METALLIC COMPOUNDS IN THE PHASE OF THE RETICULATED IONIC POLYMERS

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Abstract: In this review there are described the results of studying of iron ions state in the ion-exchange resins (KU-2, AN-31, AV-17, Varian – AD, EDE-10P), obtained by Mossbauer spectroscopy. The iron ions have been sorbet on ion exchangers, from aqueous solutions at different temperatures and air conditions. The iron state in polymer phase depends of nature of electron donor groups - amine or carboxylic. To explain the form and temperature dependence of Mossbauer spectra of polymer phase containing iron it was proposed the presence of different compounds like β-FeOOH, α-Fe$_2$O$_3$, and jarosite mineral type compounds: $(R_4N,H_3O)[Fe_3(OH)_6(SO_4)_2]$ or coordination modes: $\{RCOO\text{-}Fe(L_4)\text{-}OOCR\}^{1+}$, $\{R\text{-}CO_2=Fe(X_2)=O_2C\text{-}R\}n$, $\{R\text{-}COO\text{-}Fe(X_4)\text{-}OOC\text{-}R\}n$, and $\{(\text{-}NCH2CH2N\text{-})= Fe(X_2) =(\text{-}NCH_2CH_2N\text{-})\}$, where X= H$_2$O, OH-, SO$_4$$^{2-}$., n= from 3- to 1+. In special conditions the ultrafine superparamagnetic particles of Fe$_2$O$_3$ have been obtained.

Keywords: ion exchangers, Mossbauer spectra, iron, superparamagnetic, complexes, polymer phase.

Introduction

Reticulated ionic polymers produced in large amounts by chemical industry are widely used as ion exchangers in the water treatment of thermal and nuclear electric power plants, in waste-water and gas purification, in separation and concentration of substances, as well as in acid-basic catalysis. The ion exchange process is conditioned by electrostatic Coulomb interactions between atoms with definite electrical charges located in the polymer matrix and mobile ions (contrioni). Therefore, this process is virtually no selective in retention of micro-molecular ions.

In many cases the ion exchange is accompanied by other secondary, often uncontrolled, processes that affect polymers during their use. The ion exchangers are frequently poisoned by iron compounds, which results in reduction their service life and involve considerable additional expenses on chemical reagents and water for their regeneration [1-3]. Often the processes of the ion exchangers "poisoning" are irreversible [3]. All types of ion exchangers are "poisoned" by iron compounds. Poisoning via iron compounds presence can occur even during exchangers' production [4] by acids or bases solutions, not enough pure [5].
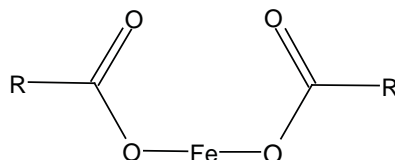
Reticulated ionic polymers containing electron donor atoms (amino groups, phenolic, carboxylic, etc..) can simultaneously participate to complexing mechanisms besides ion exchange process, too. Complexing metal cations by poly-ligands is a relatively new direction in the chemistry active polymers [6.7].. The synthesis of metal compounds in the form of ultrafine particles in the polymer phase is considered to be a new direction in physical chemistry of chemically active polymers [8, 9]. Polymers loaded with metallic compounds significantly change their physico-chemical properties. They can become catalysts [10], selective sorbents [11-14], biochemical models of transport substances [15] as well as models for experimental research of relaxation processes [16]. In order to use the metal containing polymers in different physical or chemical processes – it is necessary to know and to control the conditions of loading these metal compounds and, especially to induce the right metal cation state in the polymer phase. Knowing exactly the ions' state in polymer phase is quite difficult for several reasons. Firstly, the polymers of this class are amorphous and reticulated, which limits the number of suitable investigation methods. Secondly, the loading processes of reticulate ionic polymers with metal compounds gives simultaneously rise to other concurrent processes, and an ion exchange is generally required.

These processes depend on several factors such as nature and concentration of electrolyte, temperature, pH of the solution, contact time with the polymer solution. The processes evolve either in static or in dynamic conditions, while the presence of air in the system, nature and concentration of organic solvent, could directly or indirectly influence the processes of formation of metal compounds inside the polymer. The best methods of studying metal and non-metal ions parameters and properties in the reticulated polymer phase are the Mossbauer spectroscopy, ESR, IR, and magnetic measurements.

