

# Unforeseen Factors Influencing Fe(III)-Containing Cations Sorption on Strongly Basic Anion Exchangers

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**ABSTRACT:** The sorption and partial destruction of the Fe(III)-containing compounds in the aqueous medium in strongly basic anion exchangers AV-17 and Varion-AD phase have been investigated. It is shown that partial destruction of the Fe(III) compounds in acidulated water (pH = 2) and in K<sub>2</sub>SO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions takes place. With increasing of temperature up to 50°C, the desorption degree of the iron ions from polymer phase decreases. In dried polymer, the structural and electronic state of iron compounds, according to their magnetic susceptibility, remains

stable for a long time. The sorption of the Fe(III)-containing cations at 50°C during 12 h depends essentially on the sizes of polymer granules. Sorption increases with growing of polymer granules. For comparison of sorptional capacities, the sorption of Fe(III)-containing cations was determined on different cation and anion exchangers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2643–2647, 2008

**Key words:** ion exchangers; transition metal chemistry; supports

## INTRODUCTION

It is well known that crosslinked ionic polymers containing strongly basic groups are used largely in industry as anion exchangers. However, in certain conditions, polymers of this type are able to retain metallic cations from solutions of Fe(III), Cr(III), and Al(III) sulfates.<sup>1–3</sup> Retaining of the M(III)-containing cations on strongly basic anion exchangers from sulfate solutions as a result of anion exchange or M(OH)<sub>3</sub> compounds formation in the polymer phase is unlikely.<sup>3</sup> We have suggested that the retention of the M(III)-containing cations, namely [MOH(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>,<sup>3</sup> on strongly basic anion exchangers takes place through the formation in the polymer phase of the jarosite (alunite) mineral type compounds<sup>4</sup>: R<sub>4</sub>N[M<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>] and H<sub>3</sub>O[M<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>], where R<sub>4</sub>N<sup>+</sup> is a functional group of polymer. In the organic polymer phase, these compounds are in form of inorganic polymers of solid ultrafine particles.<sup>4,5</sup> Metallic compounds in the polymer phase modify the sorptional, catalytically and thermochemical properties of the strongly basic anion exchangers.<sup>6</sup> The obtaining and transformations of metallic compounds in the polymer phase could expand the utilization of ion exchange materials, particularly in obtaining selective sorbents,<sup>7–9</sup> catalysis and modeling of physical and biochemical processes.<sup>10</sup>

The jarosite (alunite) mineral-type compounds in polymer phase are amorphous or have a little degree of crystallinity and cannot be investigated using X-ray diffraction method. On the other hand, it is expected that their formation conditions and their stability will differ from that of naturals or synthetically obtained jarosites. So, on heating in water (*t* > 80°C) synthetically obtained jarosite compounds are converted to highly dispersed particles of α-FeOOH in superparamagnetic state.<sup>11</sup> In the phase of strongly basic anion exchangers, when boiling in water media, jarosite compounds may be converted into β-FeOOH in superparamagnetic state or relatively massive magnetically ordered particles.<sup>2,4</sup>

Native jarosite mineral is not so stable, partially being transformed into Fe(OH)<sub>3</sub>.<sup>5</sup>

It is necessary in order to apply Fe(III)-containing strongly basic anion exchangers as selective sorbents or catalysts to know their behavior in different media and sorption–desorptional features of the Fe(III)-containing cations on such kind of polymers.

In the present article was investigated concomitantly Fe(III)-containing cations sorption and desorption processes on strongly basic anion exchanger.

## EXPERIMENTAL

The commercial strongly basic anion exchangers AV-17 and Varion-AD in Cl<sup>−</sup> form were used. The exchangers are gell-type crosslinked polystyrene–divinylbenzene ionic polymers containing 8% divinylbenzene and −N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> (AV-17) and −N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>OH

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(Varion-AD) functional groups. Their full exchange capacity are 3.5–4.5 (AV-17) and 4.0 mEquiv/g (Varion-AD).<sup>12</sup> For comparison, Fe(III)-containing cations sorption have been performed on some commercial strongly basic anion exchangers, sulfonic and carboxylic cation exchangers, exchangers containing quaternary pyridinic nitrogen and atoms donor of electrons obtained at the Institute of Macromolecular Chemistry "P. Poni", Iasi, Romania.

