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New Composite Materials for Decreasing of Radioactive Molecular Iodine in the Water Coolant in Working and New Developed NPPs

Sergey A. Kulyukhin and Lubov' V. Mizina
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry
Russian Academy of Science
Russia

1. Introduction

Radioactive iodine activity in the water coolant sharply grows during shutdown of the working WWER or RBMK reactors. Therefore, it is marked that radioactivity of ^{131}I in water coolant grows in 30-200 times during shutdown of the RBMK reactor (the Leningrad and Smolensk NPPs) (Kriytskii et al., 2005). Authors of the given paper explain such increase of activity in water coolant as follows. During shutdown of a reactor the temperature of fuel inside fuel elements is reduced, that results in reduction of volume of fuel and occurrence of free space inside fuel elements. At the same time, water from coolant penetrates inside fuel elements through defects in fuel cladding and dissolves radioactive iodine and caesium, which were diffused in the fuel and accumulated in a gap between fuel and cladding at a high degree of the fuel burnup. As a result of dissolution of radioactive iodine and caesium, they are passed as ions into a water coolant. Radioactive iodine can be present in a water coolant as ionic (I^- and IO_3^-) and molecular (I_2) forms due to the oxidation-reduction reactions. Furthermore, because of a radiation destruction of the ion-exchanged resins the organic form (CH_3I) can be also formed in a water coolant. At the same time the content of radioactive iodine in a gas phase grows more than by the order as molecular and organic forms of radioactive iodine make the basic contribution to pollution of a gas phase since their distribution factors between gas and water phases are higher on some orders than similar for ionic forms. The similar effect of increase in the radioactive iodine content in the water coolant during shutdown can be also observed as on working (PWR, LWR, BWR), and on new developed (EPR /Framatome ANP/, SWR-1000 /Framatome ANP/, AP-1000 /Westinghouse/, ESBWR /General Electric/, APWR /Mitsubishi/, ABWR /Toshiba and Hitachi/) NPPs (Krebs, 1999; Reactor Design, 2002; Tomorrow's reactors, 2003).
Usually for decreasing of the radionuclide content in a water coolant the cation- and anion-exchange resins are used on NPPs during normal operation.
Moreover, the 50% decreasing in the power capacity are used on the Leningrad NPP for decreasing of the radioactive iodine content in the water coolant during shutdown of a reactor, i.e. the reactor works on 50% of the power capacity during 2-5 days (Kriytskii et al., 2005). The given approach allows to lower radioactivity of iodine in the water coolant due to short-lived radionuclides decay. However, these actions do not influence the ^{131}I behavior, which makes the basic contribution to activity of the water coolant even in 5 days.

In this connection, it was suggested to continue circulation of the water coolant during 2-5 d with its simultaneous clearing from radioactive iodine after shutdown of a reactor (Kriytskii et al., 2005).

As anion-exchange resins are capable to absorb only ionic forms of the radioactive iodine, there was a problem to develop a new material, capable to absorb molecular and organic iodine from water solutions. Absorption of all forms radioactive iodine from a water phase during shutdown of a reactor, and also, probably, and at normal operation will allow not only to lower radioactivity of the water coolant, but also will sharply lower emission of radioactive iodine into a gas phase. Thus, it is desirable to use materials, which are applied on the working NPPs to clearing coolant, for example ion-exchange resins.

We have shown previously (Krasavina et al., 2008; Kulyukhin et al., 2008, 2008a) that composite materials based on KU-2 cation exchanger, containing nanometer-sized particles of Ag and Cu in an amount of 10 wt %, are capable to take up the molecular form of radioactive iodine from aqueous solutions to 95–99%. The distribution coefficients (K_d) of I_2 exceeded 10^3 cm^3/g upon 15-min contact of the solid and liquid phases at V/m = 100 cm^3/g. The high cost of silver, which is a component of the examined sorbent, makes topical its replacement. Apparently, the most suitable for this purpose are *d*-elements whose physicochemical properties are close to those of silver, namely, Cu, Ni and Zn.

The goal of this study was to develop new composite materials based on Cu-, Ni- and Zn-containing ion exchangers, capable of decreasing the concentration of the molecular form of radioactive iodine in aqueous primary coolant of NPP.

2. Experimental

In our study we used the radionuclide ^{131}I supplied by Izotop Joint-Stock Company in the form of carrier free $Na^{131}I$ solution. The radioactivity of the nuclides was determined by γ-ray spectrometry with a semiconductor Ge–Li detector on a multichannel analyzer. The radionuclide ^{131}I was used as this study as a spike for weighable amount of inactive iodine. Therefore, designations like $^{131}I^-$ and $^{131}IO_3^-$ refer to labeled species and not to species of pure ^{131}I radionuclide. In our study we used aqueous 10^{-5} M solutions of $K^{131}I$ or $K^{131}IO_3$ with the specific activity from 2×10^3 to 3×10^4 Bq/cm^3, and also aqueous solutions of 9×10^{-4} M I_2 containing ~5 mg/cm^3 KI.

All salts, alkalis, and acids used in this study were of chemically pure grade.

Composite materials based on KU-2 cation exchanger and containing *d*-elements were synthesized in two steps, following the procedure described in the patent (Kulyukhin, 2009). In the first step, we performed sorption of *d*-elements (Cu^{2+}, Ni^{2+}, Zn^{2+}) on KU-2 cation exchanger by the following procedure. To aqueous solutions containing appropriate amounts of *d*-element nitrates, we added a weighed portion of KU-2 cation exchanger. The suspension was shaken for 2 h, and then the mother liquor was separated from the cation exchanger impregnated with *d*-elements by centrifugation. The cation exchanger was washed two or three times with distilled water. As a result, we obtained samples of KU-2 cation exchanger containing *d*-elements (Cu^{2+}, Ni^{2+}, Zn^{2+}). The content of metals in KU-2 cation exchanger was determined from the difference between the initial and residual concentrations of metals in the mother liquor and wash waters. Analysis was performed by complexometric titration with EDTA in the presence of murexide or Eriochrome Black, following standard procedures (Charlot, 1961). The results are given in Table 1.

