

Purification of spent chromium bath by membrane electrolysis

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Abstract

The present study deals with the purification of spent chromium bath contaminated by trivalent chromium, iron and aluminum. The ionic transfer of Fe(III) depends on the presence of chloride ions on the pH while aluminum transfer is not affected by chromium(III) chloride. Five different commercial cation-exchange membranes were used. Nafion[®] and PC-SK membranes showed the best results for trivalent iron and aluminum transfer.

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1. Introduction

Hexavalent chromium is highly mobile in a subsurface environment. These Cr(VI) anionic species are bioaccumulative due to their mobility across biological cell membranes and the oxidizing potential of these species make them highly toxic to biological systems. It is well known to be very toxic to plants, animals and people. Human toxicity includes lung cancer, as well as liver and gastric damage. Besides pollution abatement, chromium recovery also assumes importance as a pure-toxicity. The interest in the development of efficient techniques for separation and recovery of ions has been a motivation for testing various methods in solutions [1–3].

Electrochemical processes that take place in systems containing the main component chromic oxide (CrO₃) dissolved in water are widely used in electroplating. Chromium plating and chromate processes are widespread technologies because chromium and chromate surfaces have special properties such as hardness and corrosion resistance. Many different electrolytes exist in industry, due to basic metal differences for coating and in the required deposition quality [4]. Sulfate ion (SO₄²⁻) is a necessary catalyst in all chromium plating solutions. It is usually introduced as sulfuric acid. In the chromium plating industry, the solutions contain chromate concentration varying between

250 and 450 g L⁻¹, depending on which bath is used, with less than 10% of the chromium acid used is deposited on the metal products [5–7]. After a period of use, these chromium acid solutions become contaminated with metals such as Fe(III), Al(III), Cr(III), Cu(II), Ni(II) and other impurities. Metals may be carried into the solution on parts treated in other processes or rinsing tanks, or they may be introduced by dissolution of metals that compose the parts. The impurities could be present in concentrations varying from 10 to 25 g L⁻¹. These contaminants have undesirable effects on the plating solution including over voltages, decrease in bath conductivity and in plating efficiency. As a result of bath contamination, the solutions frequently become spent and must be disposed of. When they are treated, generally by a conventional physico-chemical process, a muddy substance is generated (galvanic sludge), and it is classified as hazardous waste [8]. There are several disadvantages to this traditional technique. For example, significant quantities of metal are being wasted. In addition, prior treatment may be required to remove complexing agents, which inhibit precipitation [7,9].

The purification of chromium baths is interesting from both environmental and economic points of view. Reducing the contamination in these baths should prolong their time of use and thereby cause a reduction of hazardous wastes [5,10,11].

Much research has been done to remove chromium from rinse waters. Methods using ion-exchange, adsorption, nanofiltration, ultrafiltration, liquid membrane and electrodialysis have been proposed [12–27]. On the other hand, little research has been done on the purification of chromium plating baths. Among the

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technologies used for purification or recovery of chromic acid, three of them stand out: ion-exchange [10,29,30], electrolysis [28,31] and the porous pot method [11,28,32]. However, all these treatment methods produce sludge.

As a possible alternative to the treatment of industrial chromium plating baths, the electro-dialysis (ED) technique has been studied. Electro-dialysis is a membrane separation technique, where ions are transported through ion selective barriers from one solution to another using an electric field as the driving force [28,33]. When current is applied to the cell, the cations flow through the cation-exchange membrane into the catholyte and this membrane restricts the flow of anions. The opposite occurs with anions. The principle of alternating cation- and anion-exchange membranes in multi-compartment electro-dialysis is the most common, but for some kinds of separation, the electro-dialysis unit may use only cation- or anion-exchange membranes [28,32,34,35]. Electro-dialysis can remove contaminant metals and also oxidize trivalent chromium into hexavalent chromium, which is the active form in chromic acid solutions, and thereby extend the useful lives of the solutions while reducing the generation of hazardous waste. The membrane process, where the reactions at electrodes are part of the process, is called electro-electro-dialysis or membrane electrolysis [36–42].

Little research has been done on the purification of chromium plating baths from spent plating solutions using membrane electrolysis. The main limitation of this method is the chemical degradation of the membranes by the oxidizing Cr(VI) [36,43]. Literature shows that the Nafion[®] cationic membrane, the Ionac MA-3475 and Fumasep[®] FAP anionic membranes are stable in chromic acid [37].

