Some Metal Compounds in the Phase of Crosslinked Ionic Polymer—Precursors for New Sorbents and Catalysts

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ABSTRACT: A commercial crosslinked ionic polymer AV-17 containing $-N(CH_3)_3Cl$ groups was used. The common compounds of Bi(III) and Al(III); Bi(III) and Cr(III); Bi(III) and Fe(III); Bi(III) and FeOOH and of three components—Bi(III), Fe(III), and Cr(III); Bi(III), FeOOH, and Cr(III) were obtained in the AV-17 polymer phase and investigated using scanning electron microscopy, powder X-ray diffraction, thermogravimetric analysis, and Fourier-transform infrared spectroscopy. It was shown that metal-containing compounds were concentrated on the surface of the polymer granules. The compounds were in the crystalline (BiOCl) or amorphous (jarosites and oxihydroxides) state. The morphology and composition of the metal-containing ultra dispersed particles were different on the surface and in the volume of the polymer granule. Most of the metal-containing compounds were in the form of pseudo spherical particles, but compounds containing Bi(III) and FeOOH in the volume of AV-17 granule, were in the form of clew of nanometer fibers. Thermogravimetric analysis (in an N_2 atmosphere) in the range 24–1000°C of the metallic compounds containing polymer was also carried out. The metal-containing polymer samples were stable up to 120°C. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2582–2593, 2012

Key words: ion exchangers; adsorption; electron microscopy; X-ray; thermal properties

INTRODUCTION

Crosslinked ionic polymers containing R_4N^+ functional groups are largely used in water treatment and other branches of industry and science as strongly basic anion exchangers. These polymers do not contain negatively charged atoms or electron donors in their matrix. Therefore, theoretically, they are able to retain from solution only anions but not inorganic cations. However, in previous studies[1–3] it has been reported that in certain conditions, strongly basic anion exchangers are able to retain Fe(III), Al(III), Cr(III)-containing cations (hydroxocomplexes) from solutions. These cations are retained by polymers from their sulfates solutions only and not from nitrates or chlorides. The retaining of cations takes place through the formation in the polymer phase of jarosite[4–6] mineral type compounds: $R_4N[M_3(OH)_6(SO_4)_2]$ and $H_3O[M_3(OH)_6(SO_4)_2]$, where R_4N^+ is a polymer group, M is Fe^{3+}, Al^{3+}, or Cr^{3+}. In the polymer phase, metallic compounds are in the form of ultra fine particles.[1,7]

It is known that on heating in water ($t > 80°C$), the synthetically obtained Fe- jarosite is converted into highly dispersed particles of α-FeOOH in super paramagnetic state.[5] However, in the polymer phase of strongly basic anion exchangers when boiling in water media, jarosite type compounds are converted into β-FeOOH in super paramagnetic state and relatively massive magnetically ordered particles.[1,7] The existence of the metallic compounds in the polymer phase modify the properties of strongly basic anion exchangers considerably. Being modified with metallic compounds, strongly basic anion exchangers become selective sorbents[8] and catalysts.

Recently,[9] we found that strongly basic anion exchangers are able to retain Bi(III)-containing cations from $Bi(NO_3)_3$ solutions. The retaining of the Bi(III)-containing cations by such kind of polymers is not due to the formation of the jarosite type compounds. By the scanning electron microscopy (SEM) investigation,[10,11] it was shown that Bi(III) compounds on the surface and in the volume of the polymer granule are in the form of ultra fine particles. On heating in water, the Bi(III)-containing particles become larger, and compounds migrate to the surface of the polymer granule. When Bi(III)-containing polymer was heated in an Na_2SO_4 solution the

modification of the morphology and structure of the Bi(III)-containing particles takes place. The powder X-ray diffraction showed the existence of the crystalline phase of BiOCl and Bi_2O_3 in the polymer samples which were heated in water and in a Na_2SO_4 solution. There was not fond a crystalline phase in the initial (before heating in water) Bi(III)-containing polymer.

To expand the use of crosslinked ionic polymers containing strongly basic groups, particularly in obtaining selective sorbents or catalysts with several active centers, a great interest presents their modification with common compounds of two or more metals.

This article reports the investigation of strongly basic crosslinked ionic polymer, containing common compounds of Bi(III) and Al(III); Bi(III) and Fe(III); Bi(III) and Cr(III); Bi(III), Fe(III), and Cr(III); Bi(III) and FeOOH; Bi(III), FeOOH, and Cr(III).The investigations were carried out using SEM, powder X-ray diffraction, thermogravimetric (TG) analysis, and Fourier-transform infrared (FT-IR) spectroscopy.

EXPERIMENTAL

The commercial strongly basic anion exchanger AV-17 × 8, containing ─N(CH₃)₃Cl groups was used. The gel-type resin had a polystyrene-divinylbenzene matrix. Its full exchange capacity is 3.5–4.5 mg of equiv/g.[12]

First of all it was prepared Bi(III)-containing polymer according to Ref. 9. The preparation took place upon the contact of 50 g of dried AV-17(Cl) during 6 h with 2 L of 0.015 mol/L $Bi(NO_3)_3$ solution with pH about 0.25 and temperature of 50°C. After that, the AV-17(Bi) polymer sample was filtrated, washed with distilled water, and dried in air. The obtained Bi(III)-containing AV-17 has been used for preparation of other metal-containing polymer samples as follows:

1. AV-17(Bi,Al)—the sample of the polymer containing Bi(III) and Al(III) compounds. The 5 g of dried AV-17(Bi) sample was 12 h in contact with 500 mL of $Al(SO_4)_2·12H_2O$ solution containing 2.5 g Al/L and having pH 3.4 and temperature of 87°C[3]. After that, the sample was filtrated, washed with distilled water, and dried at 60°C for 3 h.
2. AV-17(Bi,Fe)—the sample of the polymer containing Bi(III) and Fe(III) compounds. The 6 g of dried AV-17(Bi) sample was 8 h[13] in contact with 500 mL of solution containing 7 g $Fe_2(SO_4)_3$/L and having pH 1.95 and temperature of 50°C After that, the sample was filtrated, washed with distilled water, and dried at 60°C for 3 h.

3. AV-17(Bi,FeOOH)—the sample of the polymer containing Bi(III) compounds and β-FeOOH. The 4 g of the AV-17(Bi,Fe) sample was introduced in the 400 mL distilled water and heated for 5 h in the boiled water bath. Then polymer was filtrated and dried in air.
4. AV-17(Bi,Cr)—the sample of the polymer containing Bi(III) and Cr(III) compounds. The 7 g of dried AV-17(Bi) sample was 12 h in contact with 1 L of $KCr(SO_4)_2·12H_2O$ solution containing 2 g Cr/L and having pH 4.1 and temperature of 60°C. The pH of solution which contact with AV-17(Bi) was periodically adjusted to 4.1 using NaOH solution.[14] Then polymer was filtrated, washed with distilled water and dried at 60°C during 1 h.
5. AV-17(Bi,Fe,Cr)—the sample of the polymer containing Bi(III), Fe(III), and Cr(III) compounds. The 2 g of the AV-17(Bi,Fe) sample was in contact with 200 mL of $KCr(SO_4)_2·12H_2O$ solution containing 2 g Cr/L in the conditions of AV-17(Bi,Cr) sample preparation (Sample 4).
6. AV-17(Bi,FeOOH,Cr)—the sample of the polymer containing Bi(III), β- FeOOH and Cr(III) compounds. The 2 g of the AV-17(Bi,FeOOH) sample was in contact with 200 mL of $KCr(SO_4)_2·12H_2O$ solution in the conditions of AV-17(Bi,Cr) sample preparation.

