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ANOMALOUS ION-EXCHANGE CHARACTERISTICS OF SOME POLYNUCLEAR METAL IONS

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SUMMARY

In ion-exchange processes, preferred components exhibit favorable or linear isotherms especially at trace concentrations. In accordance with chromatographic theories, preferred components also give rise to self-sharpening type breakthroughs during fixed-bed column runs barring mass-transfer limitations. No general exception to this rule has been reported in the literature. This study identifies a series of industrially important polynuclear metal ions which would violate the foregoing principles in ion exchange systems. The underlying reasons for such anomalous characteristics have been discussed with particular emphasis on chromate and molybdate ion exchange.

INTRODUCTION

In the absence of mass-transfer limitations, preferred components in ion exchange always give rise to sharp breakthroughs during fixed-bed column runs while non-preferred components give gradual, non self-sharpening breakthroughs. The chromatographic theories[1,2] and also the experimental results with both cation- and anion-exchange systems[3,4] support the above phenomenon. In a binary ion exchange, the preferred species is the one for which the ratio of the equivalent fraction between the exchanger phase and the aqueous phase is greater than unity. Under ideal conditions, the three following types of equilibrium relationships (isotherms) are exhibited,

$$\text{favorable or convex-upward isotherm } \textit{i.e.}, \frac{\partial^2 \bar{C}}{\partial C^2} \text{ or } \frac{\partial^2 y}{\partial x^2} < 0$$

$$\text{linear isotherm } \textit{i.e.}, \frac{\partial^2 \bar{C}}{\partial C^2} \text{ or } \frac{\partial^2 y}{\partial x^2} = 0$$

$$\text{unfavorable or concave-upward isotherm } \textit{i.e.}, \frac{\partial^2 \bar{C}}{\partial C^2} \text{ or } \frac{\partial^2 y}{\partial x^2} > 0$$

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where C and $\bar{C}$ represent concentrations of a component in the aqueous phase and exchanger phase, respectively while y and x represent the equivalent fractions (normalized) of the species in question in the exchanger phase and in the aqueous phase, respectively.

A fixed-bed run is terminated when the concentration of the species to be removed reaches a predetermined value. This time and related bed volume throughput can be predicted from a knowledge of the concentration velocity of the species in question. Any concentration velocity, v_{C_i}, for a species is a function of the liquid velocity, v_0, and the local concentration gradient between the exchanger phase and aqueous phase[1].

$$v_{C_i} \equiv \left(\frac{\partial z}{\partial t}\right)_{C_i} = \frac{v_0}{1 + \left(\dfrac{\partial \bar{C}_i}{\partial C_i}\right)_z} \qquad i = 1, \ldots, n \tag{1}$$

where z and t denote distance along the path of the liquid in the column and time, respectively. Eqn. 1 is derived from a mass balance on species i neglecting axial dispersion and considering only convective flux. Stepwise derivation of eqn. 1 has been provided by Helfferich and Klein[1].

Favorable or linear isotherms, according to eqn. 1, lead to self-sharpening type breakthrough histories during column runs because the concentration velocities in these cases increase or remain constant with an increase in concentration of the species[1,2]. For an unfavorable isotherm, on the other hand, the concentration velocity increases with a decreasing concentration resulting in gradual breakthrough. Both cation- and anion-exchange equilibria have been extensively studied by various researchers[3–9] for binary and ternary systems. In none of these studies has a preferred species been found to give unfavorable characteristics. Due to its favorable or linear equilibrium characteristics, a preferred species always gives rise to self-sharpening type breakthrough[3,4] during column runs barring mass-transfer limitations.

The intent of this paper is to present examples where the foregoing general rules for predicting column breakthrough histories are not applicable, and also to provide underlying reasons for such anomalous characteristics. Specifically, ion-exchange equilibria of some polynuclear metal ions, *e.g.*, chromium, molybdenum, tungsten, etc. will be discussed. In spite of being preferred by the ion-exchange resins over other competing species, the above-mentioned ions exhibit unfavorable equilibrium characteristics resulting in gradual breakthroughs during column runs. Such unusual behaviors stem primarily from the chemistry of such metal ions. From a practical viewpoint, this phenomenon is quite important because many of these metal ions need to be removed and recovered from various process water and wastewater streams by ion-exchange processes. Due to gradual breakthrough characteristics, the effective metal removal capacities of the ion-exchange resins in conventional fixed-bed columns are greatly reduced[10,11] in spite of high selectivity.

