Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Felker, L. K. and Toth, L. M.(1988) 'Fluorine Gettering by Activated Charcoal in a Radiation Environment', Separation Science and Technology, 23: 12, 1959 — 1968
To link to this Article: DOI: 10.1080/01496398808075676
URL: http://dx.doi.org/10.1080/01496398808075676

SEPARATION SCIENCE AND TECHNOLOGY, 23(12&13), pp. 1959-1968, 1988

FLUORINE GETTERING BY ACTIVATED CHARCOAL IN A RADIATION ENVIRONMENT

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ABSTRACT

Activated charcoal has been shown to be an effective gettering agent for the fluorine gas that is liberated in a radiation environment. Even though activated charcoal is a commonly used getter, little is known about the radiation stability of the fluorine-charcoal product. This work has shown that not only is the product stable in high gamma radiation fields, but also that radiation enhances the capacity of the charcoal for the fluorine. The most useful application of this work is with the Molten Salt Reactor Experiment (MSRE) fuel salt because the radioactive components (fission products and actinides) cause radiolytic damage to the solid LiF-BeF_2-ZrF_4-UF_4 (64.5, 30.3, 5.0, 0.13 mol %, respectively) resulting in the liberation of fluorine gas. This work has also demonstrated that the maximum damage to the fuel salt by $\sim 3 \times 10^7$ R/h gamma radiation is approximately 2%, at which point the the rate of recombination of fluorine with active metal sites within the salt lattice equals the rate of fluorine generation. The enhanced reactivity of the activated charcoal and radiation stability of the product ensures that the gettered fluorine will stay sequestered in the charcoal.

INTRODUCTION

In June 1965, a molten-salt fueled demonstration reactor began operating at the Oak Ridge National Laboratory (ORNL) and continued

until December 1969, compiling 107,737 MWh of operation. The Molten Salt Reactor Experiment (MSRE) used a eutectic mixture of lithium, beryllium, zirconium, and uranium fluorides (64.5, 30.3, 5.0, 0.13 mol %) as a circulating liquid fuel salt. At shutdown, the fuel salt was drained into two Hastelloy N storage tanks to ensure criticality safety. A flush salt was also circulated and drained into a separate storage tank, and all were allowed to cool and solidify. The storage tanks are contained inside a hot cell located at the MSRE site, and numerous monitoring and surveillance programs have been in effect since shutdown.

In late 1985, a project in the Surplus Facilities Management Program began to investigate the long-term storage requirements associated with the MSRE and, in particular, the stored fuel salt (1,2). One of the major concerns related directly to the fuel salt, is the effect of actinide and fission product radiolysis of the fluoride salt with the resultant generation of fluorine gas, which could cause excessive pressures and/or corrosion during long-term storage. The stored fuel salt is a prime candidate for these radiolysis effects since the numerous fission products provide considerable alpha, beta, and gamma radiation for a number of years to the mixed fluoride solvent salt. This radiolysis effect has been well established (3,4); but most of the previous investigations have focused attention on the damage to crystal structures rather than on the generation rates, recombination rates and limiting steady state pressures of the liberated (gaseous) products. Since the generation and release of fluorine gas will leave an active metal center for recombination with free fluorine gas, a steady-state pressure should be reached where fluorine generation is equal to its recombination with active metal. One objective of this work was to investigate the radiolysis of a fluoride salt mixture (comparable in composition to that of the MSRE) and determine if such a steady state pressure exists and if this pressure were of a magnitude that could be contained in long-term storage vessels. In addition, it was desirable to determine if a suitable getter could be added to the salt mixture which would sequester the generated fluorine gas and thus reduce the steady state F_2 pressure by forming a more stable chemical system (i.e., less corrosive to the container than F_2).

Various forms of carbon appeared most attractive because of the strong C-F bonds formed when carbon reacts with fluorine. Several different forms of carbon have been examined with respect to reactivity, capacity, and stability of the final product; especially stability in a radiation field such as that expected in the MSRE fuel storage tanks. Therefore, the focus of this paper is the investigation of gettering agents for fluorine and the stability of the reaction products in a radiation environment as they relate to the long-term storage requirements of the MSRE fuel salt.

MATERIALS AND METHODS

The graphite used in this investigation was POCO EDM-3 obtained from local chemical stores. The activated coconut charcoal [6 to 14 (3.4 to 1.4 mm) mesh] was from Fisher Scientific. The spectrographic grade carbon rod was obtained from Ultra Carbon Corporation. A D-1 size cylinder of fluorine gas with an appropriate regulator were obtained from Air Products.