Results and Discussion

State of ions in the ionic reticulated polymer phase containing carboxylic groups

As a results of the investigations using potentiometric method and IR spectroscopy [17] it is known that in carboxylic polymer SG-1 type at contact with a solution of 0.003 - 0.5 M Fe (NO_3) 3 in 0.5 M $NaNO_3$ in a pH range 1-2.5 the complexes of the typeare formed.
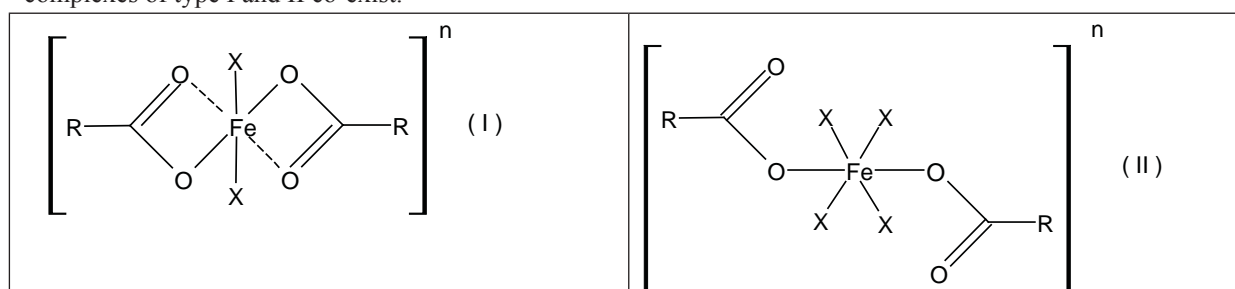

They are stable in the pH range 2.5 ~ 5.0. These complexes decompose in solutions with pH> 7 and γ-FeOOH phase is formed. According to [18], a Fe^{3+} ions from the solution of $FeCl_3$ are retained by the KB-4 polymer as a result of complexing process via carboxylic groups with final formation of a precipitate.

The presence of solvent in the polymer phase leads to increasing of Fe^{3+} ions oscillation amplitude and electric field gradient (EFG) on their nucleus. The solvent (H_2O), which molecules coordinate to metal ions, primarily affects the ion oscillations in chemical bond with ligand, as well as the oscillation of the polymer chain. The non-polar solvent influences primarily, on chain oscillation. Various measurements [19] show that the Mossbauer spectra (MS) of Fe^{3+} ions in carboxylic polymer phase (КБ-2 and others) exhibit doublet patterns. The observed differences, often essential, of iron ions state in carboxylic polymer phase [18-20] confirm that it depends on many factors, which are not always taken into account.

It is surprising that the nature of anions (Cl^-, SO_4^{2-}) influence Fe^{3+} cations complexation with carboxylic groups of cationite. Increasing of the concentration of either Cl^- or SO_4^{2-}anions have induced a diametrically opposite influence on the sorption of Fe^{3+} ions by KB-2 cationite [21].

Sorption of Fe(II) from tartaric acid solutions (0.005 N of Mohr salt, 10 mmol / L of tartaric acid) by KB-2 polymer occurs in the pH range 3-9 with a maximum at pH 6.5. In the polymer phase almost all Fe^{2+} ions being oxidized up to Fe^{3+} [22].

The Fe^{2+} and Fe^{3+} ions in cationite KB-2 phase retained from solutions of 0.005 N $^{57}Fe_2$ $(SO_4)_3$ (pH 2), $FeSO_4$ (inert gas atmosphere, pH = 5), $(NH_4)_2Fe(SO_4)_2$ in 0,01M tartaric acid (pH 5) are found in the high-spin state and in octahedral environment [19]. By keeping in air atmosphere, the oxidation of Fe^{2+} ions in the KB-2 polymer phase ends up to Fe^{3+} is occurred. But the state of oxidized ions differs from the state of Fe^{3+} ions absorbed from the Fe_2 $(SO_4)_3$ solution as described in the followings. The Fe^{2+} ions retained from $FeSO_4$ solutions are complete oxidized, and those retained from $(NH_4)_2Fe(SO_4)_2$ solutions are only partially oxidized. Existence of tartaric acid in the system from where the Fe^{2+} ions were detained from contributes to their oxidation during the storage of polymer in the air [19]. Asymmetrical lines in Mossbauer spectra of KB-2 samples, containing Fe^{3+} obtained as a result of air oxidation of Fe^{2+} ions, may be as the results that some Fe^{3+} ions are in the form of precipitate and need supplemental investigation. Although the presence of Cl^- and SO_4^{2-} anions influence in different mode on Fe^{3+} sorption by KB -2, the stabilized state of Fe^{3+} ions practically does not depend on the nature of anions in polymer phase. It is assumed that in polymer phase one part of Fe^{3+} ions is in the form of γ-FeOOH. Fe^{3+} ions from the $Fe_2(SO_4)_3$ solution with pH 1.2 are retained by the KB-2 polymer due to of their complexation with carboxylic groups only. The parameters of Mossbauer spectra of KB-2 samples retained Fe^{3+} ions from solution with pH 1.2 differ for relevancy from those who have retained cations from solution with pH 1.7 - 2.0 [19]. The effected investigations using IR spectroscopy [19] showed that the retention of Fe^{3+} cations from $Fe_2(SO_4)_3$ solutions the complexes of type I are formed in polymer KB-2 phase, but from $FeCl_3$ solutions - complexes of type I and II co-exist.
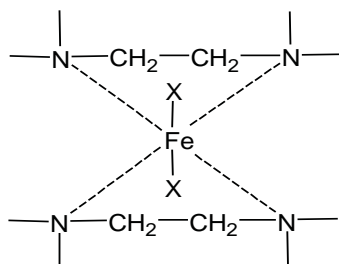

where X may be H_2O, OH^-, Cl^-, $SO4^{2-}$, and n may has the values from 1+ to 3-.