Composite material	Content of d-element in composite material		
	mM/g	mg/g	wt %
KU-2-Cu^{2+}	0.830	53.12	5.3
	0.844	54.02	5.4
KU-2-Ni^{2+}	0.931	54.93	5.5
	0.920	54.28	5.4
KU-2-Zn^{2+}	0.869	56.49	5.6
	0.872	56.68	5.7

Table 1. Content of *d*-elements (Cu^{2+}, Ni^{2+}, Zn^{2+}) in the composite material based on KU-2 cation exchanger

In this step of the synthesis we prepared precursors of the composite materials, based on KU-2 cation exchanger containing ~5.5 wt % *d*-elements. In the second step of the synthesis, the precursors of composite materials were modified. For this purpose, the materials were treated with a 1 M hydrazine hydrate (HH) solution at the metal : HH molar ratio of 1 : 3. Modification was performed at room temperature for 24 h. In all the cases we observed gas evolution and a change in the sample color: In the case of KU-2-Cu-m the color changed from light green to brown with metal lustre, in the case of KU-2-Ni-m, violet and turquoise disseminations appeared against the background of light green color, and in the case of KU-2-Zn-m the color changed from yellow to pale yellow (Fig. 1). The modified cation exchanger containing *d*-elements was separated from the mother liquor by centrifugation and then washed with distilled water until hydrazine hydrate was removed completely (to pH 6–7 of wash waters).
To study localization of ionic ($^{131}I^-$, $^{131}IO_3^-$) and molecular (I_2) iodine species, we used KU-2-M^{II}-m composites (M^{II} = Cu, Ni, Zn) and, along with distilled water, solution of the following composition: NaCl 1.17 mg/dm^3, NH_4Cl 29.96 mg/dm^3, H_3BO_3 5 g/dm^3, pH 7–8.5. The salt concentrations were chosen on the basis of data on the averaged composition of aqueous primary coolant from the first units in Russian NPPs with WWER-type reactors (Kalinin and Novovoronezh NPPs).

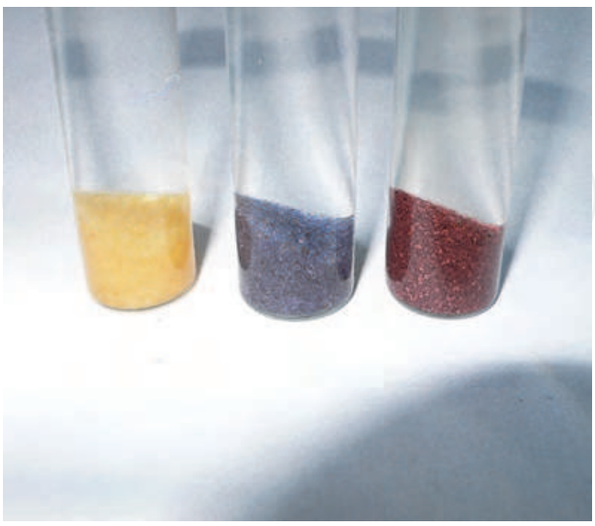


Fig. 1. Composite materials KU-2-Zn-m (pale yellow), KU-2-Ni-m (violet and turquoise disseminations) and KU-2-Cu-m (brown with metal lustre)

Experiments on sorption of $^{131}I^-$ or $^{131}IO_3^-$ from the aqueous phase on composite materials were performed as follows. To 25 cm^3 of an aqueous solution containing 10^{-5} M KI (or KIO_3) and the ^{131}I radionuclide, we added 25 mg of the composite material. The suspension was vigorously stirred for a definite period of time, after which the solid phase was separated from the mother liquor by centrifugation. The precipitate was washed two times with water. The wash waters and mother liquor were combined in one fraction, after which the content of ^{131}I in the solution and precipitate was determined by γ-ray spectrometry. Knowing the V/m ratio, from the distribution of ^{131}I between the solid and liquid phases we calculated the distribution coefficient K_d by the formula

$$K_d = (A_1 / A_2) \cdot (V/m) \quad (1)$$

where A_1 and A_2 - the content of radionuclide ^{131}I in solid and liquid phases accordingly; V - volume of liquid phase (cm^3); m - weight of the composite material based on ion-exchange resin (g).

Because in aqueous solution radioactive iodine can occur not only in molecular form, but also in several other forms simultaneously (I^-, IO_3^-, IO_4^-), it was impossible to use the radioactive tracer technique for studying localization of specifically I_2. Therefore, the efficiency of the I_2 sorption on AV-18 anion exchanger and on the synthesized composite materials was studied by colorimetry using inactive aqueous solutions of I_2.