The aim of this study was to obtain more information about the ionic transport of contaminants generated in the chromium plating baths, using the electro-electro-dialysis technique. An additional goal was to verify the behavior of other cation-exchange membranes in contact with the chromium bath, since in previously published studies only Nafion[®] cation-exchange membrane in chromium baths have been done. For this study five different commercial cation-exchange membranes were used, including the Nafion[®] cationic membrane.

2. Experimental

2.1. Membranes

Five different commercial cation-exchange membranes were used in this study. The properties of these membranes are listed in Table 1.

Table 1
Properties of commercial membranes used in the experiments

Company	Membrane	Thickness (mm)	Transport number T-Na	Electric resistance ($10^{-1} \Omega \text{ m}^2$)	Ion-exchange capacity (mequiv./g)
Selemion (Asahi glass)	CMV	0.140	>0.920	3.50	1.94
	CMT	0.220	>0.960	2.50–3.50	1.94
Du Pont	Nafion 450	0.200	0.910	1.50	0.900
Ultrex	CMI 7000	0.600	0.940	8.00	1.30–2.30
PCA (GmbH)	PC-SK	0.080–0.100	>0.880	2.50	0.370

Table 2
Bath 1 composition

Reagent	Ion	Concentration (M)	Concentration (g L^{-1})
CrO ₃	Cr(VI)	2.5	130
CrCl ₃ ·6H ₂ O	Cr(III)	0.074	3.85
Fe ₂ (SO ₄) ₃ ·5H ₂ O	Fe(III)	0.074	4.14
H ₂ SO ₄		0.36	35

Table 3
Bath 2 composition

Reagent	Ion	Concentration (M)	Concentration (g L^{-1})
CrO ₃	Cr(VI)	2.5	130
CrCl ₃ ·6H ₂ O	Cr(III)	0.074	3.85
Al ₂ (SO ₄) ₃ ·16H ₂ O	Al(III)	0.074	2
H ₂ SO ₄		0.36	35

Table 4
Solution of trivalent iron

Reagent	Ion	Concentration (M)	Concentration (g L^{-1})
Fe ₂ (SO ₄) ₃ ·5H ₂ O	Fe(III)	0.0740	4.14
H ₂ SO ₄		0.36	35

2.2. Materials, chemicals and analysis

In this work, synthetic aqueous solutions of Cr(III), Cr(VI), Al(III) and Fe(III) were used. Chromium trioxide (CrO₃) (Merck, p.a.) was used as the source of hexavalent chromium, chromium chloride [CrCl₃·6H₂O] (Vetec, p.a.) for trivalent chromium, aluminum sulfate [Al₂(SO₄)₃·16H₂O] (Vetec, p.a.) of trivalent aluminum and iron sulfate [Fe₂(SO₄)₃·5H₂O] (Synth, p.a.) of trivalent iron. Initially two synthetic baths of hexavalent chromium containing trivalent chromium were used. The compositions of the baths used in the experiments were defined as representatives of an industrial chromium bath. The first solution used also contained the contaminant Fe(III); the second, Al(III). Tables 2 and 3 show the composition of these solutions (baths 1 and 2).

Two solutions containing just trivalent iron or trivalent aluminum were also evaluated. The compositions of these solutions are shown in Tables 4 and 5.

All chemicals were reagent grade and were used as received. All reagents were dissolved in H₂SO₄ 2% (Quimex, p.a.). The membranes were immersed in the work solutions for at least 24 h prior to their use.

Table 5
Solution of trivalent aluminum

Reagent	Ion	Concentration (M)	Concentration (g L ⁻¹)
Al ₂ (SO ₄) ₃ ·16H ₂ O	Al(III)	0.074	2
H ₂ SO ₄		0.36	35

Samples of the process solution (cathodic compartment) were collected periodically and analyzed. Because of the high concentrations of hexavalent chromium and other metals, the samples were diluted before their analyses.

During the testing involving the chromic acid solution, all samples were analyzed for total and hexavalent chromium so that trivalent chromium could be determined by difference.

Hexavalent chromium, total chromium and total iron were determined with a UV–vis spectrophotometer [44]. Aluminum was determined by atomic absorption spectrometer (AAS).

The membranes were not washed after use. They were just dried by air and sent to X-ray fluorescence analysis.