Again, for unfavorable isotherms, two kinds of gradual breakthrough histories are possible depending on the curvature of the isotherm. Any unfavorable isotherm or a portion of it can be expressed in the following form,

$$\bar{C}_i = kC_i^n \qquad n > 1.0 \tag{2}$$

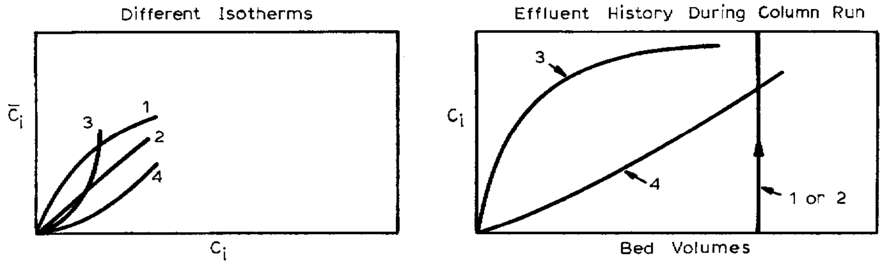


Fig. 1. Different type of isotherms and corresponding effluent histories during column runs without kinetic limitations. (1) $n < 1.0$; (2) $n = 1.0$; (3) $n > 2.0$; (4) $1 < n < 2$ in $\bar{C}_i = kC_i^n$.

where k is a constant under the operating conditions. Effluent or breakthrough history of any component i in a fixed-bed column run is the plot of its concentration, C_i, at the exit of the column *versus* time or bed volume of liquid treated. When n in eqn. 2 is greater than 2, the effluent history plot becomes convex upward *i.e.* hyperbolic[12]. However, for unfavorable isotherms with $1 < n < 2$, the effluent history plot will be convex downward type, as shown by Sengupta and Clifford[13]. Fig. 1 provides the summary of the shapes of effluent history plots for different types of isotherms in the absence of any mass-transfer limitations.

Important polynuclear complexes

Some important ionic equilibria (eqns. 3–7) showing the formation of polynuclear metal ions from their mononuclear counterparts[14–16] are given in Table I. Besides pH, the total aqueous phase concentration of each metal also affects the

TABLE I

IONIC EQUILIBRIA OF SOME POLYNUCLEAR COMPLEXES

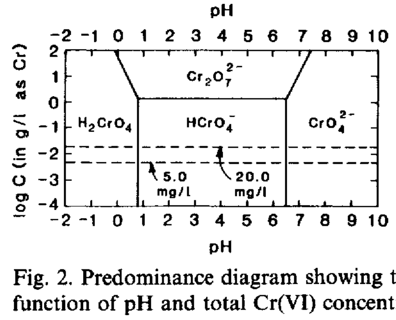
Reaction	*log K (25°C)*	*Eqn. No.*
$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$	1.52	3
$7MoO_4^{2-} + 8H^+ \rightleftarrows Mo_7O_{24}^{6-} + 4H_2O$	57.7	4
$6WO_4^{2-} + 7H^+ \rightleftarrows HW_6O_{21}^{5-} + 3H_2O$	Not available	5
$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+$	−2.9	6
$6Bi^{3+} + 12H_2O \rightleftarrows Bi_6(OH)_{12}^{6+} + 12H^+$	0.33	7
$H_2CrO_4 \rightleftarrows H^+ + HCrO_4^-$	−0.8	8
$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-}$	−6.5	9
$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$	1.52	10
$HCr_2O_7^- \rightleftarrows H^+ + Cr_2O_7^{2-}$	0.07	11
$MoO_4^{2-} + H^+ \rightleftarrows HMoO_4^-$	6.0	12
$7MoO_4^{2-} + 8H^+ \rightleftarrows Mo_7O_{24}^{6-} + 4H_2O$	57.7	13
$Mo_7O_{24}^{6-} + H^+ \rightleftarrows HMo_7O_{24}^{5-}$	4.33	14
$HMo_7O_{24}^{5-} + H^+ \rightleftarrows H_2Mo_7O_{24}^{4-}$	3.7	15

