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Fundamental and applied aspects of the chemistry of radioactive iodine in gas and aqueous media

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Abstract. The results of investigations carried out in the past 15 – 20 years in the chemistry of radioactive iodine in the gas phase and in aqueous media of various compositions are described systematically and analyzed. The prospects for practical application of the obtained data in various fields of nuclear power industry including accidents at nuclear power plants and enterprises engaged in spent nuclear fuel reprocessing are estimated. The bibliography includes 206 references.

I. Introduction

In the last 15 years, studies in the field of power engineering and energy saving have been among the priority lines of development of science, technology and engineering. Particular attention is paid to the further development of nuclear power engineering, the prospects of which are related to solution of two key problems: safe operation of nuclear power plants (NPP) and reprocessing of the spent nuclear fuel (SNF) from these plants. Due to the operation of nuclear power facilities, radioactive products get into the environment, despite the efforts undertaken to capture them. Radioactive iodine (below designated by I*) is a product of nuclear fuel fission, highly hazardous for the environment. Indeed, the IAEA classifies the accidents or other events at nuclear power facilities according to the amount of I* emission to the environment.[1]

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The stable iodine nuclide with the mass number 127 (^{127}I) was discovered almost 200 years ago. The chemical properties of various ^{127}I compounds were already studied in detail by the mid-20th century.[2] With the advent of nuclear physics and investigation of nuclear fission, it was found that other iodine nuclides with mass numbers from 115 to 141 may also exist, but their discovery and identification require cumbersome capture methods and reliable identification of their emission spectra.

The necessity to solve problems associated with the environmental safety of nuclear power engineering and SNF reprocessing required more detailed investigations of the properties of iodine radionuclides.[3 – 10] It can be seen from Table 1 that one tonne of the SNF from a pressurized water reactor (PWR) accumulates 200 to 300 g of I* at an average nuclear fuel burn-up rate of 45 GW day t^{-1}; in relation to all reactor fuel, this corresponds to $\sim$12 kg.[11] During long-term storage of fuel elements, all short-lived iodine radionuclides decay and, depending on the storage time, either two (^{127}I, ^{129}I) or three (^{127}I, ^{129}I, ^{131}I) nuclides remain in the SNF supplied for reprocessing. In this situation, of special note is the long-lived nuclide ^{129}I with half-life of 1.57×10^7 years. Annually, about 2 tonnes of ^{129}I are accumulated at nuclear plants. The problems of its isolation and storage were actively discussed in the 1970 – 1980s;[3] however, they still remain topical.[12 – 15] Reliable isolation of ^{129}I, even of that present within solid radioactive waste, for long-term storage is problematic due to the high migration ability of I* in the biosphere because of the physicochemical properties of iodine. For this reason,[129]I is currently considered as one of the possible candidates for annihilation by means of transmutation induced by irradiation with thermal and resonance neutrons.[15] Despite the considerable progress, the flow diagram for ^{129}I transmutation has not yet been elaborated in sufficient detail, as opposed to ^{99}Tc and actinides.[16 – 18] In

Table 1. Amounts and radioactivity of iodine nuclides formed in a PWR type reactor (per tonne of SNF) at an average nuclear fuel burn-up rate of 45 GW day t^{-1} (see Ref. 3).

Nuclide	Half-life	Activity /Ci	Amount /g
^{127}I	stable		39
^{128}I	25.0 min	1.3×10^{4}	2.2×10^{-4}
^{129}I	1.57×10^{7} years	3.8×10^{-2}	230
^{130m}I	9.0 min	2.8×10^{4}	1.8×10^{-4}
^{130}I	12.36 h	4.1×10^{4}	0.021
^{131}I	8.04 days	1.0×10^{6}	8.0
^{132}I	2.38 h	1.4×10^{6}	0.14
^{133}I	20.8 h	1.8×10^{6}	1.6
^{134}I	52.0 min	2.1×10^{6}	0.079
^{135}I	6.59 h	1.6×10^{6}	0.47
^{136}I	83 s	6.4×10^{5}	6.4×10^{-4}
^{137}I	24.2 s	1.7×10^{6}	4.7×10^{-4}
^{138}I	6.3 s	1.6×10^{6}	1.2×10^{-4}
^{139}I	2.3 s	1.3×10^{6}	3.3×10^{-5}

2003, transmutation of ^{129}I to ^{128}I was first performed on a laboratory scale using laser technology.[19]

An absolutely different situation may arise during accidents at NPP, especially severe (so-called beyond design basis) accidents associated with nuclear fuel meltdown. Depending on the operation time of the reactor, the amounts of I* in the fuel that gets into the atmosphere of the reactor containment shell and then may get into the environment are different and can vary from hundreds of grams to tens of kilograms. The LIRIC model (Library of Iodine Reactions in Containment) was developed for predicting the chemical forms of I* and their concentrations in the containment atmosphere during severe accidents. It includes more than 150 chemical reactions of I*, including reactions with organic impurities.[20]

Due to the large diversity of chemical forms in water or in the gas medium and high mobility in the environment, radioactive iodine presents the greatest environmental hazard and requires the development of complex protective systems for its capture both during SNF reprocessing and in NPP protective systems. In the development of capture systems, the attention is focused on CsI aerosols and compounds HI, HOI, I_2 and CH_3I in the gas phase and I_2, I^- and IO_3^- in the aqueous medium.

Since removal of I* is a topical issue, the purpose of this review is to describe systematically and analyze the results of studies dealing with I* chemistry in the gas phase and in the aqueous media of various compositions carried out in different countries during the last 15–20 years and to evaluate the prospects of the practical use of these results in various fields of nuclear power engineering.

II. Behaviour of radioactive iodine in the atmosphere

Many works devoted to the physicochemical properties of iodine and iodine nuclides as well as the capture techniques for various forms of I* during the possible emergency situations in NPP were published and summarized in several collections and monographs back in 1950–1990s.[3–10] They reported using the filtration and sorption techniques for I* capture on activated carbons, mineral natural sorbents, zeolites, oxide and organic sorbents, as well as using liquid scrubbers and sprinkler systems. Since the 1990s, apart from the upgrading and modification of traditional methods for I* capture by various materials, new methods and systems for iodine removal from gas medium started to be developed. They include agglomeration co-crystallization, sorption on hydrophilic inactive aerosols, development of new combined systems and the use of metallic filters of various types.

The greatest environmental hazard during nuclear power plant accidents comes from ^{131}I and ^{129}I nuclides. Due to the high radioactivity, ^{131}I causes enormous ecological and biological harm to the environment and especially to human health during the first several weeks after a severe accident. The ^{129}I radionuclide whose activity is about 10^7 times lower than the activity of ^{131}I, while the content and the half-life are much greater than those of ^{131}I (see Table 1) is also quite hazardous because of the chemical properties of iodine, which are responsible for its fast migration in the environment. Therefore, the consequences of the Chernobyl nuclear plant accident are still being monitored and analyzed. A number of publications[4,21–25] report the results of studies of chemical forms of I* in the Earth atmosphere after the Chernobyl accident. During the accident, about 670 PCi of ^{131}I and ^{129}I, ^{132}I, ^{133}I and ^{135}I were discharged from the crashed reactor to the environment. During a short period, radioactive gas and aerosol products spread over the atmosphere of the whole Northern Hemisphere of the Earth, and some of them got not only into the mid and upper troposphere but also the stratosphere. Considerable amounts of I* and other radionuclides reached Japan in a week, and in 10–14 days, they arrived in North America. According to studies carried out in Europe, Japan and the USA, after the Chernobyl accident, gaseous forms of ^{131}I prevailed over the aerosol forms on both the local and global scales. The aerosol-to-gas ratios for ^{131}I determined in different points of the Northern Hemisphere atmosphere always showed considerable predominance (65%–85%) of the gaseous I* forms.[22] This trend held throughout the whole monitoring period, both forms being stable in the atmosphere.[21] According to Budyka and Ogorodnikov,[25] the ratio of the aerosol to gaseous ^{131}I components in the Chernobyl region was not higher than 0.6 with allowance for the desorption correction.

Note that the chemical forms of the ^{132}I nuclide markedly differed from ^{131}I forms. The ^{132}I content in the aerosol phase predominated over its content in the gas phase. The fraction of ^{132}I in aerosols was found to be 1.5–3 times higher than that of ^{131}I. The reason is the origin of iodine radionuclides sampled 2–3 days after the accident and later. The ^{132}I nuclei that accumulated in the reactor before the accident had already decayed by that time, and the nuclei that predominated in air were mainly those formed after the accident upon the decay of the mother ^{132}Te nuclide, which was more than 90% in the aerosol form.[23,24]

The gas and aerosol components of ^{133}I proved to be full analogues of ^{131}I, and its gaseous forms accounted for 75%–80%. This provided the assumption that an identical I* distribution between the aerosol and gas phases may also be expected of ^{129}I and ^{135}I. However, it cannot be ruled out that due to the long residence time of ^{129}I in the reactor, its carriers could have different physicochemical characteristics.

When the chemical forms of atmospheric I* were investigated after the Chernobyl nuclear plant accident, not only

the aerosol : gas ratios were determined but also the contents of HOI, I_2 and CH_3I in the gas phase were estimated. Gaseous organic iodides (GOIs) were the predominant ^{131}I compounds of the Chernobyl origin. They accounted, on average, for 70% of the total atmospheric 131-iodine. The fractions of I_2 and HOI were each 5%–6%.

The degree of dispersion of aerosols and gaseous ^{131}I species was reported to affect the radiation doses inhaled by a human.[24] It was found[23] that aerosols that entered samplers can be classified into two fractions, fine (diameter < 2 μm) and coarse ones. The major part (at least 80%) of I* occurred in the finely dispersed fraction of particles with the average median diameter of 0.3–0.4 μm. This class of aerosol particles is most hazardous as regards the penetration ability into the human respiratory system.

In the 1960–1980s, studies dealing with determination of ^{127}I content and forms in the Earth atmosphere were carried out. As a result, only $CH_3{}^{127}I$ and $^{127}I_2$ are regarded as reliably identified gaseous compounds. The data on other ^{127}I species ($H^{127}I$, $H^{127}IO_3$, $^{127}IONO_2$ and so on) are based on model calculations and estimates of the rates of possible photochemical reactions.[4] The rate of solar radiation-induced photodissociation of $CH_3{}^{127}I$ and $^{127}I_2$ is much higher than the rates of reactions that occur in air. Currently, it is generally accepted that $CH_3{}^{127}I$ and $^{127}I_2$ are the primary gaseous forms of migration of ^{127}I from the ocean to the Earth atmosphere. The compounds $H^{127}I$, $HO^{127}I$, ^{127}IO and $^{127}IONO_2$ formed upon photodissociation can react in air with aerosol species, and again undergo photodissociation and other processes. Due to the high photodissociation rate, the photochemical equilibrium is established over a short period of time.

These processes can be disturbed upon severe accidents at NPP as a result of large emissions of radioactive CsI aerosols and volatile inorganic and organic compounds of I*.

In emergency situations, various chemical reactions may give rise to GOIs. Since these compounds are rather volatile, their formation increases the I* content in the gas phase. Since GOIs are not very sensitive to the action of solutions from NPP sprinkler systems, they can substantially affect the onset of the emergency situation even when the organic I* concentration is very low. Excessive concentrations of CH_4 can be formed, for example, upon the oxidation of B_4C, which is used in BWR (Boiling Water Reactors) as neutron absorber. Carbon-containing materials constitute one more source of GOIs. Under certain conditions, the reactions of I_2 with organic radicals formed upon radiolysis is the main route to GOIs. In addition, severe accidents may provoke the formation of GOIs by reactions of I_2 dissolved in water with oil films that burn on the water surface.[26]

Iodine* can get into the atmosphere not only in the case of severe accidents at NPP. Immediate sources of I* in the gas emissions from NPP are coolant leakages to utility premises, seal failure of heat insulation, reload and storage processes of leaking fuel assemblies and other factors.[27] For the Leningrad Nuclear Power Plant, the normalized permissible discharge of aerosol and gaseous ^{131}I is 0.01 mCi MW^{-1} day^{-1}. Kritskii *et al.*[27] reported the chart of formation of the gas and aerosol discharge and proposed necessary measures for decreasing the atmospheric emission of ^{131}I around the Leningrad Nuclear Power Plant. The application of these measures decreased the emission 100-fold, which markedly improved the environmental situation in this region.

A study of the atmosphere near a BWR-type reactor demonstrated that ~60% of ^{131}I occurs as CH_3I, while the rest ~40% are HOI and I_2 (see Ref. 28). In the Earth atmosphere, $CH_3{}^{131}I$ and its homologues arise upon the reaction of $^{131}I_2$ with components of the environment (CH_4, C_2H_6 and so on) or upon the isotope exchange with stable $CH_3{}^{127}I$ formed in the ocean.

In conclusion, it should be noted that volatile compounds of I* are of major biological hazard in NPP emissions during both normal operation and accidents. As found using filtering, sorption and sorption-and-filtering materials, the concentrations of gaseous radioactive iodine is often much higher than the concentrations of aerosol forms.

III. Behaviour of volatile radioactive iodine compounds in the gas and steam – air flows

Radioactive CsI aerosols are among the environmentally most hazardous volatile compounds I*. According to thermochemical analysis of SNF, CsI resulting from the reaction of elemental iodine and Cs in the fuel is the predominant I* species.[29–32] On long-term operation of the reactor, CsI is known to concentrate in the gaps between the nuclear fuel and the fuel element shell as a result of diffusion of elemental iodine and caesium along the fuel grain dislocations.[29] However, as a result of CsI radiolysis, I_2 and CH_3I ($< 0.5\%$) are also accumulated in the fuel element. On accidental damage of the fuel element or during the SNF reprocessing, CsI gets into the gas phase as aerosol. This leads to the formation of radioactive aerosols with a broad range of particle sizes (from 1–10 nm to 100–500 μm).

A study of the the behaviour radioactive CsI aerosol in air of different humidity levels demonstrated that in the absence of steam, only CsI aerosols occur in air, whereas in moist air, both CsI aerosol and CsOH are present.[33] Indeed, on contact of CsI aerosols with a steam–air mixture in strong radiation fields, oxidative hydrolysis and reactions of I_2 with environmental components (H_2O, O_2, CH_4) may occur.

$$4\,CsI + 2\,H_2O + O_2 = 4\,CsOH + 2\,I_2 \quad (1)$$

$$CH_4 + I_2 = CH_3I + HI \quad (2)$$

As a result of these reactions, the gas-phase ratio of I* species during severe NPP accidents can shift towards I_2 and CH_3I. In addition, contact of I_2 with steam at high temperature and in strong radiation field may give HOI and HI and subsequently also HIO_3. Furthermore, whereas HOI is amphoteric and extremely unstable, HIO_3 may exist as crystals fairly stable at ambient temperature. On heating to 393 K, solid HIO_3 is converted to the anhydride I_2O_5, which dissolves in water to form again HIO_3.