The content of metals in the polymer phase was determined after desorption with $3M$ HNO_3 solution at 60°C. The Bi^{3+} cations were determined photocolorimetrically with thiourea,[15] and Fe^{3+}, Al^{3+}, Cr^{3+} ions by atomic absorption spectroscopy.

Scanning electron microscopy images were obtained using Tescan SEM-EDX microscope. Powder X-ray diffraction carried out using DRON-UM1 diffractometer (Cu Kα radiation, Ni filtered, θ/2θ method).

The thermal behavior of the polymer samples containing metallic compounds were investigated under an N_2 atmosphere with Mettler Toledo TGA-SDTA 851 derivatograph in the range 20-1000°C. The N_2 gas flow rate was 20 mL/min and the heating rate was 20°C/min. The FT-IR spectra were recorded over the interval 400–4000 cm^{-1} on a Bruker Vertex 70 spectrometer. The samples were run as KBr disks (composition 1/200).
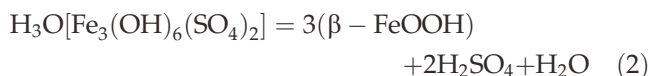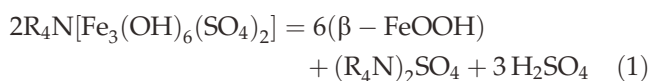
RESULTS AND DISCUSSION

Metal content in the obtained polymer samples

The metal content in the modified AV-17 polymer samples is shown in Table I.
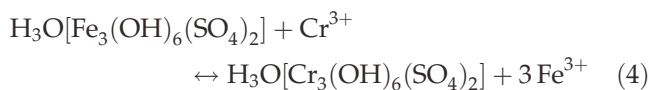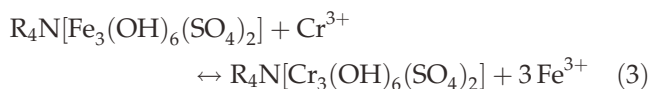
TABLE I
The Metal Content in the Polymer Samples

Samples	Metal content [mg/g]		
	Bi^{3+}	Fe^{3+}	$Cr^{3+}(Al^{3+})$
AV-17 (Bi, Al)	52.4	–	(35.0)
AV-17 (Bi. Fe)	60.5	51.0	–
AV-17 (Bi, FeOOH)	59.7	52.0	–
AV-17 (Bi, Cr)	50.0	–	97.0
AV-17 (Bi, Fe, Cr)	40.2	10.0	60.0
AV-17 (Bi, FeOOH, Cr)	42.2	12.0	30.0

When jarosite containing polymer (AV-17(Fe) sample) was heated for 5 h in the boiled water bath, the AV-17(β-FeOOH) sample was obtained,[1] according to eqs. (1) and (2):
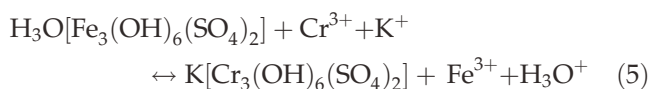
$$2R_4N[Fe_3(OH)_6(SO_4)_2] = 6(\beta - FeOOH)$$
$$+ (R_4N)_2SO_4 + 3H_2SO_4 \quad (1)$$

$$H_3O[Fe_3(OH)_6(SO_4)_2] = 3(\beta - FeOOH)$$
$$+2H_2SO_4+H_2O \quad (2)$$

The processes (1) and (2) are accompanied with passing a part of metallic cations from polymer to liquid phase.[16] But, as it is seen in Table I, obtaining of AV-17(Bi,FeOOH) sample on heating in water medium of AV-17(Bi,Fe) sample is not accompanied with iron ions lost.

The processes of obtaining the AV-17(Bi,Fe,Cr) from AV-17(Bi,Fe) sample and AV-17(Bi,FeOOH,Cr) from AV-17(Bi,FeOOH) sample are accompanied with considerable lost of iron ions. Obviously, when the AV-17(Bi,Fe) samples were in contact with KCr(SO$_4$)$_2$·12H$_2$O solution to obtain AV-17(Bi,Fe,Cr) and AV-17(Bi,FeOOH,Cr), replace of the Fe^{3+} cations in the jarosite type compounds by the Cr^{3+} ions took place according to the processes (3) and (4):

$$R_4N[Fe_3(OH)_6(SO_4)_2] + Cr^{3+}$$
$$\leftrightarrow R_4N[Cr_3(OH)_6(SO_4)_2] + 3Fe^{3+} \quad (3)$$

$$H_3O[Fe_3(OH)_6(SO_4)_2] + Cr^{3+}$$
$$\leftrightarrow H_3O[Cr_3(OH)_6(SO_4)_2] + 3Fe^{3+} \quad (4)$$

The process (5) could also take place:

$$H_3O[Fe_3(OH)_6(SO_4)_2] + Cr^{3+}+K^+$$
$$\leftrightarrow K[Cr_3(OH)_6(SO_4)_2] + Fe^{3+}+H_3O^+ \quad (5)$$

The Fe^{3+} cations were replaced by Cr^{3+} ions in the FeOOH too.

In fact, at pH 4.1 and temperature of 60°C, there were no $[Cr(H_2O)_6]^{3+}$ cations in the KCr(SO$_4$)$_2$·12H$_2$O solution,[17] but hydroxocomplexes which were destroyed in the processes (3) (4), and (5).

SEM investigation

The AV-17(Bi, Al) sample

As it is seen in the Figure 1(a,b), the surface of the polymer granule is covered with metallic compounds in the crystalline state. In the volume of the polymer granule [Fig. 1(c)], compounds particles are in the pseudo spherical form with diameter about 5 μm. The morphology of the metal-containing compounds particles on the surface and in the volume of the polymer granule is quite different. It is known that the particles sizes and morphology of Bi(III) compounds on the AV-17 granule surface depends on the temperature and SO_4^{2-} anions existence in the system upon sample preparation.[10] The obtaining of the AV-17(Bi, Al) sample carried out at temperature of 87°C in the solution of KAl (SO$_4$)$_2$·12H$_2$O, but the morphology of the metallic compounds on the polymer granule surface differ from the observed in the Ref. 10. Therefore we can conclude that existence of the Al(III) hydroxocomplexes in the polymer solution system influenced the morphology of metallic compounds on AV-17(Bi, Al) granule surface.

The elemental composition of metal-containing structural unites is listed in Table II.