State of iron ions in the phase of the anion exchangers containing amine groups

Anion exchangers containing amine groups, are able to retain both hidroxycationes of Fe^{2+} and Fe^{3+} [21], as well as their complexes from the solutions containing tartaric acid [22.23]. Opportunity to observe Mössbauer spectra at 300 K of a wet sample anion exchanger EDE-10P demonstrates unequivocally coordination of ions with amine groups of polymer [24]. The parameters of Mössbauer spectra (δ_{Na+} = 0.62-0.72 mm/s, ΔEQ = 0.72 - 0.79 mm/s (δ_{Na+} - isomer shift relative to sodium nitroprusside as reference substance, ΔE_Q- quadrupol splitting) shows that Fe^{3+} ions in polymer phase is in a high-spin state and having a somewhat perceptible distorted octahedral environment.

Relatively small values of spectral lines width Γ = 0.52 - 0.56 mm/s and no diffuse broadening of spectra with increasing temperature, especially at $T > T_{melting}$ of ice, also confirms that Fe^{3+} ions in the EDE-10P polymer phase are coordinated with electron donor atoms of poly-ligand matrix. According to the composition of polymer structural unit [4] and the results of publications [24.25] it may be considered that Fe^{3+} ions form compounds of bis-ethylenediamine type in the anion exchanger EDE-10P phase.

At the retention of iron ions in the anion exchanger AN-2FN phase, containing phenolic groups, secondary and tertiary amines [4.26], from the solution of $Fe_2(SO_4)_3$, Fe^{2+} ions were also detected in the polymer phase, too [27]. The Fe^{2+} and Fe^{3+} ions are in a high-spin state from AN-2FN polymer phase (Table 1).

Table 1

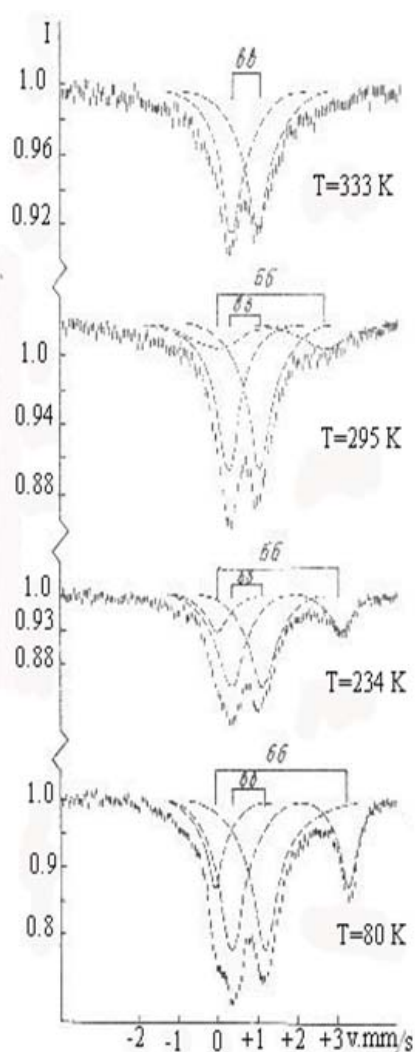**The Mossbauer spectra parameters (± 0.04 mm/s) of plymer AN-2FN**
after contacting with $Fe_2(SO_4)_3$ solution at different temperatures.

T.K	δ_{Na+}	ΔE_Q	Γ	δ_{Na+}	ΔE_Q	Γ	α f´	Fe^{2+}(%)
		Fe^{2+}			Fe^{3+}			
333	-	-	-	0.67	0.65	0.52	1.0	-
295	1.32	2.68	1.56	0.69	0.78	0.69	2.0	-
273	1.33	2.75	1.55	0.69	0.78	0.7	2.3	-
234	1.56	3.14	0.62	0.75	0.79	0.8	3.3	23
198	1.57	3.19	0.55	0.77	0.79	0.77	3.5	23
173	1.61	3.29	0.45	0.77	0.80	0.76	3.5	21
123	1.60	3.29	0.53	0.79	0.81	0.78	3.6	27
80	1.64	3.37	0.54	0.82	0.85	0.80	3.5	28

Note: α f´- a prportional value of Mossbauer effect probability (f´) for integral spectrum.

For Fe^{2+} (Tab.1) ions the sharp and essential increasing of line width (Γ) at $T > 273$ K is related to diffusion of these ions to the active centers of polymer.

