Ion Adsorption from Water When Thermo-Processed Products Subjected To Electrochemical Dimensional Processing Of Aluminum Alloy AMG-6 Are Applied.

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ABSTRACT. Fluoride ion adsorption from water solutions (concentration of fluoride ions content 10^{-4} - 3×10^{-1} mole·l^{-1}) by thermo-processed products subjected to electrochemical dimensional processing of aluminum alloy AMG-6 under 100, 200, 400, 600(^{0}C) was considered. The analysis of the conditions determining the adsorption equilibrium of fluorine ions in solution and on the surface was carried out.

KEYWORDS: Adsorption, Adsorbents, Solution, Surface, Fluoride ion, Water, Aluminum alloy AMG-6.

I. INTRODUCTION.

The theory of adsorption of dissolved ionic compounds has been developed still insufficiently in spite of the fact that the phenomena of adsorption from solutions on the surface of solid bodies underlie many chemical and technological processes, [1, 2]. Though certain attention in literature has been paid to electrolytes adsorption [3, 4], much less attention has been paid to oxyhydroxide small sized ions adsorption by [5]. Therefore authors tried to meet this drawback and by analogy with adsorption of fluorine by oxyhydroxides of aluminium tried to show the applicability of the thermodynamic approach to the description of the phenomena occurring on electrolyte solid-solution interface.

In [6] authors demonstrate basic applicability of heat treated ECDP AMG-6 alloys, as adsorbents for removal of fluorine from natural underground water ($C_{min} \approx 1$ mmole·l^{-1}). However, to approach to reasonable selection of conditions and objects of water purification or solving similar problems, it is necessary to know the regularities of the process of adsorption of fluorine on surfaces of particles of sorbents and the mechanism of ions attachment [7,8], From this point of view regular research of adsorption of F-ions from water solutions on samples AMG-100, AMG-200, AMG-400 and AMG-600 has been undertaken.

II. EXPERIMENTAL PART.

There is much literature on removal fluoride-ions [9-12] from water, but it refers exclusively to removal of ions from slightly concentrated solutions –up to 1mmole·l^{-1}.

The products of electrochemical dimensional processing (ECDP) of aluminium alloy AMG-6 have been used as adsorbents. ECDP of aluminium alloy AMG-6 electrolytes was carried on concentrated 2M solution of chloride-nitrate electrolyte at 13,7A·cm^{-2} current density. ECDP deposits were washed to eliminate ions of electrolyte to negative reaction of Cl^- ion then dehydrated and cylinders with diameter 3-4 mm were formed and air dried at room temperature.

Then the heat treatment (HT) of samples on air at temperatures 100, 200, 400 and 600(^{0}C) for 2 hours accordingly at each temperature (AMG-100, AMG-200, AMG-400, and AMG-600) continued. Based on the received samples of ECDP thermo processed products adsorption desorption isotherms of methanol vapour (a molecular platform

25 Å^2) were taken, specific surface values were determined as well as sorption volume of pores and desorption of volumes against radii were plotted [10,11]. Part of the results obtained is presented in fig.1 and tab.1.
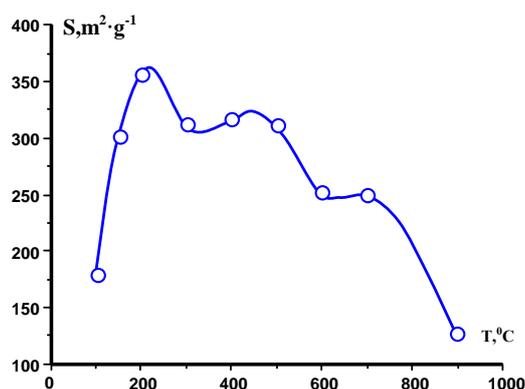
Fig.1 Dependence of the specific surface of AMG species on calcinations temperature

Table 1. Adsorption- structural characteristics and composition of thermally processed ECDP subjected aluminum alloy AMG

Thermo-treating conditions (T^{0}C)	S$_{sp.}$ м$^2 \cdot$g^{-1}	V$_s$, см$^3 \cdot$g^{-1}	R$_{ef.}$, Å	Chemical composition, H$_2$O mole amount per mole of Al$_2$O$_3$	Phase composition
20 At room temperature (untreated)	163	0,282	35	3,24	Amorphous trihydrate, paerite with pseudoboehmit
100	170	0,294	34	2,85	Crystallized paerite
200	358	0,457	26	2,00	Paerite residue, amorphous phase
400	317	0,467	29	0,35	γ - Al$_2$O$_3$, amorphous phase
600	251	0,485	39	0,089	Well crystallized γ-Al$_2$O$_3$.