Irradiation of the fluoride salt mixtures was carried out using the gamma flux from spent reactor fuel elements of the High Flux Isotope Reactor (HFIR) at ORNL (5). This gamma source was the most practical means of exposing the fluoride salt to a radiation dose that was sufficient to cause radiolytic damage in a reasonable time period. Even though alpha radiation will account for most of the radiolytic effects in the long term (1), there is a considerable intensity of gamma radiation currently associated with the stored fuel salt. Ultimately, however, it will be necessary to perform radiolysis experiments using an alpha source of sufficient intensity to produce doses equivalent to those from the gamma source. Although it is assumed that the effects of gamma and alpha doses will be similar, it will be necessary to demonstrate this in later experiments.

An equilibrium pressure of 446 kPa, corresponding to ~2% radiation damage, was obtained for the irradiation using 30 g of simulated fluoride fuel salt. When the defect sites (or active metal sites) generated by irradiation of the salt crystal structure reached ~2%, the recombination rate and the generation rate became equal and the pressure over the salt sample reached a steady state. The details of these irradiations and the results will be discussed in a separate publication (6). Since these experiments established the existence of a steady-state limiting pressure, the current work was directed towards finding a suitable getter for the generated fluorine.

A manifold for handling fluorine gas was constructed using (1) Hoke monel bellows valves, (2) monel tube fittings, and (3) an Ashcroft monel vacuum/pressure gauge. Carbon samples were loaded into the same type vessels that were designed for irradiation of fluoride salts in the HFIR spent fuel elements. This vessel (Fig. 1) was constructed of nickel with a conflat flanged top which was sealed with soft copper gaskets. The vessel was placed at the center of a spent fuel element, inside a cadmium sleeve, and a 3.2-mm-OD × 6.1-m (1/8 in. OD × 20 ft) tube extended to the top of the reactor pool to a vacuum/pressure gauge.

The basic approach (with some variations) to react the carbon samples with fluorine was to weigh carbon, graphite, or activated charcoal into a nickel vessel and heat it to 700 to 800°C under

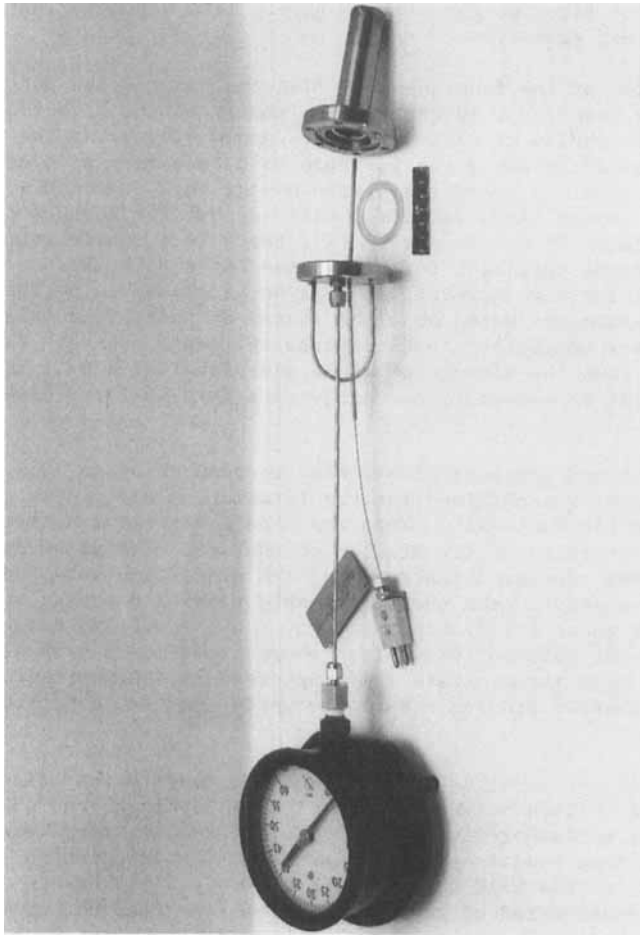

Fig. 1. Vessel for fluorine/carbon reactions and irradiations of fluorine-loaded carbon samples.

reduced pressure to remove moisture and residual gases. After cooling, the sample and vessel were weighed to obtain a tare before the sample was exposed to fluorine gas. The vessel was evactuated to <10 Pa and fluorine gas was slowly admitted into the manifold and vessel. The fluorine pressure was increased in small increments until an overpressure of 150 to 200 kPa F_2 was obtained. After the reaction was complete, the unreacted fluorine was evacuated from the vessel, which was then backfilled with helium. The vessel was removed and weighed to determine the amount of fluorine reaction.

