



Influence of long-term aqueous leaching of irradiated graphite on surface properties and behavior of radionuclides

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Abstract.

Samples of real irradiated (i-)graphite from bushings of RBMK reactor after several types of decontamination treatments were put in contact with aqueous solutions modelling underground water of Nizhnekansky massif (Russia) equilibrated with bentonite for periods up to 1.5 years. Leach rates of radionuclides and evolution of graphite surface morphology and oxidation state were monitored using nuclear spectroscopy, SEM and XPS. After the experiment, less than one third of surface carbons remains unoxidised. Extensive precipitation of secondary phases (alumosilicates, carbonates) was observed on some samples and is possibly correlated with surface oxidation extent. The leach rates of dose-forming ¹⁴C and ³⁶Cl are comparable with the leach rates of radionuclides in glassy waste forms. According to the current study i-graphite could be regarded as a waste form, which is suitable for near-surface disposal.

INTRODUCTION.

Disposal of large quantities of irradiated graphite (i-graphite) remains controversial issue and several possibilities are considered. Extensive studies have shown that thorough decontamination from principal dose-forming radionuclides such as ¹⁴C

and ^{36}Cl by chemical or thermochemical methods is barely possible without complete destruction of graphite crystalline lattice (e.g., [1-2] and references therein). The principal reason for high retention of radionuclides lies in physical mechanisms of their production, since non-negligible fraction of ^{14}C reside in graphite lattice is generated by neutron activation of ^{13}C . This fraction depends on i-graphite production method, cooling gas and fluence-temperature history of a reactor, and varies widely, but in all cases this fraction accounts for several tens percent's of total radiocarbon inventory.

In Russian Federation, two principal approaches for disposal of i-graphite are considered: a) shallow burial of the reactor graphite pile on-site with creation of multiple barriers; and b) dismantling of the pile and storage of i-graphite (possibly after partial decontamination) in shallow or deep underground repositories [3]. The selection of the approach depends, in particular, on radiological class of the radioactive waste. Eventual contact of the graphite with fluids regardless of the disposal type will likely occur at some point. The current study is devoted to investigation of radionuclides' leach rates and changes of surface properties of real i-graphite from bushings of RBMK reactor, which has contacted aqueous solutions for periods up to 1.5 years. Nizhnekamsky massif (Krasnoyarsk region, Russia) is as a main site for proposed Russian deep geological repository of radioactive waste [4]. Importantly, in this location composition of fluids in deep strata is fairly similar to that of shallow waters. Conditioned water solution modeling situation of eventual penetration of Nizhnekamsky massif fluids through engineering barriers was used for the leaching experiments. Therefore, obtained results are relevant to both types of proposed repositories – shallow and deep ones.

EXPERIMENT.

The composition of initial model water is shown in Table 1. The model water has contacted bentonite (at ratio solid/liquid = 1/10 g/l) at temperatures 25 (BS-25) and 90°C (BS-90) for 14 days with regular stirring, mimicking interaction of aqueous fluids with bentonite filling of the repository. To separate colloidal solids the solutions were centrifuged for 10 min at 8000 min^{-1} . Chemical composition of the conditioned solutions used for the leaching experiments are given in Table 2.

Table 1. Composition of model water

Anion	Concentration		Cation	Concentration	
	mg/l	%-eq		mg/l	%-eq
HCO_3^-	197,5	62,8	Na^+	74.5	62.8
Cl^-	47.9	26.2	Mg^{2+}	6.8	11.0
SO_4^{2-}	27.3	11.0	Ca^{2+}	26.9	26.2

Table 2. Composition of conditioned solution used for the leaching experiments. ICP-MS data, mg/l.

Solution	Na	Mg	Al	Si	S	K	Ca	Fe	Co
BS-25	223.8	7.39	0.016	5.96	44.2	5.88	16.1	0.0092	0.0002
BS-90	220.4	7.64	0.12	13.6	43.7	7.21	18.5	0.042	0.00014

	Ni	Br	Sr	Cs	La	Ce	Nd	Th	U
BS-25	0.0023	0.016	0.15	0.0004	0.000067	0.000068	0.000071	0.0000058	0.0052
BS-90	0.002	0.017	0.18	0.0004	0.00012	0.00015	0.00011	0.000013	0.0013

Five samples of irradiated graphite bushings from Leningrad RBMK type reactor weighing between 1-1.4 grams were studied. Two samples were used in as-received state; another two were treated by 7,5 M HNO₃ + 2%NH₄F₂ during 18 h to address influence of chemical decontamination (see [1] for details). The samples were immersed into the conditioned solution for 200 days, dried, studied by SEM and XPS and then immersed again for another 250 days. Two samples were leached at 25 and two at 90°C. The fifth specimen was used as a control for the surface studies.