The initial sample obtained from starting slime structure with Al-26,9 %, Mg-1,39%, Fe-0,15%, represented a porous material with a specific surface 163 m$^2 \cdot$g^{-1} and sorption volume 0,282 cm$^3 \cdot$g^{-1}; it's chemical composition was Al$_2$O$_3$*3,24H$_2$O. According to the radiographic analysis fig. 2 the initial sample is presented by three hydrate (bayerite) with reflexions 4,777 and 4,431 Å having a pseudo-boehmite impurity (10÷11 Å) [8,12]. Roentgenograms themselves have splays at the basis that prove a part of three hydrate and pseudo-boehmite to be amorphous.
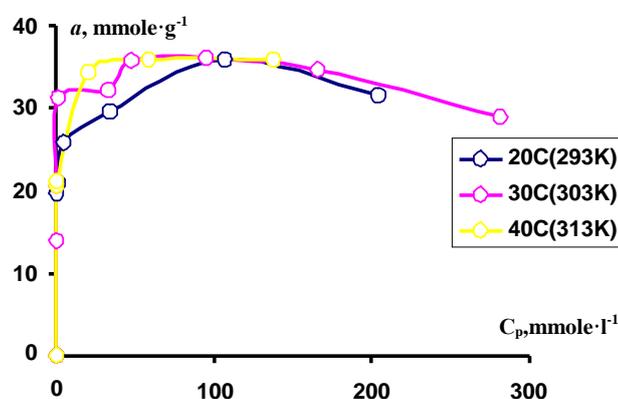
Fig. 2 Isotherm of adsorption of fluoride ions at solution temperatures at 20, 30, 40 (^{0}C) on AMG-100 species

This work is concerned with adsorption of NaF solutions with concentrations from 10^{-4} to 0,5 mole·l^{-1}. The process of adsorption was carried on at constant values of pH=5,6÷6,2 (optimum pH adsorption). Preliminary experiments on adsorption of F^- from AMG water solution samples have shown that no longer than in 10 minutes medium pH increased to ≈ 9,5 and (tab.2) meaning deviation from optimum pH of adsorptions.

Table 2 pH changes of water and NaF 0,01M solution with AMG

Sample	pH after 10 min. adsorption	
	water pH~6	p-p NaF pH ~7
AMG- init.	5,70	9,05
AMG-200	5,90	8,80
AMG-400	8,25	9,25
AMG-700	8,25	9,35

Therefore experiments were made with the use of acetate buffer (1M CH_3COONa and 0,5M CH_3COOH [14]). For maintenance of constant ionic strength of solution on adsorption 0,5m solution of Na_2SO_4 was added. In all calculations there was used activity of ions of fluorine [15].

For adsorption fractions of 0,5 mmole were selected in relation of S:L=1:250. Adsorption was carried on under constant stirring with a mechanical stirrer to balance establishment at continuous control of A concentration level with the use of fluorine-selective electrode. As the registering device ion-meter was used (pH-121), pH definition error was 0,05%, and fluorine-ions content was ±0,1 mmole·l^{-1}. The fluorine content in the solution was defined with a calibrating chart. The technique of experiments was as follows: to a certain volume of initial solution 25 ml of buffer and a quantity of water, enough to satisfy the needed concentration of ions of fluorine in the solution, was added. The buffer volume always was sustained at 50% of solution total amount. Then at constant stirring a charge of sorbent was introduced for time needed. The values of potential E (mV) were deter mined at the end of experiment and according to calibrating chart E=f(- lgC_f) concentrations of ions of fluorine in a solution were determined. Based on the difference of initial and final concentrations of fluorine the quantity of fluorine adsorbed by a surface of a sorbent was found. There were always used actual concentrations of ions of fluorine, i.e. adjusted for factor of activity of ions of fluorine at corresponding ionic force of a solution.