One sample of activated charcoal, which had been exposed to fluorine, was irradiated in a spent fuel element at the HFIR. This sample received an average gamma dose rate of 2.79×10^6 R/h over the 60 days it was in the radiation field. Daily readings of the pressure were recorded to give a profile of the pressure over the charcoal sample as a function of irradiation time. After irradiation, the sample vessel was decontaminated and heated with a heating tape to determine the stability of the reaction products at various temperatures. The sample temperature was increased in 50°C increments from room temperature to a high of 330°C, and the pressure in the nickel vessel was monitored.

RESULTS and DISCUSSION

During the course of our investigation, we realized that the high reactivity of fluorine with carbon compounds could provide a suitable getter that would form stable reaction products. It was known that graphite forms an intercalation compound with fluorine of approximate C_2F stoichiometry at ambient temperature (7). The most attractive aspect of using graphite was its compatibility with the MSRE system. Graphite was used extensively as a moderator during reactor operation (8).

The first scouting test of carbon reactions with fluorine involved a small (0.5-g) sample of a carbon rod exposed to fluorine gas. The fluorine was slowly admitted into the nickel vessel containing the carbon rod and left for three days. When the pressure had dropped to approximately 20 kPa and stabilized, the vessel was evacuated and filled with helium. A weight increase of 4.28% was noted. Based upon this result, additional testing was done using graphite having a more complex crystal structure which could possibly have a higher capacity and lead to a more stable compound.

POCO graphite was first tested with a 19-g cylinder cut from a 13-mm- (0.5-in.) diam rod. This cylinder was thoroughly outgassed at 600°C in vacuum and loaded with 0.2 g of fluorine, which is equivalent to a 1.08% weight increase. The fluorine-laden graphite with 136 kPa F_2 overpressure was then exposed to the HFIR gamma flux (1.93×10^7 R/h) for two weeks. If the 0.2 g of F_2 were completely released in the volume of the irradiation vessel, then a pressure

of 260 kPa would result. The pressure actually decreased to 124 kPa in the system.

Several approaches were used in attempts to increase the fluorine capacity of the graphite. The graphite was ground to a fine powder (<0.25 mm), crushed (>0.25 mm to <3.36 mm), outgassed in an air atmosphere, and activated using a standard steam activation procedure (9). All of the methods produced minimal, if any, improvement in the 1 to 2 wt % capacity of the graphite. The steam-activated graphite showed increased porosity (~ 0.1-mm-diam holes) under microscopic examination but had a lower fluorine capacity (less than 1% weight increase) than the nonactivated graphite.

Activated coconut charcoal was also tested because it did not have the complex crystal structure of graphite, but it did have increased fluorine capacity. Also, this charcoal was commercially available in the activated form. When a 1.0-g sample was exposed to F_2 at room temperature, a very exothermic reaction occurred with sharp rises in temperature (30 to 50°C) and surges in pressure that exceeded the gauge readings. The reaction was so rapid that only small increments of F_2 could be added, starting with an initial F_2 pressure over the charcoal of only 10-20 kPa until finally approximately 150 kPa could be left in contact with the charcoal. This sample of activated charcoal yielded a weight increase of 60%, indicative of the formation of a C/F adduct of 2.6 ratio which is consistent with the literature (7) values of 2/1 to 3/1. The fluorine also appeared to be chemically bound (as opposed to mere adsorption) to the charcoal because attemps to pump it off were unsuccessful. These results are to be contrasted with those of Lorenz, et al., where molecular iodine (I_2) was reversibly adsorbed by activated charcoal (10).

The rapid reaction rate and high capacity of the charcoal for F_2, accompanied by the stability of the resultant product, led to more serious consideration of activated charcoal as a getter material. One of the most crucial requirements, however, was the stability of the carbon/fluorine product in a radiation environment, since that is one of the criteria for a suitable getter.

Table 1 contains the results of the fluorine loading experiments on the various carbons.