For preparation of solution,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  has been used. Dried samples (0.2 g) of the polymers were contacting with 100 mL of 0.02M  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  or 7 g  $\text{Fe}_2(\text{SO}_4)_3/\text{L}$  solutions. The pH of the solution-sample system was maintained at  $1.9 \pm 0.1$  by using either  $\text{H}_2\text{SO}_4$  or  $\text{KOH}$  solutions. The sorption took place at  $50^\circ\text{C} \pm 1.0^\circ\text{C}$  according to Ref. 7. Except some kinetics studies, samples duration contact with solution was 10 h. Following contact with solution, the polymer samples were filtrated, washed with 50 mL distilled water, and dried at  $50^\circ\text{C}$  during 3 h. Content of iron ions in the dried samples was determined photocolorimetrically<sup>13</sup> after desorption with 1M  $\text{HCl}$  solution. The error of determination constituted 0.3 mg Fe/g polymer.

Some polymer samples (0.2 g) after sorption and washing with 50 mL distilled water were placed in 100-mL distilled acidulated water or 0.1M  $\text{K}_2\text{SO}_4$  solution both with  $\text{pH} = 2$  to investigate iron ions desorption at different temperature.

To determinate magnetic susceptibility Fe(III)-containing sample of AV-17 polymer was prepared. For that, 5 g of AV-17 was placed into 500 mL of  $\text{Fe}_2(\text{SO}_4)_3$  (7 g/L) solution with  $\text{pH} = 1.9$  and  $t = 52^\circ\text{C}$  during 10 h. After sorption and washing with distilled water, samples were dried at  $50^\circ\text{C}$  for 4 h.

Paramagnetic susceptibility of Fe(III)-containing AV-17(Cl) was measured at room temperature using Gouy method. The effective magnetic moment ( $\mu_B$ -Bohr magneton) of iron ion in polymer phase was calculated according to Ref. 14:

$$X_g^{p+m} = X_g^m \cdot \omega + X_g^p(1 - \omega) \quad (1)$$

$$X_g^m = [X_g^{p+M} - X_g^p(1 - \omega)] \quad (2)$$

$$X_M^m = X_g^m \cdot M \quad (3)$$

$$\mu_{\text{ef}} = 2.84(X_M^m \cdot T)^{1/2} \quad (4)$$

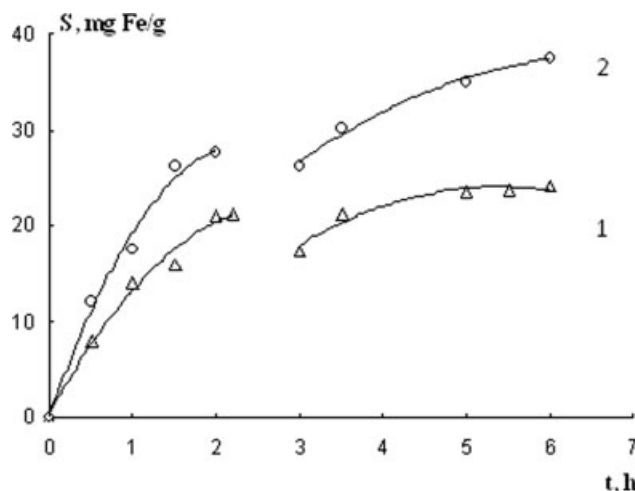
where  $X_g^{p+m}$  is the massic (gram) magnetic susceptibility of the metal (ions) containing polymer,  $X_g^m$  the massic magnetic susceptibility of the metal in polymer phase,  $\omega$  the mass part of the metal in polymer phase,  $X_M^m$  the molar magnetic susceptibility of the metal,  $X_g^p$  the massic magnetic susceptibility of polymer,  $M$  the molar mass of the metal,  $T$  the thermodynamic temperature, and  $\mu_{\text{ef}}$  the effective magnetic moment in Bohr magnetons ( $\mu_B$ ).