In order to get thermodynamic and kinetic parameters of the process isotherms of adsorption and kinetic curves at solution temperatures 293, 303 and 313(K) were developed. Oven control was carried on with accuracy of ±0,2ºC. Also there have been made experiments on desorption F^- from samples by a buffer solution at the same temperatures within 2 hours. AMG samples after adsorption of fluorine and separation of liquid phase have been washed twice with water then again fresh initial buffer at pH = 5,7 was added. The solution continued to be stirred with a magnetic mixed within two hours at temperatures 20, 30, 40(ºC) accordingly. The solution was separated by centrifugation and the quantity of fluoride-ion was determined.

III. RESULTS AND DISCUSSIONS

Isotherms of adsorption of fluorine at different temperatures by the thermo processed AMG-6 samples are presented on fig. 1-5. Apparently, isotherms of adsorption of all samples according to Gil's classification correspond to monomolecular Langmuir adsorption [9,12,13]. Interestingly, extremely high values of adsorption of fluorine at very low equilibrium concentration of fluorine-ions are observed in all samples that is characteristic of high affinity of adsorbate to adsorbent, and which indirectly prove the chemical character of adsorption.

Isotherms of adsorption NaF in all investigated samples are well described by the equilibrium concentration of sodium fluoride of 100-150 mmole·l^{-1}. It gives the possibility to find precisely enough the a_m value as a tangent of tilt angle in co-ordinates Cp/a from Cp according to the Langmuir equation in the linear form. Some isotherms of NaF adsorption are given in co-ordinates of this equation and in tab.3 values a_m, are defined experimentally and theoretically calculated according to Langmuir equation. The correspondence calculated and the experimental value of a_m is good enough.

Table 3. Langmuir equation parameters for fluorine ions adsorption by AMG samples

Sample	AMG- 100			AMG- 200			AMG- 400			AMG- 600		
T , (K)	293	303	313	293	303	313	293	303	313	293	303	313
a_m (exper) mmole·g^{-1}	35.60	36,40	36,40	36,20	40,60	39,80	22,20	26,90	34,20	19,60	18,80	28,40
Cp, mmole·l^{-1}	0,107	0,09	0,058	0,295	0,029	0,060	0,162	0,089	0,140	0,174	0,117	0,153
a_m (calc.) mmole·g^{-1}	33,58	37,89	37,41	39,11	42,86	40,65	21,32	30,40	35,97	19,06	19,52	27,42
Kp	0,330	0,377	0,668	0,056	0,115	0,351	0,095	0,066	0,132	0,087	0,171	0,608

Differences in value of a_m of the investigated samples are, perhaps, due to differences in the nature of their surface. AMG-100 samples representing actually Al three hydrates (well crystallized bayerite) and possessing a considerable quantity of hydroxyl exchangeable water are also characterized by maximum adsorptive capacity.

As it has been shown [6,10], thermo-treatment of samples at 200ºC is accompanied by phase transitions, amorphisation of structure leading to maximum S_{sp} (fig. 1). Therefore, though the quantity of water in sample AMG-200 is much lower, than in sample AMG-100, their adsorptive capacity of fluorine is the same ~ 36 mmole·g^{-1}. Sample AMG-600 which in fact represents the well crystallized $\gamma - Al_2O_3$ with minimum quantity of water, has also the minimum value of fluorine adsorption. Sample AMG-400 occupies an intermediate position.