As it follows from the Table II data, the Bi(III)-containing compounds are concentrated in the large particles on the surface and in the volume of the polymer granule. Using the data from Table II, the brut formula of the metal-containing structural units was computed. The brut formula of the structural units on the surface of the polymer granule is $Al_1O_{58.8}S_9C_{288}$ for small particles and $Bi_1Al_{0.02}O_{1.8}Cl_{0.8}C_{3.7}$ for large particles. In the volume of the polymer granule, the brut formula of the structural units is $Al_1O_{78.8}S_{10.8}C_{409}$ for small particles and $Bi_1Al_{0.07}O_{7.9}C_{25.9}$ for large particles. The small particles on the surface and in the volume of the polymer granule do not contain Bi(III) and Cl$^-$ ions. The large particles on the polymer granule surface do not contain sulfur atoms and in the granule volume do not contain sulfur and chlorine atoms. Therefore, the composition of the small and the large metal-containing particles, on the surface and in the volume of the polymer granule is different.

As it is seen in the Table II data and in brut formula, the metal-containing structural units contain a large number of carbon atoms. The metal-containing compounds cannot contain atoms of carbon; therefore, they belong to AV-17 polymer chain and its functional groups.

The X-ray diffractogram [Fig. 2(a)] of the AV-17(Bi,Al) sample is a typical spectrum of an amorphous polymer with the large broadening diffraction peaks corresponding to interplanar distances with d = 4.7 and 2.5 A^0. A sharp diffraction peaks are located on the polymer matrix curve correspond to crystalline phase of the BiOCl. Therefore, a part of Bi(III)-containing compounds represents a crystalline
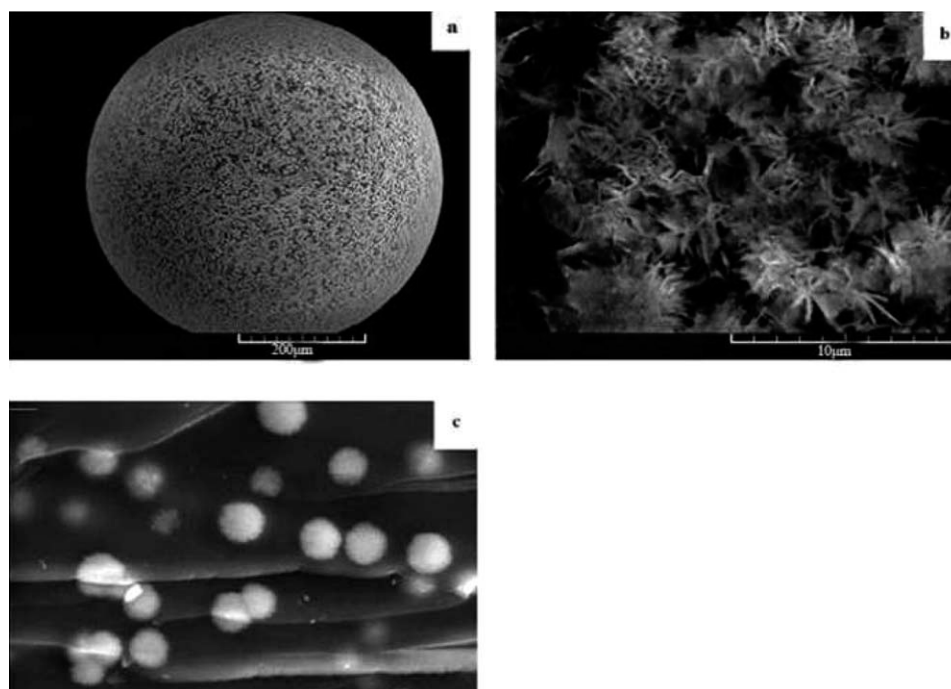
Figure 1 SEM images of the metal-containing compounds on the surface (a, b) and in the volume (c) of the AV-17(Bi, Al) polymer granule.

BiOCl which is only in the large particles on the polymer granule surface. According to the brut formula of the large particles situated on the surface of the polymer granule, Bi atoms are more than Cl ones. Therefore, we conclude that in the polymer phase exists and other compounds of Bi (III) then BiOCl. It is likely that these compounds are BiOOH because the color of the sample is the same (yellow) as BiOOH. The Al(III) compounds are probably of alunite-jarosite type. Content of the oxygen atoms in the composition of the metal-containing structural units is much more than is necessary to form BiOCl, BiOOH, Al(OH)$_3$, and jarosite type compounds, especially in the smaller particles. The AV-17 polymer matrix does not contain oxygen atoms. We propose that metal-containing particles are situated on functional groups and chains of AV-17 polymer, the oxygen and carbon atoms of the [-N(CH$_3$)$_3$]$_2$SO$_4$ groups being included in the structural unites.

Under the preparation of metal-containing polymer samples, the AV-17(Cl) was in contact with Bi(NO$_3$)$_3$ and then with Al(III), Fe(III), or Cr(III) sulfate solutions. Therefore, besides the formation of metallic compounds, in the polymer phase processes (6) and (7) took place:

$$R_4NCl + NO_3^- \leftrightarrow R_4NNO_3 + Cl^- \qquad (6)$$

$$2R_4NNO_3 + SO_4^{2-} \leftrightarrow (R_4N)_2SO_4 + 2NO_3^- \qquad (7)$$

The FT-IR spectra of all metal-containing polymer samples investigated in this article, contain intensive peaks at 1110 and 616 cm^{-1} which belong to SO$_4^{2-}$ ions and at 1384 and 1352 cm^{-1} attributed to NO$_3^-$ ions[18] (Fig. 3). As it is seen in Table II, the composition of the metal-containing structural units in the AV-17(Bi,Al) sample do not contain N atoms. The sulfur atoms contain only small particles. The data confirm that metal-containing particles are situated on the [—N(CH$_3$)$_3$]$_2$SO$_4$ and —N(CH$_3$)$_3$NO$_3$ polymer's groups and oxygen and carbon atoms of these groups are included in the composition of the structural units. As it is seen in Table II, the large particles contain more oxygen and less carbon atoms than the small particles.

The AV-17(Bi, Fe) sample

The SEM images of the AV-17(Bi,Fe) polymer granule are presented in the Figure 4. As it is seen in Figure 4(a,b), the polymer granule surface is covered with amorphous metallic compounds. In the volume of the polymer granule, there are two kinds of particles (Fig. 4c).The biggest particles have a pseudo spherical form with 4–5 μm diameter. The Table II data show that Bi(III) containing compounds are concentrated on the surface of the polymer granule. In the volume of the polymer granule, the small particles do not contain Bi and the large particles do not contain chlorine and sulfur atoms. The brut formula of the metal-containing structural unit on the polymer granule surface is Bi$_1$Fe$_{0.05}$O$_{1.47}$Cl$_{0.93}$C$_{1.42}$.