## RESULTS AND DISCUSSION

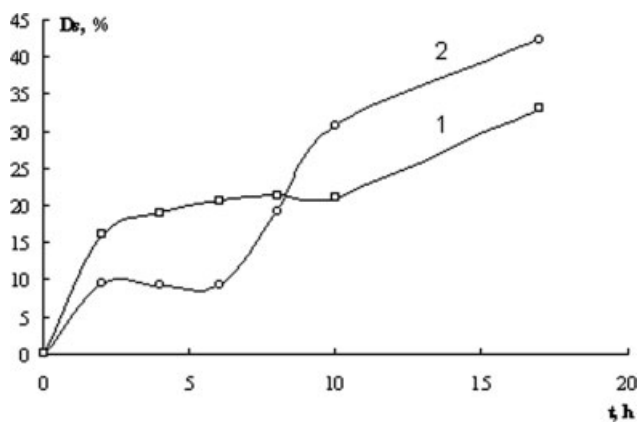
In the previous paper,<sup>3</sup> it was supposed that when strongly basic anion exchanger is in contact with  $\text{Fe}_2(\text{SO}_4)_3$  solution, the  $[\text{FeOH}(\text{H}_2\text{O})_5]^{2+}$  cations take part in formation process of compounds in polymer phase. It was shown<sup>15</sup> that the metallic cations sorption kinetics is determined by diffusion in the polymer phase. It is conditioned by the same charge sign of cations and of the ionized polymer functional groups and the high  $\text{Fe}_2(\text{SO}_4)_3$  solution concentration ( $2 \times 10^{-2}\text{M}$ ). It is known that if the sorption is determined by the internal diffusion, sorption will increase when polymer will be in contact with solution again after process interruption by phase separation.

However, as shown in Figure 1, after sorptional process interruption for 24-h Fe(III)-containing cations is less than before. It means that when polymer contacts with  $\text{Fe}_2(\text{SO}_4)_3$  solution, two concomitant processes take place: the formation of Fe(III)-containing compounds in its phase and their partial destruction.

Partial destruction of the Fe(III)-containing compounds in aqueous medium has been confirmed by next experiments. When Fe(III)-containing samples of the AV-17 polymer were introduced in acidulated water with  $\text{pH} = 2.0$  (diluted  $\text{H}_2\text{SO}_4$ ) solution, desorption of iron cations has been observed (Fig. 2). Partial desorption of iron cations from Fe(III)-containing polymer takes place and in contact with electrolyte (0.1M  $\text{K}_2\text{SO}_4$ ) solution with  $\text{pH} = 2$  (Fig. 3). As shown in Figures 2 and 3, there is a plateau on desorption degree ( $D_s$ , %) as a function of a contact duration of sample with acidulated water and  $\text{K}_2\text{SO}_4$  solution. It may be attributed to a portion of the compounds that had been destroyed in the polymer phase before introduction in solution. In this case,

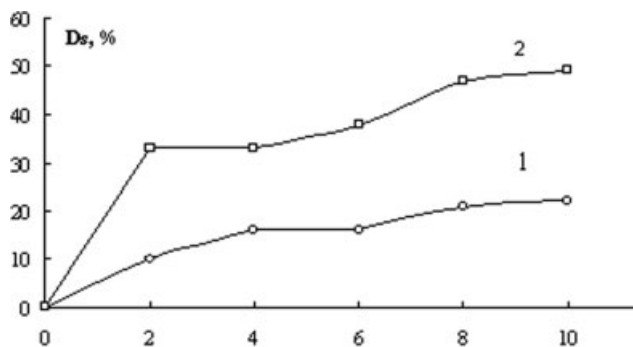


**Figure 1** Kinetics curves of the Fe(III)-containing ions sorption with interruption on AV-17 (1) and Varion-AD (2) at  $50^\circ\text{C}$ .