The shape of Mössbauer spectra and their evolution with temperature (Fig. 1), seems at the first glimps to correspond to mixed valence iron complexes ($Fe^{2,5+}$). However a thorough analysis of the results does not confirm this assumption. The sharp diminution of the Mössbauer effect probability for Fe^{2+} at $T > 273$ K is probably determined by increasing of amplitude of oscillation of the polymer chain (scheme A) affecting the Debye temperature of the whole entity. The Fe^{3+} cations form compounds with a reduced occurrence of chain oscillation (Scheme B) in the polymer.
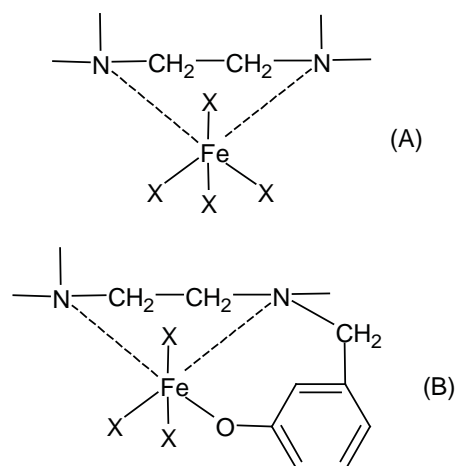
At treating of polymer sample by 3% H_2O_2 solution a part of Fe^{3+} ions is reduced up to Fe^{2+}. In this case the Mössbauer effect fraction is not zero at 300 K. So, the vibration amplitude of Fe^{2+} in the coordinative node B is lower than in A, i.e strongest bonded in composite lattice.
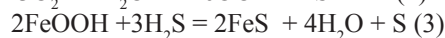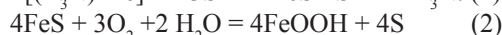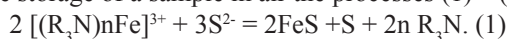
where X may be H_2O, OH^-, SO_4^{2-}.

Putting in contact a water - acetone solution and the sample of polymer EDE-10P, which contains Fe^{3+} from solution of $FeCl_3$, the Mossbauer spectra parameters δ_{Na+} and ΔE_Q have constant values both at 80 as well as 300 K [24], in the whole range of concentration of acetone from 0 to 100%. When dealing with the EDE-10P sample and water - ethanol solution the ΔE_Q value remains virtually constant throughout the all range of concentrations of ethanol, but the δ_{Na+} value is noticeable changed, especially at ~ 10-15% of ethanol [24].

Perhaps this change in δ_{Na+} value at this peculiar concentration of ethanol, is determined by the change of the solution structure [28.29]. The Mossbauer fraction data f''_{300}/f''_{80} (where f''_{300} și f''_{80} is expressing Mossbauer effect probability at 300 and 80 K respectively) indicate that with increasing the acetone concentration and, especially, the ethanol ones in their solution with water the vibration amplitude of Fe^{3+} ions is decreased [24]. Enhancing the organic component concentration in solution gives rise to augmentation of the relaxation time, which, considering the low iron content in the polymer phase (15 mg / g), it seems to be most probably of spin-lattice type. This rezoning is confirmed by comparing $\Gamma_{80K} = 0.57$ mm / s and $\Gamma_{300K} = 0.40$ mm/s for EDE-10P probe containing Fe^{3+} after its treatment with 100% acetone.

The experimental data show that the nature and concentration of anions in solution influence on Fe^{3+} ions sorption by anion exchangers containing weak basic groups [21.30]. Taking into account the high concentration of anions in the anion exchangers phase (up to 5-8 M) one may assume that some anions coordinate to Fe^{3+} ions bounded with groups-ligands of polymer. But the performed investigations using Mossbauer spectroscopy [31] did not provide clear detection of any influence of anions ClO_4^-, NO_3^-, Cl^-, SO_4^{2-} on electronic state of Fe^{3+} ions retained by the polymer EDE-10P. This fact does not exclude anions coordination to Fe3+ ions in the anion exchanger comprising weak basic groups. The state of Fe^{3+} ions in the EDE-0P polymer phase is determined by ethylenediamine groups and presence of water molecules or OH^- ions in solution and practically doesn't change it. A similar trend for δ_{Na+} values was observed for the addition of ethylenediamine to solutions of Sn(IV) halides [32].

Anions possessing red-ox or complexion character could change essentially the state of iron ions in the anion exchanger phase. When processing with Na_2S solution the majority of Fe^{3+} cations from the EDE-10P polymer phase to Fe^{2+} [33]. Reduction of Fe^{3+} ion the complexes with EDE-10P poly-ligand is blocked when FeS is formed. The FeS compounds appears as ultra fine particles which freely diffuse into the liquid phase of polymer and at $T> T_{melt}$ of ice, $f' = 0$. After prolonged exposure to air a part of Fe^{2+} ions are again oxidized to Fe^{3+}. If one assume that the parameter f' has the same value in the initial wet sample, for Fe^{2+} and Fe^{3+} at 80 K, then the Fe^{2+} ions are 74% and Fe^{3+} - 26%. Checking