Kulyukhin *et al.*[34,35] studied the behaviour of radioactive aerosols of $^{137}Cs^{131}I$ in Ar, in air and in a steam – air mixture. It was found experimentally that vaporization of 1–100 mg of ^{137}Cs- and ^{131}I-labelled CsI from a platinum heater over a period of 10–12 min in the temperature range of 900–1570 K is accompanied by oxidative hydrolysis of $^{137}Cs^{131}I$ induced by O_2 and steam to give $^{137}CsOH$ and $^{131}I_2$ aerosols. By measuring the variation of the amounts of

^{137}Cs and ^{131}I in various fractions, it was shown that the conversion of CsI in the Ar atmosphere is minor and is caused by the presence of traces of O_2 and moisture in the system. The oxidative hydrolysis of $^{137}Cs^{131}I$ is markedly enhanced as the content of steam in the steam – gas flow increases. Apart from the content of H_2O and O_2 in the atmosphere, the degree of hydrolysis is affected by the initial $^{137}Cs^{131}I$ to O_2 molar ratio.[34]

To elucidate the possibility of formation of various chemical species during oxidative hydrolysis of $^{137}Cs^{131}I$, Kulyukhin *et al.*[35] investigated the behaviour of $^{137}Cs^{131}I$ radioactive aerosols being retained in a column with the Bekipor WB metal felt under Ar, air or a steam–air mixture. The effects of the column temperature (in the range of 405–560 K), gas flow humidity (up to 60 vol.%), the flow velocity in the sorption column (2 to 6 cm s^{-1}) and the amount of $^{137}Cs^{131}I$ collected on the felt ($\sim$1 to 65 mg) on the layer distribution of ^{137}Cs and ^{131}I were studied. It was found that under certain conditions, oxidative hydrolysis may give aerosols of $^{137}Cs^{131}I$, $^{137}CsOH$ and $^{137}Cs^{131}I_3$.

The oxidative hydrolysis of $^{137}Cs^{131}I$ aerosols was also studied on a column with various filtering elements: the Krapukhin coil filtering elements (FEK), TRUMEM type metallic membrane filters with a pore diameter of $\sim$2 μm and white ribbon paper filters with a diameter of 3.5 μm and a $\sim$8000 cm^2 g^{-1} surface area. At an air flow temperature of 403–423 K, a steam content from (3–4) vol.% to 90 vol.% and a flow linear velocity of 6 to 24 cm s^{-1}, oxidative hydrolysis of $^{137}Cs^{131}I$ takes place and the hydrolysis products react with the surfaces of metallic and paper filtering elements. Depending on the experimental conditions and the filter material and inner surface area, they are able to trap from 5% to 98% of $^{137}Cs^{131}I$ fed to the system in a quantity of 0.17–70 mg.[35]

According to the results presented at the Workshop on Iodine Aspects of Severe Accident Management held in Switzerland in 2000,[36] the amount of organic compounds of I* in the containment shell atmosphere proved to be lower than it was initially expected, especially in the case of low oxygen content, in the presence of chlorine and control rods containing B_4C. The reactions of I* with painted surfaces of the containment can affect the I* volatility by either continuous adsorption of iodine on the surface or change in its chemical form. Preliminary data on the reactions of organic I* species with structural materials of NPP buildings were obtained. It was found that the rate of transformation of I_2 to IO_3^- under the action of O_3 is lower than expected earlier. However, it should be even lower if the presence of H_2 is taken into account.

In the document,[26] much attention was paid to the problem of I* aerosols in the containment shell. During an accident, I_2 and CH_3I in its atmosphere are subjected to thermal and radiation impacts. Of particular interest are reactions of I* compounds with O_3 which is formed in the shell atmosphere. Presumably, these reactions afford solid non-volatile I_xO_y products, which are regarded by the authors as I*-containing aerosols. The existence of such aerosols based on individual I* oxides is doubtful because it is known that all iodine oxides are rather unstable. An exception may be provided by $I(IO_3)_3$ or, more likely, its hydrated aerosols. However, I* can also be present in aerosols formed by compounds of other elements, in particular, non-radioactive ones.

The authors of the study[37] dealing with decomposition of $CH_3^{131}I$ induced by UV irradiation suggested that finely dispersed aerosols I_xO_y may be formed in air. This conclusion was drawn based on the results of agglomeration co-crystallization of the $CH_3^{131}I$ decomposition products with NH_4Cl formed in the gas phase by the reaction of NH_3 and HCl in air. Since NH_4I aerosols and the iodides and oxides of metals that constitute the heating units may be formed under the experimental conditions, definite information about the nature of insoluble I_xO_y species may be gained only from fundamental studies of this process.

In a study of I* removal from gas emissions of process boxes of a research water-moderated water-cooled reactor (WWER) situated at the branch of the L Ya Karpov Research Physicochemical Institute, it was found that the poorly sorbed ^{131}I form is separated from the oxidized solution of $K^{131}I$ without a carrier.[38] It was suggested that this form is HOI. The compound $HO^{131}I$, like $CH_3^{131}I$, is a volatile I* form that is difficult to trap. For example, Maypack filters retain HOI from the gas phase on activated carbons (AC) impregnated with 4-iodophenol.[4] However, the authors of the cited study[38] do not rule out the possibility of the presence of organic I* species because the observed compound was better soluble in organic solvents than in aqueous solutions. Upon UV- and electric arc discharge-induced ionization, the gaseous I* fraction was converted to aerosol. This conversion was most efficient at low I* concentration. While analyzing the data of the cited publication,[38] one may suggest that the poorly sorbed form of ^{131}I is $CH_3^{131}I$, which readily decomposes under UV irradiation to CH_4 and $^{131}I_2$. Under the experimental conditions, the resulting gaseous $^{131}I_2$ could be converted to $HO^{131}I$ and $H^{131}IO_3$ or their salts, for example, $^{131}I(^{131}IO_3)_3$. The fact of occurrence of this process was known back in the early 20th century. This process has been considered in detail for ^{127}I in the Earth atmosphere.[4]

To conclude this Section, we would like to note that the findings concerning the oxidative hydrolysis and the behaviour of volatile compounds of I* in the containment shell atmosphere are important from not only scientific but also practical standpoint because they allow estimating the amount of radioactive products that can get to the environment through leakage in the containment shell, and evaluating the efficiency of sprinkler system operation as well as developing new highly efficient systems for filtration of steam–air flows.

IV. Behaviour of radioactive iodine in aqueous media

During the mechanical cutting of fuel elements for SNF reprocessing, only 5%–10% of I* is carried away with the gas–air flow, while the rest goes to dissolution together with nuclear fuel and can subsequently reach the extraction stage being a part of solutions.[39] The distribution of I* in the organic and aqueous phases can create conditions for contamination of both final and intermediate products. This leads to accumulation of I* in wash solutions and further uncontrolled discharge to low active waste lines and then to the environment. For example, the operation of SNF reprocessing plants in Sellafield (UK) and La Hague (France) resulted in the discharge of 1400 and 3800 kg of ^{129}I, respectively, into the environment till 2007.[40] Furthermore, ^{129}I that gets into water is constantly accumulated in

bottom sediments.[41] It was found that the total concentration of ^{129}I in bottom sediments is on average $(2.34 \pm 1.43) \times 10^9$ atoms per litre of sediment, and the annual gain is $(1.25 \pm 0.30) \times 10^{12}$ atoms of ^{129}I per square metre of the bottom surface. As a result of ^{129}I influx, the $^{129}I : {}^{127}I$ ratio in the northern sea basin, in particular, in the North Sea, is $10^{-8} - 10^{-6}$ (Ref. 40). Meanwhile, the current vigorous development of nuclear power engineering in China has not yet resulted in radioactive iodine contamination of the environment. The $^{129}I : {}^{127}I$ ratio in the river water in China is $(3-5) \times 10^{-9}$. This value is more than an order of magnitude lower than that observed in Japan and two orders of magnitude lower than that in Europe.[40]

The problem of environmental protection from I* compounds is topical not only during SNF reprocessing or NPP accidents [26, 36, 42–44] but also during the normal operation of NPP.[27, 45] It is known [27] that in water-cooled NPP, due to defects in the fuel elements, some I* gets into the primary coolant. It was found [46] that during the shutdown of the water-moderated water-cooled reactor (WWER) in operating power-generating units, the activity of ^{131}I in the primary coolant increases 20–300 fold.

When it comes to nuclear propulsion plants, mounted on marine ships, studies of their operation in different water chemistry regimes (ammonia and neutral ones) demonstrated that ^{129}I and ^{131}I are the only radionuclides that are important for considering the radiation consequences.[47] The authors noted that in transient modes, first of all, during the reactor shutdown, the activity of radionuclides in the coolant increases by a factor of $10^2 - 10^4$. The maximum value is achieved after 5–20 h, and some activity decline takes place during the next 24 h.

As a result of redox reactions, radioactive iodine may be present in the primary coolant both at NPP and at nuclear propulsion plants as ionic species (I^-, IO_3^-) and as molecular iodine (I_2). Due to the presence of I_2 in the coolant during the reactor shutdown, the content of ^{131}I in the gas phase increases with time by more than an order of magnitude, because I_2 partition coefficient between the gas and the aqueous phases is several orders of magnitude higher than for the ionic forms of iodine.[46]

At the Leningrad Nuclear Power Plant, for reducing the I* content in the primary coolant upon the reactor shutdown, a 50% derating is used, *i.e.*, for 2–5 days the reactor operates at 50% power. This approach decreases the I* activity of the coolant as a result of decay of its short-lived isotopes. However, these measures hardly have any impact on the behaviour of ^{131}I, which makes the major contribution to the coolant radioactivity even after 5 days. Therefore, it was proposed to continue the coolant circulation for 2–5 days after complete shutdown of the reactor with simultaneous removal of radioactive iodine.[46]

An increase in the I* content in the primary water coolant and in the gas phase during the reactor shutdown can also be observed at operating NPP [for PWR, LWR (Light Water Reactor) and BWR]. Its appearance cannot be ruled out either at the new types of reactors being designed: WWER-1000 (Rosenergoatom, Russia), EPR, SWR-1000 (Framatome ANP, France), AP-1000 (Westinghouse, USA), ESBWR (General Electric, USA), APWR (Mitsubishi, Japan) and ABWR (Toshiba and Hitachi, Japan).[48–51]

Usually, cation and anion exchangers are employed to decrease the contents of radionuclides (including I*) in the primary coolant during normal operation of NPP. Since anion exchangers mainly absorb the ionic forms of I*, the development of materials that are able to collect I_2 in addition to other iodine species from aqueous solutions would not only reduce the coolant radioactivity but also sharply decrease the I* emission to the gas phase. Therefore, attempts are made to develop new composite sorbents using various materials that would be able to remove all forms of I* from aqueous solutions to be used for purification of the primary coolant at NPP.[52]

Investigations of the mechanisms of reactions of gaseous I* compounds with various aqueous solutions aimed at finding ways of formation of low-volatile soluble ionic forms of I* is an important and topical task for the development of new methods of I* capture not only for NPP but also for SNF reprocessing.

Haefner and Tranter [53] discussed various methods of wet removal of I* compounds from gas flows. The authors reported not only the compositions of aqueous solutions but also the mechanisms of reactions taking place in solutions. In the alkaline method of capture of $^{129}I_2$ from a steam–gas mixture using 1–2 M NaOH aqueous solution, $^{129}I_2$ is converted to $^{129}I^-$ and $^{129}IO_3^-$ ions. Unfortunately, $CH_3{}^{129}I$, which is one of the major products formed during accidents, almost does not pass to the alkaline solution.

The Mercurex process for ^{129}I capture as I_2 and CH_3I uses an aqueous mixture of $Hg(NO_3)_2$ and HNO_3 with concentration of up to 14 mol litre^{-1}. The reactions of I_2 and CH_3I with solution components afford HgI_2 and $Hg(IO_3)_2$. Upon the use of 20–23 M HNO_3 at 313–323 K in the Iodox process, the final product of ^{129}I absorption as I_2 and CH_3I is $^{129}IO_3^-$. Note that the Mercurex and Iodox processes are currently considered to be most promising for the capture of $^{129}I_2$ and $CH_3{}^{129}I$ on bubbling gas flows through aqueous solutions. In this connection, of obvious interest are studies dealing with the state of I_2 in HNO_3 solutions. Experimental measurements of I_2 solubility in HNO_3 and data interpretation are fairly complicated tasks, despite the presence of highly sensitive procedures and rather high extinction of these solutions in the visible and UV spectral regions. In oxidizing systems, I_2 can participate in numerous reactions. For example, in concentrated fuming HNO_3, iodine can be oxidized to IO_3^- almost completely, the formation of HIO_3 being irreversible.

The solubility of I_2 in 30%–55% HNO_3 at 298 K was studied;[54] it was shown that in the absence of forced stirring, the $I_2 - H_2O - HNO_3$ system does not reach equilibrium over a period of >160 h. With shaking at intervals, the equilibrium is reached in 5–6 days. The authors proposed an equation to estimate the solubility of I_2 in HNO_3; the water solubility of I_2 equal to 1.32×10^{-3} mol litre^{-1} was used in the calculation. The theoretical curve of I_2 solubility in the $H_2O - HNO_3$ system shows that for HNO_3 concentrations of up to 60 mass %–80 mass %, the solubility of I_2 is 4–5 times lower than in water, while at $[HNO_3] > 70$ mass %, the solubility increases, which may be due to the contribution of I_2 oxidation under these conditions.

Ascending frontal chromatography was used [55] to study the forms of existence of iodine in a variable redox environment in aqueous solutions. It was shown that in acidic solutions (1 and 3 M HNO_3) and in 1 M $NaNO_3$ solutions in the presence of an oxidant at pH 1–5, an unidentified iodine species is always retained at the starting point of

the chromatogram. The authors proposed that this may be either IO^- or IO_3^-. In the case of 0.1 M NaOH, iodine mainly exists in an ionic form (preferably I^-) and its mobility increases with an increase in the alkali concentration and the redox potential of the medium.

The chemical reactions of macromolecules with small molecules in solutions are of interest for the studies of processes that are important for the development of biologically active products and medical drugs.[56] The I_2-I^-–amylose complex can serve as the model for investigation of biochemical processes because iodine present in this complex is a potent biologically active factor. The effect of various surfactants on the stability of the I_2-I^-–amylose complex in aqueous solutions was studied by potentiometric titration and spectrophotometry. Surfactants actively destabilize the complex, the extent of destabilization being dependent on the surfactant nature. It was shown that surfactants decrease the stability of the complex and even destroy it, because the I_2-I^- species migrates from the amylose helix cavity to surfactant micelles, or I_2 loses the bonding to the part of the amylose helix as a result of deterioration of the helical environment needed to store polarization effects, which ensure the existence of the polyiodide chain.

In sea water, iodine mainly exists as IO_3^-, I^- and nonvolatile soluble organic iodide (total concentration of 0.45 μmol litre^{-1}). Organic iodine compounds present in sea water mainly come from marine algae. The latest studies showed that CH_3I, CH_2I_2 and other organic iodine compounds can also be formed upon fast photolysis on water surface or upon fast chemical reactions in the boundary air layer.[57] In addition, I_2 is formed in the surface layers of the ocean upon the reaction of atmospheric O_3 with I^- (Ref. 57).