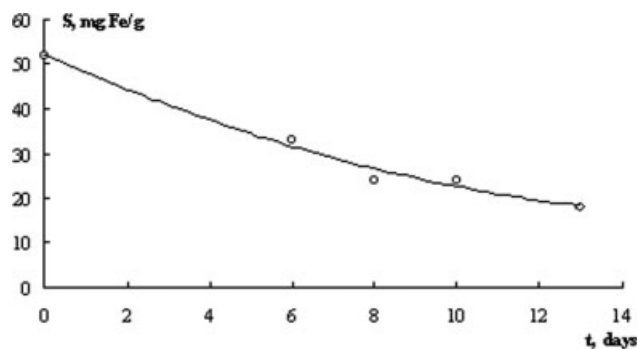


**Figure 2** Desorption degree of iron ions from Fe(III)-containing AV-17 in acidulated water (pH = 2) at 50°C (1) and 9°C (2) as a function of polymer-water contact duration.

the desorption degree of iron cations from polymer samples at 50°C is more than at 9°C  $\pm$  1°C. But with increase of the contact duration of the Fe(III)-containing samples with acidulated water, the desorption degree at low temperature becomes higher (Fig. 2). It means that Fe(III) compounds in the polymer phase are more stable at 50°C temperature. It may be that at this temperature takes place the increasing of the structuration degree of the Fe(III) compounds. The destruction of the Fe(III) compounds that has been obtained in the polymer phase at 50°C takes place when polymer samples remain after that in  $\text{Fe}_2(\text{SO}_4)_3$  solution at room temperature (Fig. 4). It confirms once more that with decreasing of temperature the destruction degree of the Fe(III) compounds in polymer phase increases. The structure stabilization of Fe(III) compounds in the polymer phase on heating is confirmed by follow results. As shown in Figure 3, desorption of iron ions in acidulated water at 50°C from dried in air at 50°C during 4 h polymer samples also takes place and desorption degree is

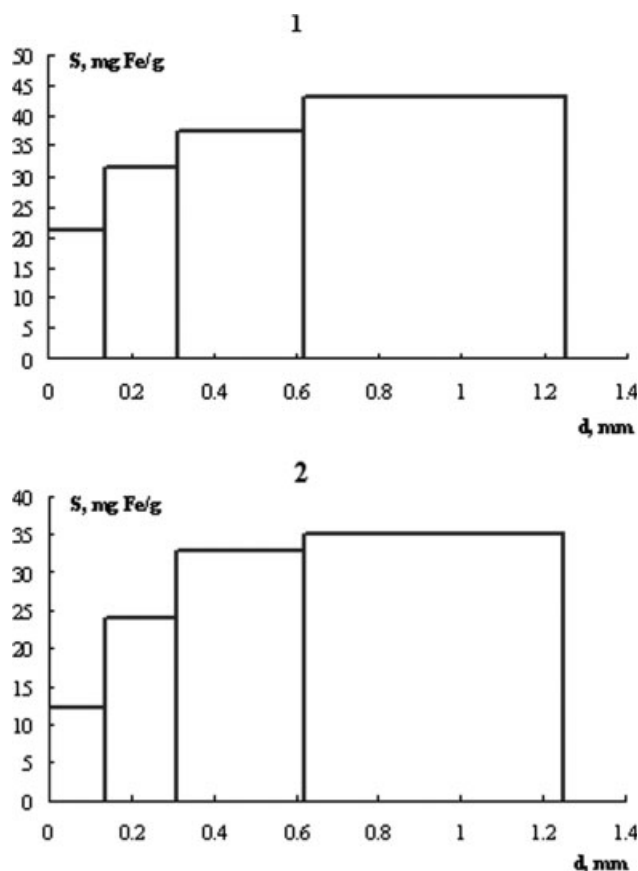


**Figure 3** Desorption degree at 50°C of iron ions from Fe(III)-containing AV-17 in 0.1M  $\text{K}_2\text{SO}_4$  solution with pH = 2 (1) and from dried AV-17 in acidulated water (pH = 2) (2) as a function of polymer-solution contact duration.