Fig. 1. The Mossbauer spectra of polymer AN-2FN retaiting the iron ions from the solution of $Fe_2(SO_4)_3$ at different temperatures.
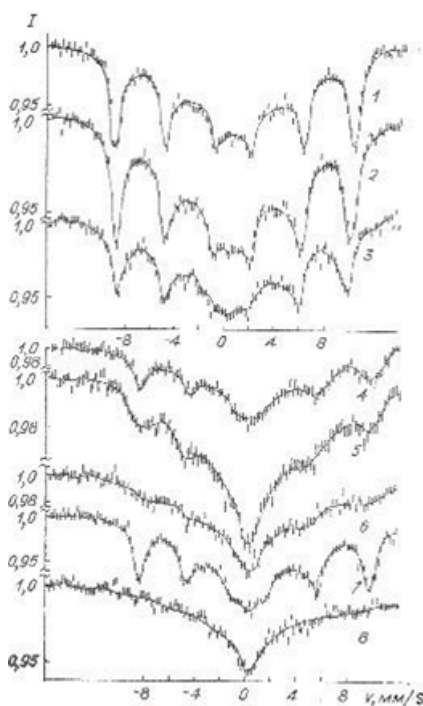
sample storage in air after 6 days, 1 and 6 months the amount of Fe^{2+} is continuously decreased to 62, 55.5 and 46%, respectively.

In the polymer phase during the storage of a sample in air the processes (1) – (3)

$$2 \, [(R_3N)nFe]^{3+} + 3S^{2-} = 2FeS + S + 2n \, R_3N. \quad (1)$$
$$4FeS + 3O_2 + 2 H_2O = 4FeOOH + 4S \quad (2)$$
$$2FeOOH + 3H_2S = 2FeS + 4H_2O + S \quad (3)$$

take place analogous to those described in [35]:

Depositing in air the EDE-10P sample processed with Na_2S solution the increase of particle size and modification of structure of compounds containing iron has involved a change the Mossbauer parameters δ_{Na+}, ΔE_Q, Γ and f´ as deduced from experimental spectra.

Fig.2. Mossbauer spectra of wetted EDE-10P polymer containing Fe(III) after treated with NaF solution at 80 (1), 116 (2), 150 (3), 172 (4), 209 (5) and 230 K (6), and a dry sample in air at 80 (7) and 300 K (8).

The low temperature Mossbauer spectra of EDE-10P sample, that retained iron ions from the $Fe_2(SO_4)_3$ solution after treating with NaF solution, are characterized by appearance of the magnetic hyperfine structure (MHS) [33]. In the EDE-10P polymer phase the paramagnetic Fe^{3+} ions are in spin blocking state and in this case the magnetic hyperfine structure is evidenced through a slow relaxation of the electronic spin [35]. With increasing temperature T> 80 K the electronic spin relaxation time of Fe^{3+} ions in the wetted EDE -10P polymer phase is diminished and from T> 230 K the MHS lines merge into a singlet component (Fig. 2) reflecting a very fast and complete relaxation of spins.

The ground term (^6S) of Fe^{3+} ions in the polymer processed by solution of NaF is spitted due to ligands crystalline field into three Kramers doublets S = ±5/2, ± 3/2 and ±1/2, which all are populated by electrons. With increasing temperature the spectral lines of the magnetic hyperfine structure (MHS) sextets became larger, but do not change sensibly their position. Since the Fe content in the EDE-10P polymer phase is small, around 2%, and taking into account the results from [16], it may be as above inferred that the evolution of MHS is characterized by a spin – lattice relaxation type.

Fluor anions completely destroy the Fe(III) compounds with groups-ligands of EDE-10P polymer as derived from Mossbauer spectra (at T> 230 K, f´ = 0 for damp sample) [34]. For air dry sample of EDE-10P the relaxation time remains quite high. In this case the formed Fe(III) compounds are located near the functional groups of the polymer. The values of δ_{Na+} = 0.70 ± 0.15 mm / s and H_{ef} = 580 ± 10 kOe (H_{ef} - effective magnetic field intensity on Fe^{3+} nucleus) indicate that iron compounds with F-anions in the polymer phase contain Fe^{3+} ions in the high-spin state and hexagonal coordination environment according to the data from [36]. Furthermore, the symmetrical ESR spectrum, with the relatively narrow spectral line (ΔH = 104 Oe at semi height) and g = 2.005 (77 K) [33], allows, according to [37], to consider that in the EDE 10P polymer phase which contains Fe (III) when processing it by the NaF solution then the $[FeF_4(H_2O)_2]^-$ ions are formed and subsequently are retained by the polymer as a result of Coulomb interactions.