Direct emission of I_2 and IO radicals upon the heterogeneous reactions of $O_{3(gas)}$ with an aqueous solution of KI was studied.[58] The amounts of the $I_{2(gas)}$ and $IO_{(gas)}$ formed are directly proportional to the KI concentration in an aqueous solution up to 5 mmol litre^{-1}. Presumably, $O_{3(gas)}$ reacts with I^- at the air–water interface to give gaseous I_2 and IO formed from the HOI and $IOOO^-$ intermediates, respectively. The yields of $I_{2(gas)}$ and $IO_{(gas)}$ are the same in NaI and KI solutions, *i.e.*, the reaction of $O_{3(gas)}$ with I^- does not depend on the nature of the cation. The authors found out that the yield of $IO_{(gas)}$ does not depend on the solution pH in the range of 2 to 11, whereas the amount of $I_{2(gas)}$ markedly decreases (approximately 7-fold) in the pH range from 2 to 4 and then remains almost invariable in the pH range from 4 to 11. At pH >11, hardly any gaseous I_2 and IO are formed; this was attributed to the following causes. First, the concentration of I^- in the interfacial layer significantly decreases due to the competitive action of HO^- ions at pH >10. Second, at pH >11, the predominant iodine form is IO^-, which is generated upon dissociation of HOI (dissociation constant $pK_a = 10.8$). It was noted that IO^- differs from HOI in terms of the chemical stability. For example, unlike HOI, the IO^- ion does not react with I^- to give I_2.

The results of a study[58] indicate that gaseous halogens play a noticeable role in the key chemical processes taking place in the troposphere. Indeed, the inclusion of halogen–ozone interactions into the block model of the atmosphere halves the discrepancy between the calculated and measured loss of ozone in the boundary layer near the sea surface.

Francis and Dodge[59] discussed the biotransformation of iodine in the environment. Germs affect the behaviour of iodine by means of processes such as formation of volatile compounds (CH_3I), oxidation of I^- to I_2, reduction of IO_3^- to I^- and intra- and extracellular bioaccumulation of iodine by bacterial cells. The microbiological formation of CH_3I upon methylation of I^- by aerobic bacteria was observed both in soils and in seawater. It was noted[60] that bacteria that oxidize I^- to I_2 can be isolated both from seawater and from natural salt water. Meanwhile, in the environment, the sulfate- and metal-reducing bacteria reduce IO_3^- to I^-. The variation of iodine species due to redox reactions can noticeably affect the I* mobility in the environment. In addition, it was noted that I^- can be sorbed on positively charged areas of the bacterial cell walls. Different bacteria have different sorption efficiency with respect to IO_3^- and I^-.

The reactions of I_2 with metallic copper, zinc and aluminium in moist atmosphere and in water have been studied.[61] In moist atmosphere, all three metals efficiently capture I_2, whereas in water, Zn and Al iodides rapidly dissolve; therefore, the metal surfaces do not absorb iodine in water.

Glänneskog *et al.*[62] also studied the reactions of I_2 with metallic Cu, Zn and Al (as wires) in the aqueous phase. The pH of the aqueous solutions was brought to 2.2 by adding H_2SO_4, in order to create conditions where iodine exists only as I_2. According to the analysis results, the aqueous solution contained absolutely no IO_3^- ions and only traces of iodide ions. Two series of experiments were carried out: the first one dealt with the conversion of I_2 to I^- on the Zn or Al surface in water and the second one considered adsorption of I_2 on the Cu surface from water. Since all of the experiments were performed in glassware, it was shown preliminarily that I_2 is not reduced to I^- on a glass surface at pH 2.2 over the whole range of studied temperatures. At pH 2.2, the reaction between the glass surface (designated by $\equiv SiO-H$) and I_2 to give $\equiv SiO-I$ and I^-does not make a significant contribution due to the high concentration of H^+ in the solution. However, at higher pH, the contribution of this reaction increases.

A study of the reactions of I_2 with Zn and Al at temperatures of 298, 323, 363 and 413 K in H_2O demonstrated that adsorption of I_2 on Zn and Al is insignificant, I_2 being mainly converted to I^- in a first order reaction. The decrease in the I_2 concentration with time is described by the equation

$$[I_2] = [I_2]_0 \exp\left(-\frac{k_{conv} At}{V}\right), \quad (3)$$

where $[I_2]_0$ and $[I_2]$ are I_2 concentrations in the aqueous solution at the initial time and at time t, k_{conv} is the rate constant for the conversion of I_2 to I^-, A is the metal surface area, V is the volume of the aqueous phase. The k_{conv} value can be found from the plot of the logarithm of I_2 concentration *vs.* time. Using the temperature dependence of k_{conv}, the activation energies for the I_2 reduction to I^- were determined to be 46.3 and 35.6 kJ mol^{-1} for Zn and Al, respectively.

In copper wire experiments, I_2 is adsorbed on the copper surface as CuI. The decrease in the I_2 concentration in the aqueous phase can be described by the equation

$$[I_2] = [I_2]_0 \exp\left(-\frac{k_{ads}\, At}{V}\right), \quad (4)$$

where k_{ads} is the rate constant for I_2 adsorption on the Cu surface.

The rate of I_2 adsorption on the copper surface, like the rate of I_2 reduction to I^- on the zinc or aluminium surface, was found to increase with temperature. Thus, the rate constant for the I_2 adsorption on the Cu surface is 2.45×10^{-6}, 11.95×10^{-6} and 17.92×10^{-6} m s^{-1} at 298, 323 and 358 K, respectively. As follows from the presented equations, the higher is the A/V ratio the shorter is the time needed for both I_2 to I^- reduction on the Zn or Al surface and I_2 adsorption on the Cu surface.

Fedushchak *et al.*[63] noted that copper nanopowders obtained by electric explosion method have a high affinity for I_2 in aqueous solutions; their reaction leads to complete decolouration of I_2 solutions in water. However, it was found that no CuI is formed in this system and the addition of $AgNO_3$ to the solution results in AgI precipitation. In the authors' opinion, Cu nanopowders, which they called 'iodine devourers', do not react with I_2 but promote its disproportionation to give HOI and HI.

The adsorption of I^- and I_2 on the silver surface in aqueous solution has been studied.[64] The reaction of I^- with Ag^0 was found to include two steps, the initial step being fast and the subsequent step being slow. A noticeable reaction between I^- and Ag^0 to give AgI can occur in aqueous solutions only under oxidative conditions, an important role being played by the state (oxidation number) of the silver metal surface. It was suggested that AgI is formed upon the reaction of Ag_2O with I^-. At pH >7 and in the absence of oxidants, the reaction almost does not proceed.

Unlike the situation with I^-, the oxidation of the silver surface does not play an important role in its reaction with I_2 in aqueous solutions. In this case, the rate of the reaction between I_2 and Ag^0 is limited by only diffusion of I_2 molecules in solution to the metal surface.

Analogous reactions involving I_2 and Ag^0 or I^- and Ag_2O can occur in the settling pond during severe accidents at NPP where the control rods are made of the In–Cd–Ag alloy.[26, 36, 43] In order to increase NPP safety during severe accidents, it was proposed [26] to add Ag^0 to the settling pond materials to retain I* in the aqueous phase.

In subsequent studies,[36] additional experimental data on the Ag^0–I* system were obtained and some conclusions on the mechanisms of Ag + I_2 and Ag_2O + I^- reactions were drawn. The problems of stability of AgI and Ag_2O under radiation remain especially important and topical as regards the capture of I* by Ag-containing materials. It was assumed that nitrogen oxides and Cl^- ions can reduce the stability of AgI.

Organic iodine compounds (OICs) are present in all natural environments (soil, water and air) that have been in contact with waters containing I*. The biosynthesis of OICs involves enzymes (iodide oxidases) that convert I^- to I_2 or CH_3I.[65] The physical and chemical processes induced by sunlight, metal oxides [66–68] and oxidants (H_2O_2, O_3 and NO_2) may also serve as routes to OICs in the environment. In aqueous solutions with pH $\sim$7–8, OICs is generated through reactions between natural organic materials (NOMs) and HOI formed upon I^- oxidation.[69–72]

Vanillin and acetovanillone were used as model compounds to study $^{129}I_2$ capture from aqueous solutions on NOMs.[60] In aqueous solutions containing $^{129}I_2$ and vanillin, two reactions may occur in parallel: $^{129}I_2$ can either iodinate the aromatic ring or be reduced to $^{129}I^-$. The latter reaction gives rise to vanillic acid in the system. Meanwhile, in the presence of acetovanillone, only one reaction is possible, namely, iodination of the aromatic ring.

Gallard *et al.*[73] studied the iodination of various organic compounds (resorcinol, 3,5-heptanedione, catechol, *m*-cresol, hydroquinone, phenol, organic acids) in water and found that these reactions occur in iodine-containing solutions at pH 5–7 in the presence of crushed birnessite (δ-MnO_2). In the absence of NOMs, the iodide ions present in the aqueous solution are oxidized to IO_3^- ions, which can be adsorbed on δ-MnO_2. In the presence of NOMs at pH <7, organic iodine compounds that can be adsorbed on δ-MnO_2 are formed in the reactions of NOMs with I_2, which appears in the aqueous solution upon oxidation of I^- in the presence of δ-MnO_2. The formation of such OICs decreases with increase in the pH and ceases almost completely at pH >7.8. This is attributable to the absence of oxidation of I^- to I_2 at high pH. Apart from the OICs that can be sorbed on δ-MnO_2, aqueous solutions were also found to contain ICH_2CO_2H, CH_2I_2 and CHI_3. Their formation also depends considerably on the pH. For example, as the pH increases from 5.0 to 6.5, the rate of formation of CHI_3 decreases more than 5-fold, while at pH >8.0 in aqueous solution, CHI_3 is not formed at all. Recently it was shown [66] that CHI_3 can also be produced upon oxidation of I^- to I_2 in the presence of PbO and NOMs.

The formation of OICs in the soils and sedimentary rocks of aquifers has been investigated.[74] Using radioactive ^{125}I and stable ^{127}I, the reactions of I_2 with soils and sedimentary rocks were studied. These reactions were shown to substantially depend on the I^- concentration, the contact time between the solid and liquid phases and the content of organic carbon. The higher is the I^- concentration, the lower is the iodine sorption. The reason is that unlike IO_3^- and OICs, which are readily sorbed on these materials, the I^- ions are not sorbed. The formation of OICs in the solution influences not only the sorbed amount of iodine but also the iodine migration in ground waters. A mechanism for OIC formation is the reaction of humic acids with I_2 or I^-. For example, under ambient conditions, OICs were the major fraction (67%) of the total soluble iodine.

A similar conclusion about the behaviour of different I* species in soils was drawn by Hu *et al.*[75] The authors noted that I^- is the most mobile I* species, while IO_3^- formed under oxidizing conditions is less mobile and can be accumulated in soils to a large extent.

It should be emphasized that the knowledge of the behaviour of I* in aqueous solutions would help not only to develop new systems for capture of radioactive iodine but also to predict its migration behaviour in the environment.

V. Precipitation methods for the removal of radioactive CsI* aerosols from the gas medium

The prevention of CsI radioactive aerosols from getting into the environment is an ecological challenge.[76] The radioactive aerosols formed are extremely non-uniform in the particle size; therefore, to prevent them from getting into

the environment, various types of protective systems are used. When designing filtration devices, all properties of the particles to be captured are taken into account; however, the particle size is most important. The larger are the particles the more easily they precipitate and the simpler is the equipment. Considerable coarsening of the particles takes place as steam condenses on them. The deliberate introduction of water drops for trapping radioactive aerosols has found wide use in condensation type dust extractors.[77–79] They can capture particles of <0.2 μm size (Venturi ultrasonic scrubber) or <1 μm (jet scrubber). However, the decontamination factors (DF) for the removal of radioactive aerosols from gas flows are only 10 and 20, respectively, for these devices. A common drawback of filtration systems is that they cannot absorb radionuclides occurring as a finely dispersed phase with a particle size of <0.1 μm in the steam–air phase. Apart from the sorption of radioactive aerosols on water droplets, agglomeration deposition on artificially formed aerosols of non-radioactive macrocomponents, for example, polyvinyl chloride, is used.[80] However, due to a number of reasons, agglomeration deposition from the gas phase proved to be of low utility.

Therefore, in the 1990s, a number of fundamental studies were performed dealing with the mechanism of formation of mixed agglomerates of CsI radioactive aerosols with inactive inorganic aerosols. In a study of co-crystallization of ^{137}Cs and ^{131}I from a steam – gas mixture with solid ammonium halides, it was found that in the presence of 1–10 mg of CsI as the carrier, ^{137}Cs forms radioactive aerosols of two types, $^{137}Cs^{131}I$ and ^{137}Cs sorbed on oxides of the metals (Fe, Ni) present as components of the aerosol generator substrate.[81,82] Both forms can be incorporated in mixed agglomerates with NH_4Cl aerosols. Co-crystallization of CsI and NH_4Cl from the gas phase affords a mixed agglomerate of nanocrystals of both compounds with a common microheterogeneous lattice.[83–85] The nanoparticles serve as the primary crystals, nanoparticle aggregates are the primary crystal aggregates, and microparticles are the secondary aggregates. Melikhov *et al.*[86] proved that the particles of mixed $CsI-NH_4Cl$ agglomerates are morphologically self-similar, whereas in the case of CsI aerosols without NH_4Cl, no self-similarity was observed.

A study of the agglomeration process of $^{137}Cs^{131}I$ with KCl from the steam–gas phase under conditions of formation of supersaturated vapours of trace and macrocomponents showed that the formation of mixed agglomerates $K(^{137}Cs)Cl(^{131}I)$ is accompanied by encapsulation of radionuclides in the trace component matrix, which prevents the subsequent I* transformations into other (inorganic and organic) forms.[87]

A similar process occurs when $^{137}Cs^{131}I$ is agglomerated with AgCl.[88] An advantage of AgCl as the macrocarrier is that the radioactive iodine it encapsulates is not almost washed away by water. An attempt to use Cu^{I} chloride, which is an AgCl analogue, for $^{137}Cs^{131}I$ encapsulation proved unsuccessful as regards the capture of ^{131}I. Although CsI has a CsCl-type crystal lattice and co-crystallizes with KCl and AgCl due to isodimorphism, it is not incorporated in the crystal lattice of CuCl.[89]

The results of fundamental research were used to develop a basically new way of removal of $^{137}Cs^{131}I$ radioactive aerosols from the gas phase based not on the filtration of the gas flow but on extraction of the radioactive aerosol in question from this flow *via* the formation of mixed agglomerates with non-radioactive macroaerosols.[90,91] As indicated above, this process occurs in steam–gas systems $^{137}Cs^{131}I-MCl$ (M = K, Ag, NH_4) and gives agglomerates that encapsulate I* and reduce the possibility of its subsequent transformation to I_2 and CH_3I.