distribution of individual species. Of all these metal ions, chromate ion exchange was most thoroughly studied due to the frequent application of the ion-exchange recovery process for chromate-laden cooling water. The predominance diagram (Fig. 2) shows the effects of pH and total concentration of chromate on the distribution of individual Cr(VI) species according to the dissociation equilibria 8–11 in Table I[14–16]. Two horizontal dashed lines on the predominance diagram indicate the range of Cr(VI) concentration (5–20 mg/l Cr) normally encountered in cooling water. It is noted that at a slightly acidic condition, $HCrO_4^-$ is by far the most predominant Cr(VI) species and $Cr_2O_7^{2-}$ is practically absent at this total chromate concentration. Total chromate concentration, $[Cr_T]$ is, therefore, equal to the $HCrO_4^-$ concentration.

Important ionic equilibria for different molybdate species are given in Table I eqns. 12–15. Fig. 3 represents the predominance diagram of different molybdate species. At neutral to alkaline pH and at total molybdenum concentration as shown by the slashed region, MoO_4^{2-} is the predominant molybdate species, and in this region total molybdate concentration, $[Mo_T]$, may be considered to be equal to the MoO_4^{2-} concentration.

Anomaly in chromate ion exchange

Chromate–sulfate and chromate–chloride isotherms were determined at acidic pH for different anion-exchange resins. For strongly basic and weakly basic polystyrene resins, the isotherms are shown in Figs. 4 and 5 at low chromate loadings where competing sulfate and chloride concentrations (2000–4000 mg/l) were kept constant in the aqueous phase. For all these isotherms, the chromate distribution coefficients (y_{Cr}/x_{Cr}) calculated from the experimental data were always much greater than unity (between 40 and 300) where y_{Cr} and x_{Cr} denote equivalent fractions of chromate in the exchanger phase and aqueous phase, respectively. Very high values of distribution coefficients indicate anion-exchange resin's tremendous chromate preference over competing sulfate and chloride. In spite of such high preference chromate–sulfate and chromate–chloride isotherms, as noted in Figs. 4 and 5, are of the unfavorable type, *i.e.*, concave upward. Again for all dynamic column runs very gradual chromate breakthrough was observed as shown in Figs. 6 and 7 even at low particle Reynolds numbers, $(Re)_p$. Sengupta and Clifford[17] have systematically



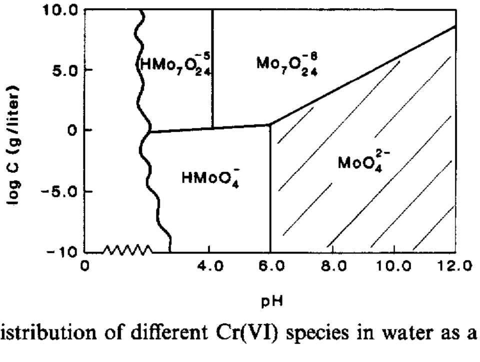
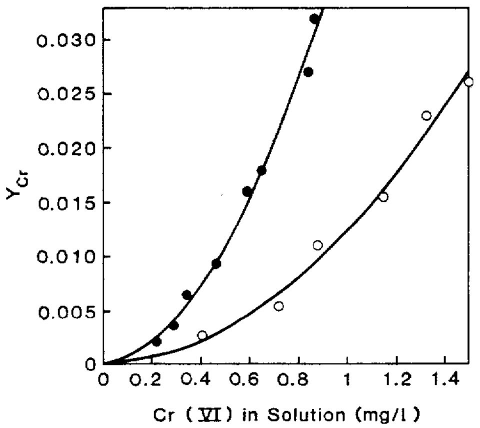


Fig. 2. Predominance diagram showing the relative distribution of different Cr(VI) species in water as a function of pH and total Cr(VI) concentration.

Fig. 3. Predominance diagram of molybdates; slashed area showing the predominance zone of MoO_4^{2-}.