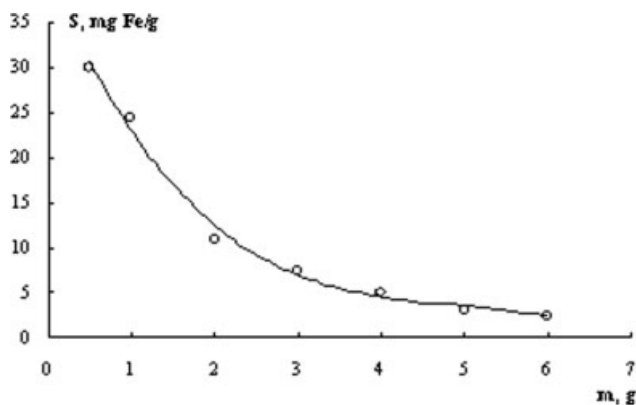


**Figure 4** Desorption degree of iron ions from Fe(III)-containing AV-17 in  $2 \times 10^{-2} \text{M}$   $\text{Fe}_2(\text{SO}_4)_3$  solution (pH = 1.9) at room temperature as a function of polymer-solution contact duration.

high. The electronic state of the iron ions in the dried polymer phase remains practically constant for a long time (at least 140 h), according to magnetic properties. The average effective magnetic moment of iron ion in the dried polymer sample at room temperature is 5.25 Bohr magnetons ( $\mu_B$ ). This magnetic moment is less than that of 5.9–6.0  $\mu_B$  for  $\text{Fe}^{3+}$  ion.<sup>16</sup> It means that in the polymer phase exist anti-ferromagnetical interactions between iron ions. The



**Figure 5** The Fe(III)-containing cations sorption dependence of AV-17 (1) and Varion-AD (2) granules sizes.



**Figure 6** The Fe(III)-containing cations sorption as a function of AV-17 mass in contact with in  $2 \times 10^{-2}M$   $Fe_2(SO_4)_3$  solution at  $50^\circ C$  and  $pH = 1.9$ .

nature of the magnetical interactions in jarosites is related in Ref. 17.

To elucidate the reason of the Fe (III) compounds instability in polymer phase supplementary investigations are needed.

On the other hand, we can mention that on sorption of some kinds of anions ( $NCS^-$  for example) Fe (III)-compounds in the polymer phase became stable.

It is well known that sorption on solid sorbents depends on specific area, and specific area depends on sorbent particle sizes. The less are particles sizes, the more the specific area and more the sorption is. As shown in Figure 5, sorption of Fe(III)-containing cations from  $2 \times 10^{-2}M$   $Fe_2(SO_4)_3$  solution with  $pH = 1.9$  at  $50^\circ C$  during 12 h essentially depends on polymer granules sizes. But this dependence is un-

usual, the large are granules sizes the more is sorption. This phenomenon may be explained only taking in consideration the partial destruction of the Fe(III)-compounds in the polymer phase and iron ions diffusion from polymer granules. On the other hand, it means that Fe(III)-compounds formation takes place in the polymer granules volume.

The sorption value of Fe(III)-containing cations on strongly basic anion exchanger depends considerably on the polymer mass and  $Fe_2(SO_4)_3$  solution volume ratio. With the increase of the polymer mass in the 100 mL of  $2 \times 10^{-2}M$   $Fe_2(SO_4)_3$  solution metallic cations sorption lows exponentially, although the solution concentration is relatively high (Fig. 6).

Sorption of metallic cations on strongly basic anion exchangers is an unusual process. The chemistry of the metallic cations sorption on such kind of polymers completely differs from the one on carboxylic or sulfocation exchangers. Therefore, it is interesting to compare the sorptional capacity of different kinds of exchangers toward Fe(III)-containing cations. For investigation, polymer samples (0.2 g) interacted at  $50^\circ C$  for 12 h with  $2 \times 10^{-2}M$   $Fe_2(SO_4)_3$  solutions having  $pH = 1.9$ . Characteristics of utilized commercial exchangers are given in Ref. 12. Some of polymer samples were obtained at the Institute of Macromolecular Chemistry "P Poni" (Iasi, Romania) by Dr. Cornelia Luca and Dr. Violeta Neagu. The obtained sorptional capacities of the investigated polymers are listed in Table I. As shown in Table I, the metallic cations sorption capacity of commercial strongly basic anion exchangers is comparable with the capacity of sulfocationite. The relatively small