TABLE II
Elemental Composition of Metal Containing Structural Units on the Surface and in Volume of A V-17 Granule

| | On the surface of polymer granule, Atoms | | | | | | | In the volume of polymer granule, Atoms (%) | | | | | | |
| | AV-17(Bi. Al) | | AV-17 (BL, Fe) | AV-17 (Bi, FeOOH) | AV-17 (Bi. Cr) | AV-17 (Bi, Fe. Cr) | AV-17 (Bi. FeOOH, Cr) | AV-17 (Bi, Al) | | AV-17 (Bi, Fe) | | AV-17 (Bi, FeOOH) | AV-17 (Bi, Fe, Cr) | AV-17 (Bi, FeOOH, Cr) |
Element	Small particles	Large particles						Small particles	Large particles	Small particles	Large particles			
Bi	–	13.51	20.52	6.36	0.44	14.73	19.19	–	2.75	–	8.69	3.06	1.54	0.16
Al	0.28	0.30	–	–	–	–	–	0.20	0.20	–	–	–	–	–
Fe	–	–	1.07	19.83	–	–	–	–	–	0.96	1.85	0.83	0.12	0.19
Cr	–	–	–	–	4.37	1.94	1.88	–	–	–	–	–	0.81	0.93
Cl	–	11.41	19.06	6.24	–	15.54	19.8	–	–	0.45	–	3.07	1.48	0.41
S	2.52	–	–	4.89	6.30	–	–	2.15	–	2.74	–	2.83	2.39	4.03
O	16.48	24.66	30.21	36.59	15.44	23.52	28.90	15.74	21.74	9.09	17.80	8.34	11.59	7.00
C	80.73	50.13	29.13	26.09	73.44	44.28	30.32	81.91	71.31	86.72	71.66	81.86	82.06	87.28

The brut formula of the structural unit of the small particles in the volume of the polymer granule is $Fe_1O_{9.47}Cl_{0.47}C_{90.3}$ and of the large particles is $Bi_1Fe_{2.1}O_{2.05}C_{8.25}$. According to the Figure 2(b), the content of the crystalline phase of BiOCl in the AV-17(Bi,Fe) is less than in the AV-17(Bi,Al) sample. Because the AV-17(Bi,Fe) sample was prepared at less temperature than AV-17(Bi,Al), in the first sample a large part of the BiOCl remained in amorphous state. Only small particles in the volume of the polymer granule contain jarosite type compounds. The Fe-containing compounds on the polymer granule surface and in the large particles in the polymer granule volume probably is FeOOH. The metal-containing particles are situated on functional groups of the polymer, and a part of C and O atoms are involved in composition of the structural units.
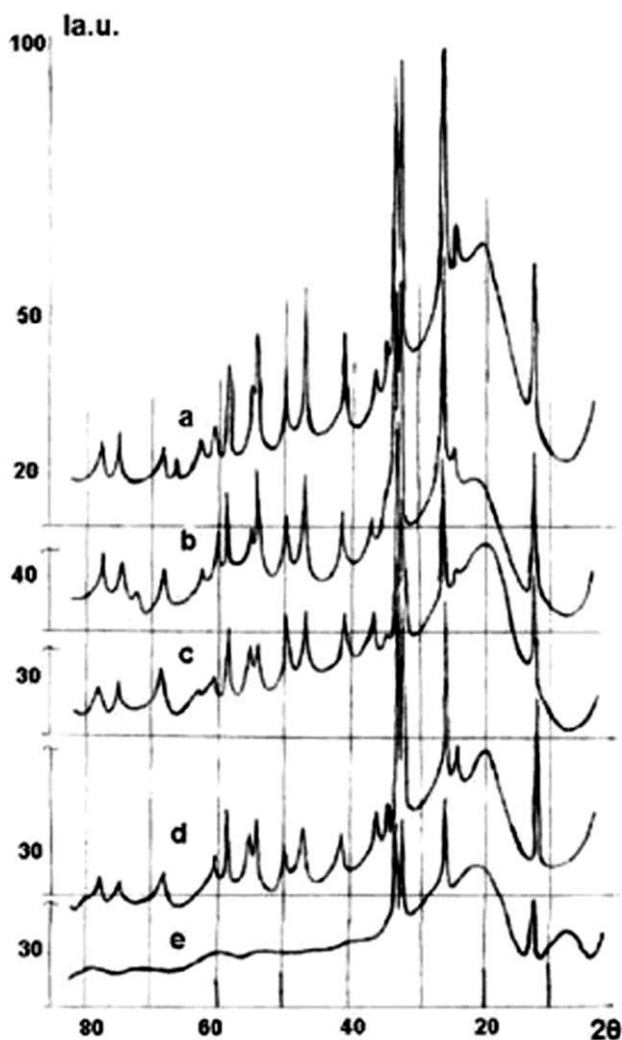

Figure 2 X-ray diffraction spectra of the AV-17(Bi, Al) (a), AV-17(Bi,Fe),(b) AV-17(Bi,FeOOH)(c), AV-17(Bi,Cr) (d), AV-17(Bi,Fe,Cr), and (e) samples.
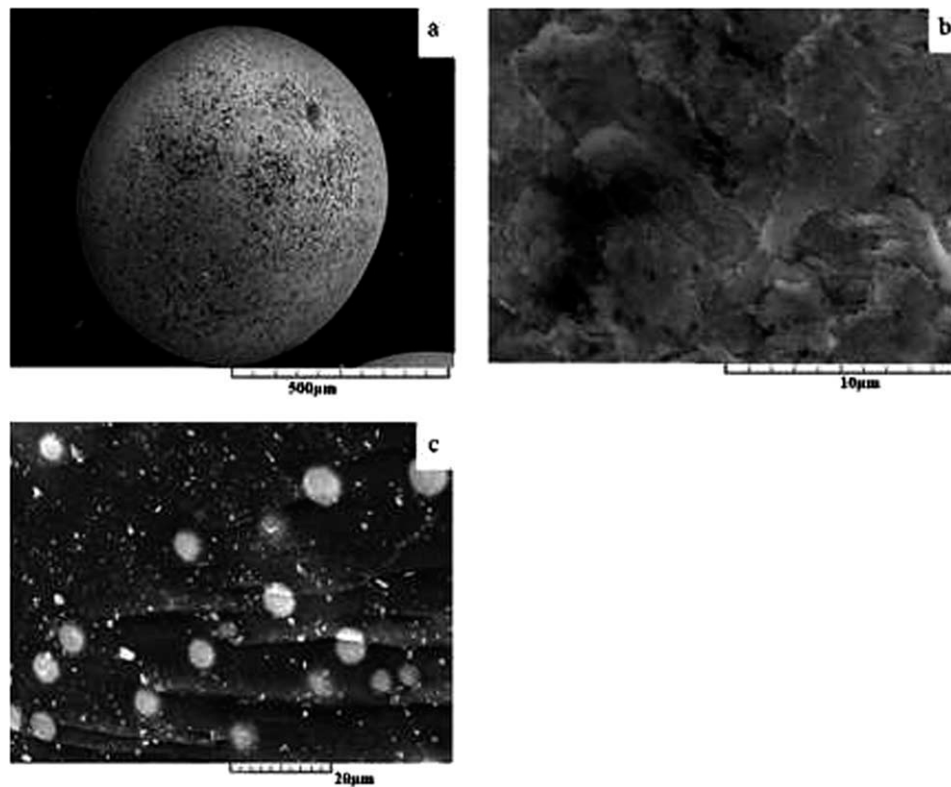
Figure 3 FT-IR spectra of the AV(Bi), (1) AV(Bi,Al) (2) and AV(Bi,Fe) polymer samples.