Data on the development of new facilities for capture of CsI aerosols from gas and steam–gas phases and from a mixture of acid gases (HCl, SO_x, NO_x) were reported.[92–95] The operation of these systems is based on the agglomeration co-crystallization of fine aerosols and larger particles from the gas phase. This type of agglomeration occurs *via* incorporation of radioactive aerosols into the internal structure of non-radioactive coarse NH_4X aerosols ($X = Cl^-$, SO_3^-, CH_3COO^-, $HCOO^-$) formed in the gas flow. The decontamination factors for the removal of problem CsI radioactive aerosols in the NH_4X-containing systems from the gas flow is 10^2-10^3 per step. Since the facility is planned to consist of three successive sections, the overall decontamination factor for the CsI radioactive aerosols can reach 10^6-10^7. The ability of the salts NH_4^+ to sublime at elevated temperature can be used to solve the problem of gas phase purification from the CsI radioactive aerosol through close-loop process.

It was demonstrated[96–98] that I* can be removed from the gas phase by co-crystallization with solid NH_4Cl and NH_4Br aerosols as $NH_4^{131}I$, which is formed in the facility upon the reaction of gaseous NH_3 with $H^{131}I$. It was found[96] that ^{131}I present as I_2 or CH_3I does not co-crystallize with the solid phase of NH_4Cl and NH_4Br. Therefore, for increasing the degee of extraction of I*, it was proposed to introduce SO_2 into the gas phase in order to reduce I_2 to HI. By using a mixture of HCl, NH_3 and SO_2 gases taken in definite ratios as the gas phase, mixed agglomerate $NH_4Cl-(NH_4)_2SO_3-NH_4^{131}I$ was obtained.

For the removal of ^{137}Cs and ^{131}I radioactive aerosols from the steam–gas phase, co-deposition of these radionuclides during the formation of non-radioactive aerosols upon hydrolysis of TaI_5, $TaBr_5$, $TiCl_4$ and during condensation of MoO_3 vapour was studied.[99–101] The macroaerosols of these substances are hydrophilic and have rather high density. It was found that ^{137}Cs and ^{131}I radioactive aerosols form mixed agglomerates with these compounds. This results in both an increase in the sedimentation rate of radioactive aerosols from a steam–gas mixture and effective purification of the gas flow from these aerosols (up to 99%). Out of all macroaerosols studied, aerosols of non-corrosive MoO_3 are most effective and promising. The advantages of MoO_3 over Ta and Ti compounds include not only the absence of corrosive products of hydrolysis (Cl^-, Br^-) but also its higher density. This process can be recommended for the protection of inner surfaces of the containment shell of the nuclear reactor.

Thus, using the results of fundamental research on agglomeration co-crystallization of aerosols, new methods for environmental protection from radioactive aerosols and volatile radionuclides were proposed. These methods are based on co-crystallization processes in the gas phase and can be used for mitigation of the consequences of accidents of various severity in nuclear power industry.

VI. Sorption-and-filtration methods for radioactive iodine capture from the gas phase

Currently, filters made of various materials (Petryanov's filtering cloth, glass fibre, glass fibre cardboard, glass fibre paper, metal felt., *etc.*) combined with scrubbers of various design are widely used to capture CsI radioactive aerosols during normal operation of nuclear power plants.[3–6,8–10] Besides, aerosol capture is performed using bed filters with various materials (sand, gravel, zeolites). The possibility of using combinations of sorbents for simultaneous capture of radioactive aerosols of CsI and other I* species is studied at the laboratory level.

Some metal-substituted zeolites (MSZ) stable at temperatures > 423 K were synthesized and tested back in the 1970–1990s.[3] They proved to be fairly effective sorbents of I* as I_2 and CH_3I. By using Ag-containing zeolites as grains of diameter 1.5–3 mm (Baylith PK 6142) to remove I_2 and CH_3I from a steam – air flow (steam : air = 2.7 : 1) at a flow velocity of 31.2 cm s^{-1}, a 99.98%–99.83% degree of iodine extraction was attained at temperatures of 415–430 K and sorbent bed height of 7.5 cm.[102] However, granular sorbents almost do not capture the CsI aerosols (< 30%); hence, they are used in decontamination facilities in combination with metal felt filters.

The works dealing with modification of MSZ sorbents for the capture of I* and CsI radioactive aerosols were also continued in the beginning of the 21st century. New sorbents based NaX- and NaA-type MSZ containing Cu^+ and Ag^+ pre-modified with acetylene in water were synthesized.[103–107] The effect of various factors on the sorption properties of the obtained sorbents was studied and it was proposed that acetylene modification of MSZ results in the formation of acetylene π-complexes with Cu^I and Ag^I; the complexes contain also H_2O molecules and anions that are present in the solution. These sorbents captured ^{137}Cs and ^{131}I from a steam – air flow with decontamination factors $> 10^2 - 10^3$ for $^{131}I_2$ and $> 10^3$ for $^{137}Cs^{131}I$ aerosols. Furthermore, Cu-containing sorbents were less efficient than their Ag-containing analogues. These sorbents were supposed to be used in a filtration module of a passive air cleaner for cleaning steam–air mixtures during severe nuclear power plant accidents.[108] The following characteristics of the filtration module were planned: column height, 1.5 m; cross-section, 3.5 m^2; capacity, 1000 $m^3 h^{-1}$; and aerodynamic resistance, 200 mm Hg. In the proposed system, the degree of decontamination of a steam – air mixture containing up to 80 vol.% of water from all chemical forms of I* was 99.95%.

Capture of CsI radioactive aerosols on a column with Bekipor WB metal felt was reported.[82] Under studied conditions, the I* absorption by the felt was almost complete (97%–99%). However, since chemical forms of iodine are highly variable, when the steam–air mixture is passed through the column for a long time, there is a possibility of I* desorption outside the column as a result of oxidative hydrolysis of CsI that has already been captured by the felt.

The development of a new filtration material based on Bekipor WB metal felt and powdered AgA and AgX zeolites was reported.[109] This filtration material is metal felt with a fibre diameter of 8 to 30 μm where each fibre is coated by a monolayer of powdered Ag-containing zeolite particles. The authors showed that a 100-cm column with a diameter of 4.5 cm at a material temperature of 420 K is suitable for almost complete (> 99.99%) removal of radioactive aerosol of CsI from a steam–air flow with a temperature of 410 K and a relative humidity of 80%. Simultaneously, the gas flow is purified from I_2 and CH_3I by 99.9%.

The possibility of using various filtration elements (FEK, membrane filter, three-layer paper filter) for the filtration-and-sorption capture of $^{137}Cs^{131}I$ aerosols (0.1×10^{-3}–100 mg of CsI) was studied.[35] It was shown that upon sublimation of < 1 mg of $^{137}Cs^{131}I$ into an air flow, the use of the FEK for capture of aerosols has low efficiency as compared with metallic or paper filters. However, when the amount of $^{137}Cs^{131}I$ is ~100 mg, FEK retains a considerable part of aerosol (up to ~70%). Apparently, in this case, coarser particles are formed and create a sealing layer when deposited on the FEK surface (so-called dynamic membrane) and thus increase the efficiency of gas flow purification from aerosol particles. In addition, it was shown that the behaviour of CsI radioactive aerosols in a steam–air flow is affected by its linear velocity in the sorption column and by the quantity of CsI entering the column. The capture of ^{137}Cs and ^{131}I from air depends most appreciably on the surface area of the filtration element, which is about 10^4 times greater for the metal felt than for FEK.[35] This indicates that the retention on FEK occurs according to the filtration principle, whereas retention on the felt column occurs by the filtration-and-sorption mechanism, which includes chemical interaction of various iodine species with the metal. This is confirmed also by the change in the physicochemical state of felt.

The development of a new sorption-filtration material Filosorb D based on impregnated OU-A carbon was reported.[110,111] This material is stable against elevated temperature (up to 390–425 K). In air purification from radioactive aerosol, its efficiency is 99.99%. Filororb D was planned for the use in iodine adsorber filters FAI-3000-1(2).[112–114]

A number of publications[103–105,115–117] report on the capture of $^{131}I_2$ and $CH_3{}^{131}I$ by metal-containing and modified NaX and NaA zeolites from Ar, air and stream – air mixtures. The modified sorbents CuX-m and AgX-m were prepared by the procedure described in a patent.[107] After drying, the metal content in the synthesized sorbents was 2 mass %–12 mass % for Cu and 7 mass %–57 mass % for Ag. The composition and the physicochemical characteristics of modified sorbents were discussed in detail.[103–105] Purification of a steam – air mixture from $^{131}I_2$, which was obtained by concentrating its solution in dilute aqueous NaCl without a carrier in the presence of hydrogen peroxide, gave DF > 10^3 for AgX-m and DF > 10^2 for CuX-m.[103,104]

Capture of $CH_3{}^{131}I$ on AgX-m and CuX-m under Ar atmosphere was studied.[115] The DF value for AgX-m containing 7 mass % Ag is much higher than for CuX-m, in particular, > 10^4 at the bed height of 6.5 cm and a contact time of the gas flow with the sorbent (τ) of 3–4 s. Under these conditions, the sorbent capacity was > 9 mg of $CH_3{}^{131}I$ per gramme of the sorbent. Also, it was established that the treatment of the used sorbent with water does not lead to I* desorption into the aqueous phase.

The effect of the following parameters on $CH_3{}^{131}I$ capture by AgX-m and AgX from a steam–air mixture was studied: Ag concentration in the sorbent (3.5 mass %–57 mass %), humidity of the steam–air flow (3.5 vol.%–78 vol.%), sorbent temperature in the column

(370–420 K) and gas flow temperature (up to 470 K). It was ascertained that AgX-m containing 30 mass %–57 mass % of Ag is effective for the removal of $CH_3{}^{131}I$ at a humidity of up to 80% and sorption temperature of 390–470 K. The degree of decontamination under these conditions exceeds 99.99% at a 7.5 cm high sorbent bed and $\tau \approx 0.2$ s.[116]

Since the DF value depends a lot on the gas flow humidity,[103,116] the effect of hydrophobization of the NaX, AgX and AgX-m zeolite surface on their sorption properties with respect to $CH_3{}^{131}I$ was studied.[117] As the hydrophobizing agent, a solution of PVC in THF with a 1 mg cm^{-3} concentration was used. After hydrophobization, the amount of PVC in the sorbent did not exceed the monolayer capacity, which ensured strong attachment of PVC on the zeolite surface.[44] The sorption of $CH_3{}^{131}I$ was also studied as a function of several parameters such as the Ag concentration in the sorbent (3.5–30 mg), the sorbent temperature (340–420 K) and the steam content in the gas flow (20 vol.%–75 vol. %). Finally, it was shown that the hydrophobization effect is the strongest for NaX. When Na is replaced by Ag, the efficiency of hydrophobization decreases ~10-fold. The subsequent modification of AgX with acetylene additionally decreases the hydrophobization effect by a factor of 1.7–4 depending on the Ag concentration (3.5 mass %–30 mass %). The hydrophobizing action of PVC takes effect for both AgX and AgX-m under rather rigorous conditions of $CH_3{}^{131}I$ absorption (sorbent temperature, 420 K; steam content in the gas flow, 65 vol. %–68 vol.%). The PVC-modified Ag-containing sorbent can retain the absorbed I* on heating up to 570 K.[117]

Silica gels (AS 6120, A-1-170, A-1-235, S-1-170) containing Ag were used back in the 1960–1980s to extract $^{131}I_2$ and $CH_3{}^{131}I$ from gas flows in SNF reprocessing techniques. They had a number of significant advantages over active carbons or MSZ but also suffered from some drawbacks including high cost of Ag and the necessity to maintain high temperature of the sorbent (~420 K). These silica gels were already used at industrial plants of the USSR, GDR, FRG and Czechoslovakia more than 30 years ago.[3] Interest in the sorbents based on silica gels still persists. This is evidenced by regular publications by scientists from different countries, who report the synthesis and applications of metal-containing silica gels to capture I* from gas flows and aqueous media.

Kulyukhin *et al.*[118] reported a granular sorbent Siloksid having high sorption characteristics with respect to I_2 and CH_3I: the degree of decontamination of gas flow from I_2 and CH_3I is more than 99.9%. However, this sorbent operates only up to 420 K, *i.e.*, it can hardly be used during severe accidents at nuclear power plants, because the temperature of the radioactive steam–air flow that comes out of the containment shell to the filtration module may be above 420 K.[102]

Data on effective sorption on silica gel impregnated with silver, MeI, EtI, Pr^iI, Pr^nI, Bu^iI, Bu^nI and CyI (Cy is cyclohexyl) were reported.[119] The DF value was determined as a function of NO_x concentration, temperature, preliminary I* loading, linear velocity of the gas flow and the column length. The results demonstrated that the Ag-containing silica gel is effective for the removal of both organic and inorganic I* species.

The catalytic influence of silver-impregnated silica gel (AS 6120) on the reaction of CH_3I with NO_2 at temperatures of 313–433 K was discussed.[120] At 393–423 K, the sorbent is stable against NO_2 present in the gas flow in concentration of 10 vol.%. However, the authors established that, apart from adsorption properties related to chemisorption according to the reaction

$$AgNO_{3\,(solid)} + CH_3I = AgI_{(solid)} + CH_3NO_3 \qquad (5)$$

(solid is silica gel AS 2120), this sorbent functions as a catalyst for CH_3I decomposition by nitrogen dioxide by the reaction

$$CH_3I + 2\,NO_2 = 0.5\,I_2 + CH_3NO_3 + NO \qquad (6)$$

Decomposition of CH_3I continues even when Ag in the sorbent has completely converted to AgI. Therefore, the sorption capacity of this silica gel may be overestimated when measured by gas chromatography or IR spectroscopy. The silver-impregnated silica gel serves as the catalyst for decomposition of CH_3I by the same mechanism as AgX.[120]

Kulyukhin *et al.*[121] captured $^{131}I_2$ and $CH_3{}^{131}I$ from the steam–gas phase using granular sorbents based on coarse-pore silica gel (SKG) impregnated with silver ions and other d-element ions (Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}). The dependences of I* sorption from a steam–gas flow on the sorbent and gas flow temperature, gas flow humidity and velocity and the amounts of $^{131}I_2$ and $CH_3{}^{131}I$ in the flow were studied. The highest sorption efficiency with respect to $^{131}I_2$ and $CH_3{}^{131}I$ from a steam – air mixture was found for the modified sorbents SKG-Ag. These sorbents effectively remove I_2 and CH_3I from a steam–air flow with a relative humidity of up to 95% in the temperature range of 300–675 K, the purification efficiency being >99.9% ($DF > 10^4$). The sorbent SKG-Ag is composed of 0.5–6.0 mm dark grains. It is stable against radiation at 1 MRad, does not initiate hydrogen ignition; radioactive iodine collected on this sorbent is retained on heating up to 875 K.