It was observed that temperature increase influences the adsorptive capacity of samples as to fluorine differently. The adsorptive capacity of AMG-100 sample with temperature practically does not change (fig. 3) that is explained by stability of its crystal structure.
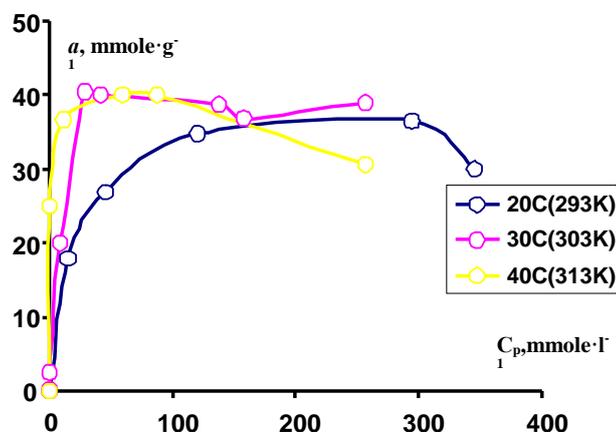
Fig. 3 Isotherm of adsorption of fluoride ions at solution temperatures at 20, 30, 40 (^{0}C) on AMG-200 species

Temperature increase of AMG-200 and AMG-400 solution leads to increase of theirs adsorptive activity: AMG-200 a_m reaches 40 mmole·g^{-1}, which exceeds the adsorptive capacity of sample AMG-100, and adsorptive capacity of AMG-400 at 400 ºC approaches to it.

Such behavior of samples is caused, apparently, by hydrothermal transformation of superfine X-ray amorphous monohydroxide and Al_2O_3 into products with plenty of hydroxyl water [5, 15].

Adsorption rate constants were calculated from curves of kinetic adsorption of fluoride-ions of the investigated samples and values were defined for three temperatures of a solution 293, 303,313(K).

Experimentally found values of residual concentration of fluoride-ions (C_F) and corresponding expose times (τ) were processed according to kinetic equation of adsorption rate $-dC_F/dt = k\tau$ in the linear form. From the tangent of tilt angle of a straight line $-lnC_{F-} = k\tau$ to axis OX numerical values of rate constants of adsorption of fluoride-ions by AMG samples (tab.4) were found. Here are also presented energy values of fluoride-ions adsorption process.

Table 4. Rate constant (k) and energy of activation (E_A) of the process of adsorption of fluoride ions by subjected to thermally ECD processed AMG-6, $k_x 10^{-4}$, $l·m^{-1}·s^{-1}$

Sample $T_{solution}$ K	AMG- 100	AMG- 200	AMG- 400	AMG- 600
293	3,00	2,73	3,00	4,00
303	4,67	3,45	4,67	4,52
313	9,33	3,47	6,17	5,06
E_A, кJ·mole^{-1}	41,4	61,9	32,3	19,2

Table 4a. Fluoride ($F^{-)}$) and water (H_3O^+) activity coefficient depending on solution ionic strength

Ionic strength, μ	0,001	0,002	0,005	0,01	0,02	0,05	0,1	0,20	0,3
γ_F	0,96	0,95	0,92	0,89	0,87	0,81	0,78	0,70	0,66
γH_2O	0,98	0,97	0,95	0,92	0,90	0,88	0,84	0,87	0,73

As one can see, the constant k value grows with the temperature of a solution rising that is natural for chemical reactions. However values E_a that change symbatically to maximum adsorptive capacities of samples which characterize the nature of process of adsorption do not fit to all chemical adsorption samples. So, for sample AMG-600 E_a it accounts to 19,2 kJ·mole^{-1}, that is natural for physical adsorption.

As in all experiments the temperature, pressure and weight of balanced system were constant the equilibrium of adsorptive process is mostly convenient to be characterized by changes of free molar Gibbs energy of adsorption (isobar-isothermal potential ΔG) or by change of chemical potential Δμº related to it, since:

$(dG/dn_i)_{p,T, nj} = \mu_i$; $\Delta\mu_i^o = \Delta H^o - T\Delta S^o = -RTlnk_i$ (1)

Where i, j – are solution components, k – adsorptive equilibrium constant.

Thus, for definition of thermodynamic functions of the process of NaF adsorption from water solutions it is necessary to know numerical values of equilibrium constants.

