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Passivation of Fluorinated Acitvated Charcoal

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Chemical Technology Division

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TABLE OF CONTENTS

LIST OF TABLES v
LIST OF FIGURES vii
SUMMARY ix
1. INTRODUCTION 1
2. PREPARATION OF FLUORINATED SAMPLES OF ACTIVATED-CHARCOAL 3
3. STABILITY OF FLUORINATED ACTIVATED CHARCOAL 4
4. LOADING OF URANIUM AND FLUORINE ON ACTIVATED CHARCOAL 8
5. PASSIVATION OF FLUORINATED ACTIVATED CHARCOAL 9
    5.1 SEARCH FOR A PASSIVATION REAGENT 10
6. PASSIVATION OF FLUORINATED CHARCOAL USING AMMONIA GAS 11
    6.1 PRELIMINARY TESTS 11
    6.2 SORPTION OF AMMONIA BY ACTIVATED CHARCOAL 16
    6.3 HEAT OF REACTION NH_3 AND FLUORINATED CHARCOAL 18
    6.4 DENATURING OF THE URANIUM-LADEN ACTIVATED CHARCOAL 21
7. PROPOSED PASSIVATION PLAN FOR THE ACB 22
    7.1 INTRODUCTION 22
    7.2 MAJOR CONSIDERATIONS FOR THE PLANNED ACB PASSIVATION TREATMENT 23
    7.3 PROCESS DESCRIPTION (CHEMICAL OPERATIONS, ACB DENATURING) 24
        7.3.1 Evacuation of F_2/UF_6 Upstream of Valve 561 25
        7.3.2 Evacuation of ACB 26
        7.3.3 Inert-Gas Backfill of the ACB 27
        7.3.4 NH_3 Dosing of ACB Inlet Region 28
        7.3.5 Pure NH_3 dosing of Remainder of ACB 29
        7.3.6 Soak Period 30

TABLE OF CONTENTS (continued)

7.3.7 Evacuation of Residual NH_3 31

7.3.8 Fill ACB with Inert Gas 32

7.3.9 Contingency Actions 32

7.4 LOGISTICAL ANALYSIS 34

8. CURRENT EXPERIMENTAL DEVELOPMENTS RELATED TO THE ACB DENATURING PROCESS 37

9. ADDITIONAL BACKUP TECHNICAL INFORMATION 41

9.1 ALLOWABLE LEAK RATE THROUGH VALVE 561 42

9.2 IMPUTING AXIAL TEMPERATURE IN ACB FROM MEASURED WALL TEMPERATURES 43

9.3 NH_3 OVERPRESSURIZATION 48

9.4 ESTIMATION OF THE LOCATION OF THE C_xF FRONT 49

9.5 RADIOLYTIC EFFECTS 51

9.6 EFFECTS ON CHEMICAL CONVERSION 52

9.7 FLAMMABILITY AND EXPLOSION LIMITS FOR NH_3 GAS 53

10. REFERENCES 54

LIST OF TABLES

Table		Page
1	Physical-chemical properties of the activated charcoal	2
2	Potential reactivity of candidate stabilization agents	11
3	Chemical reactions relevant to denaturing	19
4	ACB Denaturing operational parameter summary (provisional values)	35
5	Small column tests, NH_3 on C_xF	39
6	Full scale column, NH_3 on AC	40
7	Full scale column, NH_3 on AC/C_xF/AC	40
8	Heats of formation for pertinent chemical species	42
9	Estimates of upper bound to C_xF bed depth in MSRE ACB	50

LIST OF FIGURES

Figure Page

1 Carbon to fluorine ratio, by weight difference, in fluorinated charcoal as a function of the fluorination temperature 5

2 Comparison of TGA curves for C_xF samples prepared at -80 and 180°C showing broad and sharp thermal decomposition 6

3 X-ray diffraction analysis of C_xF particles after the NH_3 treatment showing the presence of NH_4 treatment showing the presence of NH_4F 13

4 Comparison of the DTA results for a C_xF sample before and after the treament with NH_3 gas 15

5 Ammonia sorption on activated charcoal. Loading vs pressure. Results obtained during three sorption-desorption cycles 17

6 Experimental maximum centerline temperatures during the loading of NH_3 on activated charcoal contained in a 6-in.-diam column similar to the actual ACB and corresponding fitted surface as a function of NH_3 and He flows 20

7 Temperature correlation of wall and axial thermocouple readings 45

8 Temperature history for axis and wall thermocouples (position 4) in activated charcoal adsorption experiment of July 17, 1997. Events indicated are (A) flow of 10% NH_3 at 4 std L/min; (B) flow of 50% NH_3 at 2 std L/min; (C) flow of 100% NH_3 at 1 std L/min; (D) helium purge at 7 std L/min 46

9 Axis-wall correlation. Beginning at ambient temperature (black dot), the temperatures are plotted every 10s. Events are as described in Fig. 7 46

10 Wall and axis temperature/time series for position No. 3 thermocouple (located in C_xF bed in 6-in. Column, experiment performed 8/11/97). In this experiment which used a flow of 5% NH_3 at 10 std L/min, the C_xF/NH_3 denaturing reaction occurred to a significant degree 47

11 Wall/axis temperature correlation for the data plotted in Fig. 9. Temperature correlation points are plotted at 1-min intervals. The rapid temperature rise when the axis reached approximately 80°C caused the axis temperature to deviate significantly from the correlation typical of more gradual changes 47

LIST OF FIGURES (continued)

Figure Page

12 Compositional limits for explosive mixtures of NH_3, O_2, and N_2 53

SUMMARY

The Molten Salt Reactor Experiment (MSRE), at the Oak Ridge National Laboratory has been shut down since 1969 when the fuel salt was drained from the core into two Hastelloy N tanks at the reactor site.

In 1995, a multiyear project was launched to remediate the potentially hazardous conditions generated by the movement of fissile material and reactive gases from the storage tanks into the piping system and an auxiliary charcoal bed (ACB). The drain tanks and the ACB (6-in.-diam, 24-ft-long U-tubes) were until recently connected because a shutoff valve had failed in the open position.

The MSRE ACB contains a volume of approximately 506 L of activated charcoal (6–16 mesh). The apparent density (bulk density) of the "original" activated charcoal is 0.44 g/cm^3, giving an estimated 223 kg of activated charcoal. The top 12 in. of the ACB is known by gamma scan and thermal analysis to contain about 2.6 kg of ^{233}U. According to our laboratory tests, a few feet of fluorinated charcoal are believed to extend beyond the uranium front. The remainder of the ACB, about 80 ft, should consist of unreacted charcoal.

Fluorinated charcoal, when subjected to rapid heating, can decompose generating gaseous products (CF_4, C_2F_6, etc). Under confined conditions, the sudden exothermic decomposition can produce high temperatures and pressures of near-explosive characteristics.

To proceed with the planned remediation and recovery activities at the MSRE, it will be necessary to tap into the ACB to allow the installation of piping and instrumentation. The drilling-tapping operations can result in local heating which could trigger the sudden decomposition of the ACB. To remove the potential threat, it is necessary to chemically convert the reactive fluorinated charcoal into a more stable material to safely conduct the remediation and recovery activities.

After an extensive search for a denaturing reagent, it was found that only ammonia gas could transform the potentially reactive fluorinated charcoal into a stable material that can be safely handled and heated. Ammonia can be administered to the ACB as a volatile denaturing agent that results in the conversion of the C_xF to carbon and ammonium fluoride, NH_4F. The charcoal laden with NH_4F can then be heated without risking any sudden decomposition. The only consequence of heating the treated material will be the volatilization of NH_4F as a mixture of NH_3 and HF, which would primarily recombine as NH_4F on surfaces below 200 °C. The planned scheme for the ACB denaturing is to flow diluted ammonia gas in steps of increasing NH_3 concentration, 2% to 50%, followed by the injection of pure ammonia.

This report summarizes the planned passivation treatment scheme to stabilize the ACB and remove the potential hazards. It also includes basic information, results of laboratory tests, thermodynamic calculations, process description, and operational parameters, and addresses safety concerns.

1. INTRODUCTION

The Molten Salt Reactor Experiment (MSRE) was operated at the Oak Ridge National Laboratory (ORNL) from 1965 to 1969 to test the concept of a high-temperature homogeneous fluid fueled reactor. After successful completion of this campaign, the MSRE was terminated by draining the fuel salt from the reactor circuit and solidifying it in two drain tanks at a lower level of the MSRE facility. The fuel salt has remained there for the past 27 years.[1]

In early 1994, two 1 L gas samples were withdrawn (from a gas line in the Vent House connecting to the drain tanks) and analyzed. A large amount of F_2 (350 torr) and UF_6 (70 torr) was found in these gas samples. The F_2 concentration was much larger than expected, and the presence of UF_6 was totally unexpected.

Further investigation revealed that the gas line connecting the drain tanks with charcoal beds (6-in.-diam, 24-ft-long U-tubes) was open because a shutoff valve had failed in the open position. Gamma scan and thermal analysis indicated that more than 2 kg of the ^{233}U from the drain tanks had deposited on the charcoal bed. The accompanying F_2 must have also reacted with the charcoal to form potentially "explosive" fluorinated charcoal compounds, C_xF, thereby presenting a condition of considerable concern.

Oxidizing fluorine gases, such as F_2 and UF_6, are known to react with activated charcoal to produce carbon fluorides of varying composition. The reaction between fluorine and carbon was extensively used in the early days at the K-25 Gaseous Diffusion Plant for fluorine disposal. After several violent reactions during the period 1943 to 1950, the process was discontinued. The consequences of such an explosion in the MSRE auxiliary charcoal bed (ACB) would be to scatter the radioactive and fissile materials present in the charcoal and thus created an extremely serious radiological hazard.

Before proceeding with the planned remediation and recovery activities at the MSRE, it will be necessary to tap into the ACB to allow the installation of piping and instrumentation. The drilling-tapping operations could result in local heating, which might trigger the sudden decomposition of the ACB. Therefore, it is necessary to chemically convert the reactive fluorinated charcoal into a more stable material to ensure that the remediation and recovery activities can be conducted safely.

This report summarizes the planned passivation treatment scheme to stabilize the ACB and remove the potential hazards. It also includes basic information, results of laboratory tests, thermodynamic calculations, process description, and operational parameters, and addresses safety concerns.

According to the MSRE records, the ACB is packed with a coconut-based activated charcoal (6 × 16 mesh size particles) that was provided by Calgon Carbon Corporation.[2] All of our tests, involving activated charcoal, were done using a quite similar material also provided by Calgon Carbon Corporation. The properties provided by the manufacturer are showed in Table 1.[1]

Table 1. Physical-chemical properties of the activated charcoal.[1]

Type		Coconut	
Particle size		6 × 16	Mesh
Total surface area (N_2, BET method)		1150-1250	m^2,g
Density	Apparent (Bulk) density	0.44	g/cm^3
	Particle density (Hg displacement)	0.85	
	Real density (He displacement)	2.2	
Pore volume (Within particle)		0.72	cm^3/g
Voids in dense-packed column		50	%
Iodine number (minimum)		1200	mg/g
Carbon tetrachloride adsorption		60	w%
Ash		2.62	%
Total iron		0.94	% of ash
Total sulfur		0.03	% of carbon
Hardness number		92	

The manufacturer data show that a large portion of the micropores volume consist of pores in the range 1.5 to 2.0 nm. In addition to the micropore structure, this type of activated charcoal has a system of macropores larger than 100 nm that interconnects the micropore structure and allows a rapid diffusion of gaseous species.

2. PREPARATION OF FLUORINATED SAMPLES OF ACTIVATED-CHARCOAL

The reaction between activated charcoal (AC) and fluorine is highly exothermic. The unrestricted reaction with fluorine and AC can proceed briskly causing a rapid heating that can easily inflame the AC to form carbon-fluorine compounds that further decompose into gaseous by-products such as carbon tetrafluoride (CF_4), hexafluorethane (C_2F_6), tetrafluorethylene (C_2F_4), carbonyl fluoride (COF_2), carbon monoxide (CO) and carbon dioxide (CO_2), etc.[3] The latter species originate from oxygen moieties present at the rim of the charcoal platelets.

In order to obtain reproducible carbon-fluorine compounds, it was necessary to control the speed of the fluorination and allow the heat to dissipate so that the reaction occurred at the desired temperature. In our case, the fluorine concentration was decreased using helium (He) as a diluent, which is also a relatively good heat conductor, to maintain a constant bed temperature and to promote steady flow conditions.[3]

A 5 vol% F_2/He mixed gas was prepared using a 3-L F_2-passivated nickel vessel. The gases were introduced through the bottom of the vessel to obtain homogeneous mixing. The heavier fluorine gas was introduced first followed by helium.

Initially, 1-g activated charcoal samples were fluorinated using small, annular reaction tubing made of quartz. The vessel was preheated to about 300 °C under vacuum to remove hydroxyl sites from the quartz surface. Ace®-type vacuum valves (Teflon® piston with Viton® O-rings) were used as inlet and outlet valves.

Type-K thermocouples connected to a PC-based data acquisition system were used to continuously record the charcoal bed and wall temperatures. The annular tube was fully immersed in the appropriate medium to maintain a desired temperature. A Dewar flask filled with a methanol/dry-ice slush was used to prepare samples at about −78 °C. Water/ice was used for 0 °C, a thermostatic bath was used for higher temperatures.

To avoid contamination with silicon tetrafluoride (SiF_4), the quartz vessel was replaced in the later tests by a passivated-nickel U-tube (0.5-in. OD) having Monel bellows valves at each end. Similarly, type-K thermocouples connected to a PC-based data acquisition system were used to continuously record the temperatures of the charcoal and the wall. Temperature control was as described previously except for preparations above 100 °C that utilized a hollow-tube furnace. Ten- to fifteen- gram batches of activated charcoal were fluorinated using the U-tube.

Before fluorination, the AC samples were preconditioned in their respective vessel (quartz or nickel tube) by heating to about 200–250 °C under He flow to simulate the conditions used for conditioning the actual MSRE AC bed. After the pretreatment procedure, the F_2/He gas mixture was dispensed at a very low flow rate. No attempt was made to measure the actual flow rate. A long Teflon tube connected to the vessel exhaust was used to bubble the gases through a sodium hydroxide solution. The flow of the F_2/He mixture was controlled, maintaining the charcoal temperature only slightly above the wall temperature (1 to 3 °C). The flow of reactive gases was maintained, depending on the batch size, for several days until the internal and wall temperatures were equalized. After equalization, a slow flow of pure fluorine was maintained for about two hours to ensure a complete reaction.

After completion, the fluorinated charcoal was purged with He for a few minutes to remove "nontrapped" fluorine. The fluorinated-samples were then transferred to a dry-He glovebox and weighed.

3. STABILITY OF FLUORINATED ACTIVATED CHARCOAL

The results of these experiments showed that fluorine will chemically react vigorously with charcoal to form non-stoichiometric C_xF compounds , where $4 \leq x \leq 1$ depending of the temperature maintained during the fluorination (see Fig. 1).

All our tests show that C_xF synthesized at low temperatures gradually decomposes at temperatures above 100 °C. The C_xF prepared at high temperatures also starts to decompose at temperatures in excess of 100 °C; however, the majority of the decomposition occurs in a very narrow range of temperatures around 500 °C. Figure 2 depicts the weight loss for the C_xF samples prepared at-80 °C (displaying "broad decomposition") along with C_xF sample prepared at 180 °C (showing "sharp decomposition").

Fluorine sorption on fluorinated charcoal has been reported as a possible explanation for unexpected violent decomposition reactions. Our tests indicated that fluorine sorption on fluorinated charcoal is relatively small, 1 to 3 wt%, but still significant. This sorbed F_2 can be easily removed by vacuum or by flowing an inert gas through the fluorinated charcoal.