2.3. Membrane electrolysis experiments

The experiments were conducted in a galvanostatic mode, which allowed the application of a constant current of 20 mA cm⁻². The system was tested in batch mode of operation. The length of membrane electrolysis was 6 h.

The study was carried out in a two-compartment membrane electrolysis cell, made of polytetrafluoroethylene (Teflon) due to the oxidizing media. The experiments were conducted using mechanical stirring in both compartments, separated by a cation-exchange membrane (see Fig. 1). The electrode used in the cathodic compartment was a platinum coated titanium sheet and the electrode used in the anodic compartment was a lead sheet of 20 cm² each. The effective membrane area was 5 cm². The cathodic compartment contained H₂SO₄ 20% (0.15 L) and the anodic contained the work solution (0.15 L).

After the experiments with baths 1 and 2, some other experiments were carried out with aqueous solutions without

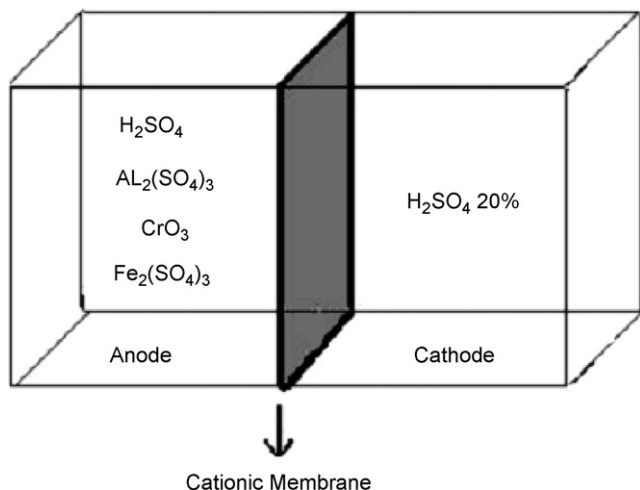


Fig. 1. The cell designed for electro dialysis experiments.

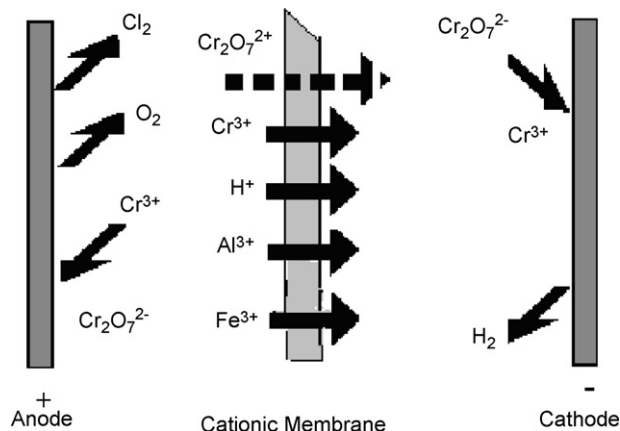


Fig. 2. Schematic diagram of the expected ionic transport through the membranes and the reactions that occur on the electrodes.

chromium, containing just trivalent iron or trivalent aluminum. These experiments were carried out to determine the influence of total chromium on trivalent iron and trivalent aluminum transport.

A schematic diagram of the expected ionic passage through the membranes is shown in Fig. 2.

The ions transport through the membrane on the two-compartment cell was evaluated in terms of removal factor RF (%) [2,3] that is defined as the variation on ion concentration in the compartments. The removal factor is expressed as follows:

$$RF = 100 \times \frac{C_0 - C_f}{C_0}$$

where C_f is the ion concentration at the end of the experiment in the cathodic compartment and C_0 is the ion concentration at the beginning of the experiment in the anodic compartment.

The ions transport through the membrane was evaluated in terms of current efficiency too, CE (expressed in %), that is defined as the ratio between the current used for the intended concentration/separation effect and the total current. The current efficiency calculated is expressed as [45]:

$$E_c = \frac{\Delta C V F}{n A \Delta t i}$$

where ΔC is the iron or aluminum concentration change (mol L⁻¹) in the volume V of solution treated (L), F the Faraday's constant, n the number of unitary cells, A the active area of the cation-exchange membrane, Δt the treatment time (s) and i is the current intensity (A).