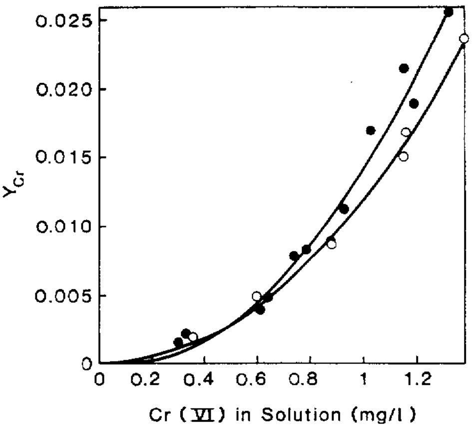


Fig. 4. Chromate–sulfate isotherms for anion-exchange resins with quaternary- and tertiary-amine functionalities. ○ = IRA 94 (tertiary amine); ● = IRA 900 (quaternary amine). Sulphate concentration 4000 mg/l; pH, 4.0.

Fig. 5. Chromate–chloride isotherms for anion-exchange resins with quaternary- and tertiary-amine functionalities. ○ = IRA 94 (tertiary amine); ● = IRA 900 (quaternary amine). Chloride concentration, 4000 mg/l; pH, 4.0.

shown that such a gradual breakthrough is not due to poor diffusion-controlled kinetics. Gradual chromate breakthroughs during columns runs have been observed also by other researchers[10]. For a highly preferred species, this behavior is quite unique and causes significant reduction in the operating capacity of the ion-exchange column[11]. Unfavorable chromate isotherms and gradual breakthroughs during column runs were observed also for other anion-exchange resins[11] and also, in the presence of other competing anions, namely, nitrate.

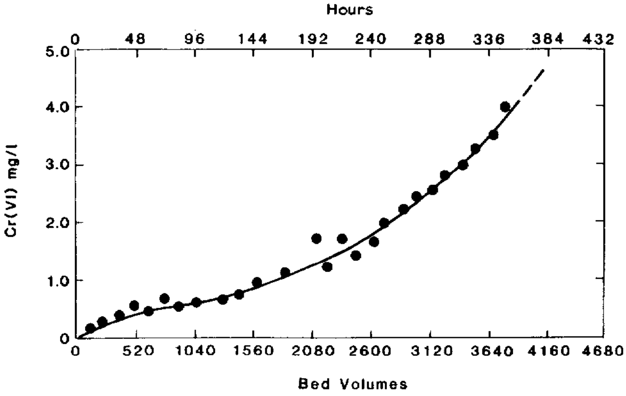


Fig. 6. Typical Cr(VI) effluent history during a column run showing very gradual chromate breakthrough for a strongly basic anion-exchange resin. Resin, IRA 900 (polystyrene–divinylbenzene, strong basic anion resin); anion concentrations: sulfate, 2000 mg/l; chloride 2000 mg/l; chromate 5.0 mg/l; pH, 4.0; superficial linear velocity: 2.15 m/h.

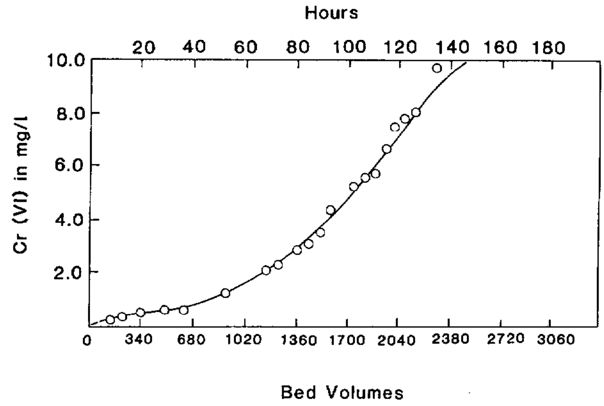


Fig. 7. Gradual chromate breakthrough for a weakly basic anion-exchange resin. Resin; IRA 94, sulfate form (polystyrene–divinylbenzene, weakly basic anion resin); anion concentrations: sulfate, 2000 mg/l; chloride, 1000 mg/l; chromate 10.0 mg/l; pH, 3.9; superficial linear velocity: 2.15 m/h; particle Reynolds number, 0.295; empty bed contact time, 4.26 min.