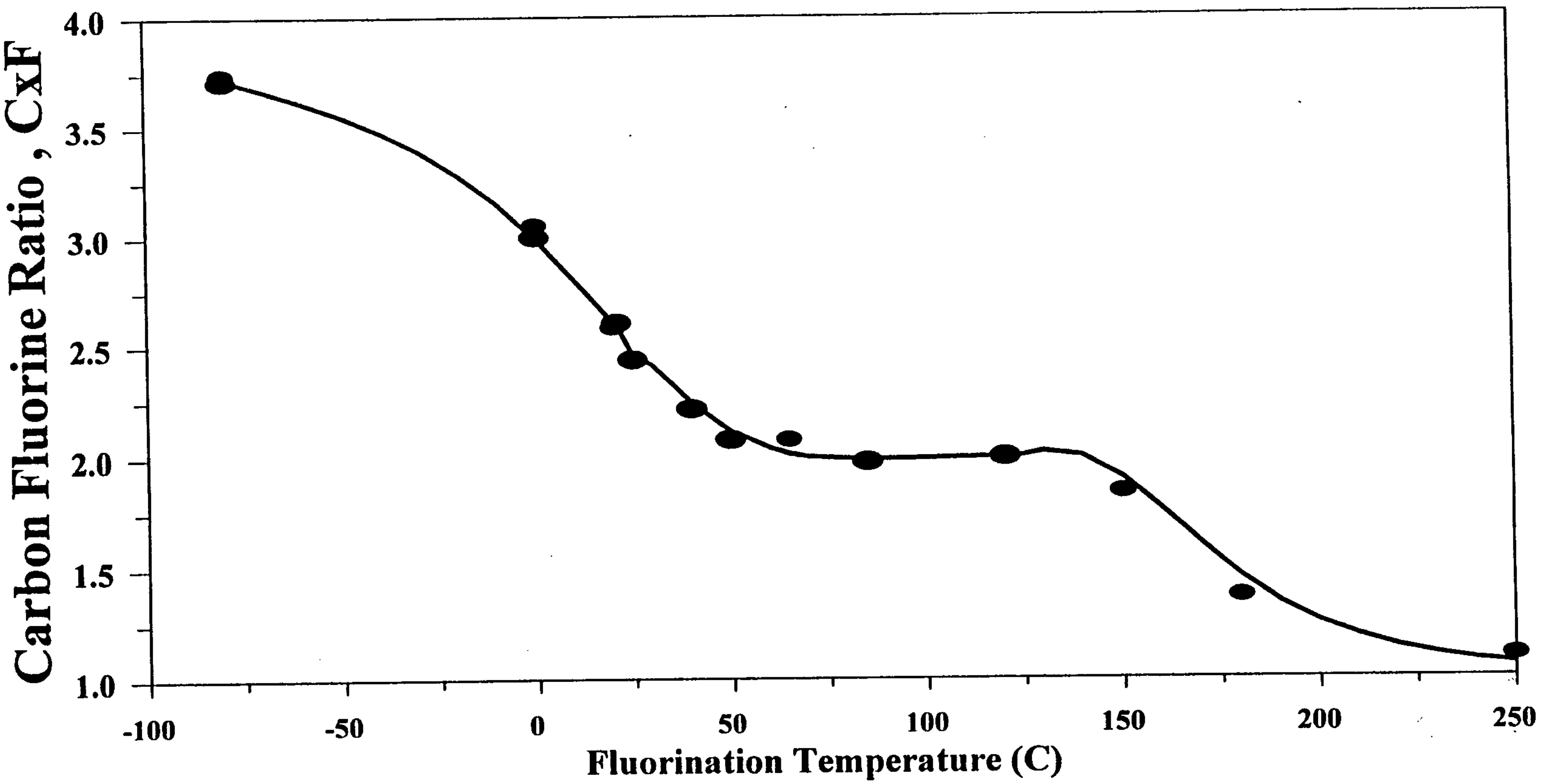

Fig. 1. Carbon to fluorine ratio, by weight difference, in fluorinated charcoal as a function of the fluorination temperature.

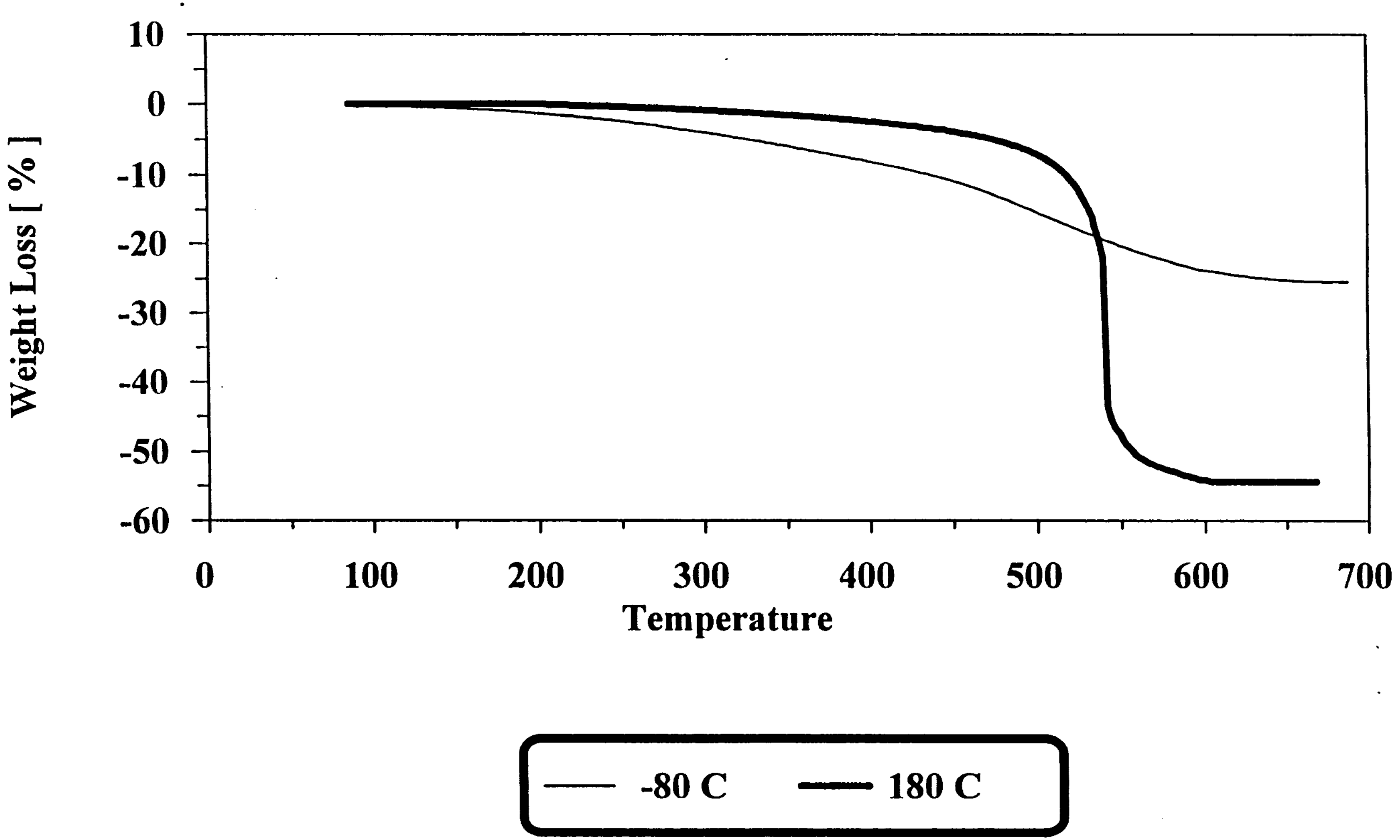

Fig. 2. Comparison of TGA curves for C_xF samples prepared at - 80 and 180 °C showing broad and sharp thermal decomposition.

Great care is needed to control the rate of fluorination and to dissipate the generated heat. Increasing the temperature during the fluorination increases the amount of fluorine chemically bound to the carbon up to the limit C≈F set by the formation, at high temperature, of the more stable whitish solid "carbon monofluoride." Uncontrolled fluorination produces high temperatures and pressures with the evolution of gaseous fluorocarbon species.

Deflagration of near-explosive characteristics can be triggered in the presence of fluorine by any process or reaction that would rapidly elevate the temperature of the C_xF. The increased temperature would initiate a positive feedback sequence by the following processes: (1) exothermic formation of a more fluorinated C_xF by the fluorine sorbed onto the C_xF (1 to 3 wt%) and the fluorine present in the pores and void volume of the trapping column; and (2) exothermic thermal decomposition of C_xF into gaseous fluorocarbons (CF_4, etc.). Once the thermal excursion is initiated, the generation of heat and gases will propagate unless there is a mechanism in place to dissipate the heat. The presence of "free" fluorine is a main contributing factor for sudden decomposition events, while the total availability of fluorine, both free and bound is the main limiting factor for the intensity of the deflagration.

In the presence of any triggering reaction a fluorine saturated trap presents the highest potential for an accident. Our laboratory experience has shown that after removal of free fluorine, by vacuum or flowing an inert gas, the potential for a "deflagration" is greatly reduced. After removal of free fluorine the deflagration is confined to a few particles near the initiation source (e.g., rapid heating using a torch). However, in the presence of "free" fluorine the thermal decomposition of C_xF would propagate and reach a significant volume of a reactor or trap, causing a "near -explosive" event.

Examples of triggering events are: (1) injection of a large amount of fluorine, (2) reaction between fluorine and water by opening a saturated trap in the presence of humid air, (3) accidental release of oil mists from a vacuum system into a trap having free fluorine, and (4) any heat source that cannot be dissipated fast enough. Most accounts of past accidents are anecdotal; however, they all seem to be explainable by the triggering events (1) to (3) and they all occurred when the charcoal traps were near saturation with fluorine.

One frequent observation after sudden decomposition events is the presence of charcoal particles having a white coating. Charcoal fluorinated at temperatures above 200 °C changes color from black to gray, then to brown, and finally to white (carbon monofluoride) at about 350 °C.

The reason for this color change is the gradual structural transformation from the de-localized graphitic electronic structure toward the Teflon-like aliphatic structure. The presence of charcoal particles having a white coating can be easily explained by the formation of carbon monofluoride at the surface of some particles, according to the temperature profile and fluorine evolution during the deflagration event. Carbon monofluoride is a much more stable material that decomposes around 700 °C.

The recovery of uranium from the MSRE charcoal trap will be followed by stabilization of the fluorinated graphite (C_xF). The stabilization procedure will mitigate the potential for unstable exothermic reactions and permit the safe disassembly of the charcoal trap.

4. LOADING OF URANIUM AND FLUORINE ON ACTIVATED CHARCOAL

Several scoping tests were performed to understand the behavior of activated charcoal when contacted with UF_6 or a F_2-UF_6 "MSRE" blend (F_2/UF_6 volume ratio of 5/1) at room temperature. These tests included batch static loading and dynamic loading through columns filled with activated charcoal. The results of the tests showed that the loading of UF_6 on activated charcoal leads to the intercalation of uranium fluorides and oxyfluorides in the graphitic structure.

The uranium-laden activated charcoal will not "deflagrate" when heated rapidly. The electron spectroscopy for chemical analysis (ESCA) determinations of the laden samples show no appreciable fluorination of carbon atoms (no C-F bonds), which explains the increased thermal stability.

The experiments also indicated that reaction between charcoal and the F_2-UF_6 MSRE blend produces C_xF, which contains intercalated uranium fluorides and oxyfluorides. The ESCA determinations of the samples contacted with the F_2-UF_6 MSRE blend show that the concentration of fluorine atoms directly bound to carbon is lower than that for the samples contacted with pure fluorine. This observation correlates with the milder decomposition of the F_2-UF_6 laden samples when rapidly heated ("mild deflagration").

The dynamic loading of the F_2-UF_6 MSRE blend through columns filled with activated charcoal showed that the fluorine front moves slightly ahead of the uranium front. Based on our laboratory experience, the measured MSRE ACB uranium front (C_xF+ intercalated uranium compounds) extending about 1 ft from the top of the ACB is probably followed by a C_xF front spanning a few feet further downstream.

It is important to mention that when water is completely excluded from the system, the visual appearance of the charcoal particles after the loading remains the same as free-flowing, virgin AC. Consequently, the laden charcoal particles can be easily removed from a column by gravity or vacuuming, as planned for the actual ACB removal. However, in the presence of humidity the charcoal particles become cemented by interstitial uranyl fluorides. These cemented chunks of laden charcoal are quite hard, and a significant mechanical force is required to separate the particles.

The significance of this laboratory observation for the ACB remediation is that hardened chunks of material could be present due to moisture intrusion. The removal of those chunks would require a special tool that could break the chunks into "vacuumable" particles. The uranyl-laden charcoal has a distinctive yellow-orange color characteristic of uranyl fluoride. Thus, the presence of interparticle uranyl fluoride could be determined by visual inspection of the top of the ACB.

5. PASSIVATION OF FLUORINATED ACTIVATED CHARCOAL

Fluorinated charcoal, when subjected to rapid heating will decompose generating gaseous products (CF_4, C_2F_6, etc). In a confined system, this sudden exothermic decomposition can produce high temperatures and pressures of near-explosive characteristics.

Before the planned remediation and recovery activities can proceed at the MSRE, it will be necessary to tap into the ACB to allow the installation of piping and instrumentation. The drilling-tapping operations can result in local heating in excess of the 100°C As shown in Fig. 2, fluorinated charcoal starts to thermally decompose at temperatures above 100°C, although attempts to produce deflagration by heating generally required higher temperatures (above 250 °C) to trigger the deflagration event. Consequently, it is necessary to chemically transform the reactive fluorinated charcoal into a more stable material to ensure that the remediation and recovery activities can be conducted safely.

5.1 Search for a Passivation Reagent

A comprehensive series of scoping tests was conducted in order to find an effective stabilization agent. The ideal stabilization agent should: (1) be volatile to allow ease of application and recovery; and (2) have sufficient reactivity at room temperature that the reaction will readily reach equilibrium with resulting favorable products in a reasonable amount of time. Several gases and some high-vapor-pressure liquids were considered for their potential for halogen exchange.

Partial hydrolysis of the fluorinated charcoal with HF formation was observed after prolonged storage in air. However, even after a 2–month exposure to humid air, the fluorinated charcoal still deflagrated under rapid heating. Additionally, the charcoal particles would clump together to form a soggy mass. Because of these considerations plus the associated criticality concerns, water was not considered as a possible denaturing reagent.

Calculations to determine the heat of reaction (ΔH_r) between the candidate reagents and fluorinated charcoal were performed to select the most promising candidates. The computations were performed with an improved version of SOLGAS. The thermodynamic library included with the latest release was entered in the spreadsheet software Quattro Pro® to compile the data input file for the SOLGAS calculations. Thermodynamic data, from refs. 3 and 7, were added to the library for acetylene, silane, boron trichloride, carbon disulfide and fluorinated graphite.

Table 2 presents the results obtained using SOLGAS for the compounds evaluated, including the calculated heat of reaction and possible products.