3. Results and discussion

It was verified during the experiments, that some membranes were more resistant to the oxidizing media than others. The resistance of the membranes was verified in terms of hexavalent chromium passage through the cation-exchange membrane into the catholyte. When the membrane was damaged hexavalent chromium solution passed immediately to the cathodic compartment, which only contained H₂SO₄. The majority of the membranes could not resist the chromium bath. Among the

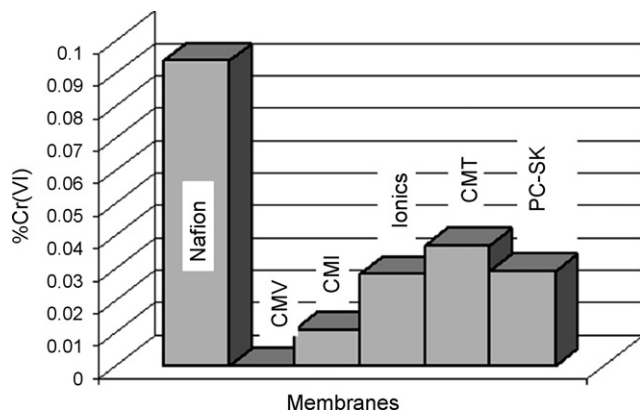


Fig. 3. Hexavalent chromium percentage that passed through cationic membranes after 6 h without applied current.

membranes, the PCA PC-SK was the least resistant and the Nafion® 450, the most resistant.

3.1. Hexavalent chromium leakage

There was some leakage of hexavalent chromium through the investigated membranes. The presence of hexavalent chromium in the cathodic compartment was indicated by the slight yellow color (Cr^{6+}) of the sulfuric acid stripping solution during experiments [10,37,46].

In chromic acid solutions, the chromium is present as different anionic species (monochromate, dichromate, trichromate, polychromate ions); the formation of large polychromate ions increases with the chromic acid concentration at low pH. Being an anion, the hexavalent chromium should not pass through the cation-exchange membrane.

Fig. 3 shows the hexavalent chromium percentage that passed by diffusion through the cation-exchange membranes after 6 h in contact with the solution without any applied current. This process could be an anion leakage through the membranes as shown for Patrick and Snyder [19].

The anion leakage through the Selemion CMV membrane was zero in three experiments; in the fourth experiment, the anion leakage was also observed with this membrane. This anion leakage may be caused by the loss of selectivity of this membrane in contact with hexavalent chromium. The Nafion® membrane had the highest anion leakage.

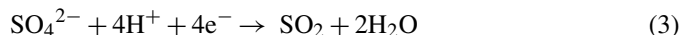
In spite of the observed passage of hexavalent chromium (anion leakage), the percentage mass transport is very small because of the high initial concentration in the bath (2.5 M). These results are according to Knill and Chessin [28] and Patrick and Snyder [19] who stated that the electro dialysis membranes are not 100% efficient more due to co-ion leakage (usually a few percent) than diffusion.

3.2. Ionic transport of Cr(III)

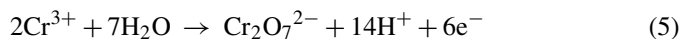
According to the schema of ionic transport (see Fig. 2), trivalent chromium is oxidized to hexavalent chromium at the anode or transported across the membrane together with the trivalent

iron or trivalent aluminum. Other reactions that occur on the electrodes are shown below.

Reduction reactions that may occur in the cathodic compartment are:



Oxidation reactions that may occur in the anodic compartment are:



No chromium deposits on the cathode were observed during the experiments.

Fig. 4 shows the trivalent chromium transport through different cation-exchange membranes.

The transport of trivalent chromium depends on the used membrane used. The experiments the PC-SK membrane showed higher trivalent chromium concentration in the cathodic compartment than for the other membranes. This result seems to demonstrate better chromium trivalent transport through this membrane. Nevertheless this result is in part due to the reduction of hexavalent chromium on the cathode, and not only due to the passage of this ion through the membrane. Experiments using membranes where the diffusion of hexavalent chromium is first very small, as CMV membrane, the passage of trivalent chromium was visible because the solution became green in the cathodic compartment. The trivalent chromium passage is shown in terms of concentration (mg L^{-1}) because it was not possible to calculate the removal factor (RF) precisely.