The AV-17(Bi,FeOOH) sample

The AV-17(Bi,FeOOH) was obtained from AV-17(Bi,Fe) sample by heating in water medium on boiling water bath. The morphology of the metal-containing particles in AV-17(Bi,Fe) and AV-17(Bi,FeOOH) samples differ very much. As it is seen in Figure 5(a,b), the surface of the polymer granule is covered with metal-containing particles, most of which are in amorphous state. The pseudo spherical particles in the volume of the polymer granule represents clews of nanometer fibers (Fig. 5c,d).

The elemental composition of the metal-containing structural units on the surface and in the volume of the AV-17(Bi,FeOOH) granule is shown in the Table II. The Table II data permitted us to calculate brut formula of the structural units which is $Bi_1Fe_{0.27}O_{2.72}Cl_{1.0}$ $S_{0.92}C_{26.71}$ in the volume and $Bi_1Fe_{3.12}O_{5.75}Cl_{1.0}$ $S_{0.98}C_{4.1}$ on the surface of the polymer granule. The Table II data show that on heating of AV-17(Bi,Fe) in water medium on boiling water bath, besides the transformation of compounds, the migration the of Fe(III)-containing compounds to the polymer granule surface takes place. On the polymer

Figure 4 SEM images of the metal-containing compounds on the surface (a, b) and in the volume (c) of theAV-17(Bi, Fe) polymer granule.
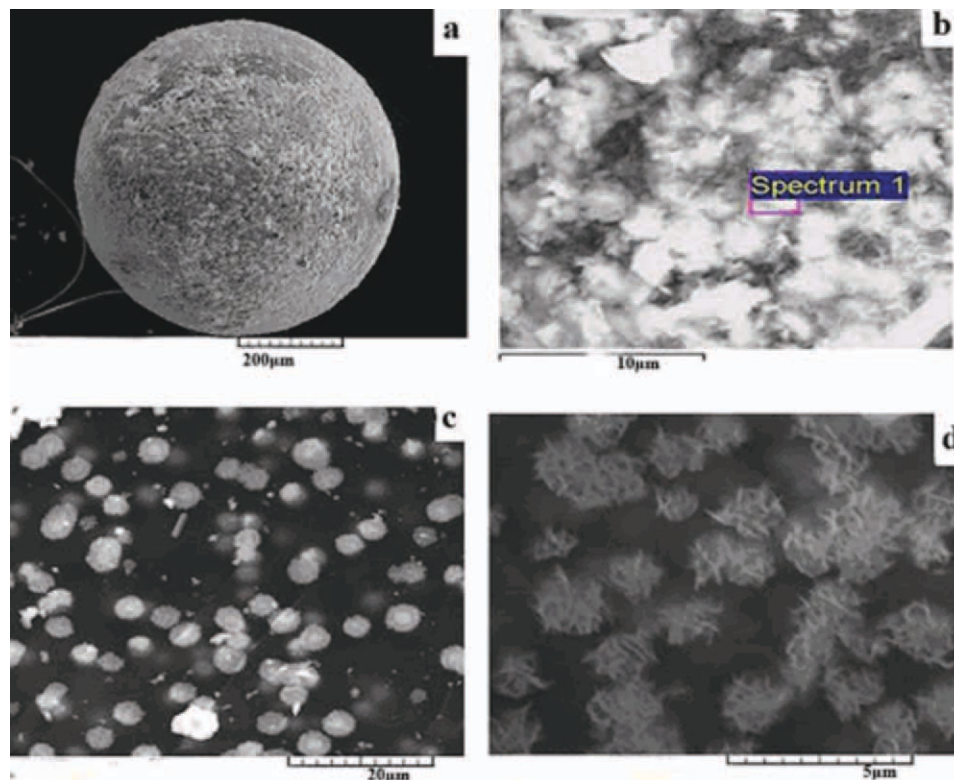

Figure 5 SEM images of the metal-containing compounds on the surface (a, b) and in the volume (c, d) of the AV-17(Bi, FeOOH) polymer granule. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
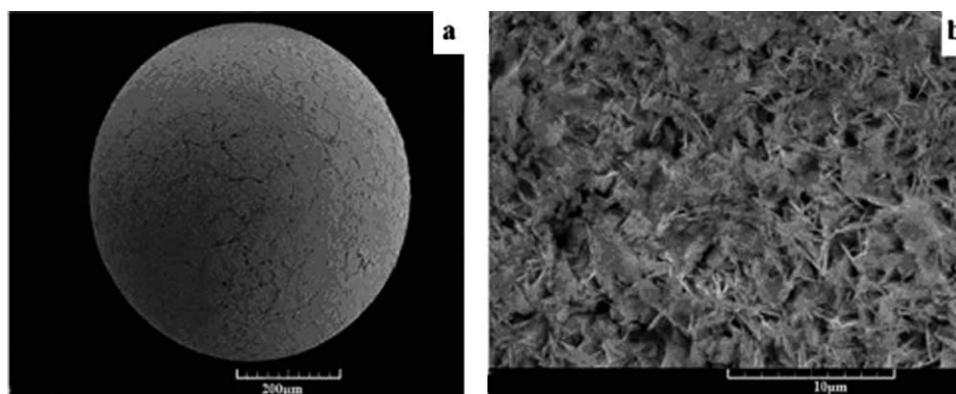
Figure 6 SEM images of the metal-containing compounds on the surface (a, b) of the AV-17(Bi, Cr) polymer granule.

granule surface, there is some crystalline BiOCl (Fig,2(c)) and much FeOOH. In the polymer granule volume, there is a compound containing both Bi(III) and Fe(III) ions. The compounds in the form of clew may be $Bi_xFe_{(1-x)}OOH$ which contains some of Cl^- ions. It is known[19,20] that β-FeOOH forming process takes place in the presence of Cl^-(or F^-) ions which entered in the β-FeOOH structure.[21,22] If to take into consideration a large content of carbon, oxygen, and sulfur atoms in the composition of metal-containing structural units, we can suggest that metallic compounds particles are situated on the polymer functional groups, especially on the $[-N(CH_3)_3]_2SO_4$ groups.