Table 2. Potential reactivity of candidate stabilization agents with fluorinated charcoal

Agent	Heat of Reaction (kJ/mol)	Primary Products
Borane, B_2H_6	-475.3	CH_4, BF_3, B, graphite
Acetylene, C_2H_2	-437.8	HF, CH_4, graphite
Nitric Oxide, NO	-436.4	N_2, CO_2, CF_4, graphite
Silane, SiH_4	-351.3	H_2, SiF_4, Si, graphite
Sulfur Tetrafluoride, SF_4	-307.6	CF_4, S, graphite
Carbon disulfide, CS_2	-266.3	CF_4, S, graphite
Sulfur dioxide, SO_2	-245.0	CO_2, CF_4, S, graphite
Carbon monoxide, CO	-235.5	CO_2, CF_4, graphite
Hydrogen iodide, HI	-214.9	HF, CF_4, I_2 , graphite
Hydrogen, H_2	-211.1	HF, CH_4, graphite
Boron trichloride,BCl_3	-162.8	BCl_3,BF_3, Cl_2, graphite
Silicon tetrachloride, $SiCl_4$	-154.9	$SiCl_4$, SiF_4, Cl_2, graphite
Phosphorous trichloride , PCl_3	-150.0	PCl_3, PF_3, CCl_4, Cl_2, graphite
Carbon tetrachloride , CCl_4	-149.3	CCl_4, CF_4, CF_3Cl, graphite
Ammonia, NH_3	-149.3	NH_3, CF_4, graphite

These results are not necessarily correlated with the actual behavior and the standard caveats with thermodynamic calculations apply : (1) the results only stipulate the equilibrium products but do not provide kinetic information (the equilibrium will not necessarily be reached at reasonable times, and intermediate products can be formed instead); (2) the data set of candidate reaction products can be erroneous or incomplete (omission of stable reaction products), thus yielding erroneous results; and (3) inaccurate thermodynamic data will yield inaccurate thermodynamic results.

All of the possible candidates were experimentally tested by using small batches of C_xF (about 1 g of material) contacted for at least 10 days with each reagent. At the end of each soaking period, the reagent was evacuated and the treated samples heated rapidly using a torch.

At the end of the selection process (from all of the reagents shown in Table 2), it was found that only ammonia gas was able to transform the potentially reactive fluorinated charcoal into a stable material that can be safely heated. Ammonia can be administered to the ACB as a volatile denaturing agent that results in the conversion of the C_xF to carbon and ammonium fluoride, NH_4F.

The charcoal laden with NH_4F can be heated without risking any sudden decomposition. The only consequence of heating the treated material will be the volatilization of NH_4F as a NH_3 and HF mixture that would mostly recombine as NH_4F on surfaces below 200 °C. Of course, the remaining charcoal would ignite in air or oxygen at higher temperatures. The following sections present the supporting work performed to define a safe and effective denaturing process

6. PASSIVATION OF FLUORINATED CHARCOAL USING AMMONIA GAS

6.1 Preliminary Tests

The first test was performed using 1 g of C_xF prepared at room temperature ($C_{2.6}F$) that was contacted with pure NH_3 inside a vacuum-tight quartz container. The NH_3 pressure was maintained slightly above 1 atm over a weekend, for a total of 3 days. Initially the reaction was relatively rapid and the skin temperature of the quartz vessel rose to above 45°C. After the treatment, the sample was transferred to an inert dry glovebox and weighed.

There were no visible changes in the appearance of the charcoal; however, the individual particles were held together at the contact points. The particles could be easily separated using a spatula As shown in Fig. 3, analysis of the particles by X-ray diffraction (XRD) indicated the presence of NH_4F. If we assume that the weight gained was due only to the retention of NH_4, then 98.7% of the available fluorine was converted to NH_4F.

The NH_3-treated sample was transferred to a fume hood and rapidly heated by using a torch to determine the denaturing ability of the ammonia treatment. The only result of the rapid heating was the gentle sublimation of NH_4F without any other visible (or audible) reaction. As expected for charcoal, the particles started burning after getting red hot. This test was repeated several times with the same results.

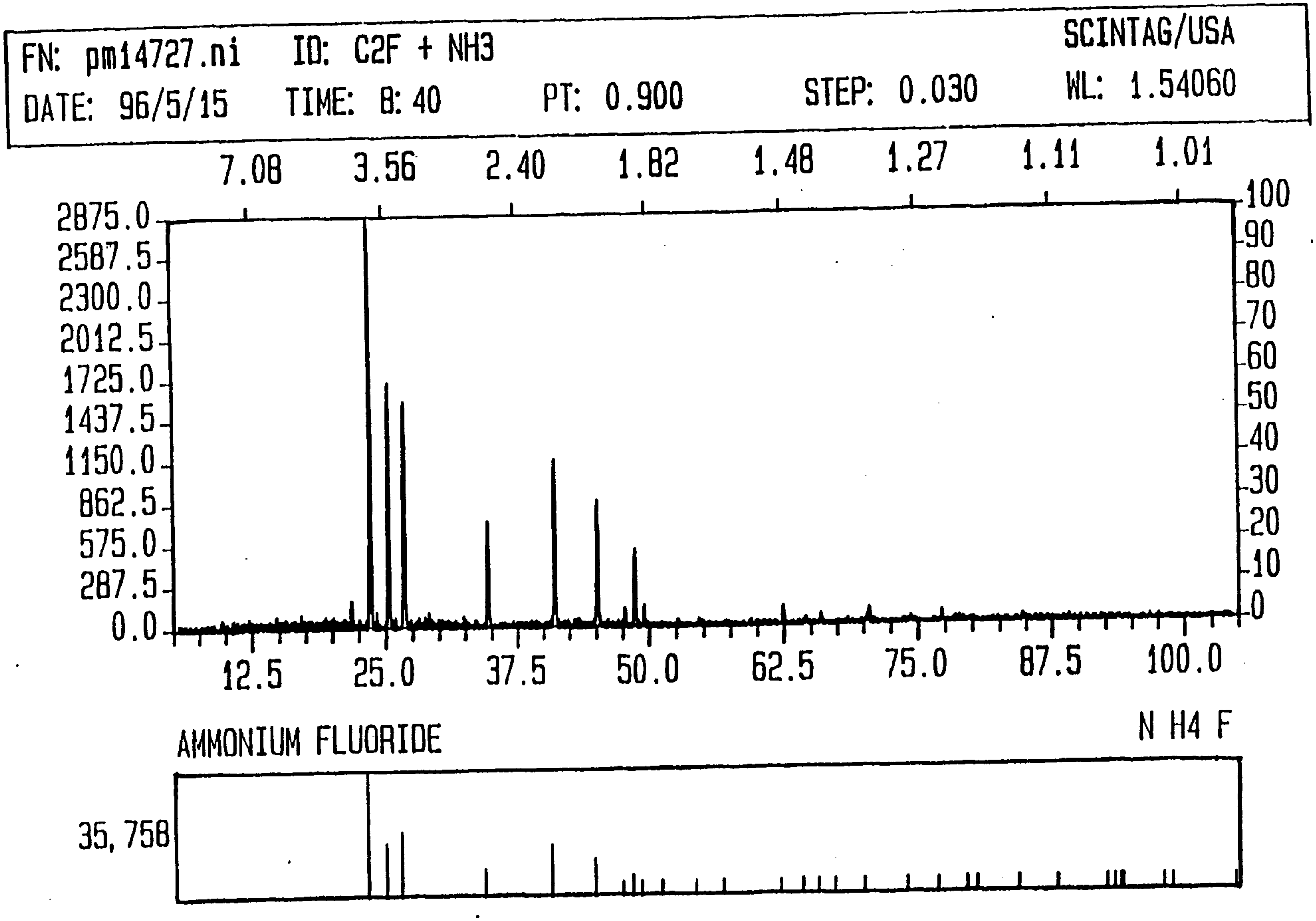

Fig. 3. X-ray diffraction analysis of C_xF particles after the NH_3 treatment showing the presence of NH_4F.

A repeat of the ammonia treatment was done on a second 1 g batch of fluorinated charcoal also prepared at room temperature. This test was done in a manner similar to that of the first test, except that the contact time was shortened to 1 day. For this test and assuming that the weight gained was due only to the retention of NH_4F, there was a 89.8% conversion of the available fluorine to NH_4F. Again, the individual particles were held together at the contact points. Similarly, rapid heating using a torch of the treated charcoal gently sublimated NH_4F without any other visible (or audible) reaction.

The results from two preliminary experiments were highly successful except for the fact that the particles were held together at the contact points. Such agglomeration would complicate any charcoal removal operation. The adhesion between particles is due to local decomposition-sublimation of NH_4F and its redeposition at the contact points of neighboring granules. In order to minimize this phenomenon, the local temperature of the particles should remain low during the reaction between ammonia and the C_xF.

To control the rate of reaction so as to maintain the temperature of the particles near room temperature to avoid particle-clustering, a third test was carried out by exposing 1 g of fluorinated charcoal to a slow flow of diluted NH_3 (10% NH_3/90% He). A slow flow was maintained overnight. On the following day, the fluorinated charcoal was contacted for 2 h with pure NH_3 to complete the reaction. After treatment, the charcoal particles remained separated and no clustering was observed. Assuming that the weight gained was due only to the retention of NH_4F, there was a 90.6% conversion of the available fluorine into NH_4F without any other visible (or audible) reaction.

Following the initial tests, several batches of C_xF and C_xF/U were treated with ammonia under different conditions. The results of these tests confirmed that after a prolonged contact with ammonia the fluorine bound to carbon is transformed into NH_4F.

Fig. 4 shows a comparison of the differential thermal analysis (DTA) results for a C_xF sample before and after the treatment with NH_3 gas. The un-treated C_xF displays the typical broad exothermic decomposition curve (before) while the NH_3 passivated sample shows only endothermic vaporization of trapped species (after).

Use of pure ammonia caused the temperature of the charcoal to rise quickly and resulted in a rapid and complete defluorination of the charcoal, which was completed in a few hours. However, the fast conversion resulted in the cementation of charcoal particles by the deposition of interstitial crystals of NH_4F. At the same time, a temperature rise approaching 250 °C must be avoided in the actual passivation scheme for the ACB because of the potential danger of triggering the decomposition of the C_xF that is not yet passivated.

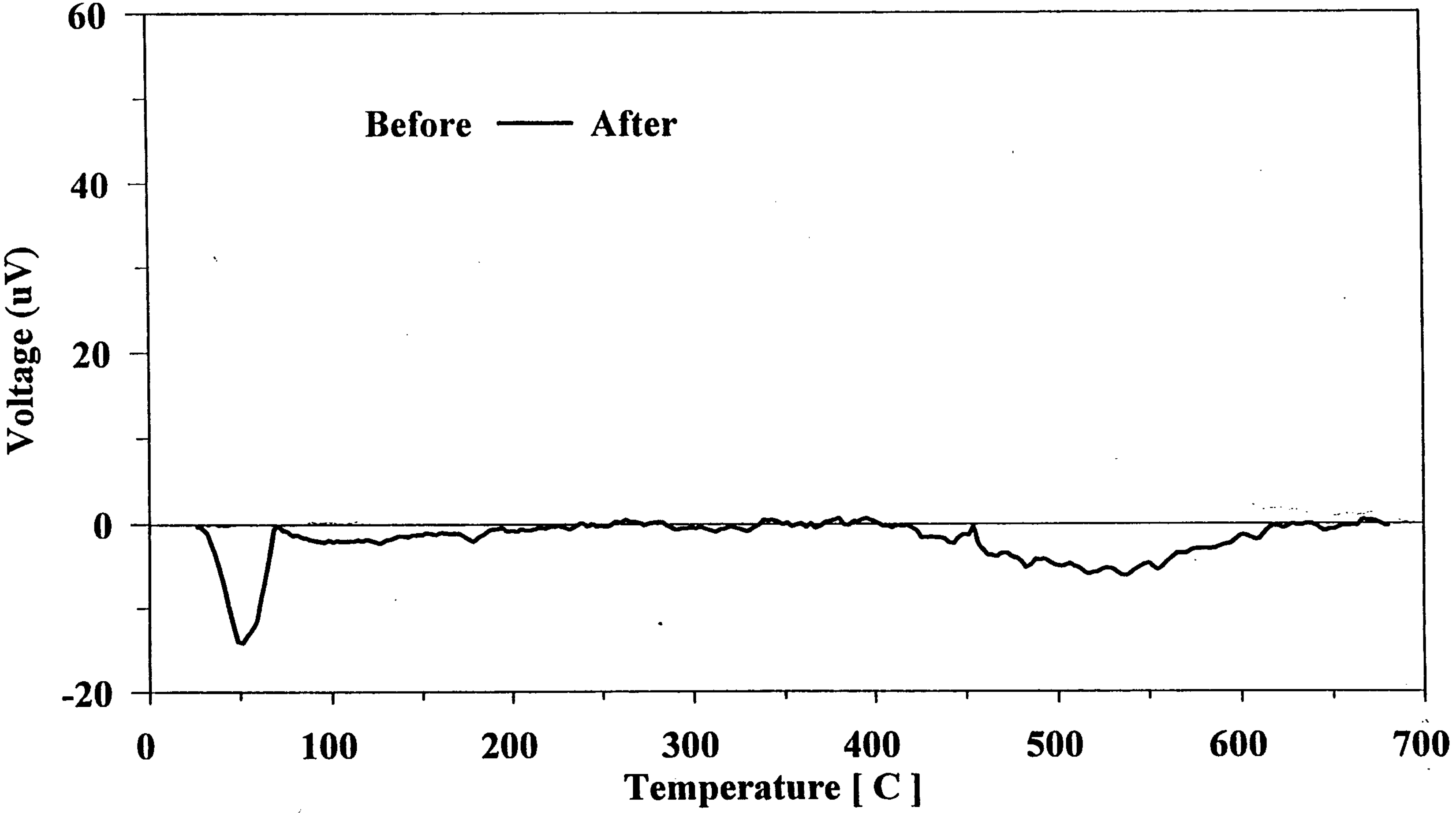

Fig. 4. Comparison of the DTA results for a C_xF sample before and after the treatment with NH_3 gas.

The de-fluorination at near room temperature using a diluted ammonia gas stream requires long contact times (2-4 weeks) to reach completion. The proposed scheme for the ACB is a combination of both processes. Initially ammonia gas diluted to low concentration will be charged, followed by successively higher concentration mixtures. This treatment will be followed by the injection of pure ammonia. After ammonia breakthrough, the ACB column will be left immersed with the ammonia gas in a static mode for about a month to ensure total de-fluorination of the charcoal by formation of NH_4F.

6.2 Sorption of Ammonia by Activated Charcoal

The MSRE ACB contains a volume of approximately 506 L of activated charcoal (6–16 mesh). The apparent density (bulk density) of the "original" AC is 0.44 g/cm^3 giving an estimated 223 kg of activated charcoal. The top 12 in. of the ACB are known to have uranium. According to the laboratory tests, a few feet of fluorinated charcoal are believed to extend beyond the uranium front. The rest of the ACB, about 80 ft, should consist of unreacted charcoal.

A fail-safe passivation of the ACB requires the flow of a reagent gas such as NH_3, through the entire ACB since there is no way of knowing precisely the location of the fluorinated front. Because of this fact, it is important to know also the loading of ammonia by unreacted activated charcoal.

For this purpose, 6.9978 g of activated charcoal that was previously heated in vacuum to ~200°C was introduced into a quartz container provided with a valve for vacuum use. The container plus sample was weighed at the beginning of the test and then connected to a manifold that included an NH_3 tank and a pressure transducer. The NH_3 was introduced through the manifold in stages and allowed to equilibrate for several hours (sorption cycle). After the pressure had become stable, the charcoal container was disconnected and weighed. Once the NH_3 pressure exceeded atmospheric pressure, NH_3 was removed in stages and the container was weighed in each step (desorption cycle).

Fig. 5 displays the results, loading vs pressure, obtained during three sorption- desorption cycles. The sorption and desorption curves do not coincide. This common phenomenon, known as "adsorption hysteresis," is due to capillary condensation. However, the results were reproducible and the weight of the charcoal always converged to the initial value under vacuum. According to these results, approximately 25 kg of NH_3 will load on the activated charcoal at 1 atm and room temperature.