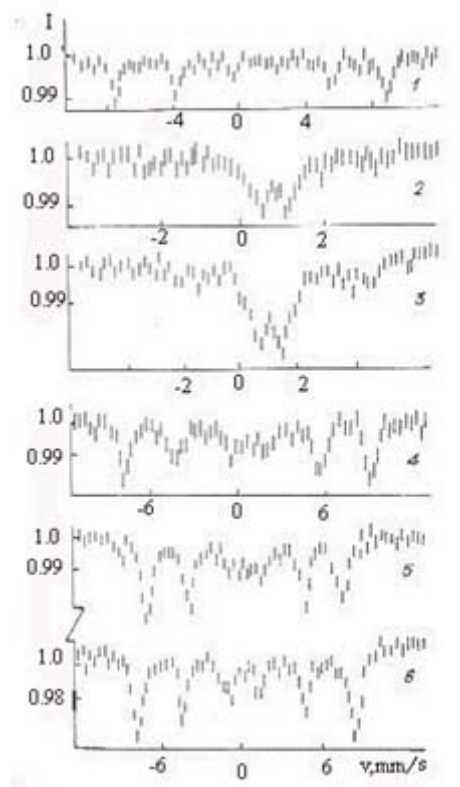**The iron ions state in outspent ion exchangers during water treatment**

Using Mossbauer spectroscopy it has been investigated the ion exchangers KU-2 and AN-31 which were depleted in water treatment in the first step and the AV-17, Varion - AD - in the second step of the Moldavian thermoelectric station [37.38]. Since the iron content in these polymers was relatively small (0.5 to 2.75 mg / g) the polymer samples were thermally treated in air at different temperatures up to 550 ºC. The Mossbauer spectra of AV-17 sample are shown in Fig. 3, and the parameters of Mossbauer spectra of AV-17 and Varion-AD samples in the Table 2.

The MS parameters show that in the phase of mentioned-up polymers iron is in the ultrafine particles of β-FeOOH, which during the thermal processing of polymer are transformed in γ- then α-Fe$_2$O$_3$. According to [39] the transformation of iron(III) oxohydroxide to α-Fe$_2$O$_3$ passes across the formation step of a paramagnetic phase x-Fe$_2$O$_3$ particles with d$_c$ = 80 ± 20 Å (d$_c$ – is critical diameter). When the particles have d> d$_c$ the x-Fe$_2$O$_3$ is transformed to γ - Fe$_2$O$_3$, and when the particles become more massive (~ 300 Å) - to α-Fe$_2$O$_3$. With decreasing of particle size of Fe(III) -oxide at d < d$_c$, in case of presence of superparamagnetism, outer sextet lines of the Mossbauer spectra became wider but reduced their intensities and are moving inward to the center until a broad relaxing singlet is formed [40]. Since the superparamagnetic state depends not only of particle size but also of temperature. In the case when the particles dimensions are slightly larger than the d$_c$ the superparamagnetic state of magnetic ordered particles appears when the temperature is increasing. Such a situation was observed in the MS with increasing temperature from 300-370 K for used-up Varion -AD sample previously thermally treated at 550°C (Fig. 4) [37].
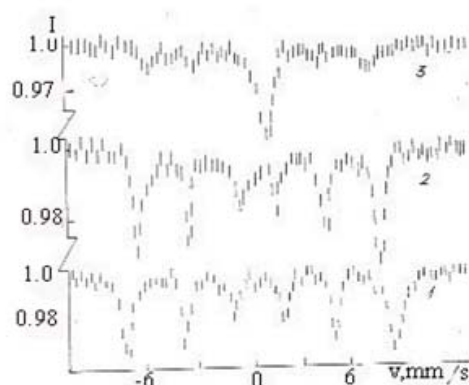
Therefore it can be concluded that there are ultrafine particles of Fe$_2$O$_3$ in the used-up and heat treated at 550°C Varion -AD polymer phase as well as there are β-FeOOH ultrafine particles in the exhausted but not heat-treated polymer.

It is known [41], that β-FeOOH is chemically more inert than other FeOOH allotropic forms, which makes difficult for regeneration of ion exchangers. The chemical stability of β-FeOOH can be explained not only by its special structure, but also due to the fact that the Cl-ions enter in its composition [41.42]. The investigations [43] have demonstrated that in this case the composition of precipitate consist of "β-FeOOH +

Fig. 3. Mossbauer spectra at 80 (1,4) and 300 K(2,3,5,6) of outspent AV-17 sample after thermo processing at 20 (1,2), 160 (3), 260 (4,5) şi 550^{0}C (6).

β-FeOOH(CL)" and has the anion exchange properties. The anions with 1- charge (NO$_3^-$) substitute the Cl$^-$ ion from β-FeOOH easier than anions with larger charge (SO$_4^{2-}$).The anion exchange capacity of β-FeOOH depends on pH and at pH 3 it is a 1 mmol (Cl^{1-})/ g [44].

It is necessary to mention, that after clearing the cause of earlier used-up limit for ion exchangers, the water source alimentation at the Moldavian thermoelectric station was changed.

Fig.4. The Mossbauer spectra obtained at 80(1), 300 (2), and 370 K(3) of exhaustive Varion–AD anionit thermoprocessing at 550°C.

