

Enhanced Recovery Of Radionuclides From Irradiated Graphite By Sulfuric Acid-Graphite Intercalation And Leaching – 14551

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ABSTRACT

In this study, a method to extract radionuclides from irradiated graphite is reported. It relies on the use of highly concentrated sulfuric acid (H_2SO_4) for graphite intercalation as well as for leaching. For this purpose, studies were first performed on non-radioactive nuclear graphite to gain insight into and to optimize the process of acid intercalation in nuclear graphite. X-Ray Diffraction (XRD) was hence used to characterize graphite prior to and after chemical intercalation reaction. After optimization of experimental conditions using inactive graphite, experiments were carried on irradiated graphite where significant fractions of radionuclide release were obtained.

INTRODUCTION

Since the beginning of the nuclear era, nuclear graphite has been used as a neutron moderator and reflector in different types of reactors, many of which are facing or will soon face decommissioning. Furthermore, a large quantity of graphite is used in high-temperature gas cooled reactors. The main issue with nuclear graphite is its contamination during reactor operation by fission products or the activation of its impurities by irradiation. From a waste management point of view, the key radionuclides are Co-60 during decommissioning if it is performed immediately after reactor shutdown, and the long-lived radionuclides C-14 and Cl-36 for long-term safety in the case of direct disposal [1] [2]. It is estimated that there is 250,000 tons of irradiated graphite worldwide that has to be managed as radioactive waste, the three possible options being underground disposal, destruction or reuse/recycling [3]. Regarding graphite decontamination as a process prior to final disposal or recycling, several authors claim that a significant part of the contamination of nuclear graphite (including C-14) can be removed by thermal, chemical or microbiological treatment [2] [4] [5].

This study proposes a simple method at room-temperature to extract radionuclides from irradiated graphite. It relies on the use of highly concentrated sulfuric acid in order to leach out radionuclides with the help of acid intercalation into graphite. Leaching of radionuclides from graphite using different acid and alkaline solutions has already been tested in order to simulate the natural release process in disposal or dismantling conditions but not with decontamination as a goal [6] [7]. Intercalation is the process whereby atoms, ions or molecules are inserted between the original layers of graphite without loss of planarity of these layers [7]. The rationale for the proposed treatment is that the penetration of intercalant species within the interlayer spaces of graphite is

expected to enhance radionuclide leaching. After the treatment, XRD analysis is used to characterize the studied samples and gamma spectrometry and liquid scintillation counting are used to control the radioactivity release for each leaching cycle.

DESCRIPTION

Samples

The samples used for this study correspond to nuclear grade graphite in its active and inactive forms. The inactive samples correspond to small blocks coming from G2 and Saint Laurent A2 (SLA2) French reactors. The SLA2 graphite block was grinded into a powder prior to experimentation. The active sample is irradiated graphite from SLA2 reactor, which was grinded into powder with a wide grain size distribution from micrometric particles to millimetric ones. The radionuclide inventory of this graphite is presented in table I.

TABLE I. Isotope inventory and specific activity of irradiated SLA2 graphite sample at 14/08/13

Radionuclide	H-3	C-14	Ni-63	Co-60	Eu-154	Ba-133	Cs-137	Cs-134
Activity (Bq/g)	1.56×10^5	1.35×10^4	3.92×10^3	7.22×10^2	31.0	21.6	37.1	5.0

Methods

The chemical intercalation reaction used is an oxidant-assisted chemical intercalation using H_2O_2 as the oxidant and H_2SO_4 as the chemical intercalant. In order to gain insight into and to optimize the process of acid intercalation, studies were first performed on inactive nuclear grade graphite. The intercalation process results in a more or less pronounced expansion of graphite which occurs along the direction perpendicular to the carbon sheets [8]. X-Ray Diffraction (XRD) is hence used to obtain information about the crystallographic structure of graphite prior to and after chemical intercalation reaction. The XRD patterns were obtained using a Siemens D5000 Bragg-Brentano $\theta/2\theta$ diffractometer with a Cu source at $\lambda=0.1541$ nm.