Experiments were performed as follows. To 25 cm^3 of an aqueous solution of 9×10^{-4} M I_2 we added 25 mg of the composite material. The suspension was vigorously stirred for 120 min, after which the precipitate was separated by centrifugation and washed two times with water. The wash waters obtained and the mother liquor were combined. The amount of I_2 remaining in the final mother liquor and wash waters and that in the initial solution were determined colorimetrically with a fairly high accuracy from a change in the absorption of I_3^- ions in aqueous solution (Ksenzenko et al., 1979). The procedure is very sensitive (detection limit 5 μg/cm^3). The molar extinction coefficient ε for I_3^- at λ = 350 nm is 25000 dm^3/mol×cm. The content of I_2 was determined as follows. An aliquot of a neutral solution being analyzed (5 cm^3), containing from 20 to 200 μg of I_2, was placed in a volumetric flask (25 cm^3), and 1 cm^3 of 1.0 M KI was added. The solution volume was brought to 25 cm^3, and the contents were thoroughly mixed. After 1 h, the solution transparence was measured using a blue color filter at the absorption band of I_3^- ions (λ = 350 nm) in 1–3-cm-thick cells. The transparence of the reference solution was also determined after 1 h. The amount of I_2 was determined with a calibration plot constructed using standard solutions with the I_2 concentration ranging from 0 to 1.0 mg. The standard solutions for the measurements were prepared for measurements by the same procedure as the solution being analyzed.

Thermal gravimetric analysis of KU-2-M^{II}-m composites (M^{II} = Cu, Ni, Zn) and of KU-2 cation exchanger was performed with a Q-1500 derivatograph (MOM, Budapest, Hungary). Samples were heated in platinum crucibles in air at a rate of 10 deg/min.

3. Results and discussion

It is known that, in aqueous solution, molecular iodine (I_2) can form complex ions of the composition I_3^-. Therefore, prior to developing new materials for localization of the molecular form in the primary coolant, it was necessary to examine the sorption properties of the anion exchangers toward I_2 in aqueous solution. The distribution coefficients K_d of I_2 on AV-18 anion exchanger from a solution of iodine in distilled water and simulated coolant are given in Table 2.

Time of contact between phases	K_d, cm³/g	
	water	primary coolant
5 min	100 ± 3	100 ± 3
15 min	130 ± 10	150 ± 12
30 min	415 ± 45	250 ± 25
60 min	532 ± 50	480 ± 50
120 min	540 ± 52	485 ± 52
24 h	7900 ± 200	9100 ± 250
72 h	> 10^4	> 10^4

Table 2. Distribution coefficients K_d of I_2 on AV-18 anion exchanger from solutions in water and simulated primary coolant at 20°C (V/m = 100 cm³/g, [I_2] = 9×10⁻⁴ M)

As can be seen, AV-18 anion exchanger fairly efficiently takes up molecular iodine from aqueous solutions. The distribution coefficients K_d of I_2 increase with the time of contact of the solid and liquid phases, and after 24 h of contact of the solid and liquid phases more than 99.0% of iodine is recovered from its solutions in distilled water and from the simulated primary coolant.

It should be noted that data on sorption of molecular iodine, given in Table 2, were obtained under static conditions. Actually the contact time of the coolant with the ion exchangers does not exceed 5–15 min (Glanneskog et al., 2006). Therefore, low rate of sorption of molecular iodine from aqueous solutions on AV-18 anion exchanger does not allow its use for efficient removal of this form of radioiodine from primary coolant both in the course of the campaign and during the reactor outage.

Data on localization of I_2 from distilled water on wet composite materials at various contact times of the solid and liquid phases are given in Table 3. To avoid oxidation of the developed materials with atmospheric oxygen, they were stored under a layer of distilled water and, in experiments on I_2 localization, used wet. As seen from Table 3, the synthesized composite materials exhibit high ability to localize the molecular form of iodine from aqueous solutions, and virtually complete localization of I_2 (>99.0%) is attained already in 5 min. At the same time, KU-2 cation exchanger does not participate in localization of the molecular form of radioiodine to a noticeable extent.

Time of contact between phases	C/C_0			
	KU-2	KU-2-Ni-m	KU-2-Zn-m	KU-2-Cu-m
5 min	< 0.0001	0.994 ± 0.004	0.993 ± 0.005	0.991 ± 0.004
15 min	< 0.0001	0.994 ± 0.004	0.993 ± 0.003	0.992 ± 0.005
30 min	< 0.0001	0.994 ± 0.005	0.992 ± 0.004	0.991 ± 0.003
60 min	< 0.0001	0.994 ± 0.005	0.992 ± 0.004	0.992 ± 0.004
120 min	< 0.0001	0.992 ± 0.004	0.990 ± 0.002	0.991 ± 0.004
72 h	< 0.0001	0.995 ± 0.004	0.995 ± 0.004	0.992 ± 0.005

Table 3. Fraction of I_2 (C/C_0) localized on various materials at various contact times of the solid and aqueous phases at 20°C ([I_2] = 1×10⁻⁵ M)

It was interesting to elucidate the mechanism of localization of molecular iodine on composite materials. A study of the I_2 localization from aqueous solutions on massive Cu, Zn, and Al plates (Glanneskog et al., 2006) showed that localization of I_2 on Cu plates occurs via adsorption with the formation of CuI on the surface, whereas in the presence of Zn and

Al plates the I_2 localization involves its conversion into ionic species. It was shown in (Glanneskog et al., 2006) that, the larger the ratio of the metal surface area to the solution volume, the higher the adsorption (or conversion) rate. In addition, the reaction rates increased with an increase in the solution temperature. To elucidate the mechanism of localization of molecular iodine from aqueous solution, it was necessary to perform experiments to examine the material balance of iodine in the liquid phase before and after localization on composite materials.