Table 2
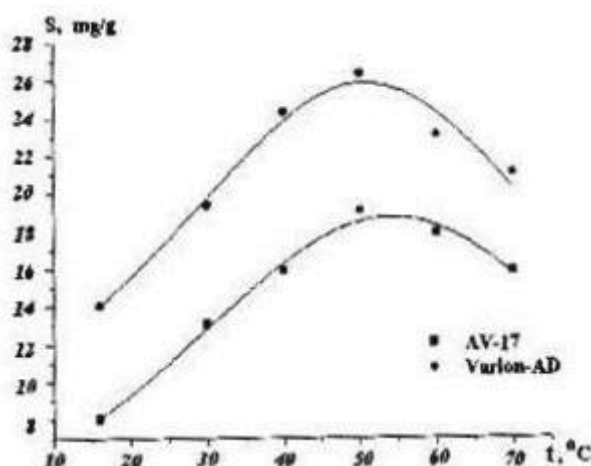
The Mossbauer spectra parameters of termo processing anionites at 300 and 80 K (in brackets).

t, ^{0}C	δ_{Na+}, mm/s	H_{ef}, kOe	δ_{Na+}, mm/s	H_{ef}, kOe	compusul
	AV-17		Varion-AD		
20	0,62 (0,62)	0 (492,5)	0,62 (0,62)	0 (480)	β-FeOOH
160	0,74 (0,68)	0 (448)	0,63 (0,70)	0 (486)	β-FeOOH
260	0,63 (0,71)	492 (518)	0,69 (0,71)	477 (512)	γ-, α- FeOOH
350	0,70 (0,65)	515 (543)	0,55 (0,60)	492 (540)	γ-, α- FeOOH
450	0,84 (0,77)	508 (546)	0,86 (0,98)	497 (528)	α- FeOOH
550	0,72 (0,78)	517 (512)	0,74 (0,69)	528 (528)	α- FeOOH

The iron ions state in the ion reticulate exchangers phase containing strongly basic groups

The monofunctional anion exchangers containing strongly basic groups (R_4N^+), do not containing in their matrix the atoms with negative charge or electron donors. In this case, theoretically, they are not entitled to retain cations from solution in static conditions. But in dynamic conditions, being in OH$^-$ form, they can retain the metal cations which are readily hydrolyzed and forming hydroxides [31]. However, surprisingly, it was demonstrated [8.21], that such polymers can retain hydroxocations of Fe (III) in the static conditions from the sulphate solutions with pH = 2.0 at equilibrium. In the same conditions these polymers do not retain hydroxocations of Fe(III) from the solutions of $FeCl_3$ or $Fe(NO_3)_3$. The curve of the Fe (III)-containing cations sorption from sulphate solutions on anion exchangers AV-17 (containing R_4N^+ group) and Varion-AD (containing R_4N^+ and ROH groups) vs. temperature passes through maximum Fig. 5) [45].

Fig. 5. The temperature dependence of Fe(III) sorbtion by AV-17 and Varion – AD polymers.

Anyhow, it can be affirmed that the retention of cations by anion exchangers containing strongly basic groups is a chemical process and not a physical one. Sorption of Fe(III) cations by strongly basic polymers takes place in a medium (polymer phase) with relatively high concentration of SO_4^{2-} anions, and in principle could form anionic complexes inside the polymer phase, which will be electrostatically retained. But it is well known that the ion exchange is the process which almost does not depend on temperature.
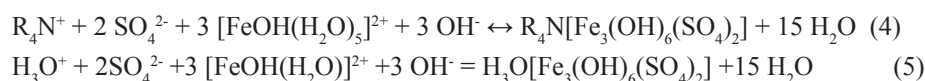
As it is shown in [8] in the AV-17 polymer phase which was in contact with $Fe_2(SO_4)_3$ solution (pH 1.7 and concentration from 0.03 to 0.06 N), there is a solid iron(III) compound (doublet in the Mossbauer spectrum) and $[Fe(H_2O)]^{3+}$, $[FeOH(H_2O)_5]^{2+}$ (sextets in the spectrum). The dimmer ions of oxo-or hydroxocomplexes of Fe (III) ions in polymer phase were not detected. There is only one type of solid Fe (III) compound in the polymer phase after contacting with $Fe_2(SO_4)_3$ solution at pH 1.85 - 2.00. The parameters of Mossbauer spectra of these compounds ($\Delta E_Q = 1$ mm / s) are close to corresponding parameters which are characteristic to Jarosite mineral: $A[Fe_3(OH)_6(SO_4)_2]$, where A may be = Na$^+$, K$^+$, H$_3$O$^+$, NH$_4^+$ and other cations [46.47], or hydrated compound $FeOHSO_4$ [46-48]. The compounds like Jarosite mineral type are obtained during hydrolytic precipitation of Fe^{3+} ions in the presence of SO_4^{2-} anions [48.50].