**TABLE I**  
Values of Sorption (S) from Solutions of Fe(III)-Containing Cations ( $2 \times 10^{-2}M$   $Fe_2(SO_4)_3$ ) by Different Polymers at  $50^\circ C$

No.	Polymer	Place of manufacture	Functional group	DVB (%)	Granules diameter (mm)	S (mg Fe/g)
1	AV-17(Cl)	Russia	$-N^+(CH_3)_3$	8	0.4-1.2	47.5
2	AV-17-2P	Russia	$-N^+(CH_3)_3$	2	0.4-1.2	49.5
3	Varion-AD	Hungary	$-N^+(CH_3)_2C_2H_4OH$	8	0.3-1.1	46.5
4	Purolyte A-400	England	$-N^+(CH_3)_3$	8	0.3-1.2	46.5
5	Amberlite IRA 410	USA	$-N^+(CH_3)_2C_2H_4OH$	8	0.3-1.2	45.0
6	4-VP- $CH_2COOH$	Romania	$\geq N^+CH_2COOH$	8	0.5	42.5
7	4-VP- $CH_2CH_2COOH$	Romania	$\geq N^+CH_2CH_2COOH$	8	0.5	11.0
8	4-VP-CB	Romania	$\geq N^+CH_2C_6H_5$	8	0.5	10.0
9	4-VP-CE	Romania	$\geq N^+C_2H_5$	8	0.5	64.5
10	4-VP-AN	Romania	$\geq N^+CH_2CH_2CN$	8	0.5	40.6
11	4-VP-AM	Romania	$\geq N^+CH_2CH_2CONH_2$	8	0.5	57.2
12	4-VP-MVC	Romania	$\geq N^+CH_2CH_2COCH_3$	8	0.5	63.8
13	KB-2	Russia	$>C-COOH$			
			$>C-COOH$	2-3	0.3-1.0	95.6
14	KB-4	Russia	$>CH-COOH$	8	0.3-2.0	25.0
15	KB-4P2	Russia	$>CH-COOH$	2-3	0.25-1.0	26.0
16	Amberlite IRS-50	USA	$>CH-COOH$	8	0.3-1.2	35.0
17	KU-2	Ukraine	$-SO_3H$	8-10	0.3-1.5	48.5

sorption capacity of the KB-4, KB-4P2, and Amberlite IRC-50 is due to inability of carboxylic groups to form chelate complexes with iron cations. Carboxylic groups of the exchanger KB-2 are able to form chelate complexes with metallic cations and its sorption capacity is much more. In the polymer phase containing pyridinic quaternary nitrogen takes place the formation of the jarosite type compounds.<sup>2</sup>

### CONCLUSIONS

When strongly basic anion exchangers contact with  $\text{Fe}_2(\text{SO}_4)_3$  solution, in their phase take place two processes simultaneously: sorption of Fe(III)-containing ions and partial destruction of formed Fe(III) compounds. Partial destruction of Fe(III) compounds in polymer phase takes place in contact with acidulated water (pH = 2),  $\text{K}_2\text{SO}_4$ , and  $\text{Fe}_2(\text{SO}_4)_3$  solutions with pH = 1.9–2.0. The desorption (destruction) degree of iron ions at low temperature (9°C) is higher than at 50°C. Desorption of iron ions from polymer phase in acidulated water takes place and from dried at 50°C Fe(III)-containing ions polymer. But, according to magnetic susceptibility measurements, electronic state of metallic compounds in the dried polymer samples apparently remains constant for a long time. It is shown that sorption capacity of polymers increases with polymer granules sizes growing. The sorption capacity of strongly basic anion exchangers towards Fe(III)-containing cations is practically the same as of sulfocationexchanger.

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