A study of sorption of $^{131}I_2$ and $CH_3{}^{131}I$ from a steam–gas mixture on SKG containing Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Ag^+ or their mixture showed[122] that only SKG-Ag can remove $CH_3{}^{131}I$ from a steam–air mixture. The degree of $CH_3{}^{131}I$ extraction was found to be >99.9%, and the sorbents SKG-Ag–Ni were more efficient than any other sorbent. Unlike SKG-Ag, the SKG impregnated with Cu, Zn, Co and Ni ions, both non-modified and modified with hydrazine hydrate capture hardly any CH_3I (<1%). Modification of the SKG containing Cu^{2+}, Ni^{2+} or Zn^{2+} was found to considerably affect their sorption properties towards $^{131}I_2$. For modified sorbents, the degree of absorption of $^{131}I_2$ from a steam–air mixture is 99.0%–99.9%, while for non-modified sorbents it does not exceed 35%.

The results related to sorption of $^{131}I_2$ and $CH_3{}^{131}I$ from a steam–air flow on MSKG silica gel-based sorbent containing d-elements were reported.[123,124] It was found that MSKG doped with Zn^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} ammines and dried at room temperature demonstrate a low degree of extraction of $^{131}I_2$ and $CH_3{}^{131}I$ from a steam–air flow (<30%). The annealing of these sorbents above 520 K hardly has any effect on the amount they retain.

Samples of MSKG silica gels containing Zn^{2+}, Ni^{2+} and Cu^{2+} nitrates remove <1% of $CH_3{}^{131}I$ from a steam–

air mixture no matter whether they are modified or not. For $^{131}I_2$, the degree of extraction from a steam–air phase with non-modified sorbents is ~70%. Analogues of these sorbents modified by a hydrazine hydrate solution using a special procedure provide a degree of $^{131}I_2$ extraction higher than 99%.[44] Sorption characteristics of these sorbents approach the values for MSKG-Ag. Thus, Ag-containing sorbents for I* capture can in some cases be replaced by cheaper sorbents based on other d-elements.

Alumina impregnated with Ag or Cu was proposed for retention of $^{131}I_2$ and $CH_3{}^{131}I$ nearly since the start of nuclear power engineering process development.[3] From the 1990s up to now, researchers engaged in this field have repeatedly addressed this sorbent. For example, Japanese scientists focus on optimizing the removal of organic and inorganic I* species from steam–gas flows at SNF reprocessing plants.[119, 125, 126]

The results on the use of Al_2O_3 impregnated with $AgNO_3$ for the removal of organic I* from gas flows during SNF reprocessing were reported.[119] It was shown that Al_2O_3-Ag is effective for the removal of MeI, EtI, Pr^iI, Pr^nI, Bu^iI, Bu^nI and CyI and inorganic iodine compounds. The DF values were determined as functions of the NO_x concentration, gas flow temperature, iodine preloading of the sorbent, linear velocity of the gas flow and column length.

An Al_2O_3-based sorbent (Al_2O_3-Ag) not only removes I_2 with at a decontamination factor of $> 10^4$ but also decreases the amount of secondary radioactive wastes after I* absorption.[125] The Al_2O_3-Ag capacity with respect to I_2 was ~230 mg g^{-1} at 24 mass % Ag in the sorbent. The Ag utilization after the sorbent use is 80%. No influence of H_2O or NO_2 on the I_2 sorption was observed up to their gas-phase concentration of ~1 vol.%. If Al_2O_3-Ag is heated to 720 K, it becomes able to retain I* for a long period of time even in water. Testing at the WAK setup in Germany showed that this sorbent can be used to purify the waste gas at SNF reprocessing plants.

The efficiency of collection of CH_3I on Al_2O_3-Ag was studied as a function of the relative humidity of gas flow.[126] It was found that the optimal average particle size of Al_2O_3 is ~60 nm and the most effective chemical form for silver impregnation is $AgNO_3$. For increasing the sorbent efficiency, a new double-pore structure of Al_2O_3 was developed.

At the Federal State Unitary Enterprise Mayak Production Association, an Al_2O_3-$AgNO_3$ sorbent is used for capture of volatile I* compounds at the stage of cutting of fuel elements.[12, 13, 127] The regeneration of the waste silver-containing sorbent with adsorbed I* by treatment with a solution of hydrazine hydrate yields mother solutions into which radioactive iodine migrates from the sorbent. Then iodine is removed from solutions by precipitation of poorly soluble CuI, which is then disposed.

In Russia, design and engineering works aimed at the development of nuclear reactors with enhanced safety are actively carried out. Particular attention is devoted to capture of I* present as I_2 and CH_3I, which are most environmentally hazardous. The sorption of these compounds by a TiO_2-based material modified by a Pb compound (product brand Termoksid-58) in N_2 atmosphere and in air under static and dynamic conditions was studied.[128, 129] Many physicochemical properties of the sorbent Termoksid-58 and a detailed description of methods for I_2 and CH_3I sorption under static and dynamic conditions from dry air and N_2 were reported.[128] The authors worked with ^{127}I compounds; therefore, they used analytical method for its determination; when the ^{127}I amount was below the sensitivity of chemical analysis, the neutron activation method was employed. The efficiency of retention of ^{127}I volatile compounds was at least 99.9% at a temperature of 410–430 K and a linear flow velocity of ~0.15 m s^{-1}. The column with the sorbent had a cross-section area of 0.87 cm^2 and a height of 50 cm. In investigations under static conditions, the capacity of the sorbent Termoksid-58 towards I_2 and CH_3I was determined as a function of temperature (in the range of 373–673 K). For CH_3I at 423 K, the maximum sorption was found to be ~106–112 mg g^{-1}. For I_2, the sorbed amount decreased monotonically from 46–53 to 4.6–9.6 mg g^{-1} as the temperature changed from 373 to 673 K.

Under dynamic conditions, the dependence of the CH_3I breakthrough ratio on the Termoksid-58 bed thickness was measured at different temperatures. The efficiency of purification of dry N_2 from I_2 in the temperature range of 383–523 K was no less than 99.9%. The major amount of ^{127}I was concentrated in upper layers of the filter, while in lower layers, the content of I_2 was below the sensitivity of the analytical method. Thus, static and dynamic investigations demonstrated that I_2 and CH_3I are irreversibly sorbed from dry N_2 *via* chemisorption at temperatures from 373 to 673 K. The authors considered[128] two principal mechanisms for interaction of I_2 and CH_3I with Termoksid-58: surface hydrolysis and chemisorption on the modifying agent. Hydrolysis of iodine compounds on the sorbent surface affords non-volatile iodine forms, sodium iodide and hypoiodite, which are weakly bound to the sorbent surface. The chemical reactions of iodine compounds with the modifying agent (Pb^{2+} compound) grafted to the sorbent surface result in the formation of low-volatile Pb^{2+} iodide, hypoiodite and iodate.

Sharygin *et al.*[129] studied the hydrothermal stability of the material Termoksid-58 and also the behaviour of this material towards CH_3I in a steam–air mixture at 373–573 K under dynamic conditions. An increase in the air humidity, all other conditions being the same, substantially deteriorates gas purification from CH_3I on this sorbent. The rate constants for the chemical reaction of the sorbate with the sorbent Termoksid-58 at a humidity from 0% to 90% varied from 15.3 to 1.7 s^{-1}, respectively. As the humidity increased, the reaction rate decreased, the decrease being especially pronounced in the range from 0% to 20% (from 15.3 to 5.1 s^{-1}). It was found that upon temperature rise, the absolute humidity remaining the same, the reaction rate constant and, hence, the efficiency of purification increase. A mechanism for the influence of steam on the rate of chemical reaction between CH_3I and Termoksid-58 was proposed. The efficiency of steam–gas flow purification from CH_3I was found to depend on the polymolecular adsorption and capillary condensation of H_2O vapour. Upon adsorption, the sorbent surface is coated by water molecules, which shield the catalytic and adsorption sites and this decreases the rate constant for the reaction. The capillary condensation results in pore filling with the condensate and complete shielding of the inner surface of the sorbent. This leads to a sharp decrease in the reaction rate. However, processes such as hydrolysis of the chemisorbed iodine compounds and catalytic oxidation of

iodides should also be taken into account. The processes can be catalyzed by the sorbent matrix, TiO_2, which has a noticeable catalytic activity. Whereas hydrolysis of chemisorbed iodine compounds leads to evolution of HI, the catalytic oxidation of iodides gives I_2.

The dynamic adsorption of I_2 vapour from air by the sorbent Termoksid-58 containing 10 mass % – 20 mass % of Pb^{II} was studied.[130] The process was performed at ~298 K and air flow rate of 0.02 – 0.3 $dm^3\ min^{-1}$. The iodine contents in the gas and in the sorbent were determined by gravimetry or by spectrometric method based on absorption bands at 360 nm for I_2 and 260 nm for CH_3I. The I_2 and CH_3I concentrations in air were 1.7 – 2.1 and 13 – 25 mg cm^{-3}, respectively, and the relative humidity of the air was 60% – 70%. The adsorption of I_2 on Termoksid-58 was comparable with adsorption on spent active carbon SKT-3, which sorbs I_2 2 – 2.5 times less efficiently than the fresh active carbon. It follows from investigation results that the efficiency of steam – gas flow purification from I_2 by the sorbent Termoksid-58 can become comparable with adsorption on fresh active carbon if a fourfold amount of this sorbent is used. Under these conditions, adsorption is largely irreversible, and up to 87% of I_2 remains in the sorbent after air purging. Thus, under the studied conditions, *i.e.*, at temperature of 295 – 297 K and a relative humidity of 60% – 70%, Termoksid-58 turned out to be less efficient than the active carbon SKT-3. This result is quite obvious because Termoksid-58 was initially meant for the use at temperatures of > 425 K.

A comparative evaluation of the efficiency of dynamic adsorption of I_2 and CH_3I from air flow on various sorbents was reported.[130] The sorbents used in the study were those recommended to be used at nuclear power facilities, in particular, to purify the vented air at the Leningrad Nuclear Power Plant. These sorbents (active carbon, Termoksid, strong-base macroreticular anion exchangers) having different physicochemical properties and different advantages and shortcomings, were tested to reveal their comparative efficiency in the gas phase purification from I_2 and CH_3I under identical conditions. Among these, the active carbon SKT-3, both fresh, impregnated and spent, is used most often in I* adsorbers. Therefore, in the study in question, the attention was focused on the sorption of I_2 and CH_3I on SKT-3 with different degrees of modification. These were active carbons impregnated with 5% KI, 5% $AgNO_3$ and 2% 1,4-diazabicyclo[2.2.2]octane (triethylenediamine, TEDA). In addition to these active carbons, the SKT-3 sorbent that had operated for 3 years in the AUI-1500IC adsorber of the third unit of the Leningrad Nuclear Power Plant was tested.

The testing showed that on fresh SKT-3, the adsorption coefficient is ~20 times higher for I_2 than for CH_3I. The performance in purification of the air flow from I_2 is 3.5 times higher and the capacity of fresh SKT-3 is 2.5 times greater. For spent SKT-3, the adsorption coefficient is 30 times lower for CH_3I than for I_2, and performance and capacity are 3.5 – 4 times lower. The efficiency of the adsorption of CH_3I (present in 0 – 150 mg amounts) decreases in the series of impregnating components 5% $AgNO_3$ > 5% KI > 2% TEDA. All parameters of the dynamic adsorption of CH_3I (stationary front velocity, duration of the protective action of the bed, required bed height and contact time, sorbent capacity, dynamic adsorption coefficient) are virtually equal for the non-impregnated (initial) and impregnated SKT-3 but the mean performance is higher for the latter material. The authors attributed this fact to different adsorption mechanisms. On the SKT-3 impregnated with potassium iodide, isotope exchange occurs by the reaction

$$K^{127}I_{(sorbent)} + CH_3{}^{131}I = K^{131}I_{(sorbent)} + CH_3{}^{127}I, \qquad (7)$$

and in the case of impregnation with silver nitrate and TEDA, chemisorption by reactions (5) and (8) takes place:

$$(CH_2CH_2)_3N_{2\,(sorbent)} + 2\,CH_3{}^{131}I = \qquad (8)$$
$$= [(CH_2CH_2)_3N_2(CH_3)_2]^{2+}(^{131}I^-)_{2\,(sorbent)}$$

Only physical sorption occurs on non-modified active carbon. Despite a wide application of the sorbents containing TEDA, they have considerable drawbacks. First, these sorbents are applicable only in the systems where the temperature does not exceed 390 K. Above this temperature, sublimation of TEDA from the sorbent material takes place.[26] Second, as the humidity of the steam – gas flow increases, the efficiency of I_2 and CH_3I sorption decreases. In the authors' opinion,[26, 131] this is due to partial hydration of TEDA:

$$(CH_2CH_2)_3N_2 + 2\,H_2O = [HN(CH_2CH_2)_3NH](OH)_2 \qquad (9)$$

In order to avoid the effect of TEDA volatility at temperatures of > 390 K, complexes of TEDA with salts of various metals, for example, with BaI_2, are used for impregnation.[132 – 136] The sorbent SKT-3IK based on active carbon impregnated with TEDA and BaI_2 is meant for the use in FAM-1500 modular adsorber filters, FID-3500 and AUI-1500IC iodine adsorber filters, and in combined filtering setups SFC-3500, SFC-7000 and SFC-10500.[137 – 139]

The sorption of CH_3I with anion exchange resins was studied using AB-17-8, Dowex-11, Relite 3AS (strong-base) and Dowex MWA-1 (macroreticular). Out of all sorbents, only the last one noticeably collects CH_3I from air.[130]

Sorption of I_2 and CH_3I from air and steam – air flows by synthetic carbon polymer sorbents, Polisorb-1 and Stirosorb, has been studied.[140, 141] The sorbent Polisorb-1 developed at the Research Institute of Polymeric Materials is prepared by styrene – divinylbenzene copolymerization (3 : 2 by mass) in the presence of an inert diluent (BR1 rubber solvent), which is taken in a quantity equal to the total monomer weight. The highly cross-linked polystyrene sorbent Stirosorb developed at the Institute of Organoelement Compounds of the RAS was synthesized by cross-linking of the styrene – 0.7 mass % divinylbenzene copolymer completely swollen in dichloroethane by monochlorodimethyl ether in the presence of Friedel – Crafts catalysts. At a flow velocity of about 0.33 cm s^{-1} and a temperature of 298 K, Stirosorb was found to absorb I_2 from the gas flow much more efficiently than Polisorb-1.[140] The capacity with respect to I_2 for Stirosorb was ~97 mg g^{-1}, that is, it was about 4 times as high as that for Polisorb-1.

The efficiency of $^{131}I_2$ trapping by Polisorb-1 depends on the gas flow humidity and velocity, the sorbent temperature in the column and the amount of $^{131}I_2$ (Ref. 141). When the relative humidity is below 100% and the temperature is between 293 and 400 K, the degree of purification of a gas flow from $^{131}I_2$ is more than 99.9% for ~22-cm

high sorbent bed and $\tau \sim 3.4$ s. However, Polisorb-1 does not trap $CH_3{}^{131}I$ under these conditions.