The AV-17(Bi, Cr) sample

The SEM images of the AV-17(Bi,Cr) polymer granule are shown in Figure 6. As it is seen in Figure 6, practically all metal-containing compounds are on the surface of the polymer granule. The polymer granule surface is covered with a dense layer of amorphous and crystalline compounds [Fig. 6(a,b)]. This layer of compounds on the polymer surface may influence considerable the sorption and catalytic kinetics on AV-17(Bi,Cr). The elemental composition of metal-containing structural unit on the polymer granule surface is shown in the Table II. The brut formula of the structural unit is $Bi_1Cr_{9.93}O_{35.09}S_{14.32}C_{166.9}$. As it is seen in the brut formula of the structural unit, there are no chlorine atoms, in its composition, although some crystalline BiOCl in the AV-17(Bi,Cr) phase was detected (Fig. 2d). Perhaps BiOCl crystals are in the volume of the polymer granule. The Cr(III) compounds in the polymer granule volume likely are of jarosite type. The metallic compounds particles are situated on the $[-N(CH_3)_3]_2SO_4$ polymer functional groups

The AV-17(Bi,Fe,Cr) sample

The SEM images of the AV-17(Bi,Fe,Cr) polymer granule are shown in Figure 7. In Figure 7(a,b), it is seen that polymer granule surface is covered with amorphous and crystalline metallic compounds. These compounds contain only Bi(III) and Cr(III) metallic cations. They do not contain Fe(III) cations and SO_4^{2-} ions (Tab. II). It means that upon AV-17(Bi,Fe,Cr) sample preparing from AV-17(Bi, Fe), the Fe^{3+} cations are replaced by Cr^{3+} cations and passed in liquid phase (in $KCr(SO_4)_2 \cdot 12H_2O$ solution). The elemental composition of the metal-containing structural unit on the surface of the polymer granule is $Bi_1Cr_{0.13}O_{1.6}Cl_{1.05}C_3$ and in the volume $Bi_1Fe_{0.08-}Cr_{0.53}O_{7.53}Cl_{0.96}S_{1.6}C_{53.3}$. The Fe(III) containing compounds are only in the volume of the polymer granule. The passing of Fe(III) ions from polymer granule to $KCr(SO_4)_2 \cdot 12H_2O$ solution, on AV-17(Bi,Fe,Cr) preparation using AV-17(Bi,Fe), is confirmed by small content of Fe (III) in the polymer phase (Tab.I). Taking into the consideration the content of sulfur and oxygen atoms in the structural units in the volume of the polymer granule, it may be suggested that there are compounds of jarosite type. In the AV-17(Bi,Fe,Cr) sample, there is some crystalline BiOCl, but less than in the precedent examined samples of metal-containing polymer [Fig. 2(e)]. A new interesting fact was observed on AV-17(Bi,Fe,Cr) sample investigation. In diffractogram of this sample [Fig. 2(e)], in spectrum of amorphous phase of the AV-17 polymer, in low range of 2θ angles, a new maximum appeared. After desorption of metals, this maximum despaired. It means that a part of the AV-17 polymer chains, including functional groups, is involved in metal-containing structural units.

The AV-17(Bi,FeOOH,Cr) sample

The surface of the polymer granule of this sample is covered with metal-containing compounds in
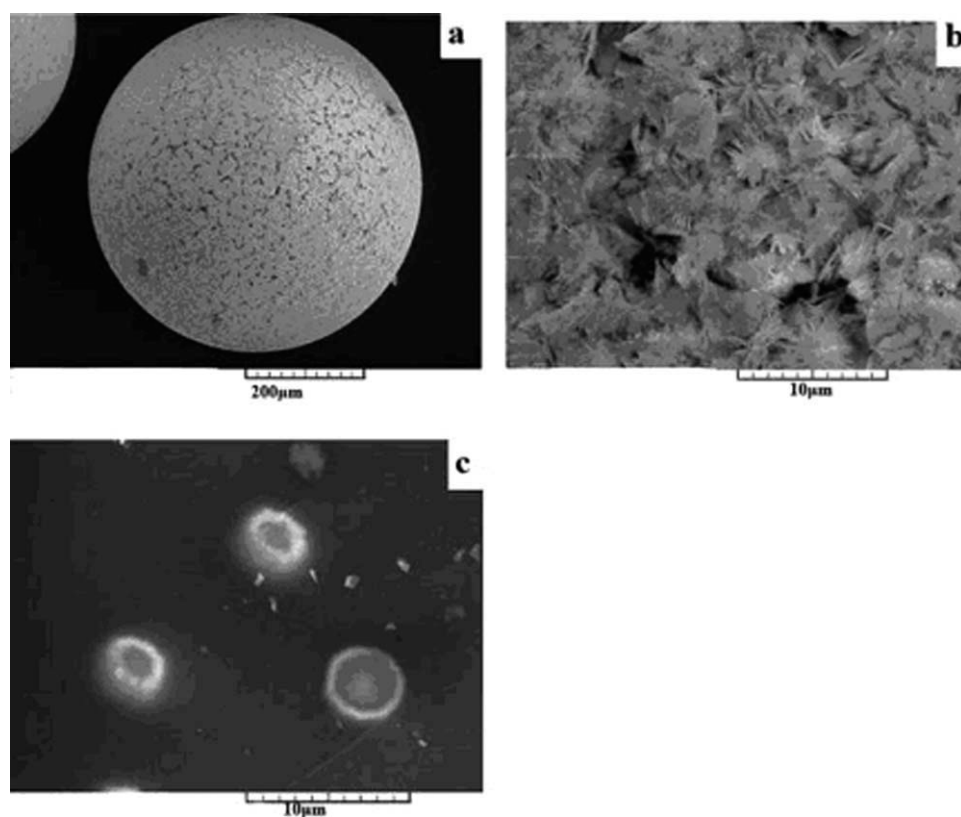
Figure 7 SEM images of the metal-containing compounds on the surface (a, b) and in the volume (c) of the AV-17(Bi, Fe,Cr) polymer granule.
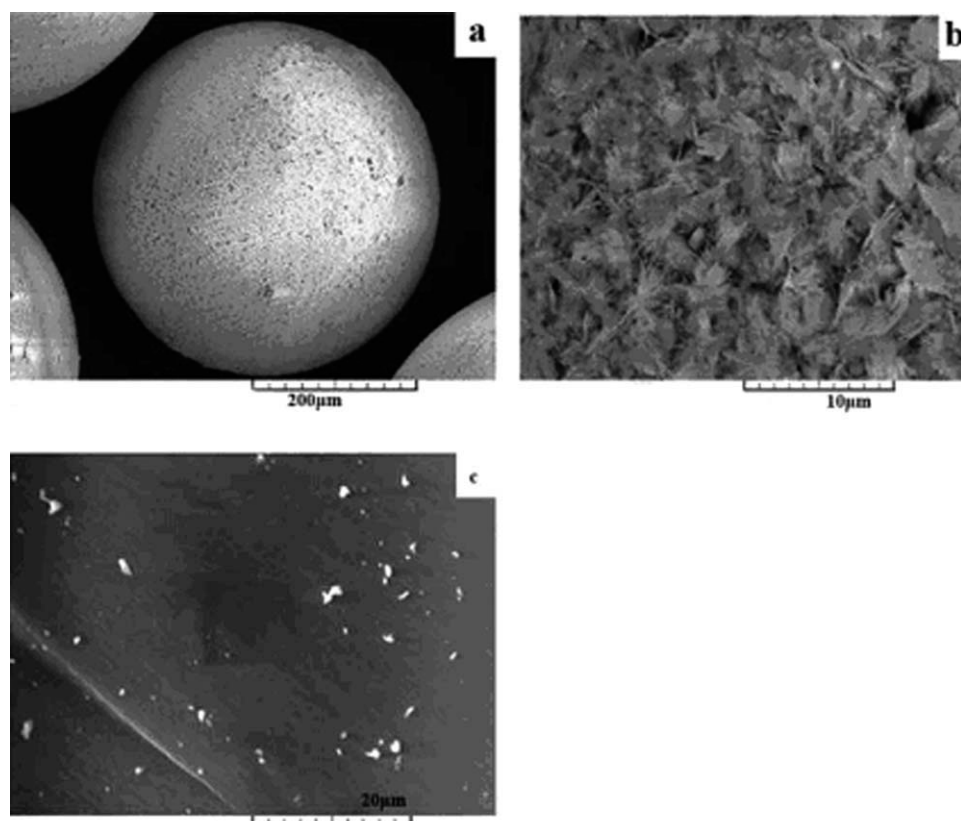