¹³⁷Cs and ⁶⁰Co content was measured using HPGe γ -spectrometer (Packard, Ortec). Actinides were measured using low-background α -spectrometer Alpha-Aria (AMETEK) after appropriate pre-concentration and separation. ¹⁴C and ³⁶Cl were measured by liquid scintillation method using Tri-Carb-3180 TR/SL after extraction procedure described in [2].

Morphological peculiarities of the samples was addressed by Scanning Electron Microscopy (SEM, JEOL320). The studied samples possessed both smooth initial faces and rough surfaces exposed by fracturing. Chemical composition of surface contaminants and speciation of C and O was studied by X-ray photoelectron spectroscopy with Kratos Axis Ultra DLD spectrometer, monochromatic Al-radiation was employed. Beamsize ~1 mm², surface sputtering was not performed. Neutralisation was not necessary due to conductive nature of the sample. Survey scan was recorded at 160 eV pass energy; detailed scans of C and O peaks performed at 40 eV pass. The samples were studied after the first (200 days) and second leaching (total 450 days) stages. Assignment of the peaks is based on [5] and some other databases.

RESULTS.

Surface morphology and C, O speciation.

SEM images of the studied samples are shown in Figures 1 and 2. As expected [6], the bushing graphite is heterogeneous on scales below several tens μ m, which reflects peculiarities of the graphite production (ratio of filler and binder, details of thermochemical treatment, etc.). Spots enriched in Al and/or Si are sometimes encountered (Fig. 1b, c, d, f); these formations are inherited from the graphite production. Immersion into the leaching solution does not alter morphology of graphite to a noticeable degree and no continuous deposits were formed. The principal difference between the control specimen and leached samples lies in amount and speciation of surface deposits. The surface deposits largely consist of individual aluminosilicate/carbonate grains with sizes up to 10-20 μ m (Fig. 1e, f; Fig. 2). In most cases, the grains appear to be randomly distributed without clear correlation with features of the graphite substrate. As indicated above, Si-Al-containing spots are sometimes present and after the leaching experiments precipitation of fine crystals are observed on some of them (Fig. 1d). The sample leached without prior acid treatment show rather contrasting behaviour in the deposits build-up: the one leached at 25°C is the least contaminated, whereas the one leached at 90°C is the most contaminated one in the whole sample set on both stages of the experiment (Fig. 2 a-e). The acid-treated samples

fall in between. After the second leach stage, many of precipitated grains are well-formed morphologically (see Fig. 2).

In general, the precipitation appears to be random without obvious correlation with morphological peculiarities of the graphite surface. Whereas drying of the solution drops after specimen removal from the liquid explains surface deposits, study of the deposited particles is of interest. First, they may take part in retention of leached radionuclides (e.g., carbonates may trap ^{14}C , ^{137}Cs , ^{241}Am). Second, the nucleation rate of the deposited crystals depends on wettability of the substrate (e.g., [7]) and thus on oxidation state of the surface. For example, morphology and number density of carbonate crystals on surfaces of the acid-treated and non-treated samples leached at 90°C differ, with fewer well-formed crystals in the former case. Note however, that some regions of the graphite samples remain virtually free from deposits (Fig. 2f).

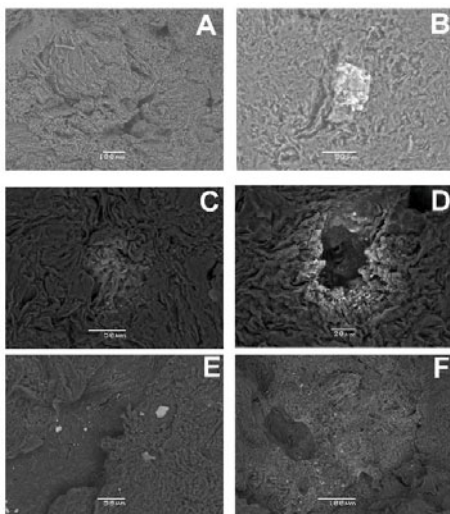


Figure 1. SEM images of the studied i-graphite samples. A, B - control sample; on B a chemically impure spot is shown. C-F - samples after 200 days of leaching.

