of retention depends slightly on t_a. Under these experimental conditions, the percentage of bound chromium varies from 48 to 58% of the initial chromium concentration when t_a increases from

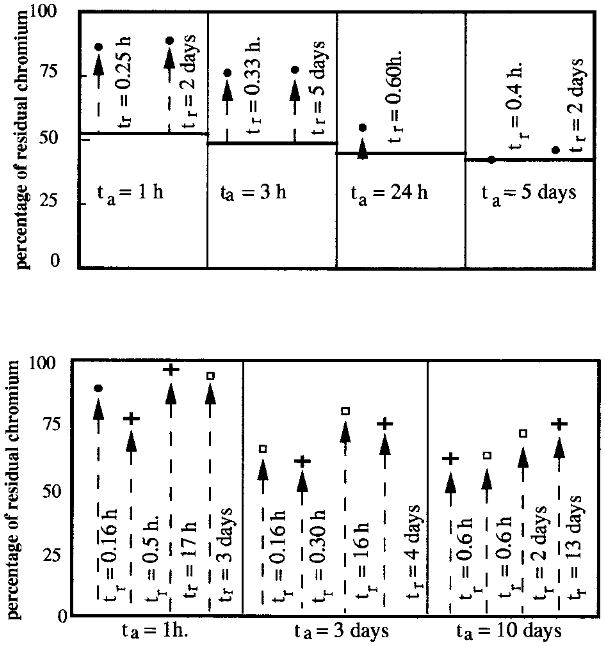
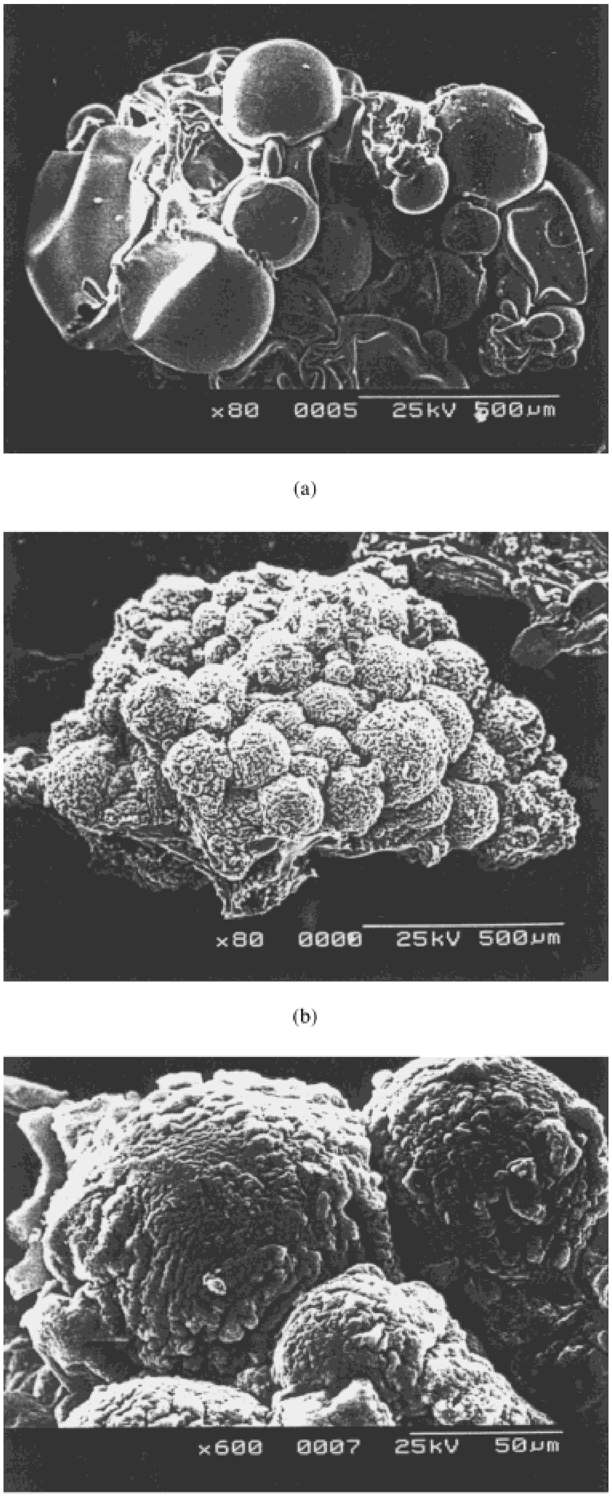