Most of the carbon samples showed a high rate of reaction with F_2 with 80 to 90% of their maximum loading occurring within a few minutes. The only exception was the graphite rod which took several days to reach maximum loading. By far the most reactive of the carbon samples was the activated charcoal, which reacted so rapidly that the F_2 had to be admitted very slowly to minimize the buildup of excessive reaction heat. (See discussion on activated charcoal.) Certainly, the difference in surface areas could play a considerable role in the reaction rates and capacities of a particular carbon sample, but little effect was noted in the rate or capacity of the graphite samples tested.

Table 1. Results of fluorine loading on various carbons

Carbon form	Special preparation[a]	Capacity (wt % increase)
Carbon rod	No outgassing or heating	4.28
Graphite rod	Outgassed in air	1.08
Graphite	Crushed	2.17
Graphite	Crushed, long-term exposure	2.17
Graphite	Crushed, no outgassing	0
Graphite	Crushed, steam activated	0.36
Graphite	Crushed, steam activated	0.41
Activated charcoal		60.00
Activated charcoal	Loaded for irradiation	50.00

[a]All samples were outgassed at 700 to 800°C under reduced pressure unless noted otherwise. Fluorine pressure = 150 to 200 kPa.

To test the radiation stability of the charcoal/fluorine compound, a 2.0-g sample of activated charcoal, loaded with 1.0 g of fluorine (50% weight increase) was placed in a nickel irradiation vessel with a F_2 overpressure of 150 kPa. This vessel was irradiated (average gamma dose rate of 2.79×10^6 R/h) at the HFIR. We expected to see a pressure increase if the products were unstable and a constant pressure if the product remained stable in the radiation field. The results of this irradiation are shown in Fig. 2. An unexpected decrease in the fluorine pressure was observed, thus indicating that the presence of radiation enhanced the reaction of fluorine and charcoal. The pressure decreased from 150 to 10 kPa and remained constant for over 20 d. Apparently, the ionizing radiation enhances the reactivity of fluorine with carbon through the formation of ·F atoms as seen by the additional (and more rapid) decrease in pressure (Fig. 2) when the otherwise stabilized F/C system was placed in the gamma flux. This phenomenon had also probably occurred to some extent in the earlier experiment where the 19-g POCO graphite sample experienced a decrease in F_2 pressure from 136 to 124 kPa in the radiation environment. The activated charcoal appears to provide the ideal getter for fluorine in the radiation environment.

After irradiation, the activated charcoal sample was returned to the laboratory to test the thermal stability of the reaction products. The temperature of the sample was increased from room temperature to 330°C in 50°C increments while pressure readings were recorded. Figure 3 shows a plot of the pressure in the system as a

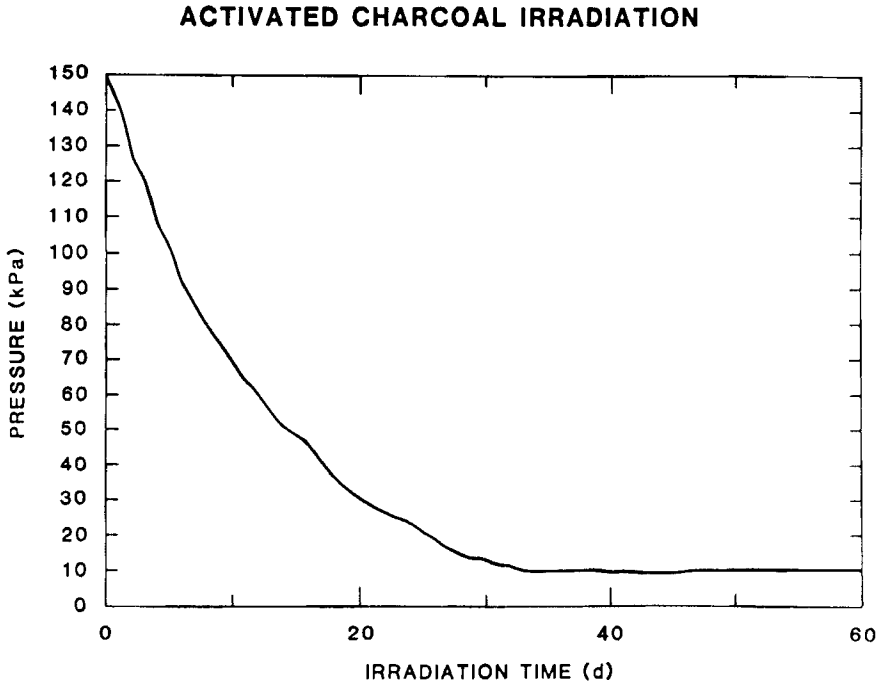

Fig. 2. System pressure vs time of irradiation for activated charcoal sample loaded to 50 wt % with fluorine.