Figure 8 SEM images of the metal-containing compounds on the surface (a, b) and in the volume (c) of the AV-17(Bi, FeOOH,Cr) polymer granule.
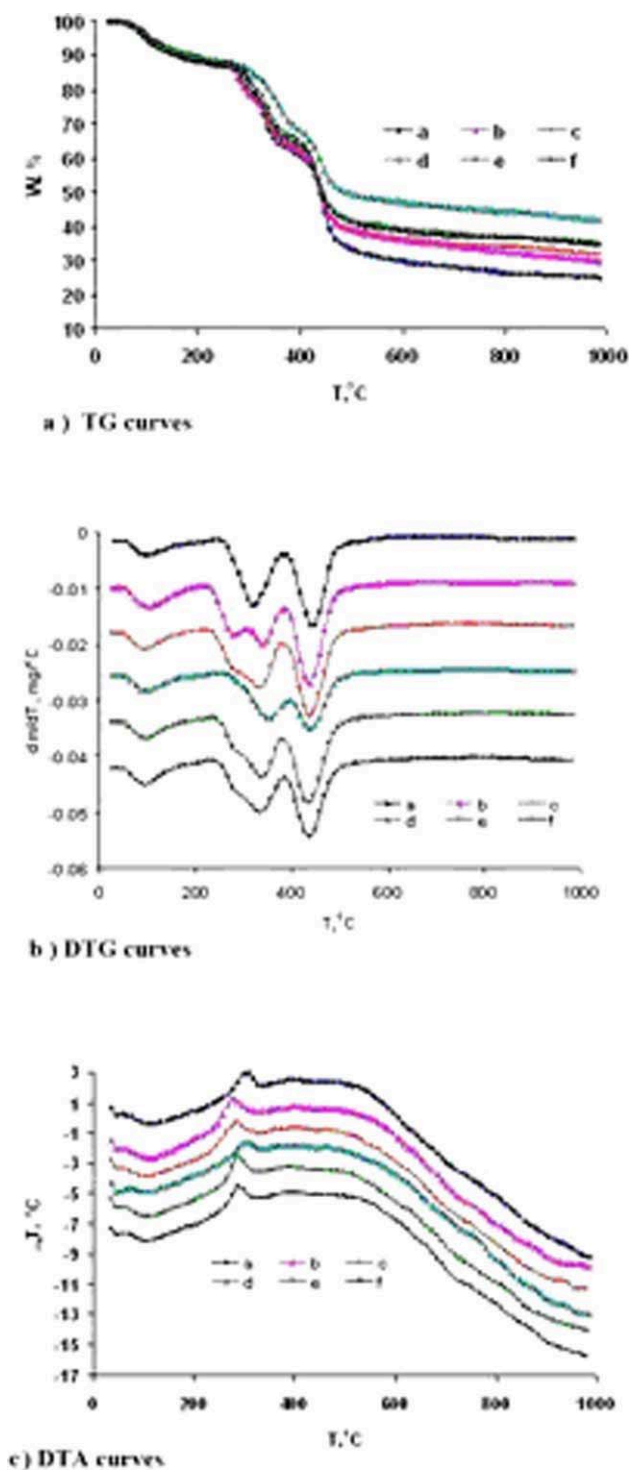
a) TG curves

b) DTG curves

c) DTA curves

Figure 9 TG, DTG and DTA curves of the AV-17(Bi, Al) (a), AV-17(Bi,Fe),(b) AV-17(Bi,FeOOH) (c), AV-17(Bi,Cr) (d), AV-17(Bi,Fe,Cr) (e), and sAV-17(Bi,FeOOH,Cr) (f), samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crystalline and amorphous state [Fig. 8(a,b)]. The morphology of the metal-containing compounds particles on the polymer granule surface looks like as in cause of AV-17(Bi,Fe,Cr) sample [Fig. 7(a,b)]. The morphol-

ogy of the particles in the volume of the polymer granule of the AV-17(Bi,FeOOH,Cr) [Fig. 8(c)] and AV-17(Bi,Fe,Cr) [Fig. 7(c)] is quite different. From Table II data, it is seen that metal-containing compounds are accumulated on the polymer granule surface of the AV-17(Bi,FeOOH, Cr). The brut formula of the metal-containing structural unite on the polymer granule surface is $Bi_1Cr_{0.1}O_{1.5}Cl_{0.99}C_{1.57}$ and in the granule volume is $Bi_1Fe_{1.19}Cr_{5.81}O_{36.8}Cl_{2.16}S_{25.2}C_{459}$. In the composition of the metal-containing compounds on the polymer granule surface, there are not Fe^{3+} and SO_4^{2-} ions (Table II), and therefore, jarosite type compounds are absent. There is some BiOCl in the crystalline state and may be the $Bi_xCr_{(1-x)}OOH$. In the volume of the polymer granule there is Cr(III)-jarosite type compounds and β-FeOOH.

Thermal behavior of metal-containing samples

The thermal behavior of the metal-containing polymer samples was evaluated by dynamic thermogravimetrical analysis in nitrogen gas, at heating rate of 20°C/min. The TG, derivative TG (DTG) and differential thermal analyses (DTA) curves, recorded under the same experimental conditions, are presented in the Figure 9.

The summary of the important TG characteristics of the sample obtained from the thermograms are listed in the Table III. For every sample, the degradation processes are not complete, for each case a residue being left. Table III reveals the TGA data such as T_i—the initial temperature thermal degradation, T_m—the temperature corresponding to the maximum degradation rate, T_f—the final temperature at which the degradation process for each step ends, and mass loss (W %), corresponding for each step.

The Table III data indicate that the thermal degradation mechanism of investigated samples is complex and occurs in several steps.

The samples AV-17(Bi,Al) and AV-17(Bi,Cr) exhibited three steps of degradation having the maximum decomposition temperature in the range 85–95°C, 319–349°C, and 440–442°C, respectively. The further samples exhibited four steps of degradation having the maximum decomposition temperature in the range 88–97°C, 272–295°C, 342–345°C, and 434–438°C, respectively. The char yields of 1000°C were in the range 25–41%.

The first step (65–175°C) for the all samples is assignable to the loss water from their structures.

The thermal degradation in the nitrogen atmosphere of the samples AV-17(Bi,Al) and AV-17(Bi,Cr) indicate one exothermic peak at 307°C and, for the further metal-containing polymer samples, at 287°C.