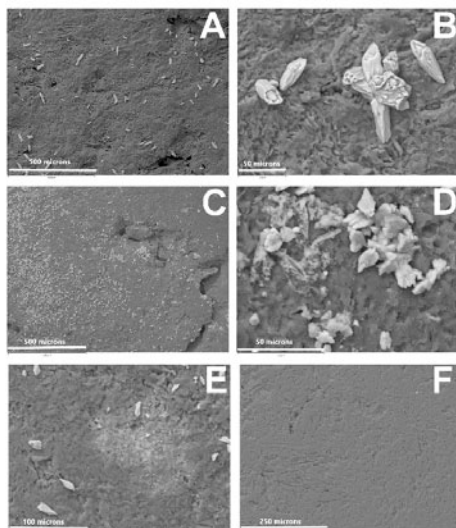


Figure 2. SEM images of the studied i-graphite samples after 450 days of leaching.

XPS results.

In addition to C and O XPS survey scans showed presence of Mg, Na, Al, Si, Ca on all samples except the control one; small amounts of Cl were occasionally. Nitrogen was detected on the control specimen (0.7 at%) and on both samples leached at 25°C (~2-2.6 at%); the second leaching stage approximately doubled the N content. Na is less abundant in comparison with Al, Mg, Si, Ca. Clearly all these elements are contained in deposited crystals and due to heterogeneous coverage of the surface detailed analysis of concentrations is ambiguous.

O1s spectra of the samples after the first leaching stage are shown in Figure 3. Usually at least two components could be resolved. Unique assignment of broad O1s peaks is difficult, but using information from C1s spectra (see below) presence of C-O and C=O species is assumed. Oxygen in hydroxyl groups is also possible. Presence of the surface deposits also influence analysis of the O1s peaks; the contribution of oxygen in the precipitates are especially pronounced on the “dirtiest” sample (no acid; 90°C).

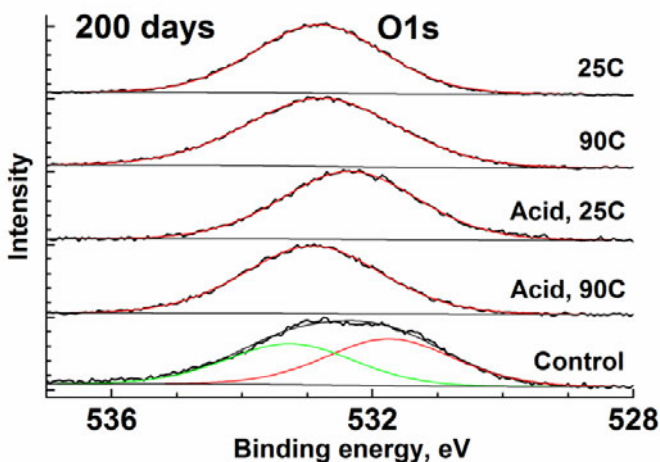


Figure 3. X-ray photoelectron spectra of O1s region for i-graphite samples after 200 days of leaching. Experimental data and example of decomposition are shown. The curves are displaced vertically for clarity.

O1s spectra are shown in Figure 4. In the control sample the graphite C-C bond at 284.3 eV accounts for >87% of total carbon, the rest is due to various oxidized forms of carbon and π - π^* shake-up satellite. The leaching experiments dramatically increase amount of oxidized carbon; the fraction of graphitic carbon drops to 26-32 at%. After the first leaching epoxy groups (C-O) are the rather abundant making 9-11 at% of all carbon; second leaching stage decreases their relative abundance. The second leaching leads to 2-3 times increase of carboxyl groups' fraction and with 18-24% they are the most abundant oxidized species. Other C,O-containing species are also present at 2-6 at% level. No clear dependence of the relative abundance of oxidized groups as a function of the treatment/temperature is observed.

The peak at 285.0-285.1 eV is assigned to sp^3 -C, possibly in hydrocarbons. This peak was weak or absent on control sample, became rather pronounced on all samples after the first leaching (up to 39 at% on acid-treated sample leached at 25°C and between 27-32 at% for other samples) and decreases after the second leaching down to 3-8 at%. Again, this peak is the strongest in sample acid+25°C.

Interestingly, the degree of surface oxidation markedly increased during the second leach test. This effect might be somewhat similar to leach rate resumption phenomena observed for some nuclear glasses (e.g.,[8]). Advanced oxidation of the graphite surface after the second leach stage increases surface wettability and enhances precipitation of surface deposits. In turn, some of the precipitates, such as carbonates, may incorporate radionuclides leached from the graphite and thus such deposits may suppress their transport. However, in presence of water oxidation of graphite facilitates intercalation and may simplify exfoliation [9]. This effect increases surface accessible to underground fluids and is clearly detrimental.