As adsorption from solutions as a rule has a displacement character and is performed by the way of rearrangement of solution components on the adsorbent-liquid interface, then the equilibrium constant should be represented as ratio of constants of adsorptive constants of components of the solution. Let us determine this relation. The chemical potential of the component is associated with its concentration in solution expression like:

$\mu_i = \mu_i^o + RTln\gamma_i * x_i$ (2)

Were x_i is component molar share i in volume phase, γ_i – it's activity at coefficient given concentration, μ_i^o – standard chemical potential i of the component in solution. Similar expression can be written and for chemical potential i of the component adsorbed on the surface of sorbent, i.e. in adsorptive layer:

$\mu_i^a = \mu_i^{oa} + RT\ln\gamma_i^a * y_i$ (3)

where by index a – we will designate the adsorptive phase, by y_i – the molar component share i in adsorptive phase, y_i^a – its activity, coefficient μ_i^{oa} – the standard chemical potential i of the component in adsorptive layer.

When in balance chemical potentials of each component of the system in adsorptive layer and in solution volume are equal, i.e. $\mu_i^a = \mu_i^{oa}$, therefore from (2) and (3) follows:

$\mu_i^o - \mu_i^{oa} = \Delta G_i^o = -\Delta\mu_i^o = RT\ln\gamma_i^a y_i / x_i y_i = RT\ln k_{ai}$ (4)

Where k – is the constant of adsorptive equilibrium for component i of a the solution, $k_{ai} = \gamma_i^a y_i / x_i\gamma_i$ (4a)

In our case we observe two phases (a solid sorbent-solution) and from multicomponent water system we will consider only water adsorption (component 1) and fluoride-ion (component 2).

Then partial equilibrium constants of water (k_{a1}) and sodium fluoride (k_{a2}) according to (4a) can be written as follows:

$(k_{a1}) = \gamma_{a1}y_1/x_1\gamma_1$ (5) $(k_{a2}) = \gamma_{a2}y_2/x_2\gamma_2$ (6)

Where y_1, x_1 is molar water share in adsorptive phase and in volume of equilibrium solution accordingly, y_2, x_2 is the molar share of sodium fluoride in the same phases.

It should be remembered that in case of porous aluminium oxyhydroxide to calculate the constants of adsorptive balance from the experiment data not only the adsorption isotherm but also the total adsorptive volume V_Σ is to be known. This volume can be presented by the sum of partial volumes of the adsorbed components:

$V_\Sigma = a_1V_1^o + a_2V_2^o$ (7)

Where a_1 and a_2 are the values o specific adsorption of solvent (in our case of water) and the solute (mole·g^{-1}), and V_1^o and V_2^o are accordingly the values of molar volumes of these components. For fluoric sodium which is crystalline at room temperature, we used the density value of its salt in a quasiliquid state – 2,79 g·cm^{-3} [5,12,16]. Then the molar volume of fluoric sodium will be equal to 0,01505 cm^3·mmole^{-1}, and that of water – 0,018 cm^3·mmole^{-1}. Total volume of adsorptive spaces V_Σ for all samples AMG was defined from impregnation of samples with water and subsequent removal of water (pumping out at 60 mm hg) [4] tab. 5.

Table 5. The values of the standard decreases in the free energy of Gibbs (ΔG^0) isosteric heat of adsorption ($\bar{Q}^o$) and standard entropy decreases (ΔS^o) during adsorption of fluoride ions by thermo-processed AMG-6 samples

Sample	V_Σ, см^3·g^{-1}	$T_{Solution}$, K	lg K$_2$	$-\Delta G_2^0$,kJ·mole^{-1}	$\bar{Q}^o$, kJ·mole^{-1}	ΔS^o, kJ·mole^{-1}
AMG -100	0,359	293	3,69	20,70	156,40	-0,463
		303	3,50	20,30	-	-
		313	3,51	21,04	156,40	-0,432
AMG -200	0,457	293	3,92	22,02	203,20	-0,620
		303	4,24	24,60	202,80	-0,588
		313	5,42	32,50	201,96	-0,541
AMG -400	0,503	293	54	19,80	-	-
		303	3,74	21,7	364,60	-1,13
		313	4,15	24,90	336,20	-0,994
AMG 600	0,502	293	3,75	21,06	174,40	-0,523
		303	3,87	22,50	186,50	-0,541
		313	4,25	22,50	177,70	-0,486