Figure 8 Release experiments with 1 g/L of PAA particles: the percentage of residual chromium after a time t_g of contact with the $CrCl_3$ solution is represented by the horizontal lines. The percentage after treatment in the presence of HCl during a time t_a (indicated vertically) is represented by (●) for freshly prepared solutions, by (□) and (+) for solutions aged 2 and 13 days, respectively. $CrCl_3$ solution (260 ppm) at initial pH 3.3 (Fig. 8a of the top) and pH 6.2 (Fig. 8b of the bottom).



(a)

(b)

(c)

Photo 2 Electronic microscopy: PAA particles dried and metalled after swelling in a $CrCl_3$ solution 4.8 $\times$ $10^{-3}M$ at pH 4, 8, (a) and pH6 (b, c).

1 h to 5 days. The percentage of released chromium is strongly dependent on t_a and varies only slightly with t_r. It is indeed possible to partially regenerate the particles if t_a is below or equal to 1 h. For $t_a = 5$ days, the amount of released chromium is negligible. It seems that the absorption of chromium ions proceeds in two steps: in a first step, the major part of the chromium is bound within the superficial layers of the particles probably only by electrostatic interactions. Thus, if the particles are added to an HCl solution, the binding is reversible. In a second step, the chromium ions diffuse into the gel and consequently there is a collapse of the particles, as seen in Figure 7. This liberates some superficial carboxylate sites which are then able to bind additional chromium ions. Moreover, it is known that the complexation of chromium on the carboxylate groups is a slow phenomenon and at the same time that diffusion occurs, stable complexes form and HCl becomes inefficient.

Outside the Solubility Range

The same experiments were carried out with a $CrCl_3$ solution of the same concentration but at a pH much higher of 6.3. Here, we consider not only t_a and t_r as parameters but also t_v, the aging time of the chromium solutions. The particles were able to absorb 100% of the chromium whatever the time t_g. Figure 8(b) shows that the release of chromium is always much more important in this case. The contact time of the particles in the $CrCl_3$ solution is an unfavorable factor for the percentage of release, but t_v has relatively small influence on the results. This confirms that when the particles are in a $CrCl_3$ solution outside its solubility domain, the chromium absorption is very high, but since the fixation is probably a surface phenomenon, the release is easy to obtain.

DISCUSSION

Finally, our observations can be summarized by the model of Figure 9, which schematizes the steps of the interactions between chromium species and PAA particles. The important factor is the initial pH of the chromium salt solutions. At pH below the solubility limit, electrostatic binding and complexation of mononuclear (and perhaps oligomeric) chromium take place. The swelling results from two antagonistic phenomena, namely the PAA hydration and the carboxylate groups complexation, and the kinetics cannot be simply interpreted. On the other hand, at equilibrium, one can expect that the amount of absorbed chromium can be calculated by taking into account the various equilibria governing the system: the ionization equilibrium of the carboxylic groups,[2] the hydrolysis equilibria of chromium ions,[1] and the three main binding equilibria.[3] We have only considered the formation of fully neutralized complexes: $Cr(H_2O)_6COO_3$, $Cr(OH)(H_2O)_5COO_2$, and $Cr(OH)_2(H_2O)_4COO$. Neither the other charged species such as $Cr(H_2O)_6COO_2^+$ or $Cr(H_2O)_6COO^{2+}$, nor the complexes which may be formed from oligomeric chromium species, are considered. The system can be reduced to two equations