The most important mass loss for the all samples has been recorded in the last stage of the thermal degradation, at temperatures onset over about

TABLE III
Thermogravimetrical and Kinetic Data Obtained, of the Samples AV-17(Bi, Al) (a), AV-17(Bi, Fe) (b),
AV-17(Bi, FeOOH) (c) AV-17(Bi, Cr) (d), AV-17(Bi, Fe, Cr) (e), AV-17(Bi, FeOOH, Cr) (f)

Sample	Step	T_i, [°C]	T_m, [°C]	T_f, [°C]	W, [%]	Residue, [%]	E_a, [kJ/mol]	n	$\ln A$
AV-17 (Bi, Al)	I	66	95	175	13.44	–	18.11 ± 0.29	1.7 ± 0.007	0.53 ± 0.04
	II	289	319	346	24.66	25.00	58.91 ± 1.23	0.88 ± 0.002	7.05 ± 0.15
	III	418	442	464	36.90	–	447.98 ± 5.74	2.95 ± 0.004	72.20 ± 1.00
AV-17 (Bi, Fe)	I	67	97	150	11.43	–	35.06 ± 0.27	2.20 ± 0.003	6.42 ± 0.27
	II	263	272	291	11.41	28.81	281.48 ± 2.98	2.31 ± 0.002	58.16 ± 0.67
	III	310	344	365	14.88	–	299.84 ± 4.34	2.84 ± 0.004	56.03 ± 0.89
	IV	407	436	467	33.47	–	374.67 ± 2.79	2.55 ± 0.002	60.17 ± 0.49
AV-17 (Bi, FeOOH)	I	65	88	156	10.95	–	40.96 ± 1.33	2.72 ± 0.006	8.74 ± 0.46
	II	259	277	295	11.59	31.28	205.90 ± 2.3 2	1.16 ± 0.002	40.67 ± 0.52
	III	320	342	354	14.75	–	469.22 ± 2.21	2.61 ± 0.001	90.43 ± 0.45
	IV	416	438	465	31.43	–	391.37 ± 1.99	2.33 ± 0.001	62.81 ± 0.35
AV-17 (Bi, Cr)	I	68	85	215	12.40	–	31.78 ± 0.93	2.50 ± 0.010	27.01 ± 0.17
	II	291	349	380	21.43	41.01	161.80 ± 2.54	1.63 ± 0.003	27.01 ± 0.17
	III	405	440	477	25.16	–	424.39 ± 6.12	3.17 ± 0.004	68.37 ± 1.06
AV-17 (Bi, Fe, Cr)	I	71	91	170	11.95	–	41.36 ± 0.96	2.81 ± 0.001	8.82 ± 0.91
	II	272	287	305	8.78	–	352.6 ± 1.74	1.62 ± 0.008	72.35 ± 0.38
	III	323	345	351	13.18	34.10	437.99 ± 2.40	2.27 ± 0.001	83.15 ± 0.48
	IV	409	435	470	31.99	–	364.26 ± 1.59	2.73 ± 0.005	58.34 ± 1.32
AV-17 (Bi, FeOOH, Cr)	I	66	89	141	12.98	–	53.88 ± 0.81	2.22 ± 0.002	13.30 ± 0.28
	II	276	295	310	9.41	33.70	28.9.90 ± 0.93	1.17 ± 0.006	58.55 ± 0.20
	III	321	342	350	13.36	–	338.31 ± 1.70	1.76 ± 0.008	63.35 ± 0.34
	IV	418	437	466	30.55	–	373.10 ± 1.20	2.55 ± 0.006	59.93 ± 2.10

410°C. Comparing the DTG curve in the Figure 8, it can be found that the degradation curves of the six samples are close to each other in shape in the last stage, the temperature corresponding to the maximum degradation rate is about 438°C

The surveys were extended with the kinetic processing of thermogravimetric data. Freeman-Caroll[23] method application is based on the Eq. (8) considers incremental differences in ($d\alpha/dT$), ($1 - \alpha$) and ($1/T$):

$$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1 - \alpha)} = n - \frac{Ea}{R} x \frac{\Delta(\frac{1}{T})}{\Delta \ln(1 - \alpha)} \quad (8)$$

where α is a normalized fractional conversion and is defined as:

$$\alpha = \frac{m_i - m(t)}{m_i - m_f} \quad (9)$$

$m(t)$ is the mass at any time t, and m_i and m_f, respectively, are the initial and final sample mass; E is activation energy; n is the reaction order, R is the universal constant of gases, and T is the temperature in K; has lead to the kinetic characteristics shown in Table III.

By plotting the graph of $\Delta\ln(d\alpha/dT)/\Delta\ln(1 - \alpha)$ dependent on $\Delta(1/T)/\Delta\ln(1 - \alpha)$ from the line slope, we can compute the activation energy E, and from origin interception, we get the reaction order n. The pre-exponential factor is computer by the equation:

$$\frac{d\alpha}{dT} = \frac{1}{a} A \exp\left(\frac{-Ea}{RT}\right) f(\alpha) \quad (10)$$

The reaction order (n) and activation energy (E) values (Table III), indicate that the thermal decomposition of the metal-containing polymer samples is a complicated process.

The small difference in the Tm values (436, 438, 435, and 437°C) and that in the values of the activation energies (375, 391, 363, and 373 kJ/mol), suggest the same degradation mechanism in the last stage of thermal degradation for the samples AV-17 (Bi,Fe), AV-17(Bi,FeOOH), AV-17(Bi,Fe,Cr), and AV-17(Bi,FeOOH,Cr).

CONCLUSIONS

By consecutive operation, the compounds of Bi(III) and Al(III); Bi(III) and Fe(III); Bi(III) and FeOOH; Bi(III) and Cr(III); Bi(III), Fe(III), and Cr(III); Bi(III), FeOOH, and Cr(III) were obtained in the phase of the commercial strongly basic anion exchanger AV-17, containing —N(CH$_3$)$_3$Cl groups. By the SEM it was shown that metallic compounds in the polymer phase were in form of ultra dispersed particles of different morphology. The main part of the metal-containing compounds is on the surface of the polymer granules. In some causes the polymer granules surface is covered with a layer of compounds in amorphous and crystalline states. The morphology of the metal-containing particles on the polymer granules surface and in the granule volume is different. Also differ and composition of the metal-containing structural units of small and large particles on the surface and

in the volume of the polymer granule, of small and large particles. The metal-containing structural unites involved in their composition and atoms (O, S, and C) of the $[-N(CH_3)_3]_2SO_4$ and $-N(CH_3)_3Cl$ functional groups.

The powder X-ray diffraction showed that in the all polymer samples there was only one compound in crystalline state BiOCl, other being amorphous FeOOH, BiOOH, $Bi_xCr_{(1-x)}OOH$, $Bi_xFe_{(1-x)}OOH$, and jarosite type compounds. The FT-IR spectra showed that all metal-containing polymer samples contain and $-N(CH_3)_3NO_3$ groups, although N atoms were absent in the composition of metal-containing structural unites.

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