In that case molar share of NaF (y_2) and water (y_1) in adsorptive phase is equal to:

$$y_2 = a_2/(a_1 + a_2) \tag{8}$$

$$y_1 = a_1/(a_1 + a_2) \tag{9}$$

Equations (8) and (9) taking into account equation (7) take the form:

$$y_2 = a_2/[(V_\Sigma - a_2 V_2^0)/V_1^0 + a_2)] \tag{10}$$

$$y_1 = (V_\Sigma\, a_2 V_2^0)/V_1^0\, [(V_\Sigma - a_2 V_2^0)/V_1^0 + a_2)] \tag{11}$$

Molar shares of NaF and water consequently (x_2) and (x_1) in the volume of equilibrium solution are equal

$$x_2 = c_2/(c_1 + c_2), \tag{12}$$

$$x_1 = c_1/(c_1 + c_2), \tag{13}$$

Where C_1 and C_2 are the concentrations of water and NaF (mole·kg^{-1}); $C_1 = 1000/18 = 55,5$ mole·kg^{-1}.

After substitution of values of molar share of solution components in equation (5) and (6) we get expressions for partial constants of adsorptive equilibrium of water (K_{a1}) and NaF (k_{a2}) from binary water solution.

It should be noticed that the relations of partial constants of adsorption equilibrium K_{a2} on K_{a1} at the same time appear to be a constant itself and looks like:

$$k_{a2}/k_{a1} = k = a_{2*} V_1^0{}_{*}55,5_{*}\gamma_{a2*}\gamma_1/(V_\Sigma - a_{2*}V_2^0)_{*}C_2\, {}_{*}\gamma_{a1}\gamma_2 \tag{14}$$

Or designating the value $K/V_1^0*55,5$ as k_2, we receive:

$$k_2 = a_{2*}\gamma_{a2*}\gamma_1/(V_\Sigma - a_{2*}V_2^0)_{*}C_2\, {}_{*}\gamma_{a1}\gamma_2 \tag{15}$$

As the value $(V_\Sigma - a_{2*}V_2^0)$ represents partial volume of solvent (water) in adsorptive phase then the relation $a_2/(V_\Sigma - a_{2*}V_2^0) = Ca_2$ is nothing but concentration of the second component, i.e. NaF in adsorptive phase being defined experimentally.

Thus K_2 value represents a selective constant of NaF adsorption equilibrium from binary water solution. From equation (15) for all thermo-processed AMG samples constants of adsorptive equilibrium were calculated. Equilibrium concentration of NaF and corresponding quantities adsorbed at sorbent surface were from initial parts of adsorption isotherms taking into consideration activity coefficients [15-16]

Constants of adsorption equilibrium and values of standard reduction of Gibbs free energy of adsorption calculated on the basis of experimental isotherms of NaF adsorption from water solution in AMG samples are presented in table 5. It can be seen that logarithm values of adsorption equilibrium constants of the investigated samples and the temperatures are in limits 3,5-5,4. Increase of temperature in the solution results in adsorption constant increase and consequently to increase of free energy of adsorption of NaF. It should be noticed that ΔGº for AMG-200 at all temperatures is higher than for all other samples. It reflects the change of porous structure of this sample due to thermal processing that leads, as a consequence, to development of amorphousness and maximum specific surface. (Tabl.1, Fig.1).

Of the given adsorption NaF data at different solution temperatures: 20, 30, 40(°C) adsorptions isosteres have been constructed, whence differential isosteric warmth $\bar{Q}$ at different values of specific adsorption *a* have been found on the equation.

$$\bar{Q} = RT^2(d\ln C_p/dT)_a, \tag{16}$$

Where C_p equilibrium concentration of fluoride-ions in solution volume at adsorption value *a*.