It has been shown in earlier works that the degree of intercalation in H_2O_2 -assisted graphite chemical intercalation depends on the H_2O_2/H_2SO_4 volume ratio which we shall refer as R in the following [9] [10]. The degree of intercalation is given by the stage number, n , which is defined by the number of graphite layers separating two alternate intercalated layers [8]. One of the goals when working on inactive samples is to determine the best value for R that will ensure the highest intercalation degree i.e. the lowest n . Hence, different H_2O_2/H_2SO_4 volume ratios were tested on G2 graphite blocks, labelled G2S1 to G2S5, as presented in table II. H_2O_2 was first added to the block sample followed by H_2SO_4 . The reaction was left for six hours after which graphite was removed from the reaction mixture as a slurry for XRD measurements. For the G2S5 sample, the analysis was performed after 24 hours of reaction. Intercalation was also performed on a SLA2 inactive graphite powder with $R=1/100$.

TABLE II. Experimental conditions for G2 graphite intercalation

Sample Name	Weight (mg)	Volume of H ₂ O ₂ (μL)	Volume of H ₂ SO ₄ (μL)	R
G2S1	156	60	300	1/5
G2S2	297	90	600	1/7
G2S3	308	60	600	1/10
G2S4	330	30	600	1/20
G2S5	315	60	6000	1/100

For leaching experiments, 250mg of the irradiated graphite were treated by adding 50μl of H₂O₂ followed by 5ml of 18M H₂SO₄ in a 40ml reaction container. The sample was agitated for 15 hours and afterwards left to decant for 8 days. After this period, 2.5 ml of the supernatant was sampled and was further centrifuged to remove any remaining particles left. 1ml of the centrifuged solution was used for gamma spectrometry analysis and the remaining solution was used for liquid scintillation counting. The separated graphite slurry was analysed by XRD. After XRD measurements, the graphite was put back in the reaction flask and 6ml of H₂O₂ was added for another leaching cycle of 7 days after which gamma spectrometry and liquid scintillation counting were performed on leachate samples as previously described.

RESULTS AND DISCUSSION

Intercalation Experiments

Figure 1 shows the picture of a G2 graphite block sample in a mixture of H₂O₂/H₂SO₄ (R=1/100). After 24 hours, swelling and disaggregation of the block are observed.

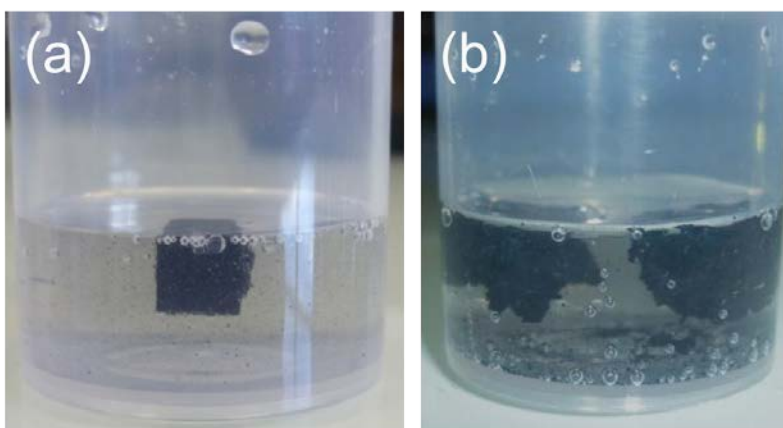


Fig. 1. G2 graphite sample (a) shortly after and (b) 24 hours after addition of H₂SO₄ into H₂O₂

XRD results obtained for treated and untreated G2 graphite are presented in figure 2(a). The patterns have been recorded in the 20° to 36° range. The XRD profiles have been smoothed and the intensity has been normalized to the peak maximum for easy

comparison. The main peak for untreated graphite is the (0 0 2) peak. In treated graphite, the main peak is shifted to shorter angles as a result of the intercalation process and owing to this intercalation, the peak indexation changes to (0 0 $n+1$) where n is the stage number.