There are literally thousands of trivalent chromium complexes, with a few exceptions, are hexacoordinated and “octahedral”. The exchange of these ligands is a common reaction, but contrary to other transition metals, the trivalent

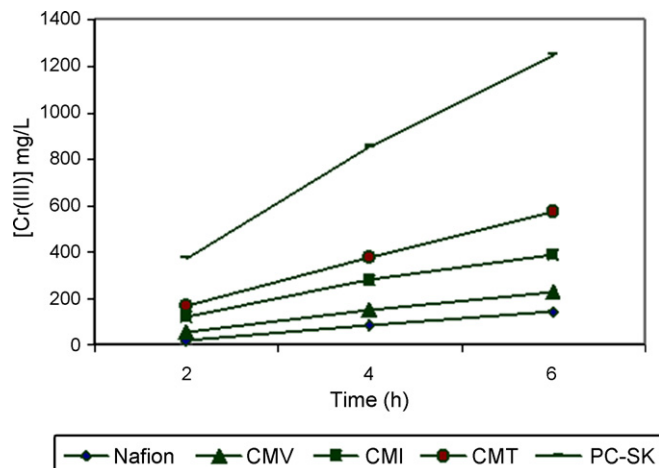


Fig. 4. Trivalent chromium passage through the cationic membranes in the chromium baths.

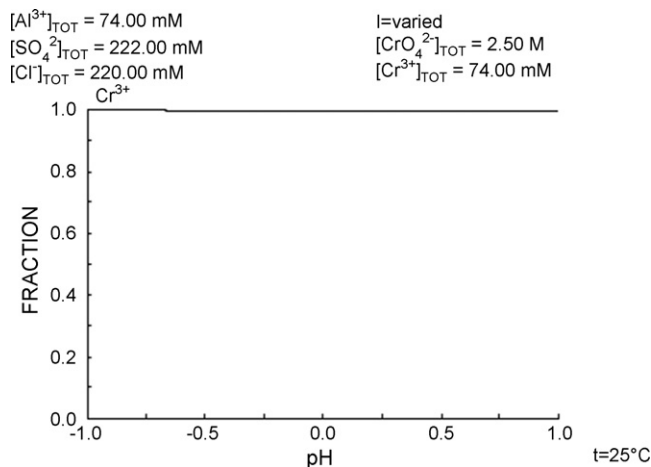


Fig. 5. Some possible forms of trivalent chromium formed in baths 1 and 2.

chromium, and do not quickly establish an equilibrium state with their ligands, including water. An important characteristic of these complexes in aqueous solutions is their relative kinetic inertness. Because of this kinetic inertness that so many complex species can be isolated as solids and that they persist for relatively long periods of time in solution, even under conditions of marked thermodynamic instability. The velocity of change of the ligands is not instantaneous. The complexes of trivalent chromium may be cations, anions or neutral molecules. They may undergo isomerism and then the number of compounds is higher [47]. Using the Hydra Medusa program [48], it was possible to see some compounds of trivalent chromium present in baths 1 and 2. These forms are presented in Fig. 5.

In Fig. 5 it is possible to observe that trivalent chromium is always present as a positive species. It indicates that the ions will be passing through the cationic membranes; but the small transport could indicate that interactions of ion–membrane are occurring.

3.3. Ionic transport of Al(III) and Fe(III)

Table 6 shows the removal factor and the current efficiency of trivalent iron in bath 1, trivalent aluminum in bath 2 and both in the solutions without chromium.

It is possible to observe in Table 6 that trivalent iron does not pass through the cationic membranes when hexavalent chromium is present. The Hydra Medusa program [47] simulated some possible complexes formed in the chromium bath containing trivalent iron with and without the presence of chlo-

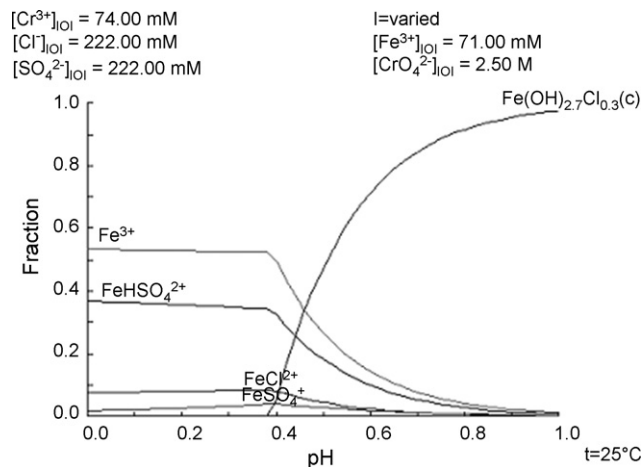


Fig. 6. Some possible complexes formed to trivalent iron in the chromium bath contaminated with chloride anions.