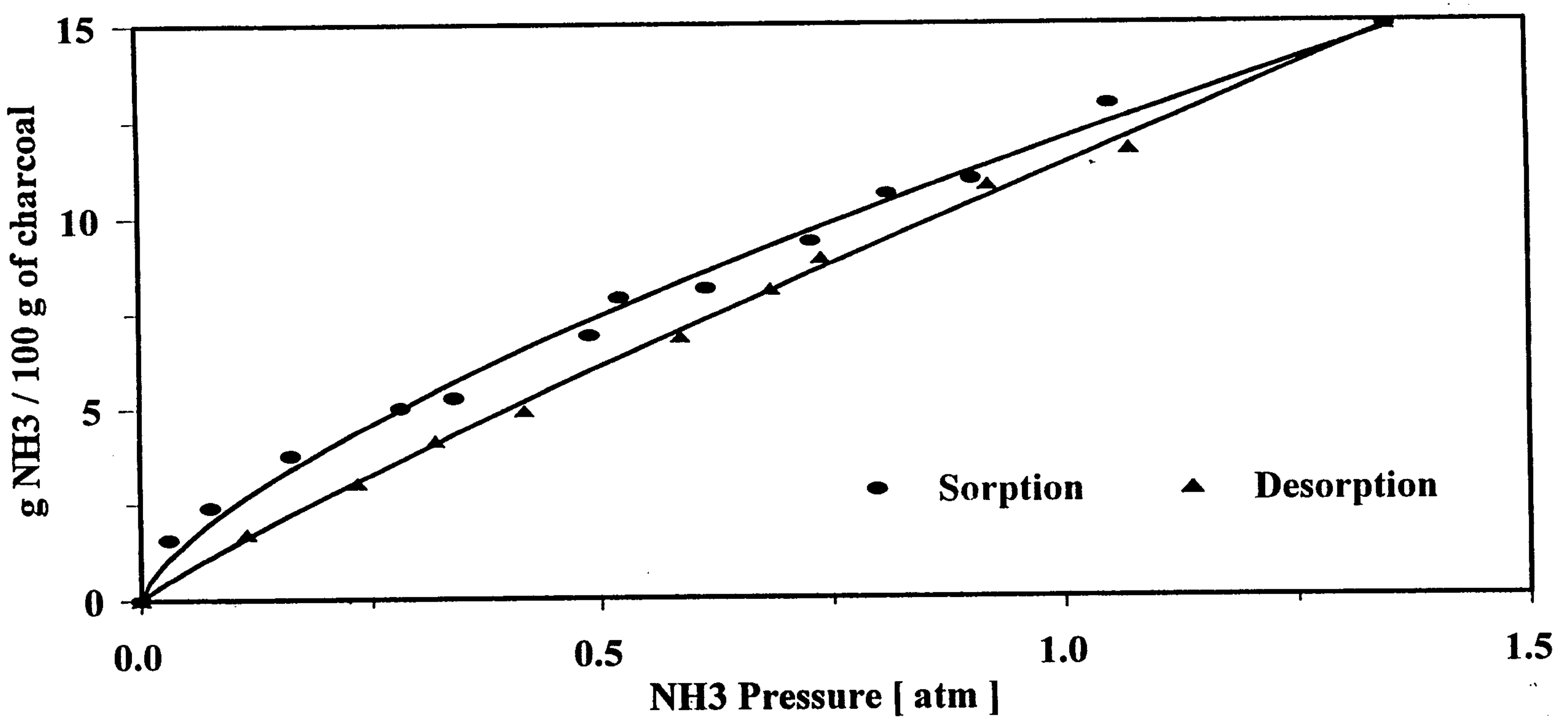

Fig. 5. Ammonia sorption on activated charcoal. Loading vs pressure. Results obtained during three sorption-desorption cycles.

6.3 Heat of Reaction Between NH_3 and Fluorinated Charcoal

The reaction of NH_3 with the C_xF will generate heat on the ACB due to both the heat of sorption of NH_3 on the AC and the heat of reaction of NH_3 with C_xF.

It has been reported that the temperature rise by sorption is proportional to the available adsorption sites of the AC. The heat of adsorption for NH_3 on carbon (Spheron, original carbon black) has been reported to be 12–13 kcal/mole at first contact followed by a nominal 9 kcal/mole up to a surface coverage of about 1 mmole of NH_3 per gram of charcoal. Spheron is capable of adsorbing appreciably more NH_3 than the heat treated carbon sorbents. Dell and Beebe have reported that as the degree of graphitization increases, the shape of the ammonia isotherm changes progressively from the characteristic type II isotherm to an isotherm that is convex to the pressure axis at low pressures. The heat of adsorption on the graphitized carbon black is virtually constant at all coverages and approximately equal to the heat of vaporization of ammonia (5.2 kcal/mol at 0 °C). The ammonia adsorption occurred in patches of one molecular layer, with the suggestion that the patches of lateral interaction are due to hydrogen bonding.

Table 3 shows the chemical reactions relevant to the ammonia denaturing process. The heat of reaction between C_xF and NH_3 to form NH_4F depends on the fluorine content. The reaction between C_xF and NH_3 at room temperature is quite slow when compared with the almost instantaneous heat released due to the sorption. If the heat of adsorption is allowed to dissipate so that the ACB column remains near room temperature then adsorption will determine the temperature of the ACB since no significant C_xF denaturing will occur.

Figure 6 shows the experimentally measured maximum centerline temperatures and temperature-fitted relation as a function of ammonia and helium flow for a 6 in.column similar to the actual ACB. As can be seen, the maximum centerline temperature (center of the bed) increases approximately with the square root of the ammonia flow and decreases linearly with the helium flow. These maximum temperatures represent the limiting-case scenario when no denaturing reaction is considered. In reality, the warming of the bed by the adsorption accelerates the rate of the denaturing reaction, initiating a positive feedback loop that is controlled by the total flow and concentration of the ammonia reaching the reaction front.

Table 3. Chemical reactions relevant to denaturing

Reaction		ΔH [KJ / mole]	Remarks
Deflagration	$C_XF_{(s)} \rightarrow C_{(s)} + CF_{4(gas)}$	-67	• Gas evolution; Explosive potential • Rate increases with temperature • Detectable heat evolution at t > 100°C • Progresses to deflagration above 250°C
Denaturing	$C_XF + {}^4/_3\, NH_{3\,(ads)} \rightarrow x\,C + NH_4F + {}^1/_6\, N_2$	-186	• Net gas removal; pressure drop • Rate is very slow at room temperature • Rate increases with temperature • NH_4F can bind charcoal particles above 100°C
Adsorption Desorption	$NH_3\,(gas) + C \rightleftarrows NH_3\,(ads) \cdot C$	-22	• Loading decreases with increasing temperature • Loading approximately proportional to pressure • Adsorption releases heat; desorption absorbs heat • Temperature rise due to adsorption can accelerate denaturing

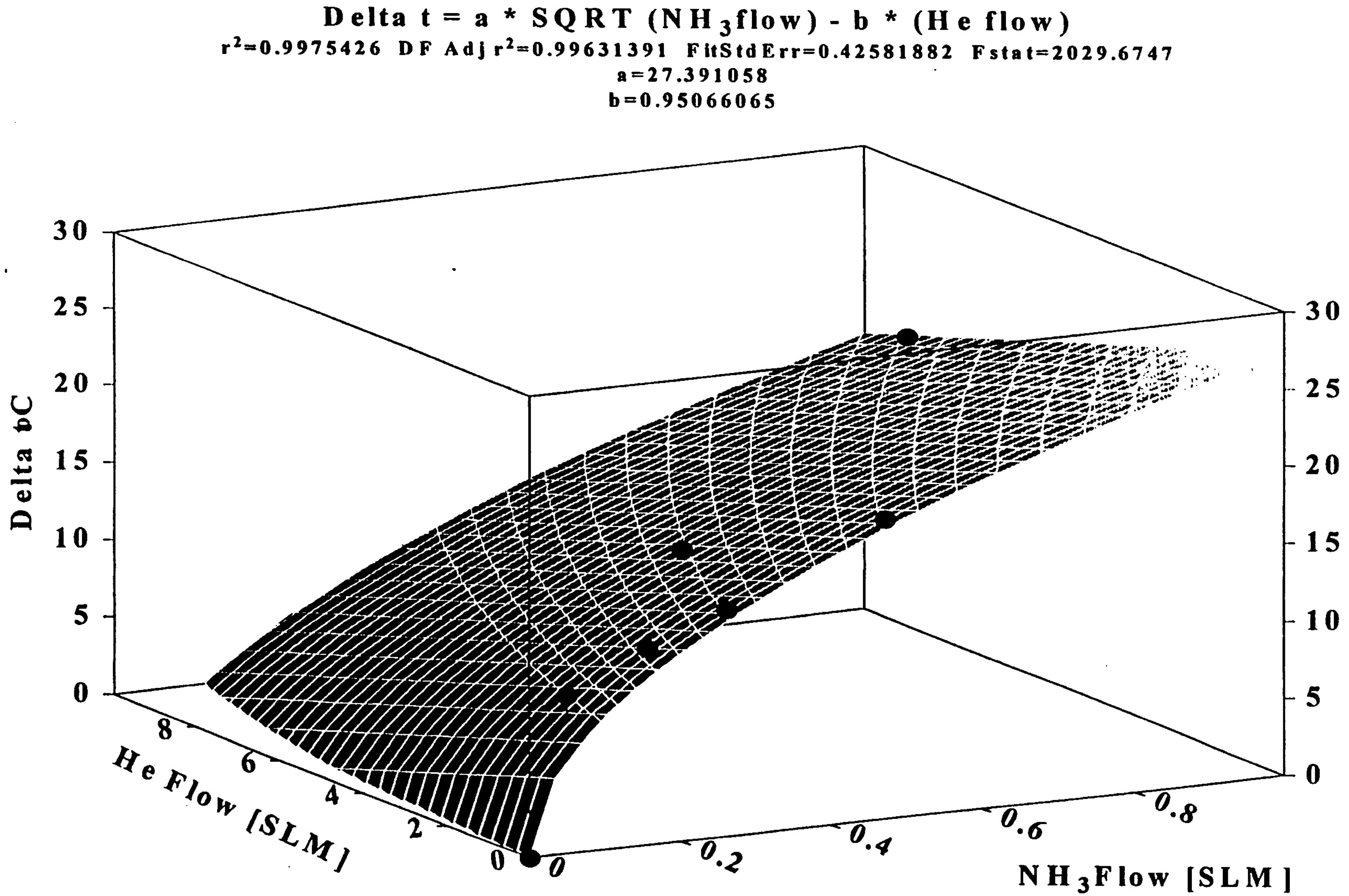

Fig. 6. Experimental maximum centerline temperatures during the loading of NH_3 on activated charcoal contained in a 6–in.–diam column similar to the actual ACB and corresponding fitted surface as a function of NH_3 and He flows.

The heat of reaction between C_xF and NH_3 to form NH_4F is significantly higher than the heat of adsorption and becomes the dominant factor determining the temperature in the ACB at higher bed temperatures (high NH_3 flow). Both reactions, adsorption and denaturing, are limited by the transport of NH_3 to the reaction front. Limiting the NH_3 flow and using a dilution with an inert gas can effectively control the denaturing process.

6.4 Denaturing of the Uranium-laden Activated Charcoal

The intercalated uranium fluorides and oxyfluorides are all trapped inside the graphitic structure of the activated charcoal. With the exception of UF_6, none of the other fluorides or oxyfluorides would react with ammonia. Accordingly, there is no conceivable mechanism for which the NH_3 gas could mobilize or remove uranium from the ACB.

The reaction between NH_3 and chemisorbed UF_6 would also produce solid UF_5 and NH_4UF_5 according to the reaction

$$4\ UF_6 + 8\ NH_3 \rightarrow 2\ UF_5 + 2\ NH_4UF_5 + 4\ NH_4F + N_2$$

As mentioned, the uranium laden activated charcoal will not deflagrate when heated rapidly. The ESCA results for the laden samples show no appreciable fluorination of carbon atoms (no C–F bonds) which explains the increased thermal stability. No significant heat is expected to be released as a result of the ammonia treatment of the uranium laden activated charcoal except for the heat of adsorption.

Nevertheless, activated charcoal laden with the 5/1 F_2/UF_6 MSRE blend will be subjected to the full passivation scheme using a 6 in. column similar to the actual ACB. The objectives of the test are to verify that the uranium-laden charcoal particles will remain free-flowing and vacuumable after the NH_3 treatment and to document the expected thermal response for the first 12 in. of the actual ACB.

7. PROPOSED PASSIVATION PLAN FOR THE ACB

7.1 Introduction

The ACB is presently isolated from the piping connected to the fuel-salt draintanks by a valve labeled 561. After this valve has been closed, any UF_6 and F_2 gases present at the top of the ACB will eventually diffuse toward the charcoal and be trapped. However, since the top portion of the ACB has an entrance void space and a length of fully reacted bed, there is always the potential for UF_6 and F_2 to be present in the space between valve 561 and the unreacted portion of the bed.

The preferred option, to eliminate the potential of having gaseous UF_6 and F_2 at the ACB entrance, is to apply vacuum on the backside of the ACB (downstream) side to pull any residual UF_6/F_2 mixture onto the charcoal to be trapped. The vacuuming operation should be done slowly over an extended period of time to avoid the possibility of heating the bed above the safe limit. The major limitation to this step is the possibility of a leakage of corrosive gases from the "drain-tank" side toward the ACB if valve 561 is not completely seated due to solid deposits. However, the reactive gas removal (RGR) team is presently proceeding with the removal and trapping of the gases contained in the piping connected to the drain-tank side. At present, the gas removal has reached the piping section immediately adjacent to valve 561, and the current plan is to fill this region with a buffer of He that would remain for the duration of the denaturing operations.

The targeted vacuum for this operation is about 10 torr which will be maintained for a period of several days to ensure the removal of sorbed gases that could energetically react with the ammonia gas (e.g., adsorbed F_2). Following this period, the ACB will be backfilled with helium.

A necessary step for the "denaturing" process is the addition of an access port at the top of the ACB. The tapping operation for the addition of this port will be done under a slightly negative pressure. Following the ACB evacuation, the tapping can be done under relatively "clean" conditions without any potential for encountering corrosive gases during the drilling operation.

The actual passivation process will be accomplished by contacting the ACB with ammonia gas, which will be introduced using the new line. Since the reaction between F_2 and NH_3 can be violent, it is necessary to ensure the complete removal of F_2 from the ACB. The previously mentioned prolonged evacuation or He purging is essential for a safe procedure.

The passivation scheme will involve the downstream flow of He/NH_3 mixtures of increasing NH_3 concentration followed by the downstream flow of pure NH_3 until breakthrough. After breakthrough, the ACB system will be left in pure NH_3 for a month to insure the completion of the defluorination by conversion to NH_4F. Pure NH_3 will be injected periodically to ensure complete saturation. (No monitoring is needed at this stage).

At the end of the ammonia soaking period, the unreacted NH_3 will be removed from the ACB prior to physical removal of charcoal by vacuum and/or He purge downstream.

Numerous laboratory tests have proved that the fluorine in the AC is converted to ammonium fluoride (NH_4F). Thus, the resulting mixture no longer has the potential chemical energy to exothermically decompose and is mechanically safe to handle.

7.2. Major considerations for the Planned ACB Passivation Treatment

A. The maximum temperature at the reaction front must be kept below 100 °C (with 50 °C suggested as a safe limit) to avoid the risk of caking (binding granules together with sublimed NH_4F)

B. The maximum temperature must be kept below 250 °C to avoid the sudden decomposition of C_XF which could lead to deflagration.

C. Reaction of NH_3 with C_XF is slow at room temperature (tens of hours to many days may be required to complete the reaction). The planned 1–month NH_3 soaking time is a rather conservative approach to ensure the completeness of the charcoal denaturing.

D. The reaction between NH_3 and C_XF is a net consumer of gases that translates into a pressure drop.

E. Adsorption of NH_3 on activated charcoal is fast, liberating considerable heat. The warming of the bed by the adsorption accelerates the rate of the denaturing reaction initiating a positive feedback loop that is controlled by the total flow and the concentration of ammonia reaching the reaction front.