However, because iodine in the aqueous phase can occur in both molecular and ionic forms, it was preliminarily necessary to examine the sorption properties of the composites synthesized toward ionic iodine species, I^- and IO_3^-. The distribution coefficients K_d of $^{131}I^-$ and $^{131}IO_3^-$ from aqueous solutions on composite materials based on KU-2 cation exchanger containing *d*-elements and on straight KU-2 resin after 120-min contact of the solid and liquid phases are given in Table 4. As can be seen, the synthesized composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn), as well as KU-2 cation exchanger, do not noticeably sorb ionic radioiodine species from aqueous solutions. The degree of sorption of $^{131}I^-$ and $^{131}IO_3^-$ does not exceed 0.02%, and K_d of $^{131}I^-$ and $^{131}IO_3^-$ is below 1.5 cm^3/g. At same time, the degree of sorption of $^{131}I^-$ and $^{131}IO_3^-$ from water solutions on composite material KU-2-Cu-m changes from 12 to 45%, and K_d of $^{131}I^-$ and $^{131}IO_3^-$ is 15-85 cm^3/g.

Composite materials	K_d, cm^3/g			
	water		primary coolant	
	$^{131}I^-$	$^{131}IO_3^-$	$^{131}I^-$	$^{131}IO_3^-$
KU-2	1.1 ± 0.05	1.1 ± 0.05	1.1 ± 0.06	1.1 ± 0.06
KU-2-Ni-m	0.4 ± 0.02	0.16 ± 0.02	0.1 ± 0.01	0.5 ± 0.02
KU-2-Zn-m	0.1 ± 0.01	0.16 ± 0.02	0.1 ± 0.01	0.1 ± 0.01
KU-2-Cu-m	14.8 ± 0.7	24.3 ± 1.2	46.8 ± 2.3	81.0 ± 4.0

Table 4. Distribution coefficients (K_d) of $^{131}I^-$ and $^{131}IO_3^-$ on composite materials from solutions in distilled water and in simulated primary coolant at 20°C ($[^{131}I^-] = [^{131}IO_3^-] = 1\times10^{-5}$ M, [NaCl] =1.17 mg/dm^3, $[NH_4Cl]$ = 29.96 mg/dm^3, $[H_3BO_3]$ = 5 g/dm^3, contact time 120 min, V/m = 100 cm^3/g)

Experiments on studying the material balance of iodine in the liquid phase before and after localization on composite materials were performed as follows. To 100 cm^3 of an aqueous solution containing definite amounts of I_2, I^-, and IO_3^-, at 20°C, we added 250 mg of the composite material. The suspension was shaken for 120 min, and the solid phase was separated from the solution by centrifugation. The solid phase was then washed two or three times with distilled water.

The mother liquor and the wash waters were combined. In the initial and final solutions, we first determined the amount of the molecular form (I_2) and then, after the reduction of I_2 with hydrazine hydrate to I^-, the total iodine content. Because the developed composite materials do not noticeably absorb ionic iodine species, from the change of the iodine amount in solution we could evaluate the localization of I_2. Similar experiments were performed at 40 and 60°C, but first we examined the effect of temperature on the dissociation of I_2 in aqueous solution. The experiments were performed as follows. Ampules with an aqueous I_2 solution of known concentration were placed in a BINDER drier oven and kept at a definite temperature for 5, 15, 30, 60, and 120 min. The I_2 concentration in the final solution was determined, and the degree of dissociation of I_2 was calculated from

difference. This correction for the change in the I_2 concentration was taken into account both when constructing the iodine balance and when performing experiments on I_2 localization from various solutions. Data on the kinetics of variation of the I_2 content in aqueous solution at 20, 40, and 60°C are given in Table 5. As can be seen, at 20 and 40°C the I_2 concentration in the solution does not change for 120 min, whereas at 60°C in 120 min the I_2 concentration in the solution decreases by approximately 20%. Because in all the experiments the contact time of the solid and liquid phases did not exceed 120 min, it was unnecessary to perform thermostating of I_2 solutions for a longer time.

t, min	20°C	40°C	60°C
5	220 ± 3	220 ± 3	220 ± 3
15	220 ± 4	220 ± 2	200 ± 2
30	220 ± 3	220 ± 2	190 ± 4
60	220 ± 2	220 ± 3	185 ± 2
120	220 ± 3	220 ± 4	180 ± 3

Table 5. Concentration of I_2 in aqueous solution (mg/dm^3) in relation to thermostating time *t*

Data on the iodine balance in the aqueous solution–composite system at 20, 40, and 60°C are given in Table 6. As can be seen, in all the cases, excepting system "water solution - KU-2-Cu-m" at 20°C, the total amount of iodine in the system before and after the interaction with the composite materials coincides. Each value of the I_2 and ΣI amount in the initial and final solutions was calculated as the mean value from three replicate runs. This fact suggests that, in all the systems, in the presence of the developed composite materials I_2 undergoes conversion to ionic species. In the case system "water solution - KU-2-Cu-m" at 20°C about 20% of I_2 absorb on the composite material and about 80% of I_2 converse to ionic forms. So, in what follows we study the localization of I_2 in the system "water solution - KU-2-Cu-m" at 20°C without isolation of each processes contribution.

Data on localization of I_2 from aqueous solutions on wet composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn, Cu) at 20, 40, and 60°C are given in Table 7. As can be seen, wet composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn, Cu) exhibit high localizing ability toward molecular iodine both in distilled water and in simulated primary coolant of water-cooled water-moderated reactors. Despite certain decrease in the degree of I_2 localization in the simulated primary coolant, the degree of localization exceeds 95%. The study of the kinetics of these processes shows that already after 5-min contact of the solid phase and solution the degree of localization of I_2 exceeds 95%.