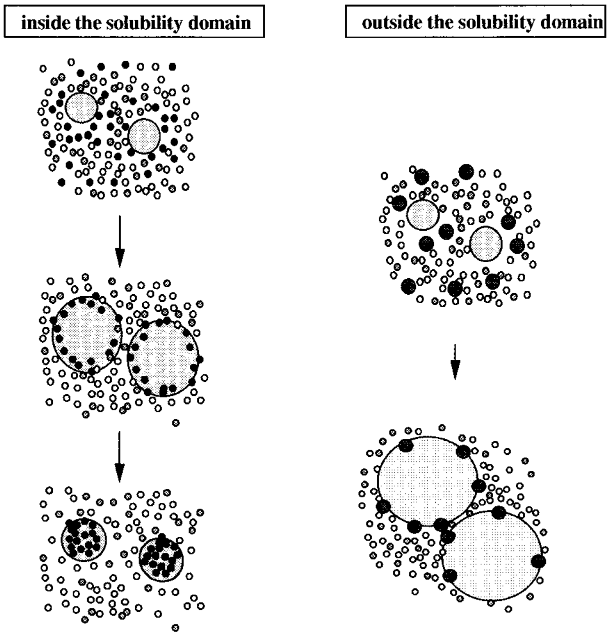


Figure 9 Scheme of the interactions between PAA particles and chromium ionic species versus time of contact.

$$[COO^-] + \frac{[COO^-][H^+]}{K_a} + \frac{[COO^-][Cr^+]}{K_{11}} + 2\frac{[COO^-]^2[Cr^{2+}]}{K_{12}} + 3\frac{[COO^-]^3[Cr^{3+}]}{K_{13}} = c_p \quad (2)$$

with

$$[Cr^{2+}] = \frac{K_{c1}[Cr^{3+}]}{[H^+]}; \quad [Cr^+] = \frac{K_{c1}K_{c2}[Cr^{3+}]}{[H^+]^2}; \quad [COOH] = \frac{[COO^-][H^+]}{K_a} \quad (3)$$

and

$$[\mathrm{Cr}^{3+}]\left[\frac{K_{c1}}{[\mathrm{H}^+]}+\frac{K_{c2}}{[\mathrm{H}^+]^2}+1\right]+\frac{K_{c1}\cdot K_{c2}[\mathrm{Cr}^{3+}][\mathrm{COO}^-]}{K_{11}[\mathrm{H}^+]^2}$$

$$+\frac{K_{c1}[\mathrm{Cr}^{3+}][\mathrm{COO}^-]^2}{K_{12}[\mathrm{H}^+]}+\frac{[\mathrm{Cr}^{3+}][\mathrm{COO}^-]^3}{K_{13}}=c_s \quad (4)$$

where $[Cr^{3+}]$, $[Cr^{2+}]$, and $[Cr^+]$ are the molar concentrations of the ions $Cr(H_2O)_6^{3+}$, $Cr(OH)(H_2O)_5^{2+}$, and $Cr(OH)_2(H_2O)_4^+$, $[COO^-]$ and $[COOH]$ the molar concentrations of the ionized and acid carboxylic groups. The ionization constant of PAA was taken equal to that of PAA at $\alpha = 0.3 \times 10^{-5}\ \mathrm{mol}^{-1}$. As explained above, K_a varies with α but in the case where the chromium binding is important, α is expected to slightly increase. This approximation will be discussed later. The values of K_{c1} and K_{c2} were taken from refs. 22–25; they are respectively equal to 1.6×10^{-4} and $1.5 \times 10^{-6}\ \mathrm{mol}^{-1}$.