F. Results of loading tests using 5/1 F_2/UF_6 mixtures showed that the F_2 front moves slightly ahead of the uranium front. Based on laboratory tests, the known top 1 ft containing uranium is followed by only a few feet (1–4) of C_xF further downstream. This experimental observation is in agreement with the calculations using the best estimate of the radiolytic yield for F_2 generation (G value). The bulk of the ACB remains as activated charcoal (~80 ft). Additional details are available in Sect. 9.

7.3 Process Description (Chemical Operations, ACB Denaturing)

The chemical operations activities will be accomplished in two phases. Activities in the first phase, which will take place before the hot tap installation in the vicinity of valve 561 are as follows:

1. evacuation of F_2 / UF_6-containing gas from the MSRE off gas system (OGS) piping region upstream of valve 561 (in the region measured by PT-518), followed by inert gas buffering of that region;
2. evacuation of the ACB (to remove possible high concentrations of F_2 and UF_6 in the inlet region) via a vacuum system in the vicinity of valve 562; and
3. Inert-gas backfill of the ACB.

The hot tapping operations will occur following the initial evacuation and inert-gas backfill. After the completion of the tapping, new line installation, and system readiness checkup (including all appropriate hardware and instrumentation, especially the gas inlet system, the bottle station and the thermocouples on the ACB), the following operations can be conducted:

4. stepwise dosing of the ACB inlet region with NH_3/He mixtures of increasing NH_3 concentration, ending with pure NH_3;
5. dosing of the entire ACB pure NH_3;

6. NH_3 soaking period, with periodic addition, to make up pressure loss (if any), but at a minimum adding sufficient gas to displace a portion of the ACB volume and replace it with fresh NH_3.
7. purging and evacuation of residual (gaseous plus reversibly adsorbed) NH_3; and
8. refilling the ACB with inert gas.

Step 8 is the end of the scope of the chemical operations relating to denaturing of the ACB. A more-detailed description and discussion of the operational steps follows.

7.3.1. Evacuation of F_2 / UF_6 Upstream of Valve 561

A major safety concern is the reaction of NH_3 with F_2 due to inadvertent mixing of gas streams. The reaction of these gases is highly exothermic. Secondarily, it is necessary to avoid loading additional F_2 on the AC at uncontrolled rates. Isolation of the ACB via existing valves is apparently not adequately reliable from a safety evaluation standpoint, so other operational parameters must be controlled to prevent mixing of residual MSRE gas with ammonia. The obvious way to assure that F_2 is not leaking into the ACB is to evacuate the adjacent region and buffer it with an inert gas to a pressure which ensures that any gas leakage (if it occurs) is in a direction that will not carry F_2 into the ACB (or NH_3 into regions containing F_2).

Our plan is to introduce this helium buffer in the PT-518 region and maintain it while NH_3 is present in the inlet region of the ACB. Should the buffer fail (e.g., rapidly lose pressure), NH_3 operations will cease, and a backup buffer will be imposed by introducing helium into the inlet piping and headspace of the ACB to displace gaseous NH_3 from that region.

Accomplishment of this step is partly a program integration issue, as removal of reactive gases from adjacent zones is a function of reactive gas removal system (RGRS) operations. The timing of that removal and the ability to reliably buffer an adjacent zone of the OGS with inert gas are dependent on activities beyond the scope of the Uranium Deposit Removal (UDR) portion of MSRE remediation.

7.3.2. Evacuation of ACB

Radiation profiling has shown that the first foot or so of the ACB is loaded with uranium. There must be a similar zone of AC loaded with F (to form C_XF), but the extent of loading is not known from direct evidence. Estimates have been made based on indirect evidence which suggest that the cumulative F_2 loading has probably produced a bed of C_XF less than 2.9 ft long, but definitely no more than 12 ft long (using the least favorable combination of uncertainties in that estimate). Additional details are available in Sect. 9.5. Both estimates are upper limits in the sense that undiscovered sinks for F_2 (e.g., solid UF_5 or UF_6 deposits or corrosion of materials of construction) would reduce the quantity available for production of C_XF.

The piping that leads to the inlet of the ACB, the void space at the inlet, and the void space in the already-loaded region *may* contain free F_2 (or may not, since F_2 in a static system would diffuse over time to the "sink" represented by the AC). Without access to gas analysis or knowledge of the volume of this region, it is prudent to assume that gaseous F_2 may be present. Further, the fluorine-loaded AC may have a small quantity of adsorbed unreacted F_2.

If free F_2 in large quantities were suddenly forced into the unloaded zone of the ACB, excessive reaction heating could occur. To remove such a possibility, evacuation of the ACB (via a vacuum system) in the vicinity of valve 562 is planned. Evacuation will be done at a controlled rate to limit reactive heating as the gas expands into the unreacted AC. Laboratory tests are planned to determine a flow rate at which F_2, if present, would produce an observable temperature rise bellow the safe limit. The location of the reaction front, if F_2 were present, would indicate the position of the interface between the C_xF and the virgin charcoal.

Evacuation of the isolated charcoal bed via the downstream (562) end will result in gas expansion toward the vacuum system. For example, a flow rate of 100 std cm^3/min (sccm) at the evacuation end will result in an effective flow rate of 10 sccm 90% of the distance toward the inlet end (8 ft from the inlet), assuming there is no flow of gas into the ACB inlet.

Thermocouples on the wall of the ACB will be available to measure temperature for the first several feet of the bed, and an additional thermocouple can measure the temperature at approximately the halfway point in the bed. Laboratory tests are determining the heating rate and temperature limits for a variety of flows, which should lead to firmer flow limitations.

The general strategy for this step is to evacuate at a safe rate so that a small but appreciable rise in temperature could occur in the ACB. If F_2 is actually present in quantity in the ACB void space then a discernable rise in temperature would reveal the location of the boundary between the C_XF and the unreacted activated charcoal. Knowledge of the location of this boundary would allow us to accelerate the dosing operations conducted later .

7.3.3. Inert-Gas Backfill of the ACB

The ACB will be backfilled (from the 562 end) with an inert-gas —probably He most although nitrogen or argon would serve as well— to approximately atmospheric pressure. This addition of inert gas will allow the subsequent hot tapping operation to be conducted against a pressure differential that is minimal. The hot tapping operation will, create a new access point into the system between valve 561 and the inlet of the ACB. That operation is outside the scope of chemical operations in denaturing. Once the hot tapping is complete and all appropriate hardware and instrumentation are operational, the subsequent operations will be initiated.

7.3.4. NH_3 Dosing of ACB Inlet Region

A gas flow of helium containing a low concentration of NH_3 will be injected via the bottle station and hot tap into the inlet of the ACB. This operation will be done in a series of stages utilizing increasing concentrations of NH_3. There are several reasons for utilizing this approach, all of which are based in one way or another on the need to minimize the temperature rise during dosing.

It should be noted that two modes of adsorption are of interest here: (1) irreversible reaction with C_XF to form NH_4F and N_2, and (2) reversible adsorption of NH_3 on activated charcoal. In addition, the decomposition of C_XF, highly unlikely under the planned conditions, represents a third exothermic reaction This is the reaction which, at higher temperatures, can lead to the deflagration which this entire denaturing process is intended to prevent. All three of these reactions liberate heat.

The reversible adsorption process generates less heat than the other two reactions and has a negative temperature coefficient (adsorption is reduced at higher temperatures); however, it occurs readily at room temperature. The denaturing reaction generates more heat per unit mass of reactant, but has a very slow rate at room temperature. Its temperature coefficient is positive: the reaction rate increases with increased temperature.

The dosing process must permit the adsorption reaction to proceed to equilibrium at the desired partial pressure of NH_3 of each stage of the process while allowing time for the heat generated to dissipate. This procedure avoids a temperature increase above ~250 °C where the reactions of C_XF take place to an appreciable extent.

A second temperature threshold, which is not of concern from a safety standpoint but is operationally very important, is that where NH_4F can cause caking of the AC granules. During the course of the entire denaturing operation, the reactions of NH_3 with AC and C_XF, sorption, and passivation, will release, at completion, a total amount of heat of the order of 21000 kcal over half of this heat will be generated in the first few feet of the bed where the denaturing reaction takes place. The details of the dosing scheme are predicated on dissipation of this heat without generation of excessive temperatures.

Dosing, at least of the inlet region of the ACB where C_XF may be present, will be accomplished by a stagewise introduction of dilute mixtures of NH_3 in He. The use of mixtures will allow better control of the rate of arrival of NH_3 into the adsorption zone of the ACB than would the use of pure NH_3. Each increase in concentration of NH_3 will be associated with an incremental increase in equilibrium adsorption —and thus heat generation. Laboratory tests of dosing on full-diameter AC and C_XF beds are still under way, so the exact procedure has not yet been fully determined.

The two controlling factors are NH_3 dilution and NH_3 flow (total flow times dilution factor). At the beginning of the process, the dilution is quite high and the total NH_3 flow is low to avoid any potential risk. As the reaction progresses, the NH_3 concentration and NH_3 flow are increased sequentially in order to maintain a smooth reaction and allow the heat to safely dissipate over an extended period.

Whatever the specifics of the final dosing procedure, the general course of each stage (a "stage" is determined by a prescribed NH_3 concentration and total flow rate) will be as follows:

1. Initiate the flow of mixture at about one-third of the nominal flow for this stage.
2. Allow the flow to proceed until the first 18 in. to 24 in. of the ACB has equilibrated with this concentration.
3. Increase the flow rate to the nominal flow rate for this stage
4. Allow the flow to proceed until the adsorption front has passed the furthest possible extent of the C_XF.
5. If the temperature of the inlet region of the ACB has not returned to within a degree or two of the ambient temperature, stop the flow and wait for the region to cool.
6. Proceed to the next stage of the dosing procedure.

Gas for each stage will be purchased as pre-mixed bottles of He/NH_3 and fed through a flow control module from the bottle station via the hot tap. The final stage will consist of pure NH_3. During all dosing stages, the temperatures (as read by external thermocouples, one infrared (IR) thermometer, and one coaxial thermocouple) will be continuously monitored. If excessive temperature rises (or trends in that direction) should develop, the gas flow will be reduced or stopped as needed, to keep the temperatures within prescribed limits.

Temperature limits for control are still under development since a number of factors must be considered. Because caking has been observed at temperatures above 100 °C, a temperature limit of 50 °C has been suggested. The temperature at which the onset of heat evolution from the C_XF auto decomposition reaction was observed is also 100°C, although deflagration did not occur in laboratory samples until the temperature have been increased to at least 250°C. At present, it appears that a core temperature limit of 40–60 °C would allow adequate temperature control.

Result of tests indicated that a relationship between temperature rise measured at the core of the bed vs that at the wall exists, with a time lag of 2–4 minutes, (see Sect. 9.3 for more details).

7.3.5. Pure NH_3 dosing of Remainder of ACB

Following the step dosing of the inlet region of the ACB, the entire ACB will be filled with pure NH_3. If this were not the case, NH_3 would tend to desorb from the inlet regions (which are equilibrated to 1 atm of NH_3 in the final stage of the inlet dosing process) and migrate downstream to adsorb on unladen AC.

Over the long term, this NH_3 in the inlet region will react with fluorinated AC according to the equation (the N_2 by-product was not analyzed since it is not measurable by IR analysis):

$$^4/_3\,NH_3 + C_XF \rightarrow NH_4F + x\,C + {}^1/_6\,N_2$$

The currently proposed flow rate for this step is 5 std L/min. At the anticipated ACB NH_3 demand, this flow rate leads to dosing times of 60 to 90 h. Since the loading of NH_3 on AC is a self-limiting process (higher-temperature AC has less capacity for adsorbed NH_3) and there are no particular reasons to limit bed temperature in areas remote from C_XF, the dosing of this section can likely be increased to reduce the duration of the step.

A commercial thermal conductivity detector will be used to determine the completion of the NH_3 loading. In addition, plumbing fixtures for connecting other analytical methods of gas analysis (FTIR, sample bottles, etc.) are being designed for incorporation into the evacuation system. An obvious advantage of FTIR or batch gas sampling and remote (e.g., gas chromatograph or mass spectrometer) analysis is their ability to detect the unexpected.

7.3.6. Soak Period

After the NH_3 dosing period, the NH_3-loaded ACB will be allowed to remain idle for about 4 weeks to ensure the completion of the denaturing reaction All laboratory tests have shown complete passivation at shorter times than the planned four weeks of ammonia soaking. However, the extra reaction time adds a reasonable margin of assurance that the reaction has gone to completion..

The contact time can be considered to begin when the inlet region is first exposed to substantial concentrations of NH_3 (say, 20% or more). Assuming that the dosing stages are completed in less than the required 4-weeks of contact time, an idle period will be initiated. During this period, makeup NH_3 will be needed as the C_XF reaction proceeds.

Assuming the equation $^4/_3\,NH_3 + C_XF \rightarrow NH_4F + x\,C + {}^1/_6\,N2$ represents the chemical process involved here, the reaction of C_XF and NH_3 will be accompanied by a pressure change.. Although the loss of 4/3 mol of NH_3 is accompanied by the production of only 1/6 mol of N_2, nearly all (~99%) of the NH_3 present is adsorbed. Thus, it is likely that a larger proportion of the N_2 produced will be in the gas phase.

Some pressure change is expected as the reaction proceeds, but its magnitude and direction are not quantitatively known.

As NH_3 is depleted in the C_XF region, it will tend to desorb from both the immediate vicinity and more remote areas of the ACB, but a diffusion block of N_2 may build in the vicinity of the C_XF. A periodic makeup of pure NH_3 is planned in order to keep the local NH_3 concentration constant. This makeup of NH_3 will serve to replace the consumed NH_3 and also to displace N_2 from the vicinity of the C_XF zone. Present plans are to make up any pressure drop in the event that one should occur; in any case, NH_3 will be in a quantity sufficient to displace approximately 10% of the ACB void volume, twice a week during the idle period.

7.3.7. Evacuation of Residual NH_3

After the reaction has the opportunity to go to completion, the residual NH_3 will be removed. Otherwise, the ACB, laden with approximately 24 kg of reversibly adsorbed NH_3, would tend to maintain a partial pressure of about 1 atm of NH_3, which would complicate the vacuuming of the uranium-laden charcoal to follow.

The main issue during this evacuation step is that the trap, and hence the vacuum pump effluent, will be nearly pure NH_3. While not generally considered a fuel, NH_3 is potentially flammable in air. However, it is very difficult to ignite, requiring a much higher ignition temperature than more common gaseous fuels (see Sect. 9.7). Pumped to the building stack, it will quickly be diluted in air to below flammable limits; however, there would be a plume of flammable gas between the stack inlet and the point at which dilution eliminate the risk. No obvious ignition source exists other than perhaps, static discharge.

The probability of ignition of this plume is very minimal. However, the possibility of ignition can be eliminated by diluting the NH_3 with sufficient inert gas (e.g. He) that no possible mixture of air and the diluted NH_3 is flammable (for more details, see Sect. 9.7).

A He:NH_3 dilution as low as 1:3 would suffice to keep the effluent out of the explosive region. In practice, a greater degree of dilution, 1:1, will be employed to ensure a wide margin of safety. Diluent gas flow will be monitored by a flowmeter and will mix with NH_3 at the exit of the vacuum pump, which will not lengthen the duration of the evacuation process. The evacuation process will probably require 1 or 2 (24 h) days.

The evacuation of residual NH_3 will be accompanied by a slow purge of inert gas (He) from the bottle station/hot-tap piping (~ 1 std L/min), as this purge should assist in the removal of, especially, the last traces of adsorbed ammonia as the evacuation process goes to completion.

7.3.8. Fill ACB with Inert Gas

After the evacuation has been completed, the ACB will be filled with inert gas (He from the bottle station) to a pressure just below 1 atm. This will allow the ACB breaching operation to be conducted against little or no pressure differential into a largely inert gas atmosphere.

7.3.9 Contingency Actions

In the event of abnormal or unfavorable developments, certain contingency actions may be warranted. The motivation for these may be operational control (to minimize duration of operations), avoidance of later operational difficulties (e.g., avoiding AC caking), or avoiding safety problems (e.g., avoiding deflagration).