Taking into account high reduction potential of the Ni^{2+}/Ni^0 and Zn^{2+}/Zn^0 couples [–0.234 and –0.763 V, respectively (Lidin et al., 2006)] and the capability of Ni^{2+} and Zn^{2+} ions to form stable complexes with hydrazine [log*K* = 2.76–11.99 for Ni^{2+} and 2.4–6.3 for Zn^{2+} (Chemist's Handbook, 1964)], we could expect that modification of the materials with hydrazine hydrate could involve partial or complete reduction of metal ions to the metallic state or formation of complex ions $[M^{II}(N_2H_4)_n]^{2+}$ (M^{II} = Ni, Zn) in the composite materials. Figure 2 shows electron micrographs of the composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn), obtained with an EM-301 electron microscope (Philips). As can be seen, the materials developed contain nanometric M^0 particles (M = Ni, Zn) of the size that does not exceed 50 nm. However, their concentration is low. Therefore, we could assume formation of complex ions in the composite material on treatment of the precursor with hydrazine hydrate.

Figure 3 shows the results of thermal gravimetric analysis of the synthesized materials KU-2-M^{II}-m (M^{II} = Ni, Zn). As seen from Fig. 3a, in the DTA curve of KU-2-Ni-m at 252°C there

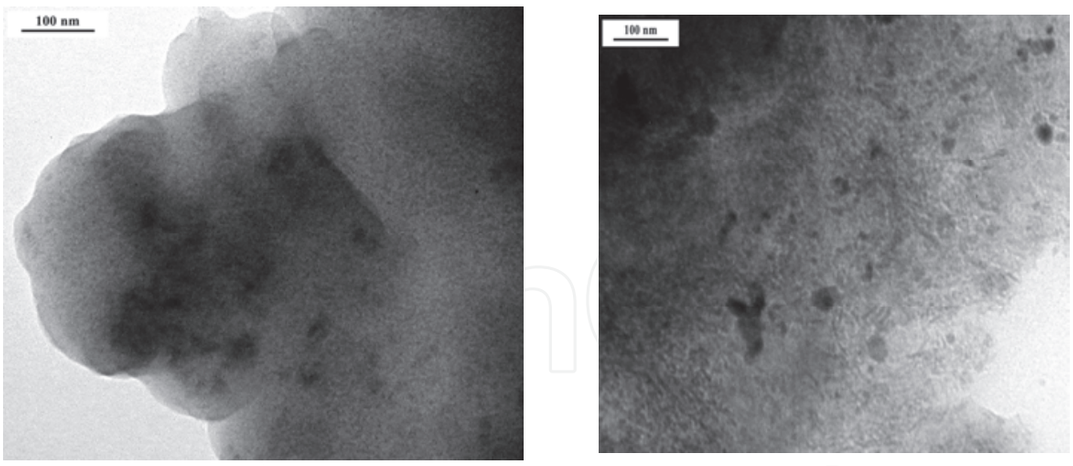
is an exothermic effect accompanied by a sharp weight loss. This effect is parently associated with decomposition of the complex $[Ni(N_2H_4)_n]^{2+}$ in the material. The subsequent exothermic effect is due to combustion of the ion-exchange matrix. In the DTA curve of KU-2-Zn-m (Fig. 3b), there is also an exothermic effect accompanied by a sharp weight loss. It is observed at 285°C and is, apparently, associated with decomposition of the complex $[Zn(N_2H_4)_n]^{2+}$ in the material. The subsequent exothermic effect, as in the case of KU-2-Ni-m, is due to combustion of the ion-exchange matrix. The data we obtained allow a conclusion that treatment of the precursor, KU-2-M^{2+} (M^{2+} = Ni, Zn), with hydrazine hydrate mainly involves formation of complex ions $[M^{II}(N_2H_4)_n]^{2+}$ (M^{II} = Ni, Zn) in the composite material and only partial reduction of *d*-element ions to the metal. It should be noted that both diagrams of thermal decomposition of KU-2-M^{II}-m materials (M^{II} = Ni, Zn) differ from the curves of thermal decomposition of KU-2 (Fig. 4). Thus, the localizing effect of KU-2-M^{II}-m composites (M^{II} = Ni, Zn) is based on the reduction of molecular iodine to ionic species with hydrazine molecules incorporated in the complex $[M^{II}(N_2H_4)_n]^{2+}$ (M^{II} = Ni, Zn) in the structure of the materials.

Composite material	T, °C	Initial solution		Final solution		Composite material
		I_2	ΣI	I_2	ΣI	
KU-2-Ni-m	20	0.039 ± 0.002	0.064 ± 0.003	< 0.0001	0.064 ± 0.003	< 0.0001
	40	0.037 ± 0.001	0.062 ± 0.002	< 0.0001	0.062 ± 0.002	< 0.0001
	60	0.038 ± 0.002	0.063 ± 0.003	< 0.0001	0.063 ± 0.003	< 0.0001
KU-2-Zn-m	20	0.039 ± 0.002	0.064 ± 0.003	< 0.0001	0.064 ± 0.003	< 0.0001
	40	0.037 ± 0.001	0.062 ± 0.002	< 0.0001	0.062 ± 0.002	< 0.0001
	60	0.038 ± 0.002	0.063 ± 0.003	< 0.0001	0.063 ± 0.003	< 0.0001
KU-2-Cu-m	20	0.039 ± 0.002	0.064 ± 0.003	< 0.0001	0.056 ± 0.002	0.008 ± 0.001
	40	0.037 ± 0.001	0.062 ± 0.002	< 0.0001	0.062 ± 0.002	< 0.0001
	60	0.038 ± 0.002	0.063 ± 0.003	< 0.0001	0.063 ± 0.003	< 0.0001

Table 6. Iodine balance (content, mM) in the aqueous solution–composite system at various temperatures