The molar concentrations of the complexes can be deduced from:

$$\frac{[\mathrm{Cr}^+][\mathrm{COO}^-]}{[\mathrm{CrCOO}]}=K_{11};\quad \frac{[\mathrm{Cr}^{2+}][\mathrm{COO}^-]^2}{[\mathrm{CrCOO_2}]}=K_{12};$$

$$\frac{[\mathrm{Cr}^{3+}][\mathrm{COO}^-]^3}{[\mathrm{CrCOO_3}]}=K_{13} \quad (5)$$

$[CrCOO]$, $[CrCOO_2]$, and $[CrCOO_3]$ are the molar concentrations of the complexes $Cr(OH)_2(H_2O)_4$-COO, $Cr(OH)(H_2O)_5COO_2$, and $Cr(H_2O)_4COO_3$, respectively.

Figures 4 and 5 show that a reasonable agreement with the experimental results can be obtained with

$$K_{11} = 10^{-3}\ \mathrm{mol},\quad K_{12} = 10^{-6}\ \mathrm{mol}^2,$$

$$\text{and } K_{13} = 8 \times 10^{-7}\ \mathrm{mol}^3$$

Such values are only approximate because of the limited number of experimental points. However, it seems possible to predict the order of magnitude of the residual chromium as a function of the initial chromium concentration and the amount of PAA particles. Figure 10 shows in a particular case (1 g/L of PAA particles and molar concentration of chromium 0.0032*M*) the variation of the distribution of the different charged and uncharged species versus pH. It appears that the main species is the complex $Cr(OH)(H_2O)_5COO_2$. The fraction of $Cr(H_2O)_6COO_3$ is always lower than 1% and is not represented. Under such conditions, the ionization degree of the carboxylate groups reach nonnegligible values and the hypothesis that K_a is constant is not justified. If its decrease when α increases was taken into account, the fraction of complexes would be lower than shown in Figure 10. When the concentration of PAA is low (as compared to the chromium concentration), the formation of complexes will be favored and the hypothesis will then be more correct.

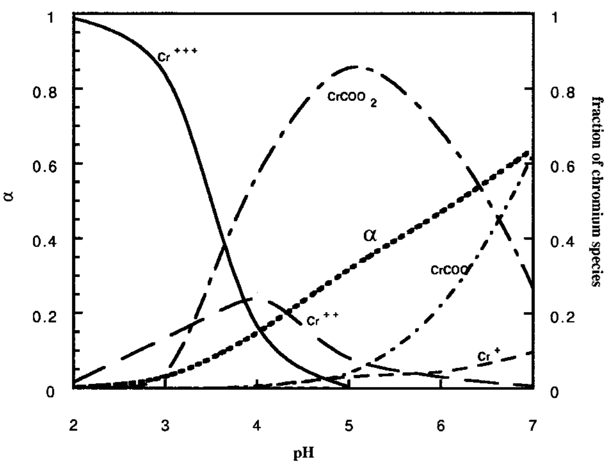


Figure 10 Distribution of the different species calculated as described in Discussion.

CONCLUSION

The interactions of PAA particles with chromium species in aqueous solutions have been investigated as a function of the initial pH of the chromium solution. This parameter affects both the chromium retention in the PAA particles and its release under acidic conditions. Two different mechanisms have been identified according to the solubility of the chromium species.

At pH below the solubility limit, interactions between the carboxylate groups and mononuclear ionic chromium ions occur, and formation of complexes take place which appear irreversible at the time scale used in this work. When pH increases, the fraction of bound chromium at equilibrium increases and a deswelling of the PAA particles results from the decrease of their average charge. The chromium ions can be assumed to diffuse in the whole volume of the particles and to interact with the almost totality of the carboxylic groups. It is possible to predict the degree of ion retention by simply considering the complexation equilibria.

At pH above the solubility limit, chromium hydroxide species which have a residual positive charge and dimensions close to 100 nm are the main species present in solution. Interactions with the PAA particles occur with a much higher chromium retention than at lower pH, and at equilibrium, the swelling of the PAA particles is about the same as in pure water. The chromium desorption under acidic conditions is almost complete and fast. These results suggest that the hydroxide chromium species are not complexed within the PAA particles but only adsorbed at their surface due to electrostatic interactions.

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