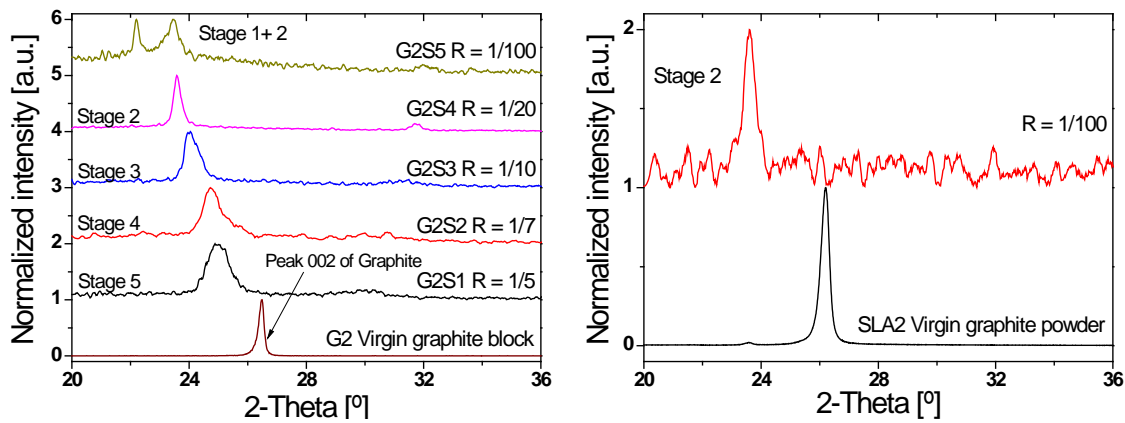


Fig. 2. XRD patterns for (a) treated samples G2S1-S5 (G2S5) (b) SLA2 graphite powder

In order to determine n from the new peak positions, the following formula has been considered:

$$l_c = d_i + 1/2c_0 \times (n-1) = l \times d_{obs} \quad (\text{Eq.1})$$

where l_c is the repetition period, d_i , the intercalated layer thickness, c_0 , the initial c-lattice parameter of graphite (=0.6717 nm), l , the Miller index (for the strongest peak equal to $n+1$) and d_{obs} , the corresponding observed interplanar distance.

The calculated n , considering d_i varying in the range of 0.79-0.80 nm, is reported in figure 2 (a) next to its corresponding pattern. n is found to vary consistently with R . As R is lowered, n is also lowered. The lowest stage structure obtained corresponding to the highest intercalation degree is a mixture of stage 1 and 2 obtained for $R=1/100$.

Figure 2(b) shows the results obtained on the SLA2 sample using $R=1/100$. In this case, the intercalation degree is a stage 2 structure.

Based on the results showing the best intercalation data, the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ mixture with $R=1/100$ is chosen for the following leaching experiment performed on irradiated graphite.

Leaching Experiments

The intercalation of the irradiated graphite after one 8-day leaching cycle is evidenced by XRD as shown in figure 3.

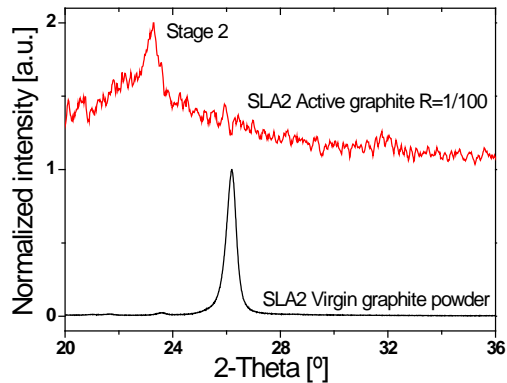


Fig. 3. XRD patterns for SLA2 virgin graphite and treated irradiated graphite

With respect to the virgin SLA2 graphite powder, the main peak is shifted to shorter angles and the new peak position allows us to deduce a stage number of 2 similar to what was observed for the virgin SLA2 sample treated with the same H₂O₂/H₂SO₄ volume ratio (figure 2b).