Composite materials	T, °C	C/C_0	
		water	primary coolant
KU-2-Ni-m	20	0.992 ± 0.004	0.960 ± 0.004
	40	0.982 ± 0.005	0.958 ± 0.005
	60	0.985 ± 0.007	0.963 ± 0.006
KU-2-Zn-m	20	0.995 ± 0.004	0.968 ± 0.004
	40	0.993 ± 0.005	0.961 ± 0.005
	60	0.991 ± 0.007	0.966 ± 0.006
KU-2-Cu-m	20	0.991 ± 0.004	0.963 ± 0.004
	40	0.987 ± 0.005	0.957 ± 0.005
	60	0.984 ± 0.007	0.955 ± 0.006

Table 7. Degree of conversion of I_2 (C/C_0) into ionic species with wet composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn, Cu) from a solution in distilled water and from simulated primary coolant at various temperatures ($[I_2] = 1\times10^{-5}$ M, [NaCl] = 1.17 mg/dm^3, $[NH_4Cl]$ = 29.96 mg/dm^3, $[H_3BO_3]$ = 5 g/dm^3, contact time 120 min)



A B

Fig. 2. Electron micrographs of the composite material KU-2-Ni-m (A) and KU-2-Zn-m (B).

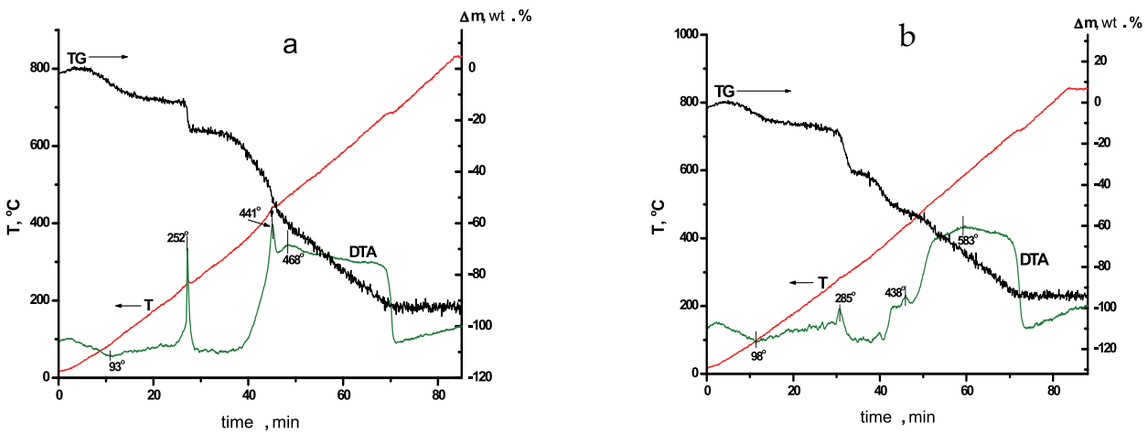


Fig. 3. Results of thermal gravimetric analysis of (a) KU-2-Ni-m (sample weight 69.0 mg) and (b) KU-2-Zn-m (sample weight 62.6 mg).

Based on the data of conversion of I_2 in the presence of copper nanometric particles (Fedushchak et al., 2008), it was interested to study the structure of developed composite material KU-2-Cu-m.

During reduction of Cu by hydrazine hydrate the formation of metal particles can take place. On the dependence from reduction conditions the size of metal particles can change more then order (Fedushchak et al., 2008). The higher copper concentration in material, the bigger particle formed during reduction.

Figure 5 shows electron micrographs of the composite material KU-2-Cu-m, obtained with an EM-301 electron microscope (Philips). As can be seen, the materials developed contain nanometric Cu^0 particles of the size that does not exceed 50 nm. Due to the formation of nanometric particle of Cu^0 the conversion of I_2 takes place in these systems.

At the same time the $[Cu(N_2H_4)_n]^{2+}$ can formed during treatment of the precursor with hydrazine hydrate (HH). Figure 6 shows the results of thermal gravimetric analysis of the synthesized materials KU-2-Cu-m. As seen from Fig. 4 and 6, the decomposition curves of KU-2 and KU-2-Cu-m are similar. The DTA curve of KU-2-Cu-m does not include additional

exothermic effect in comparison with DTA curve of KU-2. These data allow us to conclude that during treatment of the precursor KU-2-Cu^{2+} with HH the reduction of Cu^{2+} to Cu^{0} take place.

Figure 7 shows comparative data on localization of the I_2 from simulated primary coolant on AV-18 anion exchanger and on wet samples of the developed composite materials. As can be seen, contact for 15 min ensures virtually complete localization of I_2 (>99.0%) on the materials we developed, whereas on AV-18 anion exchanger the degree of the I_2 sorption is as low as 60%.

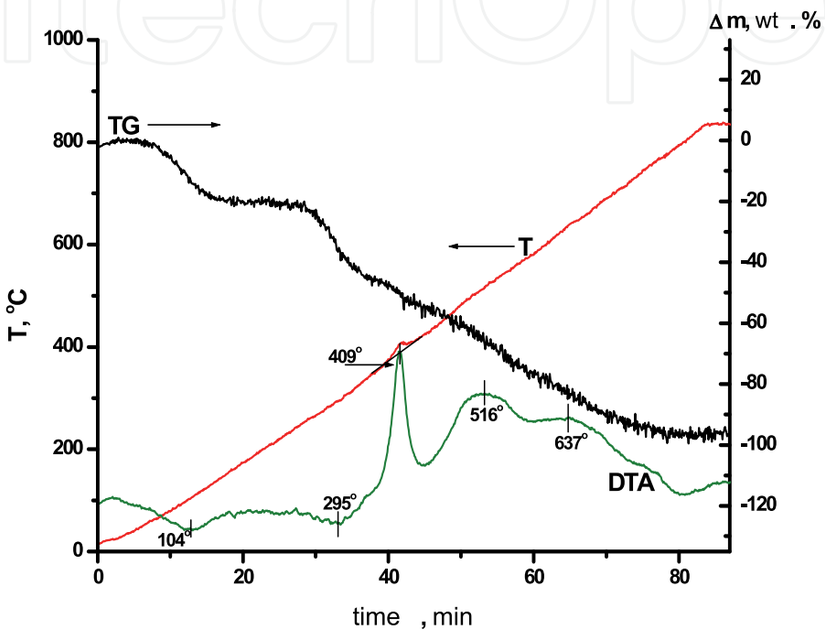


Fig. 4. Results of thermal gravimetric analysis of KU-2 (sample weight 60.4 mg).