The information available to the operator will be limited to gas flows at the inlet and possibly outlet of the ACB, gas pressures in several locations, and the temperature readings on the ACB wall (plus a single location in the ACB axis). The temperature of greatest interest is that at the axis of the ACB in the C_XF region, especially the uranium-laden portion thereof, since the axis is the region most likely to reach higher temperatures. Prediction of axis temperatures from observed wall temperatures will rely primarily on laboratory observations of the temperature behavior of a test column with dimensions and materials similar to those of the ACB.

Available data to date (see Sect. 9.3) indicate that the wall temperature can lag the axis temperature by up to a few (1–4) min and (lags ignored) experience rises about 50 % of those experienced at the axis. Operational response to such temperature rises will require estimates of ACB axis temperatures imputed indirectly from measurements at the wall. Whatever the source of reactive heating, the control of temperature requires decreasing the rate of reaction. Several actions can be taken to reduce the heat load. First, the rate of influx of NH_3 can be reduced.

Since the operations will utilize premixed He-NH_3 bottles, it may not be practical to reduce the concentration from that currently in use during a given operation, as such an action would require changing bottles (perhaps to a mix not immediately available). It is, however, possible to easily reduce the flow of the NH_3 mixture (to reduce the chemical, and hence the thermal, load). This can be and likely will be, done manually to control temperatures that are moving toward undesirable levels. (Conversely, if it appears that the prescribed flows are generating minimal temperature rises, it may be desirable to increase the flow to save time,).

If in doubt, the flow can be stopped manually by the operator; however, current designs include a feature by which the NH_3 flow will be shut off if any of the thermocouples on the ACB indicates temperatures above prescribed levels. The precise set points not yet determined will be dictated by the need to avoid AC bed caking, which occurs at a lower temperature than deflagration.

In addition to simply shutting off the flow of NH_3, additional measures could be taken which could actually provide some cooling to the ACB. Substituting a flow of He for the mixed or pure NH_3 would begin a purge of the previously adsorbed NH_3 from the AC. Just as adsorption of NH_3 releases heat, desorption absorbs the equivalent amount of heat —thus cooling the bed. Partial evacuation of the ACB would have a similar, but less localized effect, as a reduction in overall pressure would result in partial desorption of NH_3, cooling the bed. Of course, either of these would, in the short term, draw additional NH_3 into the bed (gas held up in the inlet lines).

The helium purge concept appears to be the most locally efficacious, and at present is to be preferred if simply reducing or stopping the flow of NH_3 fails to bring a temperature rise under control. Whatever the amelioration action, several minutes of observation will be required before temperature sensors will register the effect of any temperature control effort.

One type of failure that would require special backup action relates to the gas buffer between the ACB and other regions of the MSRE OGS. It is contemplated that an inert gas (He) buffer should be instituted in the region just past valve 561, and that it would be maintained at some pressure difference (e.g., 1 psi) higher than the maximum of the operating pressure in the ACB or the equilibrium pressure in the remainder of the MSRE OGS. The reasoning is that in such a case, any leakage would consist of inert gas flowing from the buffer region to both the ACB and to the rest of the OGS.

This buffer region is bound on one side by valve 561, but on the other possibly only by a piping plug of indeterminate character. Should the buffer fail under circumstances in which is could not be maintained and in which F_2-containing gas might pass from the OGS to the ACB, then temporary protective measures would have to be taken to prevent the mixing of large quantities of F_2 and NH_3 (which could react with a release of considerable energy).

In such an event, a backup buffer would be instituted in the inlet region of the ACB by (1) stopping the flow of NH_3, (2) flowing sufficient He into the inlet to displace NH_3 from the inlet area, and (3) closing the exit stream of the ACB and allowing the pressure to build up (with additional He) to the point that the ACB pressure equals or exceeds the OGS pressure.

7.4 Logistical analysis

Provisional operational parameters have been specified based on results of laboratory experiments or, in cases where such results are not available, on intuition and extrapolation. A cursory analysis of the logistical implications of the combination of steps and provisional operational parameter values is summarized in Table 4. For example, for each dosing stage, the specified flow rate of ammonia was combined with experimental values for the demand for adsorbed NH_3 by AC and with the quantity of AC in the ACB to calculate the duration of the pure NH_3 dosing step, the number of bottles of NH_3 needed, and the frequency of bottle changes.

In computing the number of hours required for each stage, it is further assumed that no time is required for the ACB to cool between dosing stages. It is also assumed that the temperature is controlled to a sufficiently low level that no significant reaction of NH_3 and C_XF occurs during the mixed gas dosing (see discussion below). Results of laboratory tests provide evidence that some denaturing occurrs during the adsorption step.

Our current best estimate of the demand for NH_3 due to the denaturing reaction is 5.3 kg (or less). During the initial stages of the passivation, some $C_XF + NH_3$ reaction can be expected while flowing the dilute He/NH_3 mixtures. A reasonable estimate for NH_3 consumption is 10 to 30% of the total denaturing demand. Since each Ne/NH_3 mixture bottle contains about 0.2 Kg of NH_3, three to eight additional mixture bottles may be needed above those required for satisfying the adsorption demand.

To reiterate, the specifics of the itemized stages are provisional at this point, in that this exact sequence has not been tested in the laboratory at for a full diameter test bed loaded with C_XF.

Table 4. ACB Denaturing operational parameter summary (provisional values)[a]

1. RGRS evacuates and He buffers the PT-518 region of OGS.

2. Initial evacuation step: Minimum flow = 100 std cm^3/min; duration = 58 h

3. Inert backfill: Maximum flow = 5000 std cm^3/min; duration = 1.2 h, using 0.05 bottle He

4. Dosing inlet region of ACB: (Provisional) dosing sequence for initial 12 ft of ACB

	2 mol %	5 mol %	10 mol %	20 mol %	35 mol %	50 mol %	100 mol %
Flow, std cm^3/min	10000	10000	10000	5000	3000	2500	2000
Duration, h	8	5	4	8	11	9	20
No. of bottles	1	1	2	4	6	9	0.4
Bottle replacement interval, h	24	6	2	2	1.9	1.1	55

[a] *Notes: 1. Initial 18 in. of ACB will be dosed at no more than one-third the above rates.*

2. Above values ignore the estimated 5-kg ammonia demand due to C_XF.

Table 4 (Continued)

5. Dosing remainder of ACB with pure ammonia

Flow	10,000 std cm^3/min
Duration	54 h
No. of 10-kg bottles	3
Bottle replacement interval	21 h

6. NH_3 supplement: Approx. flow 5000 std cm^3/min; duration = 0.04 h or more, if pressure noticeably declines. NH_3 use is insignificant unless unexpected behavior occurs. Total C_XF demand for NH_3 is estimated to be less than 5 kg.

7. Final evacuation step:

Pump at	3	ft^3/min;
Duration	27	h (or longer; actual duration will probably depend on heat balance in ACB);
Pressure	0.25	atm
Inlet purge	1,000	std cm^3/min , using 1 bottle He
Net removal	20,300	std cm^3/min adsorbed ammonia
Exhaust dilution,	42,600	std cm^3/min (on average), using ten bottles He, changing bottle each 2.7 h

8. Inert gas fill

Flow	10,000	std cm^3/min;
Duration	0.6	hrs using 0.05 bottle He,
Pressure	0.95	atm

8. CURRENT EXPERIMENTAL DEVELOPMENTS RELATED TO THE ACB DENATURING PROCESS

As presented in Secti. 5.1, after an extensive search for a denaturing reagent, it was found that only NH_3 gas could transform the potentially reactive fluorinated charcoal into a stable material that can be safely handled and heated. Preliminary tests, Sect. 6.1, demonstrated that the fluorine bonded to the charcoal reacts with NH_3 to form NH_4F most likely according to the reaction

$$^4/_3\,NH_3 + C_XF \rightarrow NH_4F + x\,C + {}^1/_6\,N_2 .$$

The consumption of NH_3 and by-products formation was analyzed using a FTIR; NH_4F generation was confirmed by XRD (see Section 6.1). Since N_2 does not absorb IR light, the actual formation of N_2 gas was not corroborated . A possible competitive reaction is as follows:

$$C_XF + {}^2/_3\,NH_3 \rightarrow {}^1/_6\,NF_3 + {}^1/_2\,NH_4F .$$

However, NF_3 was not detected by FTIR analysis of the gases, and in any case; this reaction is significantly less exothermic than the previous reaction.

The charcoal defluorination reaction is slow at room temperature requiring several days to go to completion while at higher temperatures (above 70 °C) all the fluorine bonded to the charcoal is transformed into NH_4F in a few hours. At even higher temperatures, the reaction is completed in minutes.

The study of the mechanism and kinetics of the denaturing reaction is beyond the scope of this task. However, it can be assumed to be controlled by the interlamellar diffusion of NH_3 in the micro graphitic charcoal structure.

As mentioned previously, the reaction of NH_3 with C_xF will generate heat on the ACB (see Sect. 6.3 for more details). This heat generation results from both the heat of sorption of NH_3 on the AC and the heat of reaction of NH_3 with C_xF.

The primary objective of the passivation process is to completely denature the CxF in a progressive and controlled fashion in a reasonable length of time. In order to achieve this goal, it was decided to use mixtures of an inert gas, He, and NH_3 in steps of increasing NH_3 concentration. The major controlling factors are the NH_3 concentration and the flow rate (see Sect. 7). A series of bench-scale experiments are being completed to determine the optimal procedure for denaturing the ACB while maintaining the temperature in a safe margin.

The maximum temperature rise during the NH_3 loading depends on process variables that can be controlled, such as flow rate, NH_3 concentration and the actual physical and chemical conditions at the ACB.

Accurate prediction of the temperature profile by mathematical modeling requires reliable transport and kinetics parameters that are usually determined from previous experimental work. At present, there is no background literature to support the accurate modeling of the ACB system.

The actual ACB is believed to consist of three layers of charcoal materials. The top 12 in. of the ACB are known to contain uranium and a few feet of fluorinated charcoal extend beyond the uranium front. The remainder of the ACB, about 80 ft, consists of unreacted charcoal. Accordingly, the tests encompass the loading of NH_3 /He mixtures at different flow rates and temperatures on the three charcoal layers: charcoal, fluorinated charcoal covered by layers of activated charcoal, and uranium-laden activated charcoal.

The approach for the current tests includes scoping tests using small columns at different superficial velocities and full-size experiments using a column similar to the actual MSRE-ACB. The primary goal is to define the boundary condition for the safe and efficient dosing of NH_3 for the actual ACB denaturing operation.

Tables 5–7 display a compilation of conditions and major results for all the tests already conducted. (A detailed report will be issued at the completion of the tests). The main experimental results consist of temperature and front profiles that would permit correlation with the actual ACB conditions for the optimal denaturing scheme.

Table 5. Small column tests, NH_3 on CxF

Test	Load/run	Column ID (in.)	Area (cm^2)	NH_3 (Vol %)	Total flow (std cm^3/min)	Face velocity (m/s)	Init. temp. (°C)	Max. temp (°C)	Δt (°C)
NH3MAX01	I-1	0.8	3.24	10	10-300		20.5	28.0	7.5
NH3MAX04	II-1	0.8	3.24	50	100.0	5.14E-03	20.6	126.0	105.4
NH3MAX08	III-1	0.8	3.24	10	16.6	8.54E-04	20.8	24.0	3.2
NH3MAX11	IV-1	0.8	3.24	30	16.6	8.54E-04	21.3	28.9	7.6
NH3MAX14	V-1	1.375	9.58	10	49.2	8.56E-04	20.1	30.9	10.8
NH3MAX17	VI-1	1.375	9.58	20	49.2	8.56E-04	20.2	27.0	6.8
NH3MAX21	VII-1	1.375	9.58	30	49.2	8.56E-04	21.7	45.8	24.1
NH3MAX24	VIII-1	1.375	9.58	20	49.2	8.56E-04	22.0	44.1	22.1
NH3MAX25	IX-1	0.375	0.713	20	3.66	8.56E-04	20.7	21.1	0.4
NH3MAX28	X-1	0.375	0.713	30	3.66	8.56E-04	21	25.3	4.3
NH3MAX30	XI-1	1.375	9.58	100	100.0	1.74E-03	21.2	146.6	125.4
NH3MAX31	XII-1	0.375	0.71	10	100	2.35E-02	21.4	37.4	16.0
072997a	XIII	4.25	91.48	10	445	8.11E-04	24.1	27.50	3.4

Table 6. Full scale column, NH_3 on AC

Test	Load/run	Column ID (in.)	Area (cm^2)	NH_3 (vol%)	Total flow (std cm^3/min)	Face velocity (m/sec)	Init. temp. (°C)	Max. temp. (°C)	Δt (°C)
071197A	I	6.375	205.93	10	1000	8.09E-04	20.3	29.4	9.1
071497A	I	6.375	205.93	20	1000	8.09E-04	21.7	33.4	11.7
071597A	I	6.375	205.93	30	1000	8.09E-04	22.6	36.4	13.8
071697A	I	6.375	205.93	50	1000	8.09E-04	24.2	42.9	18.7
071797A	I	6.375	205.93	10	4000	3.24E-03	23.6	37.6	14
071897A	I	6.375	205.93	10	10000	8.09E-03	23.7	42.4	18.7
071497B	II	6.375	205.93	100	1000	8.09E-04	30.2	56.5	26.3
071597B	II	6.375	205.93	100	1000	8.09E-04	32.4	53	20.6
071697B	II	6.375	205.93	100	1000	8.09E-04	34.5	47.9	13.4
071797A	II	6.375	205.93	50	2000	1.62E-03	32.7	47.8	15.1
071897A	II	6.375	205.93	50	4000	3.24E-03	24.2	49	24.8
071797A	III	6.375	205.93	100	1000	8.09E-04	44.7	54.3	9.6
071897A	III	6.375	205.93	100	1000	8.09E-04	26.2	47.6	21.4

Table 7. Full scale column, NH_3 on AC/C_xF/AC

Test	Load/run	Column ID (in.)	Area (cm^2)	NH_3 (vol%)	Total flow (std cm^3/min)	Face velocity (m/sec)	Init. temp (°C)	Max. temp (°C)	Δt (°C)
081197A	I	6.375	205.93	5	10000	8.09E-03	23.3	162.7	139.4
081497A	II	6.375	205.93	5	10000	8.09E-03	23.3	39.6	16.3

9. ADDITIONAL BACKUP TECHNICAL INFORMATION

The topics indicated by the tittles of the following subsections have arisen in recent discussions of safety analysis or operational control issues. The material offered here will serve as backup documentation for these various topics.

9.1 Allowable Leak Rate Through Valve 561

One scenario that might cause temperature excursions in the ACB, in the extreme case leading to deflagration of the C_XF, is the leakage of reactive gases from the MSRE OGS into the ACB via valve 561. Although that area should be buffered with inert gas, the possibility is considered that the buffer could fail and F_2-containing gas could leak into the ACB region. For purposes of evaluating the consequences of such a leak, an arbitrary value of 10 std cm^3/min leakage through valve 561 is assumed. This leak rate is probably larger than that which would actually be experienced when more accurate measurements are made (at present only limited information is available on this point).

In the following discussion, the heat release is estimated for various chemical scenarios. Assuming that the MSRE off-gas consists of 80% F_2 (which is higher than the actual content measured to date), a 10-std cm^3/min leak rate corresponds to 8-std cm^3/min F_2 influx. There is no particular reason to suppose that the leakage rate would change other than in response to changes in pressure difference.