Apparently from the table (6) and drawing differential isosteric figures (3, 4, 5) warmth depends on Θ degree of filling of a surface molecules with NaF, and its absolute value for all samples AMG decreasing with Θ growth. This reduction of warmth of adsorption is concerned both with increase in solubility of fluoride of sodium due to solution temperature, and owing to reduction of chemical potential of a solution. Curve extrapolation to $\bar{Q} = f(\theta)$ at θ=0 in the assumption of linearity $\bar{Q}$ from Θ numerical values of standard isosteric warmth of adsorption (or standard decreases of adsorption enthalpy ΔH**º=-$\bar{Q}$º**) were found. Values of $\bar{Q}$**º**, apparently from the table (5) little depend on solution temperature, but are strongly different from all investigated samples AMG, changing from 156 to 364 kJ·mole^{-1}.

Table 6. Dependence of adsorption heat of fluoride ions by AMG on the degree of surface filling (Θ).

Sample	a, mmole·g^{-1}	C_p, mmole·l^{-1}	Θ_1	C_p, mmole·l^{-1}	Θ_2	$\bar{Q}$, kJ·mole^{-1}
AMG-100		293 K		313 K		
	28	17	0,77	2	0,77	81,33
	30	36	0,82	4	0,82	82,16
	32	58	0,88	9	0,88	70,79
	34	82	0,93	18	0.93	57,66
	a_m =36,4 mmole·g^{-1}			a_m =36,4 mmole·g^{-1}		
AMG-200		293 K		313 K		
	26	42	0,72	2	0,64	115,80
	28	51	0,78	3	0,69	107,88
	30	66	0,83	5	0,74	98,00
	32	85	0,89	7	0,78	94,91
	a_m =36,0 mmole·g^{-1}			a_m =40,8 mmole·g^{-1}		
AMG-400		303 K		313 K		
	16	14	0,66	1	0,46	207,39
	18	20	0,67	2	0,52	180,92
	20	30	0,75	4	0.57	158,34
	22	42	0,82	8	0,63	130,29
	24	58	0,90	13	0.69	117,49
	a_m =26,8 mmole·g^{-1}			a_m =34,8 mmole·g^{-1}		
AMG-600		293 K		303 K		
	12	20	0,62	5	0,65	101,61
	14	50	0,73	13	0.76	99,10
	16	84	0,83	30	0.87	75.77
	a_m =19,2 mmole·g^{-1}			a_m =18,4 mmole·g^{-1}		
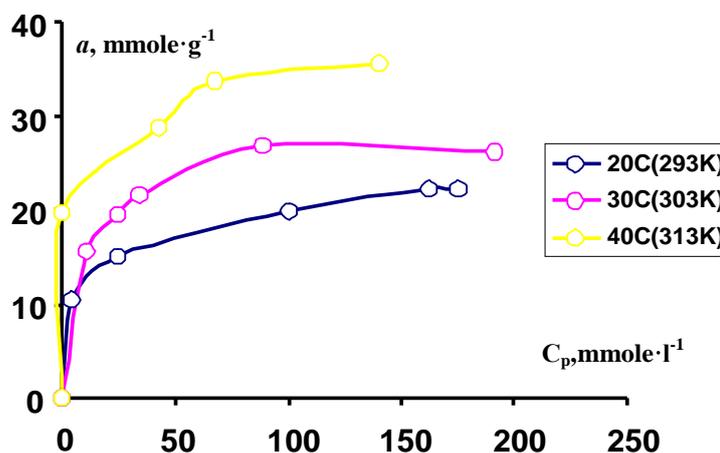
Fig. 4 Isotherm of adsorption of fluoride ions at solution temperatures at 20, 30, 40 (^{0}C) on AMG-400 species
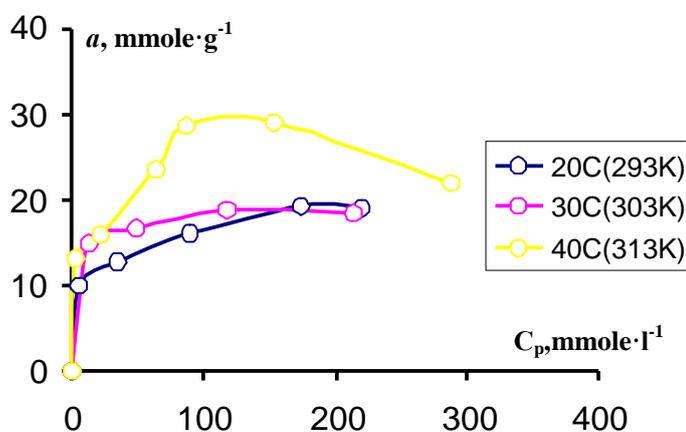
Fig. 5 Isotherm of adsorption of fluoride ions at solution temperatures at 20, 30, 40 (^{0}C) on AMG-600 species