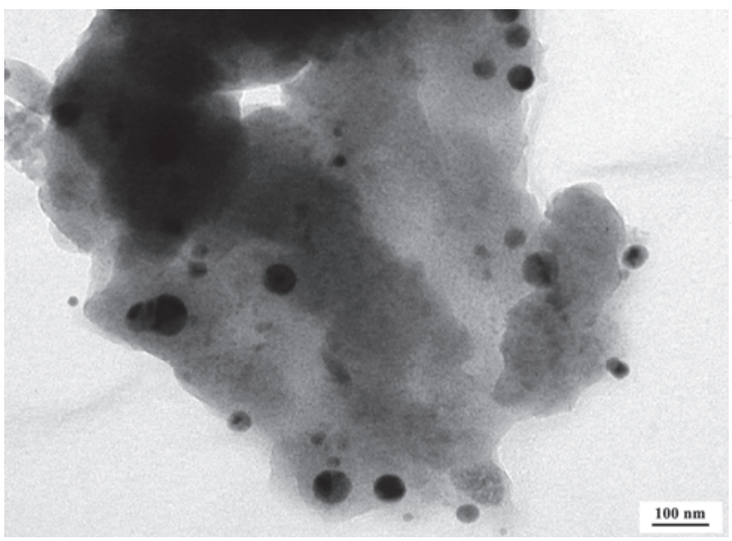


Fig. 5. Electron micrograph of the composite material KU-2-Cu-m.

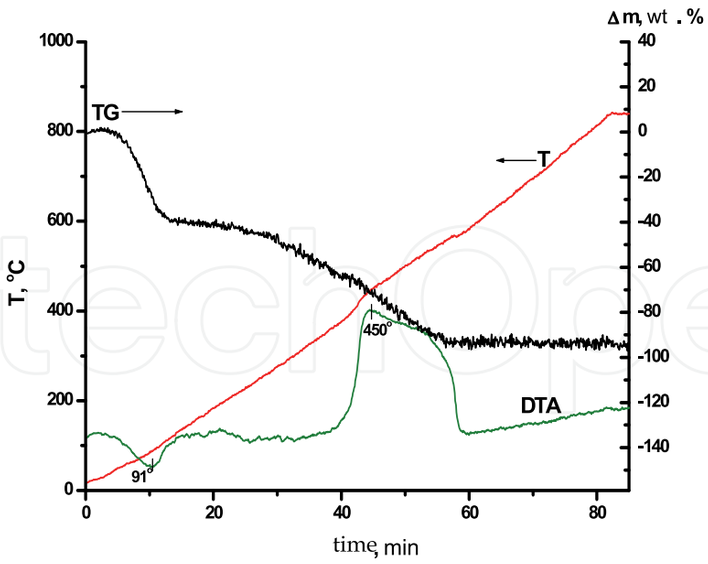


Fig. 6. Results of thermal gravimetric analysis of KU-2-Cu-m (sample weight 54.2 mg)

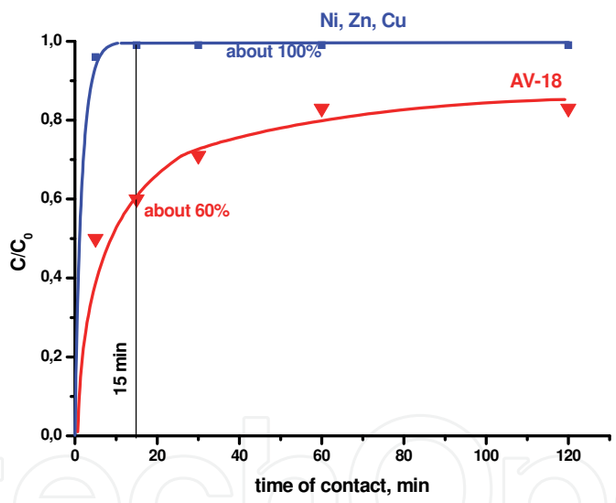


Fig. 7. Fraction of I_2 taken up by AV-18 anion exchanger and by wet samples of composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn, Cu) as a function of the contact time of the solid and liquid

Thus, wet composite materials based on KU-2 cation exchanger containing *d*-elements, after modification with hydrazine hydrate, show high localizing ability toward molecular iodine in aqueous solutions. At the same time, from the viewpoint of possible application of these materials and their transportation to the site of use, it is important to evaluate the localizing properties of these materials after their drying to the friable state. Below are data on the degree of localization of molecular iodine in simulated primary coolant in the presence of dried composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn, Cu) (Table 8). The analogous data for the wet samples are given for comparison.

It can be seen that the degree of I_2 localization from simulated primary coolant in the presence of dried Ni and Zn-containing samples is close to that obtained with the wet samples. At the same time, the localizing ability of the Cu-containing samples decreases on drying by a factor of approximately 5. This may be due to the fact that drying of the Cu-containing materials is accompanied by changes in the state of a part of metallic copper. Thus, KU-2-M^{II}-m composites (M^{II} = Ni, Zn) can be used in both wet and dried state.