In the absence of NH_3, F_2-containing gas leaking through valve 561 will diffuse to the activated carbon, reacting approximately as follows:

$$F_2 + 5.2\,C \rightarrow 2\,C_{2.6}F \qquad \Delta H_{Rxn} = -333\ \text{kJ/mol} \qquad Q\,(10\ \text{std cm}^3/\text{min}) = 2.0\ \text{W} \qquad (1)$$

where the heat of reaction is derived from heats of formation from the references in Table 8. Assuming that valve 561 has been leaking, this reaction should have been occurring all along. In the event that F_2 should leak into the ACB during NH_3 operations, it will react with the NH_3 by one of the two following mechanisms:

$F_2 + {}^{8}/_{3}\,NH_3 \rightarrow 2\ NH_4F + {}^{1}/_{3}\,N_2$ $\Delta H_{Rxn} = -805$ kJ/mol Q (10 std cm^3/min) = 4.8 W (2)

$F_2 + {}^{1}/_{3}\,NH_3 \rightarrow {}^{1}/_{3}\ NF_3 + HF$ $\Delta H_{Rxn} = -300$ kJ/mol Q (10 std cm^3/min) = 1.8 W (3)

For comparison, the heat load thought to exist in the ACB inlet due to radiation heating from uranium and its daughters is about 2.6 W, and has resulted in only a slight temperature increase above ambient.

These reactions should take place immediately on mixing the gases, namely in the inlet piping near valve 561 and the hot tap, approximately 20 ft from the ACB inlet. Adiabatic temperature rises in the reacting gases could, in theory, heat the gases to high temperature, but the heat production rate is sufficiently slow that it necessarily will be communicated to the piping rather than be transported elsewhere with the gas.

For example, a 10 std cm^3/min flow, reacting according to eq. (2) will displace the gas in 5 cm of pipe in 1- min and generate 288 J of heat. This is sufficient to increase the temperature of 5 cm of piping during that minute by 7.9°C (assuming no conductive losses along the pipe or heat dissipation elsewhere to the surroundings).

Distributed over the entire pipe leading to the ACB, the temperature rise would be on the order of 0.1 °C/min, if we ignore any heat dissipation to the surroundings.

Table 8. Heats of formation for pertinent chemical species

Compound	ΔH_f°(25 °C) [kJ/mol]	Source	
$NF_3(g)$	-132.1	(Ref. 4)	
CF_4	-933.2	(Ref. 4)	
$NH_3(ads)$	- 67.9	(Ref. 5-8)	($P > 0.1$ atm)
$NH_4F(s)$	-463.9	(Ref. 8)	
$NH_3(g)$	- 46.1	(Ref. 8)	
$C_{2.6}F$	-166.3	(Ref. 9)	

Laboratory experiments are planned to determine the maximum flow rate of F_2 into activated carbon permissible without an intolerable temperature rise; however, until they are completed, this analysis suggests that a 10-std cm^3/min flow should not lead to any serious consequences in the ACB during NH_3 treatment. The times and heat loads are such that considerable time would be available to observe and react to the loss of the buffer gas. Even if F_2-containing gas were to enter the ACB region during NH_3 operations at the above rate, the heat generation would not impose harmful temperature rises.

9.2 Imputing Axial Temperature in ACB from Measured Wall Temperatures

Temperature control is important in the ACB denaturing operation. Accordingly, a series of thermocouples will be mounted along the exterior of the ACB in and beyond the region likely to contain uranium and C_XF. Heat generation due to adsorption will likely be uniform throughout the bed, but heat dissipation will occur primarily at the wall. For that reason, the temperature extremes are more likely to occur in the core (i.e. on the axis) of the ACB. Unfortunately, we will have only a single thermocouple monitoring an axial position, and it will be located just a few inches inside the inlet (in the uranium-laden region).

For purposes of operational control, it will be necessary to deduce the approximate axial temperature based on wall temperature measurements. A series of laboratory experiments has been conducted on a test bed that simulates the geometric and material configuration of the ACB. This test bed, which was 6 in. diam., is packed with similar material of similar size. It was instrumented with a series of thermocouples reading the wall temperature, as well as a series of thermocouples at corresponding locations at the axis of the bed.

Several experiments have been performed to study the temperature behavior of AC upon the adsorption and desorption with NH_3 at various flows and concentrations, in one experiment, the C_XF was similarly loaded with NH_3. Several general observations can be summarized as follows:

1 There was a clear correlation of temperature change at the axis vs temperature change, as measured at the wall of the bed. This correlation is depicted in Fig. 7.

2 Rapid changes in heat load (rapid increases in concentration or flow rate) tend to produce temperature changes at the axis that are not immediately reflected in readings at the wall. A delay of 2 to 4 min is required before the wall temperature and the axis temperature again follow the correlation depicted in Fig. 7.

3 In the one C_xF full-diameter test performed thus far, the temperature at which exothermic chemical reactions began at a rate sufficient to result in thermal runaway (i.e., resulting in thermal excursion above the desired operational limits) was about 80°C in the bed axis, or 40°C as measured at the wall.

Figures 8–11 depict two examples of wall-vs- core temperature correlations from two different experiments. Points are plotted each 10 s(Fig . 9) or 60 s (Fig. 11) as the overall bed temperature rose due to heat of adsorption and reaction. Figures 8 and 9 illustrate that temperature changes which occur reasonably slowly approximately follow the correlation shown in Fig. 6. Figures 10 and 11, on the other hand, show that a rapid temperature excursion at the axis of the bed can lead to divergence from the temperature correlation for a period of time before the wall temperature responds.

To keep the temperature in control in the actual ACB dosing campaign, it will necessary to make changes in potential heat load slowly. Further, following any change, it will be necessary to wait for a short period of time (3 to 5 min) to ensure that the wall readings are reflecting the situation at the axis, prior to making any further changes.

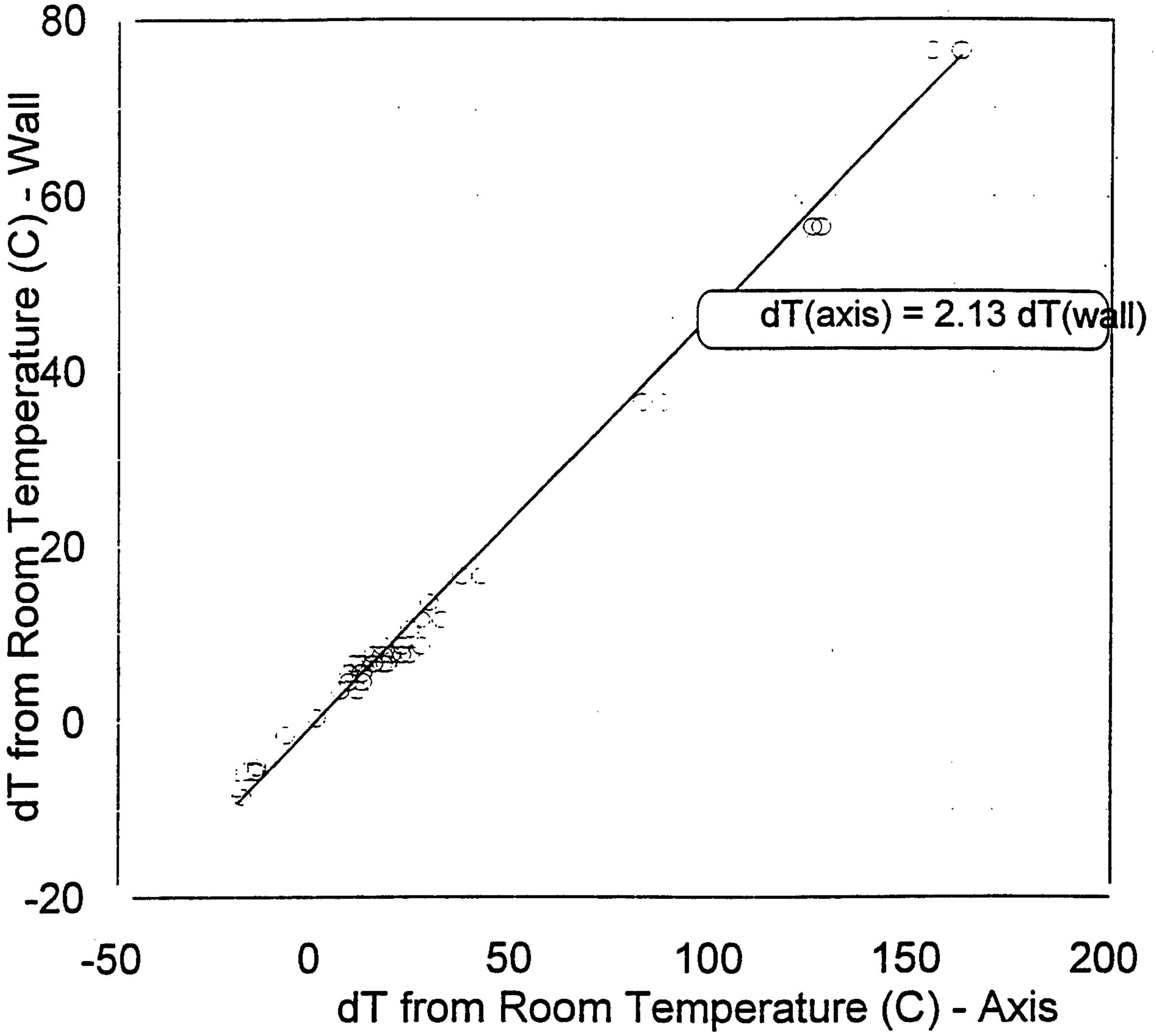

Fig. 7. Temperature correlation of wall and axial thermocouple readings.

The magnitude of changes to potential heat load, however, can now be predicted fairly well based on laboratory data obtained to date, and will be further refined based on future laboratory results. Once the AC has been equilibrated with a certain partial pressure of NH_3, the heat load due to a change in concentration and flow can be predicted fairly well from the product of the new flow rate and the incremental increase in partial pressure.

The laboratory experiments provide the information needed to adjust the flow rate and the concentration increments so as to maintain temperature control.

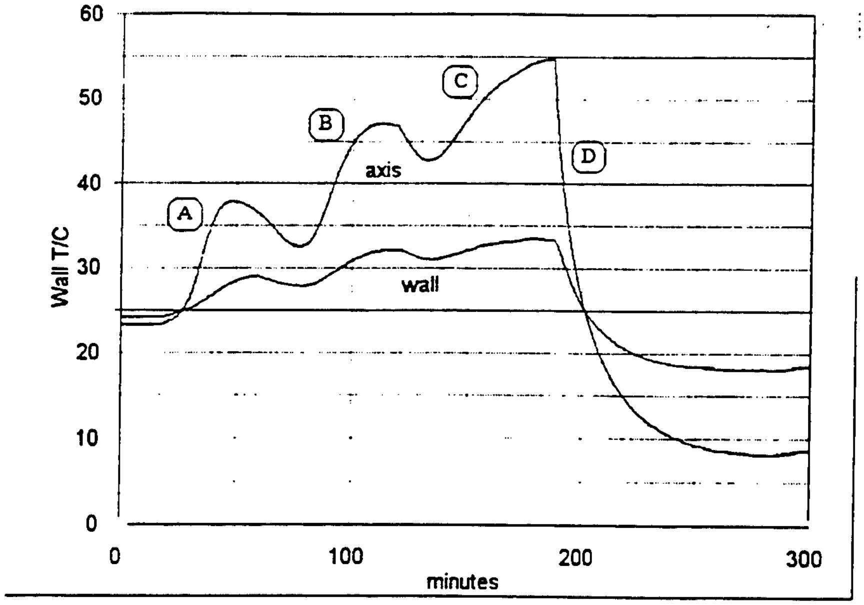

Fig. 8. **Temperature history for axis and wall thermocouples (position 4) in activated charcoal adsorption experiment of July 17,1997. Events indicated are (A) flow of 10% NH_3 at 4 std L/min; (B) flow of 50% NH_3 at 2 std L/min; (C) flow of 100% NH_3 at 1 std L/min; (D) helium purge at 7 std L/min.**

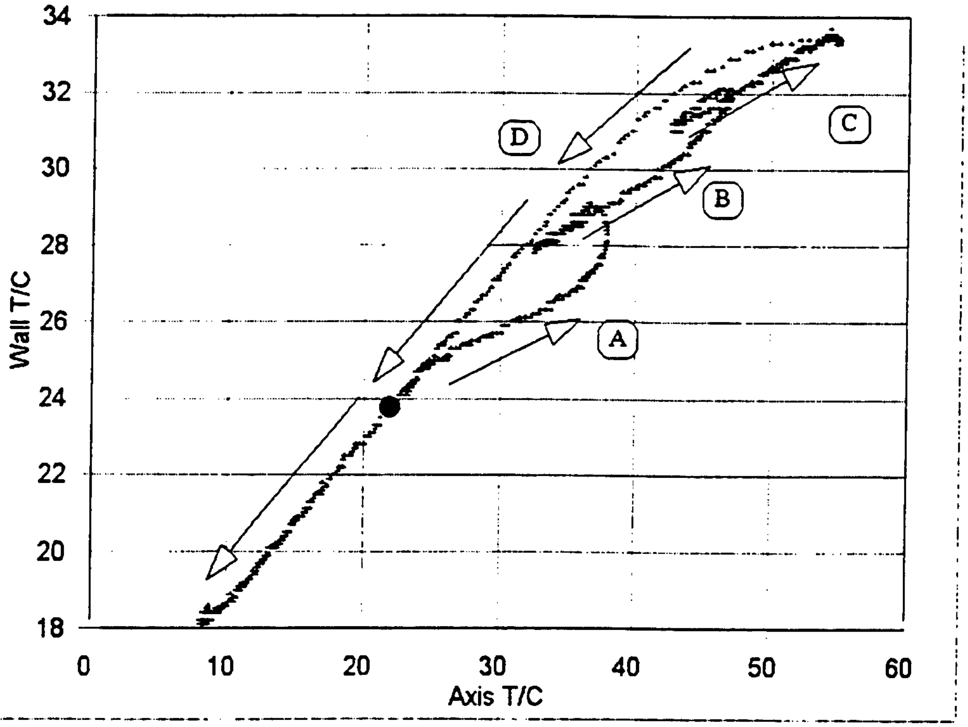

Fig. 9. **Axis-wall correlation. Beginning at ambient temperature (black dot), the temperatures are plotted every 10 s. Events are as described in Fig. 7.**

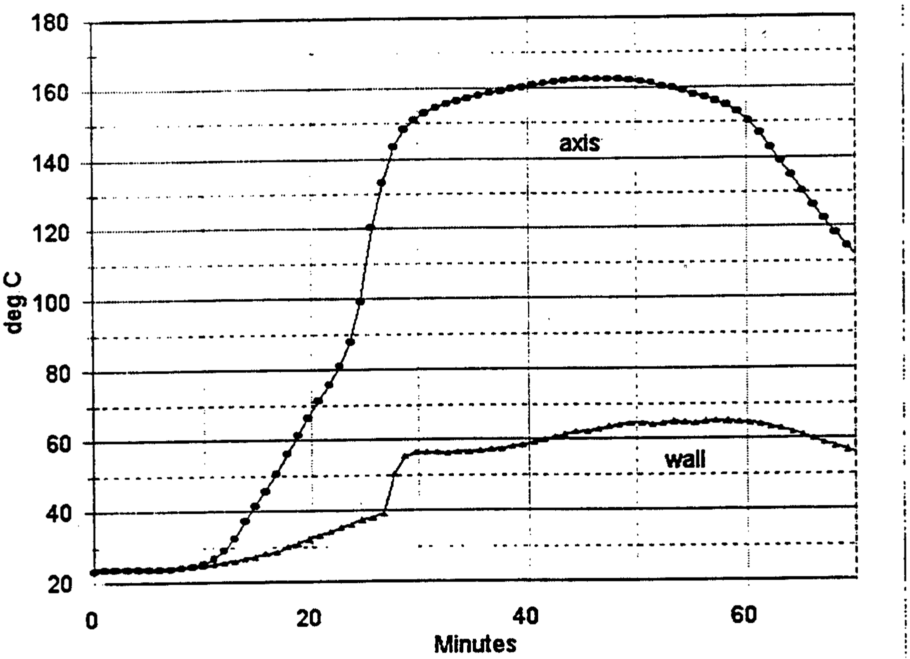

Fig.10. Wall and axis temperature/time series for position No.3 thermocouple (located in C_xF bed in 6-in. column, experiment performed 8/11/97). In this experiment which used a flow of 5% NH_3 at 10 std L/min, the C_xF/NH_3 denaturing reaction occurred to a significant degree.