EXPERIMENTAL

The resins used in this study were conditioned following the standard procedure of cyclic exhaustion with 2 *N* hydrochloric acid or sulfuric acid and regenerations with 2 *N* sodium hydroxide. Finally, the resins were converted into air-dried SO_4^{2-} and Cl^- forms. Isotherm data (23 ± 2°C) were generated by a batch equilibration technique where a weighed amount of resin was gently agitated for about 6 h with a fixed volume of solution containing sulfate and chromate or chloride and chromate of known initial composition. At the end of the equilibration, solution composition was determined again to calculate the exchanger-phase concentration of different components. Equilibrium was attained in less than 4 h.

Column runs were carried out at room temperature (23 ± 2°C) using plexiglass columns and constant flow, positive-displacement pumps. Since the study was aimed at investigating the equilibrium behavior, the superficial liquid phase velocity (SLV) and particle Reynold's number $(Re)_p$, were kept very low as indicated in the figures.

Chromium was analyzed using atomic absorption spectrophotometry; sulfate and chloride were analyzed using a Dionex ion chromatograph. All the chromium in the aqueous phase was found to be in the hexavalent form. Mass balance checks showed that less than 2% of the total chromium removed by the ion-exchange resins was converted to trivalent chromium. Other experimental details have been provided by Sengupta[11].

RESULTS AND DISCUSSION

Origin of the anomaly

For the range of total chromate concentration considered in this study and as illustrated in Fig. 2, $HCrO_4^-$ is the most predominant chromate species in the aqueous phase, while $Cr_2O_7^{2-}$ is practically absent. Between $HCrO_4^-$ and $Cr_2O_7^{2-}$, however, an anion-exchange resin prefers $Cr_2O_7^{2-}$, first due to its higher charges and conse-

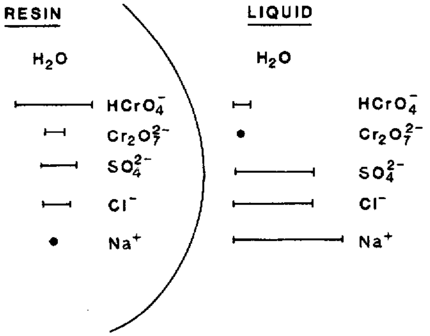


Fig. 8. Schematic partitioning of various counter-ions and sodium (co-ion) between the ion-exchange resin and water.

quently, increased electroselectivity[18]; and secondly due to its relatively hydrophobic, double-tetrahedra structure[19]. As a result, $Cr_2O_7^{2-}$ is significantly present inside the exchanger phase along with $HCrO_4^-$ although it is practically absent in the aqueous phase. This phenomenon may be viewed as an exchanger-phase dimerization of $HCrO_4^-$ into $Cr_2O_7^{2-}$ in accordance with eqn. 3 and can be predicted from the Donnan membrane principle[17]. Schematically, the chromate ion-exchange mechanism is represented in Fig. 8 showing the qualitative partitioning of different species between the liquid phase and the solid exchanger phase. The following aspects are worth-mentioning and the proofs in support of such observations have been provided elsewhere[17]:

(i) $Cr_2O_7^{2-}$ is practically absent in the liquid phase but significantly present in the exchanger phase;

(ii) monovalent $HCrO_4^-$ is preferred by the anion-exchange resin over divalent SO_4^{2-} and, this is due to the selectivity reversal effect[18,20] at the prevailing ionic strength;

(iii) the capacity of the anion-exchange resin being high, sodium ion (co-ion) concentration in the exchanger phase is considered negligible due to the Donnan exclusion effect.