The interrelation between the basic thermodynamic functions of any system is defined by correlation

$$\Delta G^0 = \Delta H^0 - T \Delta S^0, \tag{17}$$

where $\Delta G°$, $\Delta H°$, $\Delta S°$ - standard free energy of adsorption of Gibbs, enthalpy and entropy of adsorption. The values calculated on this equation (17) $\Delta S°$ (in our case $-\Delta H^0 = \bar{Q}^o$) for adsorption of fluorides-ions from water solutions on samples AMG (table 5) testify that they little change with temperature of a solution for the same sample, but differ 1,5-2 times concerning other samples. Nevertheless by absolute value the standard change of entropy of adsorption is not so considerable ($0{,}49 \div 1{,}13$ kJ·mole^{-1}·К$^{-1}$). All this testifies about strong interaction of fluoride-ions (F$^-$) and aluminum cations as on the surface so inside the AMG samples. Most strongly fluorine ions are held on the surface of AMG-200 samples and AMG-400: they demonstrate maximum reduction of negative standard entropy of adsorption.

Let's consider the mechanism of adsorption of ions of fluorine on the surface of sorbents. As it has already been noted, the investigated samples represent oxy hydrates of aluminium with different degree of hydration - the water maintenance fluctuates from 2,85 to 0,089 mole·mole^{-1} of aluminium's oxide. Depending on the nature of connection of hydroxigroups with a sorbent surface following mechanisms of ionization of superficial groups are possible [2]

$$Al(OH)_3= [Al(OH)_2]^++OH^-$$

$$AlOOH= AlO^++ OH^-$$

$$Al_2O_3+3H_2O=2Al(OH)_2^++2OH^-$$
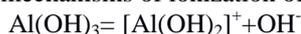
A s a result, in all cases voltage- determinative ions are those of positively charged cations of hydroxy aluminium.

Apparently, under investigated conditions fluorine adsorption is shown to be carried out in two stages - the ionic exchange of fluorine with superficial groups OH$^-$ at the beginning taking place:

$$=Al-OH+F^-\rightarrow =Al^+F+OH^-$$
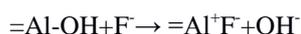
This fact is proven by results of experiences on adsorption of fluorides-ions from water solution in absence of the buffer: increase pH a solution from 7 to 9,5 is observed (tab.2). Then formation of a chemical bond of a fluoride-ion with cation surface aluminum takes place

$$=Al^+F\rightarrow =Al-F$$
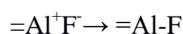
Experiments on desorption fluorine from samples testify in favour of this statement. Triple washing of samples in the conditions identical to conditions of adsorption (application of the acetate buffer, temperature equaling 20, 30, 40(°C), at constant washing within 120 minutes) leads to desorption of only 0,39 % and 1,2 % of fluorine for AMG-400 and AMG-600 samples accordingly. The initial content of fluorine in these samples was 34,75 mmole·g^{-1}and 22,75 mmole·g^{-1}.

As to sample AMG-200, fluorine from its surface practically is not desorbed (not registered in eluates).

IV. CONCLUSION

1. It was shown that for all samples the increase of solution temperature (20-40^{0}C) results in increase of adsorptive capacity as to fluoride-ions that indicate chemical fixing of fluoride ions on the surface. The latter is supported by the experiments on fluoride-ions desorption on the surface of samples.

2. Fluoride-ions adsorption kinetic curves were built and constants of adsorption rate and energy values of adsorption process were calculated. Changes of differential free mole energy, isosteric heat and entropy of fluoride ions depending on samples surfaces filling were considered

3. There was advanced the mechanism of fixing of fluoride ions on the surface of modified alumina oxy hydrates that is anion exchange of fluoride ions with OH groups of surfaces which form covalent link subsequently being transformed into ionic one.

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