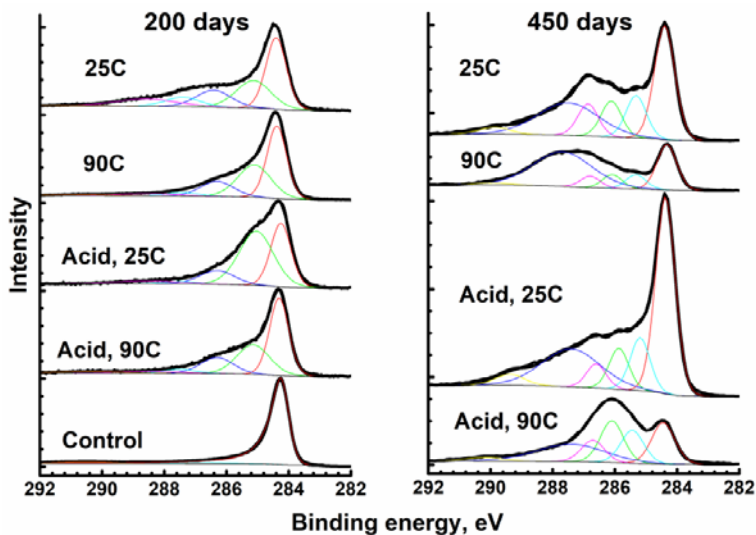


Figure 4. X-ray photoelectron spectra of C1s region for i-graphite samples after 200 and 450 days of leaching. Experimental data and example of decomposition are shown. The curves are displaced vertically for clarity.

Leaching results.

Amount of radionuclides leached in the first 200 days is higher than during the second leaching stage. ^{137}Cs , ^{14}C , ^{14}C , ^{36}Cl and minor amounts of fission products and actinides were found in the solution. At 25°C $1.8 \times 10^{-2} \%$ of total ^{14}C and 0.6% of ^{36}Cl were leached in the first 200 days; subsequent 250 days additionally removed $8.2 \times 10^{-3} \%$ of ^{14}C and 0.2% of ^{36}Cl . Leaching at 90°C removed larger amounts: $2.0 \times 10^{-2} \%$ ($1.7 \times 10^{-2} \%$) of ^{14}C and 2.6% (0.94%) of ^{36}Cl (first 200 and subsequent 250 days, respectively). At both temperatures the leach rate decreases with time; similar behavior was observed in previous studies (e.g., [1, 10]).

Leaching of ^{137}Cs intensified markedly at 90°C ; for Pu and Am inverse behavior is observed. Leaching of ^{60}Co is temperature independent. Acid treatment prior to the leaching experiments removed a fraction of Pu and Am [1], explaining their lower amounts in the leachate even despite long duration of the experiment. It should be noted that our extensive work on different types of i-graphite show that leaching of activation products and of actinides is strongly sample-dependent and may vary at least an order of magnitude. This is logically explained by highly heterogeneous distribution of these nuclides in the graphite due to variations in manufacturing process and history of reactor campaigns.

CONCLUSIONS

Alteration of surfaces of real i-graphite samples and leaching behavior of several important radionuclides during long-term (1.5 years) exposure to simulated

underground solutions are investigated. Whereas morphological changes of the graphite are too subtle to be reliably observed, pronounced surface oxidation clearly occurs. After the experiment, less than one third of surface carbons remains unoxidised. With time, the oxidation may lead to exfoliation of graphite, and increase of surface exposed to fluids. Deposition of small crystals of secondary phases (carbonates, aluminosilicates) on graphite is observed and broad correlation of crystal morphology and nucleation rate with degree of surface oxidation possibly exist. The secondary phases may incorporate a fraction of leached radionuclides, but efficiency of this process remains unknown.

Leach rate of ^{14}C and ^{36}Cl increases with temperature, but gradually saturate with time. Formation of secondary carbonate phases will immobilize part of leached ^{14}C . Radiochlorine is characterized by higher, albeit strongly variable leach rates. This is explained by its heterogeneous distribution in graphite pile after the production processes ([2, 11]) and thus the absolute amounts of ^{36}Cl in solutions remain low. The leach rates of these radionuclides are comparable with losses of long-living nuclides from nuclear glasses. In summary, the current investigation shows that i-graphite could be regarded as a waste form, which is suitable for near-surface disposal.

Acknowledgements.

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