function of temperature. Also shown is the calculated pressure increase expected from thermal expansion of the residual gases. There appears to be some release of gaseous reaction products from the activated charcoal when the sample was heated, but there was also some additional reaction at 200°C as indicated by the reduction in pressure at this temperature. If the total amount of fluorine were released, the pressure would increase to 869 kPa, but the pressure remained below 100 kPa in the temperature range studied. This latter increase in pressure with heating would pose no problem in the actual MSRE salt storage since such an increase (to 330°C) in temperature is very unlikely and a pressure in this range (100-150 kPa) is very manageable.

APPLICATION

The results obtained by these experiments yield a promising solution to the long term storage requirements of the MSRE fuel

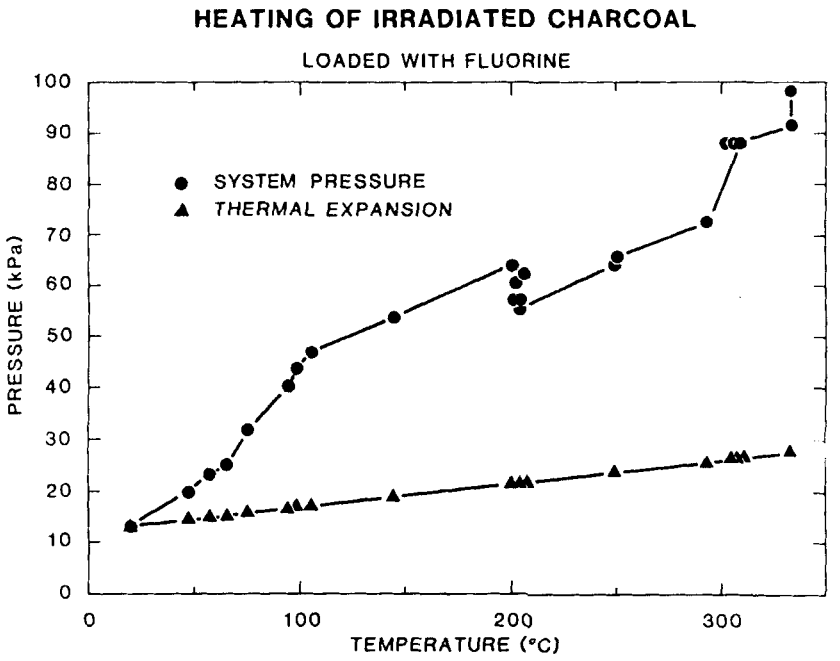

Fig. 3. System pressure vs temperature for activated charcoal sample loaded with fluorine and irradiated for 60 d.

salt. Calculations were made to determine the effect of 2% radiation damage on the actual stored salt. The two drain tanks contain a total of 4650 kg of solidified fluoride salt and have a combined void volume of 1331 L (1). Assuming 2% radiation damage in the fluoride salt, 64.7 kg (1704 mol) of fluorine gas could be generated. Assuming that all of the generated fluorine is liberated to the void space in the drain tanks and the increased pressure does not cause an equilibrium shift, a fluorine pressure of 3.2 MPa could result, which is well above any pressure considered safe for long term-term storage.

If the stored salt did reach the 2% radiation damage level, it would require 129 kg of activated charcoal (assuming 50% weight increase gettering capacity) to react with the 64.7 kg of generated fluorine. The volume associated with this amount of activated charcoal is 244 L, which is only 18% of the void volume in the storage tanks. Therefore the activated charcoal could be added

on top of the existing solidified salt to getter the fluorine as it is generated thus reducing the heat generated by the exothermic reaction of carbon and fluorine.

Use of the activated charcoal to getter the fluorine in this particular application is very attractive. The reaction of the activated charcoal and fluorine is enhanced by the radiation field and stable reaction products are obtained, even at elevated temperatures. The reaction products are also believed to be non-corrosive to the Hastelloy N containers. Even though no cost estimate has been made for this application, the cost incurred using the activated charcoal should be significantly lower and require less capital investment than other methods such as electrochemical reduction or reprocessing. Other applications are also possible where the gettering capacity for fluorine and reaction product stability in a radiation environment are desired.

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