Again, our primary objective in the ion-exchange separation process is to remove chromium atoms regardless of the ionic species they form. Considering chromate–sulfate ion exchange, $HCrO_4^-$ and SO_4^{2-} are the two prime counter-ions in the aqueous phase while in the exchanger phase, three counter-ions, namely, $HCrO_4^-$, SO_4^{2-} and $Cr_2O_7^{2-}$ are present. Total exchanger-phase chromium concentration is then contributed by both $HCrO_4^-$ and $Cr_2O_7^{2-}$. Various equilibrium relationships and the associated reactions are given as follows:

$$\overline{[RCr_T]} = \overline{[RHCrO_4]} + 2\,\overline{[R_2Cr_2O_7]} \tag{16}$$

$$\overline{R_2SO_4} + 2HCrO_4^- \rightleftarrows 2\,\overline{RHCrO_4} + SO_4^{2-} \tag{17}$$

$$\overline{R_2SO_4} + Cr_2O_7^{2-} \rightleftarrows \overline{R_2Cr_2O_7} + SO_4^{2-} \tag{18}$$

$$[Cr_2O_7^{2-}] = K_3\,[Cr_T]^2 \tag{19}$$

where [ ], R and overbar indicate molar concentration, resin and exchanger-phase, respectively. $[\mathrm{Cr_T}]$ and K_3 denote total chromate concentration and equilibrium constant for eqn. 3, respectively. The overall chromate–sulfate ion exchange, after solving eqns. 16–19, is given by Sengupta[11] as follows:

$$\overline{[\mathrm{RCr_T}]} = \overline{[\mathrm{RHCrO_4}]} + 2\,\overline{[\mathrm{R_2Cr_2O_7}]}$$

$$= \left(\frac{K^{\mathrm{I}} f_{\mathrm{S}} \overline{[\mathrm{R_2SO_4}]}}{[\mathrm{SO_4^{2-}}]}\right)^{1/2} \left(\frac{[\mathrm{Cr(VI)}]}{f_{\mathrm{HCrO_4^-}}\gamma_1} + \frac{2K_3 K^{\mathrm{II}} f_{\mathrm{S}} \overline{[\mathrm{R_2SO_4}]}}{f_{\mathrm{Cr_2O_7^{2-}}}\,[\mathrm{SO_4^{2-}}]} \frac{[\mathrm{Cr(VI)}]^2}{\gamma_1^2}\right) \tag{20}$$

where f_{S} and γ_1 indicate exchanger-phase activity coefficient of the sulfate ion and aqueous-phase activity coefficient of a monovalent ion, respectively. K^{I} and K^{II} denote equilibrium constants for reactions 17 and 18. When chromate is a trace species and the concentration of the competing sulfate ion is constant, all the terms on the right hand side of eqn. 20 become constant excepting total chromate concentration. Also, equivalent weights of $\mathrm{HCrO_4^-}$ and $\mathrm{Cr_2O_7^{2-}}$ as chromium are the same. Under these conditions, eqn. 20 degenerates into the following form:

$$y_{\mathrm{Cr}} = A_1 x_{\mathrm{Cr}} + A_2 x_{\mathrm{Cr}}^2 \tag{21}$$

This is the equation of a parabola where the first term on the right hand side represents the contribution of $\mathrm{HCrO_4^-}$ in the exchanger phase while the second term represents the contribution of $\mathrm{Cr_2O_7^{2-}}$. The second term also accounts for the unfavorable characteristic of the chromate isotherms *i.e.*, for eqn. 21, $\partial^2 y/\partial x^2 > 0$. A_1 and A_2 are constants which depend on the type of anion-exchange resin used, total sulfate concentration, various equilibrium constants, etc. Such an unfavorable characteristic is an equilibrium property of chromate ion exchange and was observed in the presence of other competing anions ($\mathrm{Cl^-}$, $\mathrm{NO_3^-}$) for all types of anion-exchange resins studied, *e.g.*, anion resins with (i) weakly and strongly basic functionalities, (ii) polystyrene and polyacrylic matrices, and (iii) gel and macroporous structures[11].

Again, if the unfavorable isotherm, as shown in eqn. 21, is fitted to the form of either

$$y_{\mathrm{Cr}} = k x_{\mathrm{Cr}}^n$$

or

$$\overline{C}_{\mathrm{Cr}} = k C_{\mathrm{Cr}}^n$$

the exponent n will always lie between 1 and 2, when chromate is a trace species. It was confirmed[11] by statistically fitting four sets of experimental binary isotherm data as shown in Table II. Since the exponent n is less than 2, the Cr(VI) effluent history according to Fig. 1, should be concave upward. The column run data, as shown in Figs. 6 and 7 and for others[11] not included here, are in agreement with the foregoing prediction.