The Jarosite mineral is not notably stable in the normal atmospheric environment, partially transforming in to $Fe(OH)_3$ [50]. The $Fe_2(SO_4)_3$ solution interacts with freshly precipitated $Fe(OH)_3$ giving rise, in dependence of
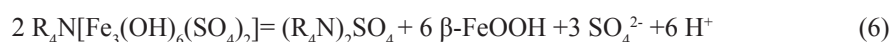
temperature, to soluble or insoluble $FeOHSO_4$ [51.52]. The Jarosite mineral type compounds are stable up to about 230^0C on heating in air, and at $T > 230^0C$ one of the thermodecomposing products is $FeOHSO_4$ [53]. Following the thermal dehydration of $FeOHSO_4$, the ΔE_Q value grows considerably. Boiling in water the iron(III) compounds such as Jarosite are transformed into α-FeOOH in superparamagnetic state [47].

Under thermal treatment in air up to 200^0C of Fe (III) Jarosite mineral type compounds in the AV-17 polymer phase the red-ox processes take place and the Fe (II) compounds as well as stable libber radicals are formed [54]. Mossbauer spectra parameters of AV-17 sample containing Jarosite do not change essential when the sample was heated up to 180^0C. So in the AV-17 polymer phase there is not formed $FeOHSO_4$ when it is in contact with solution of $Fe_2(SO_4)_3$. Furthermore, when boiling in aqueous medium the Jarosite from polymer phase is converted to ultrafine particles of FeOOH showing superparamagnetic state.

During a few cycles "sorption of Fe (III) then boiling in water", one part of the magnetic particles become relatively large and magnetically ordered, while another part remains in superparamagnetic state due to location in narrow pores of the polymer [55]. In the solution of $Fe_2(SO_4)_3$ with pH 2.0 there are $[Fe(H_2O)_6]^{3+}$, $[FeOH(H_2O)_5]^{2+}$ and $[Fe_2(OH)_2(H_2O)_8]^{4+}$ ions [55.56]. The dimeric hydroxocomplexes were not detected in the polymer phase via contacting with $Fe_2(SO_4)_3$ solution. These complexes are hardly changed to organize in new structural units [57]. The $[Fe(H_2O)_6]^{3+}$ ions does also not directly participate in the formation of compounds like Jarosite mineral. So in the polymer phase the $[FeOH(H_2O)_5]^{2+}$ ions participate to the formation of compounds of Jarosite mineral type:

$$R_4N^+ + 2\ SO_4^{2-} + 3\ [FeOH(H_2O)_5]^{2+} + 3\ OH^- \leftrightarrow R_4N[Fe_3(OH)_6(SO_4)_2] + 15\ H_2O \quad (4)$$
$$H_3O^+ + 2SO_4^{2-} + 3\ [FeOH(H_2O)]^{2+} + 3\ OH^- = H_3O[Fe_3(OH)_6(SO_4)_2] + 15\ H_2O \quad (5)$$

In boiling aqueous solution the iron compounds such as mineral Jarosite decompose according the scheme (6):

$$2\ R_4N[Fe_3(OH)_6(SO_4)_2] = (R_4N)_2SO_4 + 6\ \beta\text{-}FeOOH + 3\ SO_4^{2-} + 6\ H^+ \quad (6)$$

Jarosite mineral formation can take place only in the presence of water. When this mineral was found on Mars it was deduced that water is present there too and latter confirmed.

The Jarosite mineral type compounds are formed as layers of 3 or 6 octahedral cycles [49]. The OH- groups are located in the equatorial plane, forming a bridge between metal ions and SO_4^{2-} groups are located in axial position, each coordinating 3 metal ions of 3 octahedrons.

The Jarosite mineral type compounds presence in polymers phase changes essentially their physical-chemical properties. The R_4N^+ and H_3O^+ ions from compounds can be exchanged with different cations but at the same time the anions SO_4^{2-} connect with different other anions or molecules able to form coordination bonds with the central metal ions.

The alunit type mineral $K[Al_3(OH)_6(SO_4)_2]$ is izostructural with Jarosite mineral. So, at contacting with $Al_2(SO_4)_3$ solution in the phase of strongly basic anion exchangers it may be formed compounds such alunit [13]. Moreover, in the analogical conditions it may be formed compounds like Jarosite mineral type containing other cations species which differ of Fe3+ or Al^{3+} [12].

The reticulated ionic polymers containing in their matrix not only strongly basic groups, but other chemically active functional groups such as - COOH,-CN etc, also may retain metal cations (M^{3+}) from the solutions of sulfate as a result of training compounds like Jarosite mineral, as well as function of coordination with electron donor atoms of the polymer [58].

Conclusions

To understand more deeply the formation of metal compounds in chemical active reticulate polymer phase and the processes connected with utilization in different areas of these composites uploaded with metallic compounds polymers it is imperiously required their investigation using various complementary physical methods, including Mossbauer spectroscopy in special.

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