TABLE III. Gamma activity release for the two successive leaching cycles

Radionuclide	Fraction released in Cycle 1 (Intercalation)	Fraction released in Cycle 2 (H ₂ O ₂)	Cumulative fraction released
Co-60	71.7% ± 0.8%	15.7% ± 0.4%	87.4% ± 1.2%
Eu-154	71.0% ± 1.8%	23.3% ± 1.1%	94.3% ± 2.9%
Ba-133	45.9% ± 5.6%	14.5% ± 3.8%	59.4% ± 9.4%
Cs-137	64.6% ± 11.0%	22.4% ± 6.6%	87.0% ± 17.6%

Table III shows the activity release of major gamma emitters for cycle 1 and 2 together with the cumulative fractional releases for both cycles. It can be seen that the measured fractions of radionuclides released are significant (over 40%) for the first cycle of 8 days in acid. For instance, up to 70% of the Co-60 is released during the first cycle. The addition of H₂O₂ as last leaching solution allowed the extraction of an additional 14-23% of the remaining radionuclides. The cumulative fractional releases vary from 59.4% for Ba-133 to 94.3 % for Eu-154.

Liquid scintillation counting (LSC) was used to obtain an estimate on the amount of β radioactivity released in the leachate. In order to do so, actual counting for the leachate sample was compared with that of reference samples formed from pure C-14, Ni-63 and H-3 in the same acidic conditions and with comparable activity levels. It was found that the major part of β activity measured is due to H-3 and the fractional release is estimated to be 51% for both H-3 and Ni-63 for the first cycle. No C-14 was clearly detected since its level of activity was initially much lower than H-3 and in such acidic solutions the C-14 released most probably formed volatile molecules and left the solution in the gaseous form. With regards to a full scale process, one of the possibilities to collect C-14 lost by volatilization is to capture it in concentrated NaOH solution and to precipitate it as CaCO₃ by addition of Ca(OH)₂. The precipitated CaCO₃ can then be filtered and conditioned in containers.

Furthermore, we expect that a fraction of H-3 could also have been released in the same way in the gaseous form. Therefore, in the case of the H-3, the activity release measured in the leachate is the lower limit of activity release for this radionuclide. In a future work, the beta emitter release in the leachate and in the gaseous form will be studied more precisely by the use of separation methods coupled with liquid scintillation counting. This work will allow us to determine the H-3, C-14, Ni-63 activity released fractions and any Cl-36 release.

Since the fractions of radionuclides released are significant compared to what is generally observed for graphite leaching in aqueous solutions [11] [12] [7] [6], we can conclude that the intercalation indeed plays a role in the enhanced activity release by leaching. This enhanced activity release is not enough however to reclassify the treated graphite to a lower level waste category since the remaining fractions of radionuclides are non-negligible. One main reason could be that these fractions correspond to those radionuclides forming stable compounds with graphite. For instance, in a recently published work [13], it has been shown that cobalt could form stable carbides with graphite which are insoluble in water and most acids. Going one step further, we suggest that radionuclides forming stable compounds may withstand long-term leach attack. In that case, our technique can be used as an efficient treatment for graphite ahead of disposal. For this disposal, the treated graphite may be rinsed with water to remove acidity and any remaining H_2O_2 that has not been decomposed to water and oxygen during the treatment. The rinsed graphite can then be conditioned according to the current technologies available.

CONCLUSIONS

The leaching experiments performed on irradiated graphite allowed us to obtain fractional releases over 80% for gamma emitters such as Co-60, Eu-154 and Cs-137. Fractional releases of at least 50% were recorded for Ba-133 and β emitters such as H-3 and Ni-63. Such significant values can be attributed to the chemical intercalation of the graphite structure by the intercalant species coming from the leachant. It is highly probable that the unreleased part of radionuclides corresponds to those forming stable compounds with graphite rendering them resistant to long-term leach attack. On this basis, we propose that our technique can be used as an efficient treatment ahead of disposal. Successful intercalation in small graphite blocks indicates that for a full scale process, the grinding of graphite to a powder is not needed. However the extent to which the size of the graphite blocks can be upscaled without adverse effect on the intercalation process has to be studied. Furthermore, based on the disaggregation properties of the acid-graphite intercalation process, it can also be used as an effective method to separate graphite from other materials during dismantling operations.

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