TABLE II

BEST-FIT EQUATIONS FOR VARIOUS ISOTHERMS AT pH 4.0

Resin	*Competing anion concentration, C_i (mg/l)*	*Best-fit equation* $y_{Cr} = kx^n_{Cr}$
IRA-458	2000 mg/l sulfate	$y_{Cr} = 127\, x_{Cr}^{1.39}$
(Acrylic, SBA)	2000 mg/l chloride	$y_{Cr} = 2200\, x_{Cr}^{1.7}$
IRA-900	2000 mg/l sulfate	$y_{Cr} = 7430\, x_{Cr}^{1.59}$
(Sty-DVB, SBA)	2000 mg/l chloride	$y_{Cr} = 2930\, x_{Cr}^{1.35}$

Molybdate ion exchange

Unfavorable characteristic of a preferred component is unique but not necessarily limited to chromate ion exchange. This phenomenon may be observed for other polynuclear metal ions, *e.g.*, molybdenum, tungsten, iron, bismuth and probably a few more. Molybdate ion exchange will be treated as an example in the following discussion showing how molybdates may give rise to unfavorable characteristics and consequently, gradual breakthroughs during ion exchange column runs in the presence of other competing ions.

As shown in the predominance diagram (Fig. 3), MoO_4^{2-} is practically the only molybdate species in the slashed region. Therefore, total molybdenum concentration,

$$[Mo_T] = [MoO_4^{2-}] \tag{22}$$

However, at a given pH a very trace amount of $Mo_7O_{24}^{6-}$ will always be present in the aqueous phase according to the equilibrium given by eqn. 4.

$$Mo_7O_{24}^{6-} = 57.7\,[H^+]^8\,[MoO_4^{2-}]^7 = \text{constant} \cdot [Mo_T]^7 \tag{23}$$

Due to its higher charges, $Mo_7O_{24}^{6-}$ will have much greater electroselectivity[18] towards anion exchange resins compared to MoO_4^{2-}. As a result, in spite of being practically absent in the aqueous phase, it will be a significant molybdate species inside the ion-exchange resin. Total exchanger-phase molybdenum concentration is now given by,

$$[\overline{RMo_T}] = [\overline{R_2MoO_4}] + 7[\overline{R_6Mo_7O_{24}}] \tag{24}$$

Considering molybdate–sulfate ion exchange where molybdate is a trace species, and proceeding the same way as done for chromate ion exchange, the equilibrium distribution of molybdenum between the exchanger phase and the aqueous phase is given by

$$y_{Mo} = Ax_{Mo} + Bx_{Mo}^7 \tag{25}$$

y_{Mo} and x_{Mo} are equivalent fractions of molybdate in the exchanger phase and the aqueous phase, respectively while constants A and B will depend on the type of ion-exchange resin used, various equilibrium constants, total sulfate concentration, etc. First term in the right hand side of eqn. 25 is due to MoO_4^{2-} in the exchanger phase while the second term is contributed by the presence of $Mo_7O_{24}^{6-}$ in the exchanger phase. The second term will cause a strong unfavorable isotherm even though molybdate is a preferred species with respect to competing sulfate anions. During ion-exchange column runs, molybdates will, therefore, exhibit gradual breakthrough characteristics like chromates. It is to be noted that such unfavorable characteristics are not due to any non-ideality in the exchanger phase, but stem primarily from the chemistry of the metal complexes.

CONCLUSIONS

This study identifies a series of polynuclear metal ions which, in spite of their greater selectivities towards ion-exchange resins, can give rise to unfavorable characteristics, especially at concentrations, which are relatively low compared to the competing ion concentrations. This is caused due to the presence of the polynuclear metal ions in the exchanger phase although they are practically absent in the aqueous phase. In ion-exchange separation processes, these anomalous characteristics lead to early, gradual breakthroughs of these metal ions during fixed-bed column runs and greatly reduce the operating capacities of the ion-exchange resins.

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