It was noted that upon failure of the primary circuit, I_2 is the major gaseous form present in the containment shell atmosphere in the initial instant of time. However, after several days, GOIs resulting from the reactions of molecular I* with the paint-and-lacquer coatings become the major compounds.[36] Therefore, much attention is currently paid to studies of the I_2 and CH_3I behaviour upon their absorption from the gas phase by organosilicon and epoxide coatings that are used in new NPP units. The use of these coatings may become one of the possible passive methods of capture of volatile I* forms in the confined containment shell space.

Aleksandrov *et al.*[142] investigated I_2 and CH_3I adsorption from the gas phase under static and dynamic conditions on the OS-51-03 organosilicate coating and epoxide coatings based on EP-525 and EP-574 enamels by gravimetric and spectrophotometric techniques. The concentrations of I_2 and CH_3I in the gas phase were calculated from the plots for saturated vapour pressure *vs.* temperature. The authors demonstrated that in emergency the adsorption of I* by organosilicates and especially by epoxide coatings can play a significant role in the retention of volatile iodine species in the airtight zone. For example, I_2 adsorption by the OS-51-03 coating at 363–373 K can be ~ 0.1 μg cm^{-2} and epoxide coatings may absorb up to 3 μg cm^{-2}. Since the coating surface area in the airtight zone of the containment shell is tens of thousands of square metres, it can capture up to 500 g of I*. These calculations did not take into account the effects of steam, irradiation and coating ageing on the efficiency of adsorption and retention of I_2. In the case of depressurization of the containment shell, complete desorption of I* from these coatings occurs within 24 h.[142]

The formation of GOIs upon surface processes is discussed by Cantrel.[143] For predicting the role of iodine evolved upon reactor accidents, the amounts of CH_3I formed on some surfaces, including paints, from the adsorbed I^- ions were measured over a broad range of concentrations. The obtained results were used to develop a computer model of the surface reactions. Reactions of this type were earlier established to occur in catalytic processes. Apart from the GOIs, the volatile inorganic form I_2, which is also formed in surface reactions, was also identified.

To summarize the foregoing, sorbents containing silver ions are most efficient for sorption of I* from the gas phase. However, due to high cost of silver, a topical task is to develop sorbents with low silver content and high sorption characteristics with respect to I* compounds. This objective can be achieved by either modification of sorbents with low silver contents or introduction of additional components to enhance the performance of Ag-containing sorbents.

VII. Combined systems for capture of various radioactive iodine forms from the gas medium

The problems of simultaneous capture of all I* forms and compounds and minimization of consequences of severe nuclear power plant accidents could be successfully solved only relying on the optimal design and engineering works, including the design of combined systems for the capture of radionuclides; the results of research along this line have been published since the 1990s.[99–101,138,139]

Mikheev *et al.*[101] presented examples of protective systems being used or being developed at that time in various countries for removal of radioactive aerosols and various I* species from gas flows. These systems cost 50 to 100 million US dollars. An example of combined systems for I* capture is the German system based on the simultaneous use of a stainless steel fibre filter (for the separation of aerosols and possible condensed water drops) and a column with the Baylith PK 6142 sorbent (for the removal of various gaseous and vapour forms of organic and inorganic I*). This system was developed for LWR type reactors operated in Germany, and its assessed cost may apparently exceed 3 million US dollars.[93,102]

The combined filtration units described in a number of works[138,139] include a series of modules for capture of aerosols and volatile I* forms (HI, HOI, I_2 and CH_3I). Aerosols are captured using a two-stage filter. The first stage is made of a 10 mm-thick non-woven polyester cloth with a surface density of 100–200 g m^{-2} and a fibre diameter of 30 μm, while the second stage is made of a 0.5 mm-thick three-layer glass fibre paper with a fibre size of 0.8 to 0.4 μm.[144] In these setups, the volatile forms of I* are captured using impregnated active carbon SKT-3IK.[132]

The use of modified SKG-Ag and MSZ-Ag provides the removal of up to 99.95%–99.99% of aerosols and all gaseous forms of I* from gas flows.[90–95,102–108,115,116] Given appropriate design and engineering support, these setups can serve as efficient and relatively low-cost combined systems for removal of I* from gas flows. For example, a basically new passive system for capture of accidental gas emissions was included into the design of a new-generation nuclear power unit.[145–148] This system ensures the point-source emission of a steam–gas mixture from the space between the containments during severe accidents with full switching-off of power sources. The key element of the passive filtration system (PFS) is a modular filter heated to 575 K mounted in the upper part of the containment shell. The first stage of the filter purifies the emitted gas from aerosols, while the second stage removes volatile inorganic and organic I* compounds. A pilot PFS module was tested at a rated air flow and proved to fully comply with the design characteristics in the temperature range of 293–573 K. It can be used at relative humidity of up to 100% and even in the presence of condensed moisture and aerosols of corrosive compounds such as NaCl.

Thus, by means of combined systems being designed, it is possible not only to avoid leakage of a radioactive steam–air mixture to the environment at any scenarios of accident development at the NPP but also to considerably increase the safety of the operating plants and new plants being designed.

VIII. Sorption and other methods for removal of radioactive iodine from aqueous solutions of various compositions

It was proposed[12,13] to use solutions of $Cu(NO_3)_2$ in the presence of $N_2H_4 \cdot n\,H_2O$ for isolating ^{129}I from the alkaline solutions formed during regeneration of Ag-containing sorbents. The precipitation of $Cu^{129}I$ provides almost quantitative removal of ^{129}I from solutions.

Kulyukhin *et al.*[149] studied the process of removal of ^{131}I from a model solution of NPP floor drain water by coprecipitation with silver salts, $Ag_4[Fe(CN)_6]$ and AgCl, and

demonstrated that co-precipitation with AgCl removes ~96% of ^{131}I, while co-precipitation with $Ag_4[Fe(CN)_6]$ binds only 65% of ^{131}I.

In recent years, a number of new composite sorbents based on zeolites, silica gels, ion exchange resins, inorganic and organic matrices modified by various metals (Ag, Cu, Bi, Ni, Zn, Pb, *etc.*) and natural sorbents (bentonite, montmorillonite, peat, coal, mica, tripolite, *etc.*) have been studied. In the studies,[90, 103–105, 107, 150] Ag- and Cu-containing sorbents based on 13X and 4A zeolites were used for effective adsorption of I* as I^- and IO_3^- from aqueous solutions. These particular metals were selected in view of the possibility to retain I* in sorbent matrices *via* the formation of insoluble compounds of these elements in +1 oxidation state with I^- and IO_3^-. For increasing the efficiency of sorption, the Ag^+- and Cu^+-containing zeolites were additionally modified by treatment with acetylene in aqueous solution.[107] The materials obtained in this way can remove I* as I^- and IO_3^- from aqueous solutions with partition coefficients (K_d) of more than 10^3-10^4 cm^3 g^{-1}. The dependences of K_d of I* in aqueous solution on the metal concentration in the sorbent, free pore volume of the sorbent and the nature of the anion were established. As regards their sorption characteristics, the acetylene-modified sorbents in aqueous solutions exceed the initial Ag^+- and Cu^+-containing NaX and NaA zeolites. It was noted that the sorption efficiency of modified Cu^+-containing sorbents towards I^- and IO_3^- in aqueous solutions is much higher than the sorption efficiency of Ag^+-containing analogues.

Leaching of I* from AgI-containing zeolites 13X (maximum pore size), 5AP and Amoco A (minimum pore size) into aqueous solutions was studied.[151] Zeolites with sorbed I* were annealed at temperatures of 473, 673, 873, 1073 and 1273 K and then brought in contact with water. Zeolite 13X was found to retain its structure up to 873 K, leaching of I* being 20%–30% of the total adsorbed amount. Leaching of I* from the Amoco A zeolite was 85%; the authors attributed this to the I* sorption–desorption processes on the sorbent surface. The best results were obtained for 5AP: even after annealing at 1273 K, leaching of I* into water was only 4%.

Apart from Ag-containing zeolites, the properties of Cu-containing 13X and 5AP zeolites were studied.[151] Copper-containing zeolites were found to have, first, smaller sorption capacity and, second, higher degree of leaching into water after heat treatment as compared with their Ag-containing analogues.

An unusual method has been proposed for removal of I* from alkaline solutions.[151] This method is based on the zeolite growth around a iodine-containing anion directly in an alkaline solution, for example, of NaOH. The crystalline layered cancrinite can be easily synthesized by adding kaolinite clay to a highly concentrated solution of NaOH and subsequent heating of the mixture at 363 K for several days. During the growth, cancrinite should incorporate I* ions into its structure. To verify the possibility of trapping I* by cancrinite, various amounts of I^- and IO_3^- were added to the solution of NaOH. It was found that both I* forms can be trapped in cancrinite; furthermore, in some experiments, the amounts of I* adsorbed by cancrinite and Ag-containing zeolites were nearly equal. The drawbacks of this method for removal of I* include the following. First, a different zeolite structure is often formed instead of the layered cancrinite structure. Second, when I*-containing cancrinite is washed with distilled water at 363 K, some of the trapped I* migrates to the aqueous solution. However, this method was regarded by its authors as a promising way for trapping I* from the liquid phase.

The Ag-mordenite ion exchanger has been also tested as a material for removal of I* from aqueous solutions.[151] The material was grey-coloured due to the silver coating on the zeolite external surface. However, the authors did not answer the question of how much silver and in what form is present in the zeolite pores. The studies showed that Ag-mordenite removes I* from aqueous solutions with a ~90% efficiency. However, on drying and subsequent annealing of I*-laden Ag-mordenite samples to 1923 K, desorption of I* to the gas phase takes place. The degree of I* desorption is 59%–62%, whereas for 13X zeolite samples, it is only 10% under similar conditions.

The sorption of $^{131}I^-$ and $^{131}IO_3^-$ (concentration $4\times10^{-5}-6\times10^{-5}$ mol litre^{-1}) from the aqueous phase at 298 K on MSKG silica gels with particle size of 0.25–2.00 mm containing Ag and other d-elements (Cu, Ni, Zn, Co) was studied.[123] The sorbents were prepared by sorption of d-elements on MSKG from ammonia solutions. The sorbents containing Ag, Cu, Ni, Zn and Co ammines have low K_d values for $^{131}I^-$ and $^{131}IO_3^-$ in water: $\leqslant$150 cm^3 g^{-1} at $\tau = 120$ min and $V/m = 1000$ cm^3 g^{-1} (V is the solution volume, m is the sorbent weight). The annealing of the sorbents at 423 K resulting in the partial change of the chemical state of ammines in the sorbent matrix does not cause a noticeable change in K_d for I^- and IO_3^- in water with respect to non-annealed sorbents.

The sorption of I_2, $^{131}I^-$ and $^{131}IO_3^-$ from aqueous solutions at 298 K on MSKG containing d-element nitrates (Zn, Ni, Cu, Co) was studied.[124] The sorbents were obtained by slow drying of the MSKG impregnated with an aqueous solution of the corresponding nitrates, in air for 24 h at 373–383 K. The materials containing d-elements were additionally modified by treating with a solution of $N_2H_4\cdot n\,H_2O$ (10 mol litre^{-1}) for 1 h at room temperature. This gave sorbents containing reduced forms of either individual d-elements or their combinations. Such sorbents have low K_d for $^{131}I^-$ and $^{131}IO_3^-$ ($K_d < 10$ cm^3 g^{-1} at $\tau = 120$ min and $V/m = 1000$ cm^3 g^{-1}).[124] Under these conditions, non-modified sorbents almost did not collect I_2 from the aqueous phase ($K_d < 10$ cm^3 g^{-1}). However, their modified analogues did collect I_2 under the same conditions and had K_d for I_2 of ~170–250 cm^3 g^{-1}. In the case of the Ni-containing sorbent, treatment with hydrazine hydrate induced partial hydrolysis of Ni^{2+} to give numerous Ni–OH bonds on the sorbent surface. The presence of HO^- groups able to undergo anion exchange increased K_d for $^{131}I^-$ and $^{131}IO_3^-$ ($K_d \approx 100$ cm^3 g^{-1} at $\tau = 120$ min and $V/m = 1000$ cm^3 g^{-1}) but had almost no influence on K_d for I_2.

A study of the I_2, $^{131}I^-$ and $^{131}IO_3^-$ sorption on MSKG containing $AgNO_3$ or its mixture with other d-element nitrates demonstrated that at $\tau = 120$ min and $V/m = 1000$ cm^3 g^{-1}, the sorbents have rather low K_d values for all I* forms ($K_d < 100$ cm^3 g^{-1}). However, the $N_2H_4\cdot n\,H_2O$-modified sorbents containing Ni and Ag collect not only I_2 ($K_d \approx 270$ cm^3 g^{-1}) but also $^{131}I^-$ and $^{131}IO_3^-$ ($K_d \approx 3100$ and 1500 cm^3 g^{-1}, respectively) from the aqueous medium.

For some modified sorbents, desorption of ^{131}I into aqueous solutions was studied. After 24 h of the contact between the solid and liquid phases, the degree of desorption of ^{131}I does not exceed 25% of its total amount sorbed as $^{131}I^-$ and $^{131}IO_3^-$. As regards desorption of ^{131}I that was sorbed as $^{131}I_2$, after 24 h of the contact of the solid and liquid phases, the content of ^{131}I in the aqueous phase was lower than the detection limit of the colorimetric method, *i.e.*, $^{131}I_2$ was retained by these sorbents almost completely. Thus, the use of MSKG-based sorbents containing Ni and Ag in various process flow charts is suitable for extracting both molecular and ionic forms of I* from the aqueous phase with high partition coefficients, which implies lower consumption of the sorbent.

Sorption of ^{131}I and ^{137}Cs from a model solution of NPP floor drain water was studied.[149] The highest degree of extraction of ^{131}I (>99%) can be achieved by using granular sorbents of the brand Fizkhimin based on coarse-pore silica gel KSKG containing Ag and Ni in 1 : 4 ratio (K_d for ^{131}I are $>10^5$ cm^3 g^{-1} at $\tau = 120$ min and $V/m = 1000$ cm^3 g^{-1}). An increase in the solution temperature to 313 K does not affect the degrees of removal of ^{131}I and ^{137}Cs. Unfortunately, the degree of extraction of ^{137}Cs did not exceed 35% in all experiments.

Currently, cation and anion exchangers of various brands are widely used at NPP for collection of radionuclides present as cations or anions in the aqueous phase. Anion exchangers find use for collection of ionic forms of I* such as I^- and IO_3^- from the primary water coolant of different NPP. However, there still exists the problem of removing I_2 and organic iodine compounds, in particular, CH_3I, from primary water coolants both during the reactor shutdown and during accidents.