Composite material	C/C_0	
	Wet sample	Dried sample
KU-2-Ni-m	0.960 ± 0.004	0.961 ± 0.003
KU-2-Zn-m	0.968 ± 0.004	0.970 ± 0.005
KU-2-Cu-m	0.963 ± 0.004	0.180 ± 0.001

Table 8. Degree of conversion of I_2 into ionic species (C/C_0) with the KU-2-M^{II}-m composites (M^{II} = Ni, Zn, Cu) in simulated primary coolant at 20°C ([I_2] = 1×10^{-5} M, [NaCl] = 1.17 mg/dm^3, [NH_4Cl] = 29.96 mg/dm^3, [H_3BO_3] = 5 g/dm^3, contact time 120 min)

Along with studying the localizing ability of the materials synthesized, it was interesting to estimate the maximal amount of I_2 that can be converted in aqueous solutions and to compare the data obtained with the analogous characteristics of AV-18 anion exchanger. The experiment was performed as follows. A 250-ml Erlenmeyer flask was charged with 500 mg of KU-2-M^{II}-m composite (M^{II} = Ni, Zn, Cu) or AV-18 anion exchanger. Then 100 cm^3 of a 9×10^{-3} M aqueous solution of I_2 was added. The suspension was vigorously stirred for 120 min. Then an aliquot was taken from the solution, and the I_2 amount in it was determined colorimetrically. If the sample contained no I_2, one more portion (100 cm^3) of the same aqueous solution of I_2 was added. The experiment was performed until unchanged I_2 appeared in the mother liquor. The maximal amounts of I_2 localized from various aqueous solutions with the materials developed are given in Table 9. As can be seen, for distilled water and simulated primary coolant the results are well consistent. The amount of I_2 localized with wet KU-2-M^{II}-m samples (M^{II} = Ni, Zn) is considerably higher than with AV-18 anion exchanger.

Material	Aqueous solution	Localized I_2, mg/g	
		wet sample	dried sample
KU-2-Ni-m	Water	> 3100	> 3100
	Primary coolant	> 3100	> 3100
KU-2-Zn-m	Water	> 3100	> 3100
	Primary coolant	> 3100	> 3100
KU-2-Cu-m	Water	> 3100	101 ± 5.05
	Primary coolant	> 3100	81.5 ± 4.40
AV-18	Water	-	158 ± 7.6
	Primary coolant	-	208 ± 10.0

Table 9. Maximal amount of I_2 converted into ionic species in the presence of the developed materials in distilled water and simulated primary coolant at 20°C ([NaCl] = 1.17 mg/dm^3, [NH_4Cl] = 29.96 mg/dm^3, [H_3BO_3] = 5 g/dm^3, contact time 120 min)

Thus, composite materials KU-2-M^{II}-m (M^{II} = Ni, Zn) that we developed allow more than 95.0% localization of molecular iodine from aqueous solutions. At the same time, it should be taken into account that iodine after the conversion remains in the solution phase, i.e., its back conversion to the molecular form is probable. Therefore, we developed a two-step procedure for iodine localization from aqueous solutions. The experiment on two-step localization of molecular iodine was performed as follows. To 100 cm^3 of a 1×10^{-5} M I_2 solution, we added 500 mg of the composite material KU-2-M^{II}-m (M^{II} = Ni, Zn) and vigorously stirred the suspension for 5 min. Then the mother liquor was separated by decantation, the composite material was washed with two portions of distilled water, and the wash waters and mother liquor were combined. An aliquot of the combined solution was taken for colorimetric determination of the concentration of molecular iodine. After that, the combined solution was spiked with ^{131}I and thoroughly mixed for 5 min, and 5.0 g of AV-18 anion exchanger was added. The suspension was vigorously stirred for 15 min. The anion exchanger was separated by centrifugation and washed with two portions of distilled water. The mother liquor was combined with the wash waters. The amounts of ^{131}I in the solution and resin were determined by γ-ray spectrometry. Below are results of experiments on localization of molecular iodine from aqueous solutions by the two-step scheme (Table 10). As can be seen, the use of the two-step treatment first with the composite material and then with AV-18 anion exchanger allows more than 95.0% localization of the molecular form of radioactive iodine from aqueous solutions of various compositions.

Material	C/C_0	
	water	primary coolant
KU-2-Ni-m	0.956	0.961
KU-2-Zn-m	0.959	0.966

Table 10. Degree of I_2 localization (C/C_0) from aqueous solutions by two-step treatment first with the composite material and then with AV-18 anion exchanger at 20°C ($[I_2] = 1\times10^{-5}$ M, [NaCl] = 1.17 mg/dm^3, $[NH_4Cl]$ = 29.96 mg/dm^3, $[H_3BO_3]$ = 5 g/dm^3, contact time 120 min)

4. Conclusion

It should be noted in conclusion that the use of the materials we developed does not require changes in the NPP design and significant changes in the units for treatment of aqueous primary coolant. At the same time, these materials ensure not only a decrease in the amount of radioactive iodine in aqueous primary coolant, but also a decrease in the radioactive iodine discharge into working rooms of an NPP. That is, the load on iodine filter is reduced both in the course of the reactor outage and spent nuclear fuel reloading and at normal NPP operation.

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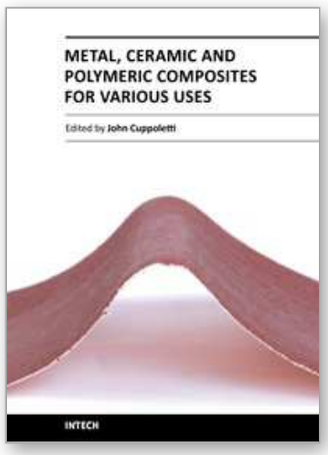
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