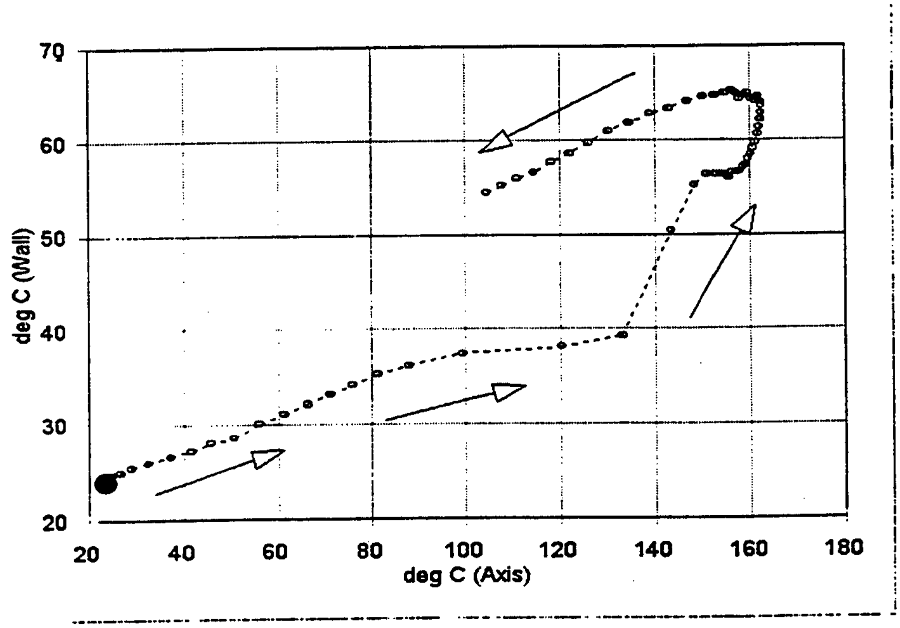

Fig.11. Wall/axis temperature correlation for the data plotted in Fig. 9. Temperature correlation points are plotted at 1-min intervals. The rapid temperature rise when the axis reached approximately 80 °C caused the axis temperature to deviate significantly from the correlation typical of more gradual changes.

9.3 NH_3 Overpressurization

Overpressurization of the MSRE OGS is an accident scenario that is considered in safety analyses. For purposes of analysis, mixtures of NH_3 and He will no be different from bottles of pure He except that the quantity of gas they contain will be lower. This is due to the fact that NH_3 is condensable . Also, the mixture, in order to remain as pure gas when compressed, is limited to having no more than a specific partial pressure of NH_3 in the bottle, regardless of the overall composition.

Commercial mixtures in full-size gas cylinders apparently come with this quantity of NH_3 set such that the dew point of the material inside is about 40 to 45°F, which translates to a mass of NH_3 of about 0.2 kg per bottle. The result is that the quantity of He, for a given mixture, will be limited to a value well below the He content of a standard He cylinder of the same size. The quantity will vary with the mixture (and we will be using a range of mixtures); however, for example, a 10% NH_3–He mixture will contain gas at a pressure of about 730 psig, as compared to over 2000 psig in a pure He cylinder. Pure NH_3 comes in cylinders containing primarily liquid NH_3 under its vapor pressure. The quantity of material in the cylinder is much larger than in the mixed-gas cases. Some typical commercial sizes are 5, 100, and 150 lb, although we can obtain, by special order, cylinders with any desired quantity of NH_3.

Regardless of the quantity of material present, NH_3 can maintain a pressure no greater than its vapor pressure at the coolest spot in the system. Vapor pressure measurements at 60, 70 and 80°F are 107, 128, and 153 psia, respectively, which are higher than desirable for the MSRE OGS. If NH_3 were allowed to freely expand into the OGS (or some subset thereof) from an unlimited source, it could increase the pressure to these levels, although evaporative cooling in the NH_3 bottle would limit the rate of pressure rise somewhat. The entire volume of the OGS could hold about 20 kg of NH_3 at its 60 °F vapor pressure of 107 psia (calculated from the non ideal gas density of NH_3), neglecting any reactions with F_2 that might take place.

Ammonia is expected to be introduced only via the hot-tap region in the vicinity of the ACB. Thus, the presence of activated carbon would act as a sink for most of the incoming NH_3. The adsorption capacity of activated carbon for NH_3 is, in the range of interest, approximately proportional to partial pressure of NH_3, with the adsorbed loading given by

$$m(NH_3\ ads) = 0.12\ \ m(C)\ \ P(NH_3,\ atm)$$

where m is the mass of the indicated material and P is pressure.[5]

For example, if the partial pressure of NH_3 over the carbon is 2 atm, 1 g of carbon can adsorb 0.24 g of NH_3. This neglects NH_3 in the vapor phase between granules, which would add only about 1% to the capacity being considered.

The ACB contains approximately 210 kg of carbon (at a bulk density of 0.44 g/cm^3 in 480 L), so the capacity of the ACB is approximately 25.2 kg of NH_3 (per atm NH_3 partial pressure). If a 100-lb bottle of NH_3 (45 kg) were attached and the contests dumped to the system, the generated pressure would be about 1.8 atm absolute (26.4 psia or 11.8 psig). Since we do not expect to need more than about 25 kg of NH_3, we do not intend to procure a full 100-lb cylinder in any case.

The above reasoning is based on the following conditions:

(1) The NH_3 can get to the ACB. This will not be completely correct if the ACB exit valve is closed, as the diffusion block of inert gas might prevent access to some fraction of the ACB.

(2) The ACB can dissipate the heat of adsorption. Adsorption releases heat, and at higher temperatures, the loading capacity of the activated carbon's is reduced. Thus, reaching an equilibrium room-temperature loading would not be an instantaneous process, but would proceed as rapidly as the heat could be dissipated.

(3) A compensating factor for item 2 is that NH_3 from the original tank is in liquid form and can evaporate no faster than heat can arrive to allow it to boil. Thus, the accidental dumping of a bottle of NH_3 would require considerably more time than the similar accidental dumping of a bottle of compressed gas.

9.4 Estimation of the Location of the C_XF front

Williams[1] has estimated the quantity of F_2 generated by radiolysis from the shutdown of the MSRE through the end of 1994. These estimates were based on experimental radiolysis rates combined with the calculated decay energy deposited in the MSRE fuel and flush salts. Two estimates were provided, one based on the best estimate of the G factor (the F_2 generated per unit radiation energy deposited), and the other using the maximum credible value of this G factor (see Table 9).

These values are used to generate a best estimate (designated as A in the accompanying table) and a maximum estimate (designated as B) for equivalent F_2 generation. Radiolysis rates displayed in that report were used to extrapolate to 1996, when the ACB was isolated from the rest of the off-gas system.

The quantity of F_2 in the MSRE off-gas inventory was recently reevaluated by our team based on initial pressures and compositions determined in recent RGRS operations, who arrived at a figure of 193 mol accounted for as gaseous F_2 and UF_6 (conversion of UF_4 in the fuel salt to UF_6 would consume 1 mol of F_2 per mol of UF_6 produced). Additionally, 7 mol for MoF_6 are also present as a minor constituent in the off-gas. The MoF_6 was presumably produced directly or indirectly from metallic molybdenum in the Hastelloy materials of construction, consuming 3 mol F_2 per mol of MoF_6 raised. This total F_2 accounted for outside the ACB is 200 mol.

Table 9. Estimates of upper bound to C_XF bed depth in MSRE ACB.

Estimate	A (best)	B (max)
G factor (molecules of F_2/100 eV)	0.02	0.045
F_2 generated as of 1994, mol	300	650
F_2 generated as of 1996, mol	316	690
F_2 accounted for , mol	200	200
F_2 unaccounted for, mol	116	490
C_XF bed depth, cm	88	373
C_XF bed depth, ft	2.9	12.2

The formula for the C_XF, based on our recent work on AC fluorination at room temperature is $C_{2.6}F$.[2] Using the known bulk density of 0.44 g/cm^3 for the activated charcoal (particles not change physical size on fluorination) a nominal 6-in. sched. 10 pipe (inner diameter of 15.8 cm) will contain 86 g of carbon per cm of bed.

Allocating the 200 mol of unaccounted for F_2 at the C:F ratio of 2.6:1, results in a maximum bed depth of (A) 88 cm and (B) 373 cm, as listed in the above table. These are both upper limits in that other plausible sinks of fluorine are not considered. For example, the presence of F_2 will produce some corrosion on the Hastelloy.

Evidence of solid deposits of UF_6 has been observed in RGRS operation in the form of sublimation. Other, non-volatile uranium fluorides (e.g., UF_5) are probably present in the OGS piping and drain tanks. The gas pressure in the drain tanks may also plausibly be higher than the value used in this estimate, and the F_2 concentration (at the source of F_2) may similarly be higher than the average observed to date. All these areas represent internal sinks for radiolytic F_2 which would reduce the quantity of "free" F_2 that could have migrated toward the ACB.

A second line of indirect evidence for location of the C_XF front comes from our laboratory work. Using gases emulating the F_2 / UF_6 / He mixture found recently in the MSRE, loading tests were done on AC columns in the laboratory. The loading of the F_2-UF_6 MSRE blend through columns filled with activated charcoal showed that the fluorine front moves ahead of the uranium front.

Based on our laboratory experience, the measured MSRE ACB uranium front (C_XF + intercalated uranium compounds) extending about 1 ft from the top of the ACB is probably followed by a C_XF front spanning a few feet (1 to 4 ft) further downstream, which is consistent with the estimated upper limit based on mass balance and radiolysis.

Based on both these lines of reasoning, the most probable location for the C_XF front is 2 to 4 ft beyond the uranium front. This estimation is based on the maximum quantity of F_2 generated by radiolysis minus the residual fluorine-containing gases remaining in the piping system (F_2, UF_6, and MoF_6).

9.5 Radiolytic Effects

Results of our laboratory tests clearly indicate that the fluorinated charcoal is quite stable toward gamma irradiation. Four samples irradiated to a total integrated doses of 2.3×10^8 R showed no significant changes as compared with the original material, and no detectable radiolytic species were generated. Accordingly, it can be assumed that no significant changes should be expected in the physico-chemical behavior of the fluorinated charcoal as a result of the self-irradiation at the MSRE ACB.

9.6 Effects on Chemical Conversion

The ultimate purpose of the denaturing is to render the material in and near the uranium-laden zone of the ACB chemically inert so as to allow safe physical removal and, ultimately, conversion of the uranium to a stable form for long-term storage. Although outside the scope of the denaturing activity, it is important that the stability of the denatured C_XF greatly facilitates subsequent processing.

Several batches of passivated fluorinated charcoal were initially heated to 600 °C while flowing helium, followed by F_2 burning, as part of the recovery and conversion process. During these tests the exhaust gases were analyzed by FTIR and the pressure was continuously monitored using pressure transducers. In each test, the passivated charcoal released NH_4F that condensed in a collecting trap with no other decomposition products. The heating and further fluorine burning of the passivated charcoal proceeded smoothly and uneventfully to completion, while the pressure remained stable at the preset values.

9.7 Flammability and Explosion Limits for NH_3 Gas

Ammonia burns in air with great difficulty to produce N_2 and H_2O; the flammable limits are 16 to 25 vol %.[10] Information in the literature[11] indicates that the ignition temperatures of ammonia - air mixtures lie above 900 °C, which is higher than most common gas mixtures thought of as flammable, and is consistent with qualitative observations that NH_3 is difficult to ignite.

Figure 12 shows the explosion limits of ternary mixtures of NH_3 / O_2 / N_2 .[11] Points on the explosive composition boundary are plotted.. Dashed lines depict mixtures of NH_3 with various O_2 / N_2 mixtures of fixed composition, the lowest one (that intersects the y-axis at 20%) approximates the composition of air.

The solid line labeled as "1:3 He-NH_3 dilution" depicts all possible mixtures of a 25% helium–75% ammonia mixture with air. All points on this line fall outside the explosive mixture boundary. On the assumption that helium and nitrogen have substantially the same diluent effect, one would conclude that no combination of these two mixtures can explode.

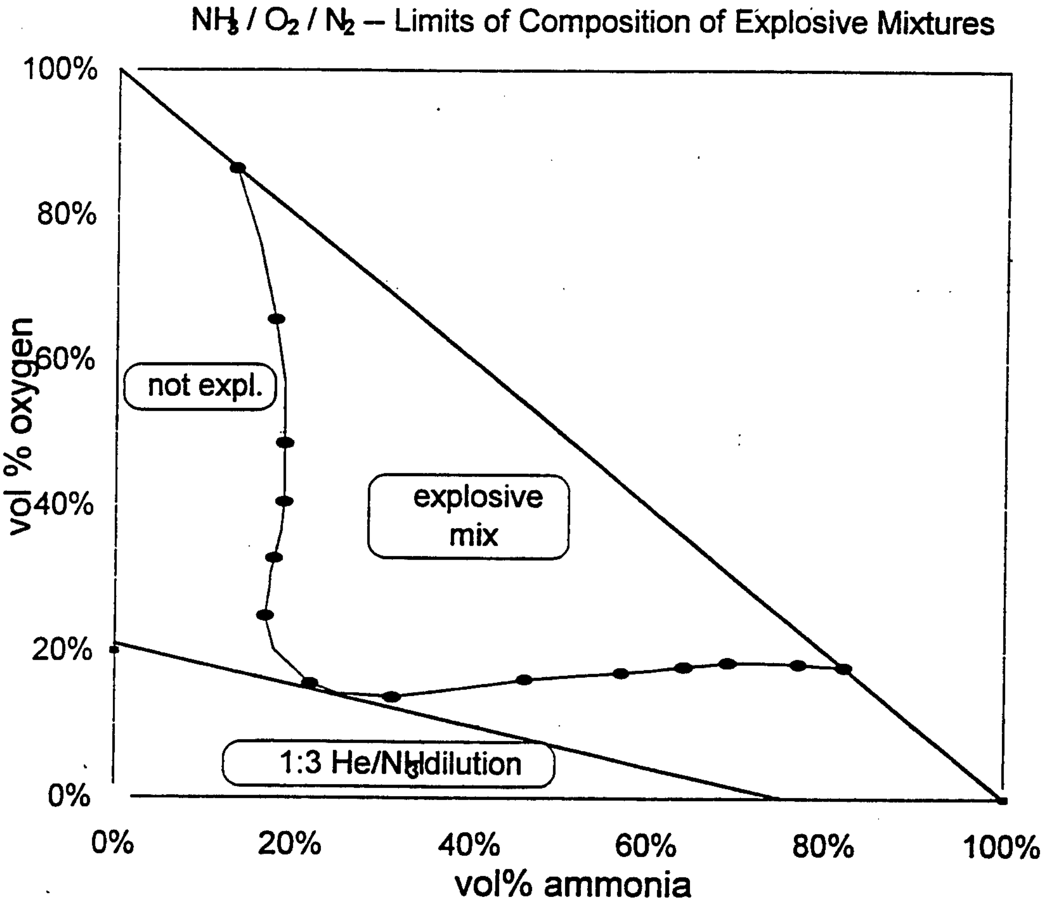

Fig. 12. Compositional limits for explosive mixtures of NH_3, O_2, and N_2.

In the ACB denaturing operation, we will likely utilize an even higher dilution (1:2 or 1:1) to ensure that the NH_3 exhausted during its final removal from the ACB cannot form even a transient explosive mixture as it enters the stack; however, the chance of ignition even in the absence of inert-gas dilution, seems remote.

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