The synthesis of new composite materials based on a KU-2 cation exchanger containing nanoparticles of Cu, Ni, Zn and Ag compounds was described.[52, 152–157] These materials are meant for fast and effective trapping of I_2 in the primary water coolant of WWER and LWGR type reactors. The composite materials based on KU-2 containing ~5.5 mass % of Cu and Ag were synthesized by a procedure reported in a patent.[153] It was also shown[154–157] that nanocomposites that contain Cu and Ag can rapidly and efficiently remove I_2 from an aqueous solution having the same composition as the primary coolant of WWER type reactors. During a 15-min contact of the liquid phase and the composite, >99% of I_2 is removed from aqueous solutions. In this case, the K_d value for I_2 is greater than 10^3 cm^3 g^{-1} for $V/m = 100$ cm^3 g^{-1}. However, the efficiency of these composite materials with respect to $CH_3{}^{131}I$ in aqueous solutions proved to be low ($K_d < 11$ for $V/m = 100$ cm^3 g^{-1}). Simultaneously it was shown[155] that only after 24 h of the contact between the liquid phase and the anion exchanger AV-18, the degrees of extraction of I_2 and $CH_3{}^{131}I$ from aqueous solutions resembling the primary water coolant of the WWER type reactor are >99% and 60%, respectively. The K_d value for I_2 is $>10^3$ cm^3 g^{-1} for $V/m = 100$ cm^3 g^{-1}, whereas this value for $CH_3{}^{131}I$ does not exceed 200–300 cm^3 g^{-1}.

Due to the decrease in the efficiency of absorption of I_2 by Cu-containing nanocomposites after their air drying and also due to the high cost of silver present as a component of the materials used, Cu and Ag were replaced by Ni and Zn, which have similar physicochemical properties. The composite materials containing ~5.5 mass % Ni and Zn were synthesized by the procedure reported in a patent.[158] At temperatures from 293 to 333 K, these composites can convert more than 99% of I_2 to ionic forms. This refers both to distilled water and to aqueous solutions with a composition corresponding to the primary coolant of NPP with WWER type reactors. It was found that almost complete conversion of I_2 (>95%) is attained in 15 min.[52]

The conversion of I_2 molecules to I_3^- and I^+ in various solvents in the presence of highly electron-dense solid matrices (zeolites, MgO, γ-Al_2O_3, TiO_2, mesoporous silica gel, ordered mesoporous organosilicates) have been studied.[159, 160] The formation of I_3^- in solution, which promotes a decrease in the volatility of I*, was studied by spectrophotometry, because due to higher extinction coefficient of I_3^- compared with I_2, there was a possibility of reliable determination of I_3^- in the presence of I_2. Simultaneously, the solid matrices stabilized the I^+ ion in the system.

Studies by Kulyukhin *et al.*[123, 161] are devoted to sorption of $^{131}I^-$ and $^{131}IO_3^-$ from 10^{-5} M KI and KIO_3 aqueous solutions by composite materials based on γ-Al_2O_3 with particle size of 1.0–2.0 μm containing Cu and Ni. The composites were prepared by sorption of Cu and Ni ions by γ-Al_2O_3 from ammonia solutions during 24 h at 298 K. The materials had K_d values for $^{131}I^-$ and $^{131}IO_3^-$ commensurable with analogous characteristics of MSKG-Ag (for $V/m = 1000$ cm^3 g^{-1}, $K_d \approx 3100$ and 1500 cm^3 g^{-1}, respectively).[123, 124] It is noteworthy that commensurable K_d values for $^{131}I^-$ and $^{131}IO_3^-$ are attained by using a composite in which the Ni content is ~10 times lower than the Ag content in MSKG. The annealing of the samples at 1273 K results in some additional increase in K_d for $^{131}I^-$ and $^{131}IO_3^-$. It was concluded that the use of composite sorbents based on γ-Al_2O_3 modified by Ni or Cu ammine makes it possible not only to remove I* ionic forms from the aqueous phase but also to replace expensive Ag-containing sorbents in this process.

The use of microporous acetyl cellulose membrane impregnated with Ag or Bi is suitable for extracting $^{131}I^-$, $^{131}IO_3^-$ and $^{131}IO_4^-$ from a reactor water coolant.[162, 163] The membranes were prepared by impregnating the matrix with an aqueous solution of the corresponding nitrate followed by the reduction of Ag or Bi ions to the metallic state. The metal content in the membrane was ~0.3 mg cm^{-2}. It was shown that $^{131}I^-$ and $^{131}IO_4^-$ are collected by these membranes more efficiently (than $^{131}IO_3^-$) (K_d values are 10^3–10^5 cm^3 g^{-1} for $^{131}I^-$ and $^{131}IO_4^-$ and 600–900 cm^3 g^{-1} for $^{131}IO_3^-$). Therefore, it is recommended first to stabilize I* as $^{131}I^-$ by sulfite reduction in the acetate buffer (to pH 3.2–3.5).

Amosova *et al.*[163] found that traces of $^{131}I^-$ are removed almost quantitatively from a 0.5 M NaCl solution on Ag-containing membranes. However, in solutions of KBr with concentrations of >0.01 mol litre^{-1}, the $^{131}I^-$ sorption efficiency is much lower. This difference in the behaviour of $^{131}I^-$ in the presence of Cl^- or Br^- ions was attributed to different rates of sorption of halide ions on silver. Indeed, from 10^{-3} M solutions of the corresponding halide, $^{131}I^-$ is sorbed on the Ag^0 surface with monolayer coverage in 0.23 s, whereas sorption of Br^- and Cl^- ions requires 2 s and 20 h, respectively. For halide mixture, the rate of $^{131}I^-$ sorption on the Ag surface does not depend on the presence of Cl^- and Br^- ions in the solution.

For membranes containing Bi^0, the Cl^- and Br^- ions have a considerable competitive effect on the sorption of $^{131}I^-$ because the rates of sorption of halide ions do not differ much. For this reason, Bi-containing membranes are recommended for collection of $^{131}I^-$ only from desalted aqueous solutions. A study of I* removal under dynamic condition showed that both Bi- and Ag-containing membranes are able to capture I* with efficiency of 80% to 98% at the aqueous solution flow rate of ~ 0.5 cm^3 min^{-1} through a membrane of diameter 35 mm. For metal-free acetyl cellulose membranes, the efficiency was 74% under similar conditions.

Data on the use of polymer composite materials based on phenol formaldehyde resins for capture of I_2 from aqueous solutions were published.[164] Highly cross-linked resol resin was prepared from phenol and formaldehyde in 5 : 6 molar ratio in the presence of a catalyst (NaOH or NH_4OH). The sorption capacity with respect to I_2 varied depending on the total volume of sorbent pores and on the sorbent specific surface area. For sorbents with similar total pore volumes, the sorption capacity relative to I_2 increases with increase in the specific surface area. For sorbents with a total pore volume of ~ 0.80 cm^3 g^{-1} and specific surface areas of 780 and 720 m^2 g^{-1}, the sorption capacities are 880 and 710 mg of I_2 per gram of the sorbent. The authors suggested that the increase in the sorbent specific surface area caused by the development of microporisity upon sorbent activation with pure steam has a substantial effect on the sorption activity relative to I_2. On the other hand, for sorbents having similar specific surface areas but different total pore volumes, the sorption capacity with respect to I_2 slightly decreases with increase in the total pore volume. For example, for sorbents with a specific surface area of ~ 785 m^2 g^{-1} and total pore volumes of 0.79 and 0.91 cm^3 g^{-1}, the sorption capacities are 880 and 840 mg of I_2 per gram of the sorbent, respectively.

For the capture of I* during reprocessing of liquid radioactive wastes (LRW), it was proposed[165] to use the anion exchanger AV-17. Together with sorbed I*, this anion exchanger is planned for incorporation into the solid matrices $KMgPO_4 \cdot 6H_2O$ meant for prolonged storage of radioactive wastes. However, this solution requires long experimental verification to make sure that properties of the matrices chosen for the disposal of radioactive wastes would not change due to the radiation instability of the anion exchanger and the possibility of the subsequent formation of gaseous and other products.

The sorption of $^{131}I^-$ and $^{131}IO_3^-$ on the polymeric sorbents Polisorb-1 and Stirosorb from the aqueous medium was studied.[140, 166] In the experiments carried out under static conditions, the sorbents virtually did not collect $^{131}I^-$ and $^{131}IO_3^-$ from aqueous media: for $\tau = 30$ min and $V/m = 500$ cm^3 g^{-1}, the K_d values did not exceed 0.01 cm^3 g^{-1}. Meanwhile, both sorbents efficiently collect $^{131}I_2$ from a 2 M HNO_3 aqueous solution at 298 K. The partition coefficients for $^{131}I_2$ at $\tau = 120$ min and $V/m = 1000$ cm^3 g^{-1} are ~ 1350 and ~ 590 cm^3 g^{-1} for the Stirosorb and Polisorb-1 sorbents, respectively.

It is known that the structure of specially prepared calcium hydroxide phosphate $Ca_5(PO_4)_3OH$ (or hydroxyapatite, HAP) can be described as a calcium phosphate framework pierced by channels formed by Ca^{2+} ions; these channels accommodate HO^- ions. The possibility of isomorphous replacement of HO^- ions in Ca channels by other anions depends appreciably on the strain of P—O bonds in the framework.[167–169] This material can, in principle, be promising as an inorganic sorbent for collecting various forms of I* from aqueous solutions.

The sorption of $^{131}I^-$ and $^{131}IO_3^-$ from aqueous solutions on the HAP $Ca_5(PO_4)_3OH$ was studied.[170] The authors suggested the possibility of isomorphous replacement of HO^- and PO_4^{3-} ions by $^{131}I^-$ and $^{131}IO_3^-$, respectively. However, it turned out that $^{131}I^-$ and $^{131}IO_3^-$ are nor sorbed on $Ca_5(PO_4)_3OH$ from aqueous solutions. The partition coefficients for $^{131}I^-$ and $^{131}IO_3^-$ did not exceed 0.1 cm^3 g^{-1} at $[K^{131}I] = [K^{131}IO_3] = 2-5$ mg dm^{-3}, $V/m = 200$ cm^3 g^{-1}, $\tau = 5$ min. Hence, it was concluded that the Ca channels of HAP are much smaller than the $^{131}I^-$ and $^{131}IO_3^-$ ions, and the PO_4^{3-} groups of the HAP framework cannot be isomorphously replaced by $^{131}I^-$ or $^{131}IO_3^-$ due to the considerable difference between the structural parameters of these anions and, perhaps, also due to kinetic limitations.

The sorption of $^{131}I^-$ and $^{131}IO_3^-$ on Ca, Sr and Ba hydroxide phosphates was ivestigated.[122, 171–173] The researchers assumed that upon replacement of Ca^{2+} ions by analogous Sr^{2+} and Ba^{2+} ions, the size of the channels that accommodate the mobile HO^- ions would increase, and this would create conditions for accommodating $^{131}I^-$ and $^{131}IO_3^-$ ions. However, no sorption of $^{131}I^-$ or $^{131}IO_3^-$ ions on any of HAP samples was observed in experiments. The K_d values for $^{131}I^-$ and $^{131}IO_3^-$ were not more than 15 cm^3 g^{-1} for $[K^{131}I] = [K^{131}IO_3] = 10^{-5}$ mg dm^{-3}, $V/m = 500$ cm^3 g^{-1}, $\tau = 30$ min. It was also shown that increase in τ to 120 min has almost no influence on the K_d value for $^{131}I^-$ and $^{131}IO_3^-$ for their sorption from aqueous solutions on $Ca_5(PO_4)_3OH$.

Betenekov *et al.*[174] used the radiation-resistant composite sorbent Termoksid-5 manufactured by JSC Scientific and Production Company TERMOKSID (Zarechnyi) presaturated by Ag ions to capture I* from aqueous alkaline eluate during the extraction of ^{99}Mo from irradiated uranium blocks. The proposed process indicates that it is possible to obtain radiochemically pure ^{99}Mo concentrates with high purification from fission products including iodine radionuclides.

Metal hydroxides and mixed compounds based on them take an important place among inorganic anion exchangers. Among divalent metal hydroxides, $Ni(OH)_2$ stands out for its anion exchange capacity. Also, it is a typical representative of compounds with the brucite structure containing active HO^- groups.[175, 176] The $Ni(OH)_2$ grains are agglomerates of crystallites the space between which (macropores) is filled by the solution, which ensures the anion migration from the aqueous solution inside the grain. There are two key mechanisms of the anion exchange on crystallites: exchange on the crystallite surface and diffusion into the interlayer space of the crystallite structure.[175]

In view of the possible formation, as a result of corrosion, of hydroxides of the metals present as components of structural materials, in particular $Ni(OH)_2$, in the aqueous solution of the primary coolant of a WWER and LWGR type reactor, Kulyukhin *et al.*[177] studied sorption of $^{131}I^-$ and $^{131}IO_3^-$ on the $Ni(OH)_2$ solid phase from aqueous solutions at 293 K. It was found that upon increase in the $^{131}I^-$ and $^{131}IO_3^-$ concentration from 10^{-5} to 10^{-3} mol litre^{-1}, the K_d values in the aqueous solution decrease, after 120 min of the liquid and solid phase contact

at $V/m = 500$ cm^3 g^{-1}, from 16.4 to 5.3 cm^3 g^{-1} for $^{131}I^-$ and from 113.6 to 30.8 cm^3 g^{-1} for $^{131}IO_3^-$. This decrease was assumed to be caused by the low sorption capacity of $Ni(OH)_2$.[178] The effect of various anions (Cl^-, NO_3^-, SO_4^{2-}, BO_3^{3-}) on the $^{131}I^-$ and $^{131}IO_3^-$ sorption by solid $Ni(OH)_2$ from aqueous solutions was studied.[177] Upon increase in the concentration of these anions from 10^{-5} to 10^{-1} mol litre^{-1}, the K_d values for $^{131}I^-$ and $^{131}IO_3^-$ decrease 3–10-fold. These results were attributed to strong competitive effect of the studied anions both during the ion exchange with the OH groups in $Ni(OH)_2$ and during the formation of the corresponding mixed salts with $Ni(OH)_2$.

In recent years, layered double hydroxides (LDH) have attracted considerable attention of researchers.[179–185] They have the composition $M^{2+}_{1-x}M^{3+}_x(OH)_2[(An^{n-})_{x/n}\cdot 0.5\,H_2O]$, where M^{2+} and M^{3+} are metal cations and An^{n-} is almost any anion or anionic complex, $0.2 \leqslant x \leqslant 0.33$. These compounds have a layered structure with positively charged $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$ layers and anions located in the interlayer space. An important feature of LDH is stability of their layered structure over a broad range of cation and anion sizes; furthermore, the anions in the interlayer space can be replaced without destruction of the layered structure. Hence, anions can be easily introduced or withdrawn. As a rule, the anions are arranged in the interlayer space of LDH in such a way as to minimize the space.

The anion exchange in LDH was studied and the relationship was established between the anion nature and interaction with atoms in the LDH structure both through Coulomb forces and through hydrogen bonding.[180] The LDH of Mg and Al containing NO_3^- and Cl^- in the interlayer space (below referred to as LDH-Mg-Al-NO_3 and LDH-Mg-Al-Cl) interact only weakly with the studied anions in aqueous solutions and, under equilibrium conditions, they demonstrate a type V sorption isotherm. The authors noted that for LDH-Mg-Al-NO_3, the maximum adsorption of iodide ions occurs at $x = 0.33$, whereas for LDH-Mg-Al-Cl, the maximum adsorption is observed at $x = 0.25$. It was suggested that the Coulomb interaction plays a predominant role in the ion exchange in the case of LDH-Mg-Al-Cl, whereas for LDH-Mg-Al-NO_3, hydrogen bonds play an important role in exchange reactions.