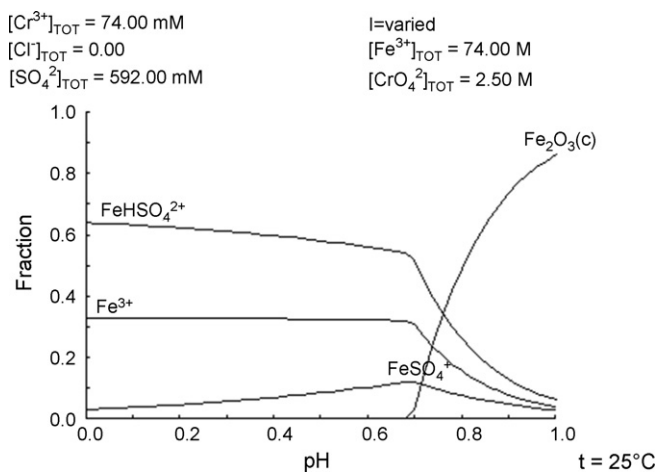


Fig. 7. Some possible complexes formed to trivalent iron in the chromium bath contaminated without chloride ions.

ride ion (Figs. 6 and 7). In Fig. 6 it is observed that the quantity of free trivalent iron is approximately forty and five percent on pH 0.5; after that this compound decreases quickly and a crystalline compound is formed in high quantity. During the 6 h of experiment the pH of the anodic compartment increased from -1 to 1 in the baths. At pH 0.4 a precipitated species, probably $\text{Fe(OH)}_{2.7}\text{Cl}_{0.3}$, was formed in high percentage. This species was visible on the membrane and verified by X-ray fluorescence (Table 7). The precipitation of this crystalline compound did not permit the passage of trivalent iron through the membranes.

Table 6
Removal factor and current efficiency of Fe(III) and Al(III) in the presence and absence of chromium

Membrane	Fe(III) in the chromium bath		Fe(III) without chromium		Al(III) in the chromium bath		Al(III) without chromium	
	RF (%)	CE (%)	RF (%)	CE (%)	RF (%)	CE (%)	RF (%)	CE (%)
Nafion 450	0.14	0.27	9.60	3.92	14.4	1.42	18.2	1.81
CMV	0.12	0.22	1.00	0.39	4.10	0.41	4.70	0.47
CMT	0.22	0.42	3.90	1.59	12.9	1.27	20.5	1.01
CMI	0.08	0.14	2.00	0.79	0	0	0	0
PC-SK	0.48	0.88	9.70	3.94	10.3	1.02	36.6	3.63

Table 7
X-ray fluorescence of membranes used in the experiments

Sample	%Pb	%Cr	%Cl	%S	%Fe
Nafion	14.2926	4.5129	1.6731	61.4916	16.1605
CMV	38.4596	0.1805	2.0769	28.1858	28.0545
Ionics	15.2359	–	–	25.8910	54.0375
CMT	3.5487	5.2835	8.0341	15.5377	63.5958
PC-SK	3.9897	7.2077	5.5625	65.7406	15.7070

It is important to control the pH bath during the experiments in order to avoid the formation of this precipitate. Observing Fig. 8, it is possible to see that another crystalline compound is formed too, but at a pH of around 0.6. Comparing these diagrams, it is possible to see that it makes no difference whether the chloride ion or sulfate ion is used, because in both diagrams crystalline compounds are formed. It is believed that interactions between membrane–chloride or membrane–sulfate do not permit the passage of iron.

The Nafion® and PC-SK membranes presented the best results for trivalent iron and the RF was very similar. With the CMV membrane there was very little passage of trivalent iron. For aluminum, the RF was greater with Nafion® 450, PC-SK and CMT membranes than with the other cationic membranes. The PC-SK membrane had the best RF for aluminum without chromium. There was no aluminum transport through CMI membrane in any of the solutions. All experiments of RF showed better results with the absence of chromium.

Observing the results obtained in Table 6 for current efficiency, it can be seen that the values had been extremely low for always membranes, and thus like in the RF the gotten values had been bigger in the absence of chromium. It believes that this phenomenon indicates the low transport of trivalent ions through the membranes.