A study of sorption of $^{129}I^-$ from aqueous solutions on the LDH-Mg-Al-Cl solid phase showed that this process is fast and at $[^{129}I^-] = 4.25\times10^{-5}$ mol litre^{-1}, the equilibrium is reached as soon as after 48 h.[186] The sorption of $^{129}I^-$ was found to be due to ion exchange, and the adsorption isotherm can be described by the Freindlich and Dubinin–Radushkevich equations. It was found that in the pH range from 3.5 to 8.5, the adsorption of $^{129}I^-$ does not depend on the solution acidity. However, despite the favourable kinetic characteristics, the amount of $^{129}I^-$ sorption is low and amounts to ~50% at $[^{129}I^-] = 4.25\times10^{-5}$ mol litre^{-1}. This value corresponds to exchange capacity of $\sim 2 < 10^{-6}$ mmol g^{-1}. As the Cl^- concentration increased, the $^{129}I^-$ sorption sharply declined. Whereas in the presence of 0.05 mol litre^{-1} of $MgCl_2$, sorption occurred by 30%, in a 0.1 M solution of $MgCl_2$, no sorption of $^{129}I^-$ on the solid LDH-Mg-Al-Cl was observed. The observed effect is caused by higher affinity of Cl^- compared to $^{129}I^-$ towards LDH-Mg-Al; for singly charged anions the exchange constant decreases in the following order: $HO^- > F^- > Cl^- > Br^- > NO_3^- > I^-$.

The thermal decomposition of LDH at temperature of > 573 K gives layered double oxides (LDO). An important property of LDO exhibiting the 'structural memory effect' is their ability to reduce the LDH structure upon getting into aqueous solution. Together with HO^- ions, other anions present in the solution are also incorporated in the LDH structure. Sorption of I* on the solid phase LDO- Zn-Al from aqueous solutions was reported.[187] Unfortunately, the authors did not indicate in what chemical form I* was present in the solution. As noted above, LDH-Mg-Al and LDO-Mg-Al are suitable for the collection of various anions from aqueous solutions.[179, 183, 185]

Data on the sorption of $^{131}I^-$ and $^{131}IO_3^-$ from aqueous solutions on LDH-Mg-Al-CO_3 and LDH-Mg-Al-NO_3 were reported.[188–191] It was shown that for $[K^{131}I] = [K^{131}IO_3] = 10^{-5}$ mol litre^{-1}, after 60 min of contact of the liquid and solid phases, the K_d values for collection of $^{131}I^-$ and $^{131}IO_3^-$ from aqueous solutions on solid LDH-Mg-Al-CO_3 are 38 and 34 cm^3 g^{-1}, respectively. It was concluded that the exchange of HO^- groups and CO_3^{2-} ions present in LDH-Mg-Al-CO_3 with $^{131}I^-$ and $^{131}IO_3^-$ occurs to a moderate extent both due to steric hindrance and due to higher affinity of HO^- and CO_3^{2-} compared to IO_3^- and I^- (Refs 180 and 186). However, since the $^{131}I^-$ and $^{131}IO_3^-$ ions are secured insufficiently strongly in the LDH interlayer space, they are easily replaced with time by the CO_3^{2-} ions that are formed in solution upon adsorption of CO_2 from the surrounding atmosphere. These data are in good agreement with conclusions of another study.[180] Under similar conditions, the K_d values for $^{131}I^-$ and $^{131}IO_3^-$ on LDH-Mg-Al-NO_3 are almost 7 times lower ($K_d <$ 5 cm^3 g^{-1}) than those for LDH-Mg-Al-CO_3. Meanwhile, the K_d values for $^{131}I^-$ and $^{131}IO_3^-$ on LDO-Mg-Al obtained by thermal decomposition of LDH-Mg-Al-CO_3 at 823 K in aqueous solutions after 14 h of contact between the aqueous solution and the solid phase ($V/m = 50$ cm^3 g^{-1}) were ~8000 and ~7000 cm^3 g^{-1}, respectively.

A study[192] of sorption of $^{125}I^-$ (as analogue of $^{129}I^-$) from aqueous solutions on various minerals under aerobic and anaerobic conditions was reported. As the solid phase, various minerals (pyrite, chalcopyrite, galenite and cinnabar) and their mixtures with bentonite were tested. The sorption experiments were carried out by reactions of crushed and sieved mineral or their mixture with bentonite with aqueous solutions containing ^{125}I. The contact time was varied from 1 to 43 days, the equilibrium being attained by the 32th day. Under aerobic conditions, the distribution coefficients for $^{125}I^-$ were as follows:

Sorbent	K_d/cm^3 g^{-1}	Sorbent	K_d/cm^3 g^{-1}
Bentonite	3.23	Pyrite	1.93
Chalcopyrite	72.42	Cinnabar	55.48
Galenite	118.9		

Thus, the maximum sorption of $^{125}I^-$ was observed for chalcopyrite (Cu content of 33.27 mass %), galenite (Pb content of 85.99 mass %) and cinnabar (Hg content of 85.74 mass %). The K_d values for $^{125}I^-$ were higher than those for $^{125}IO_3^-$. Indeed, for $^{125}IO_3^-$, the K_d values on galenite and chalcopyrite were 15.95 and 22.27 cm^3 g^{-1}, respectively. In addition, it was shown that K_d of $^{125}I^-$ and $^{125}IO_3^-$ decreased with increase in the pH of the solution.

For example, as pH was increased from 2.25 to 12.26, the K_d value for $^{125}I^-$ on a galenite–bentonite mixture (1:9) decreased from 17.69 to 2.62 $cm^3\ g^{-1}$, *i.e.*, ~6-fold. Under anaerobic conditions, the K_d values of $^{125}I^-$ and $^{125}IO_3^-$ substantially decreased to become 88.48 and 42.8 $cm^3\ g^{-1}$ for galenite and 6.47 and 2.39 $cm^2\ g^{-1}$ for chalcopyrite, respectively. A study of ^{125}I desorption from galenite and chalcopyrite after sorption of $^{125}I^-$ and $^{125}IO_3^-$ from aqueous solutions demonstrated that the sorption of these ions on these minerals is irreversible. On the basis of these results, it was concluded [192] that galenite (lead glance) is the best sorbent for $^{125}I^-$ and $^{125}IO_3^-$ both under aerobic and anaerobic conditions.

A study [193] dealt with sorption of ^{125}I from aqueous solutions of medium-activity LRW on various inorganic materials (Al_2O_3, Fe_2O_3, MnO_2, TiO_2, CeO_2, SnO_2, bentonite, silica gel). At 5–6, the best ^{125}I decontamination factor equal to 2 was achieved on Al_2O_3. If $FeCl_2$ is simultaneously used as a coagulating agent, ^{125}I decontamination factor at pH 5–7 increases to 5.

In the case of sorption on clays containing goethite (FeOOH) and iron hydroxides, the degree of extraction of ^{125}I as IO_3^- was 90%–97%.[193] A solution containing only $^{125}IO_3^-$ ions was obtained when $^{125}I^-$ was first oxidized to $^{125}IO_3^-$ with sodium hypochlorite at pH 4.8–5.8.

Goba *et al.*[194] compared the sorption properties of various sorption materials (carbon and mineral) and composite sorbents based on them with respect to a mixture of radionuclides including ^{131}I. As sorbents, they studied the active carbon BAU, sulfonated carbon, technical oxidized carbon DOU, fossil coals (brown coal, semicoke, saline coal, anthracite), peat, natural zeolites from various deposits, mordenite, limestone, ash from the Triplosky condensation power plant and sorbents based on biomass. In addition, composite sorbents based on these materials were studied. It was shown that zeolites, ash and limestone rather efficiently collect $^{134,137}Cs$ and ^{140}Ba, whereas carbon materials well extract ^{131}I. Thus the degrees of extraction of ^{131}I from water by ash and anthracite were 95% and 100%, respectively. Unfortunately, none of the studied sorbents exhibited universal sorption behaviour with respect to the whole spectrum of radionuclides. Therefore, the authors concluded that simultaneous removal of all radionuclides from aqueous solutions may be accomplished by using mixed composite sorbents. Relying on the experiments for large-scale water treatment units, the authors recommended the following composite sorbent mixtures: peat + zeolite, brown coal (or anthracite) + limestone + zeolite and ash + limestone + zeolite.

Peat was used to remove $^{129}I_2$ from the aqueous phase.[60] At pH 6, the reaction of $^{129}I_2$ with peat is partially caused by the reduction of $^{129}I_2$ to $^{129}I^-$ and is partially due to absorption of $^{129}I_2$ in the peat matrix. The authors noted that the reaction of $^{129}I_2$ with peat is substantially accelerated with increase in the pH of the solution.

It was shown [195] that electrostatic interaction of $^{129}I^-$ with positively charged surfaces of organic compounds or iron oxides promotes the adsorption of $^{129}I^-$ on these materials. The degree of adsorption depends appreciably on the pH of the medium. Upon increase in the acidity of the medium, the adsorption of $^{129}I^-$ increases due to increase in the number of positively charged sites on the surface of materials.

Investigations showed [196] the absence of sorption of $^{129}I^-$ from aqueous solutions on some minerals present in argillaceous ores (quartz, montmorillonite, dolomite, kaolinite and calcite). Meanwhile, other mineral components of argillaceous ores (pyrite, illite) weakly sorb $^{129}I^-$ (Ref. 196). One of the causes of $^{129}I^-$ sorption on the argillaceous ore is the possibility of isotope exchange between $^{129}I^-$ in the solution and ^{127}I in the ore where its content is $\sim 10^{-6}$ mol kg^{-1} (Ref. 197).

Wittebroodt *et al.*[198] investigated sorption of $^{129}I^-$ on argillaceous ore from Tournemire (France), which contained ~50% of clay minerals (illite, illite-smectite, kaolinite), ~20% of quartz, ~20% of calcite, pyrite and siderite at a ~1% total content of organic carbon.[199] In the $^{129}I^-$ concentration range from 10^{-2} to 10^{-3} mol $litre^{-1}$, no sorption took place and $K_d \approx 0$. When the $^{129}I^-$ concentration varied from 10^{-4} to 10^{-5} mol $litre^{-1}$, K_d was 0.01–0.02 $cm^3\ g^{-1}$.

Layered bismuth oxyiodides were proposed as possible I* collecting agents.[151] Treatment of a mixture of aqueous solutions of $Bi(NO_3)_3$ and KI taken in different ratios with a 1 M NaOH solution gives bismuth oxyiodides of various compositions: BiOI (Bi : I = 1.00), Bi_5O_7I (Bi : I = 5.00), $Bi_7O_9I_3$ (Bi : I = 2.33), $Bi_4O_5I_2$ (Bi : I = 2.00). The iodine content in the samples varied from ~5 mass % to ~30 mass % for Bi_5O_7I and BiOI, respectively. A study of the solubility of these compounds in water demonstrated that in the temperature range from 298 to 363 K, the solubility is higher than 5 ppm. However, the solubility value is affected by the presence of HCO_3^- in the aqueous solution. For example, a study of the effect of 0.005 M $NaHCO_3$, Na_2SO_4 and NaCl solutions on the solubility of Bi oxyiodides showed that in the presence of SO_4^{2-} and Cl^-, their solubility does not exceed 10^2 ppm, whereas in the presence of HCO_3^-, it increases to $(1-2)\times 10^3$ ppm.

The preparation of hydrated uranyl iodate $UO_2(IO_3)_2(H_2O)$ from aqueous solutions was reported.[200–203] This was accompanied by intercalation of HIO_3 into the layered structure to give $UO_2(IO_3)_2(H_2O)\times 2\,HIO_3$. The authors noted that this mechanism is the key route of the I* capture as IO_3^- by layered uranium compounds. By a similar mechanism, I* is captured as IO_3^- in the uranophane $Ca[UO_2(SiO_3OH)]_2\cdot 5\,H_2O$.[204]

Three new layered uranyl phosphates described as $Ba_3(UO_2)_2(HPO_4)_2(PO_4)_2$ (BaUP), $Ba(UO_2)F(PO_4)$ (BaUPF) and $Cs_2(UO_2)_2(PO_4)_2$ (CsUP) were synthesized under mild hydrothermal conditions.[205] The synthesized compounds were characterized by various methods, in particular, their ability to collect I* as $^{129}IO_3^-$ *via* replacement of $PO_3(OH)^{2-}$ or PO_4^{3-} ions in the compounds was studied. The $^{129}IO_3^-$ collection process from aqueous solutions by the solid phases BaUP, BaUPF and CsUP was studied in two independent experiments. In one case, the above-listed phosphates were synthesized from solutions containing $H^{129}IO_3$, whereas in the other case, uranyl phosphate phases were made to react with a $H^{129}IO_3$ solution under mild hydrothermal conditions (463 K, 5 days). In all experiments, the stoichiometric ratio $U : {}^{129}IO_3^-$ was 10 : 1. Finally, it was found that in both cases, $^{129}IO_3^-$ was captured in solid uranyl phosphate matrices. The contents of I* in BaUP, BaUPF and CsUP were 4162, 2923 and 100 ppm in the former case and 412, 1241 and 139 ppm in the latter case. It was concluded that

the mechanism of incorporation of $^{129}IO_3^-$ into the listed compounds is replacement of various phosphate groups in uranyl phosphates. Different coordination of phosphate groups in uranyl phosphate structure results in different degrees of inclusion of $^{129}IO_3^-$. In conclusion, the authors assumed that $^{129}IO_3^-$ can be accumulated in the environment in natural minerals based on uranyl phosphate, for example, in phurcalite $Ca_2(UO_2)_3(PO_4)_2O_2 \cdot 7\,H_2O$.

IX. Conclusion

The information presented in the review concerning the behaviour of I* in the gas and aqueous phases demonstrates that studying the I* behaviour in these media still remains highly important both for further successful and safe development of nuclear power engineering and for maintenance of the environmental safety.

The Fukushima nuclear power plant accident (Japan) in March 2011 resulted in I* emission to the environment, which led to radioactive contamination of the sea water and atmosphere. As a result of air mass movement, the ^{131}I and $^{134,137}Cs$ radionuclides were detected not only in the Pacific Ocean and in North America but also in Europe.[206] It is owing to the use of modern instruments based on new sorption-and-filtering materials to monitor the atmosphere of Europe, the experts were able to detect the presence of ^{131}I in the atmospheres of most European countries. Therefore, effective capture of various I* forms both for atmospheric monitoring and for accident prevention at nuclear power industry facilities requires advancement of research aimed at the development of new relatively cheap sorbents that would be able to replace Ag-containing materials. Simultaneously, it is necessary to search for new composite materials suitable for converting I* compounds that are difficult to capture to simple forms that are easily sorbed. The presence of such materials would not only simplify but also make cheaper the environment protection systems at nuclear industry facilities.

The importance and topicality of the problem considered in this review is beyond doubt, because provision of the radiation and environmental safety at nuclear industry facilities and preservation of the environment are vital for the sustainable development of the mankind.

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