These results are consistent with Ahmed's results [49], where it was verified that the transport of ions through Nafion® 117 cationic membrane was inversely proportional to ionic radii. In addition, small ions promoted strong interactions with the sul-

fonated groups into the membrane. Among ions Cu(II), Ni(II) and Fe(III), more resistance to the transport through the membrane by Fe(III) was shown, regardless of being the smallest one. He proposed that the trivalent iron could be complexed with sulfate or hydrated into the membrane.

Total chromium interferes very little in the passage of aluminum, except with CMI membrane, since the results obtained by way of aluminum transport are very similar with or without chromium.

Using the Hydra Medusa program [48] it is possible to note some complexes formed in chromium bath contaminated with trivalent aluminum and chloride. These complexes are shown in Fig. 8. It is observed that positive complexes are formed. These complexes do not obstruct the passage through the cation-exchange membranes.

Another important characteristic in the study of membranes is the interaction among membranes and ions, because this characteristic is related to the ionic transport. It is well known [50] that the transport of ions in ion-exchange membranes depends on the pair formed with the ionic group inside the membrane. It is assumed that monovalent and other ions compete in the system, and that a monovalent ion can be easily transferred when compared to Cr(III), Al(III) or Fe(III). Trivalent ions do not move easily because of their low ionic motion in the solution and in the membrane, and their mobility is less than H⁺ ions transport.

Chaouki [51], Sata [52] and collaborators verified that the membranes that contain more sulfonated sites show better ion transport. They also verified that ions having the same valence show interactions between specific ion-exchange groups and particular ions or interactions with the membrane matrix. This could explain the differences in the passage of the ions through the membranes. As the membranes have different chemical compositions, the interactions among them with ions and chromium baths resulted in different behavior. The findings show that chromium restricts the passage of trivalent iron much more than trivalent aluminum. The results obtained agree with Tor [53] who studied the simultaneous recovery of Cr(III) and Cr(VI) and demonstrated that the recovery of hexavalent chromium was more effective in the absence of co-existent ions and that the presence of co-ions did not affect the passage of trivalent chromium.

4. Conclusion

In this study, the membrane electrolysis technique was used. Five different cation-exchange membranes were evaluated by Fe(III) and Al(III) transport in spent hexavalent chromium baths. Without chromium, the RF of Fe(III) through the membranes is higher than the RF of Al(III). The joined values of CE had been also low. Chloride ions and/or sulfate ions hinder that the trivalent iron pass through the membranes. Total chromium interferes in the passage of these ions, much more for Fe(III) than Al(III). The chloride ions interfere more than sulfate ions on the transport of trivalent iron, because a precipitated is formed in high amount from pH 0.4.

Nafion® 450 and CMI were more resistant than the other membranes in the oxidizing media.

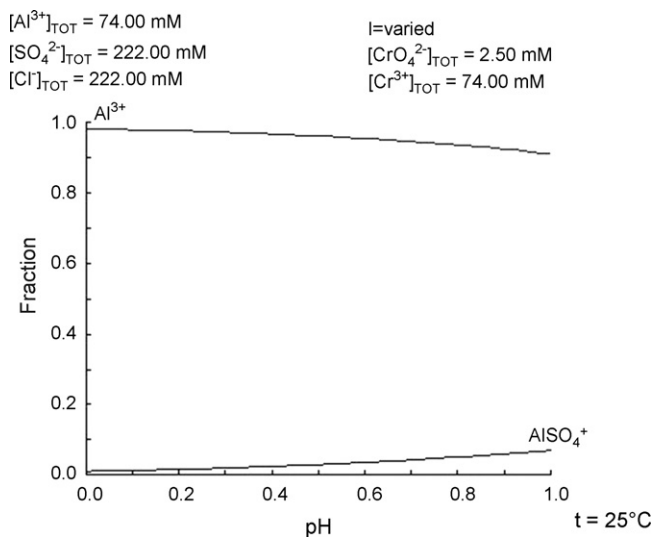


Fig. 8. Some complexes formed in the chromium bath contaminated with Al(III).

The results show that a treatment in continuous system should remove trivalent chromium and trivalent aluminum; to remove trivalent iron, the pH bath must be controlled.

The membrane electrolysis technique could be applied for purification of hexavalent chromium baths, but a modification of the membranes for a better resistance to the oxidizing media would be important.

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