An Overview of Radiolysis Studies for the Molten Salt Reactor Experiment (MSRE) Remediation Project

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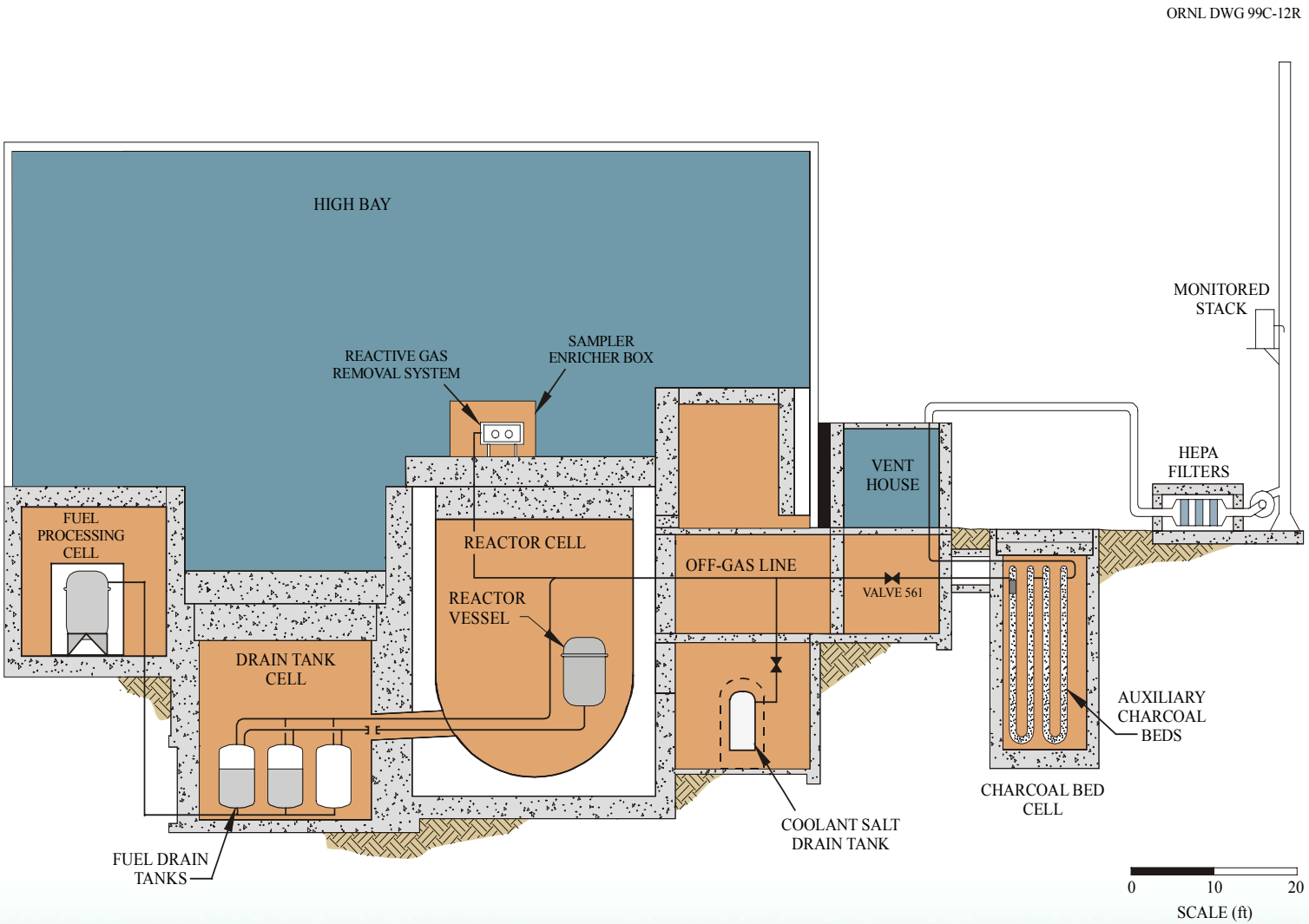
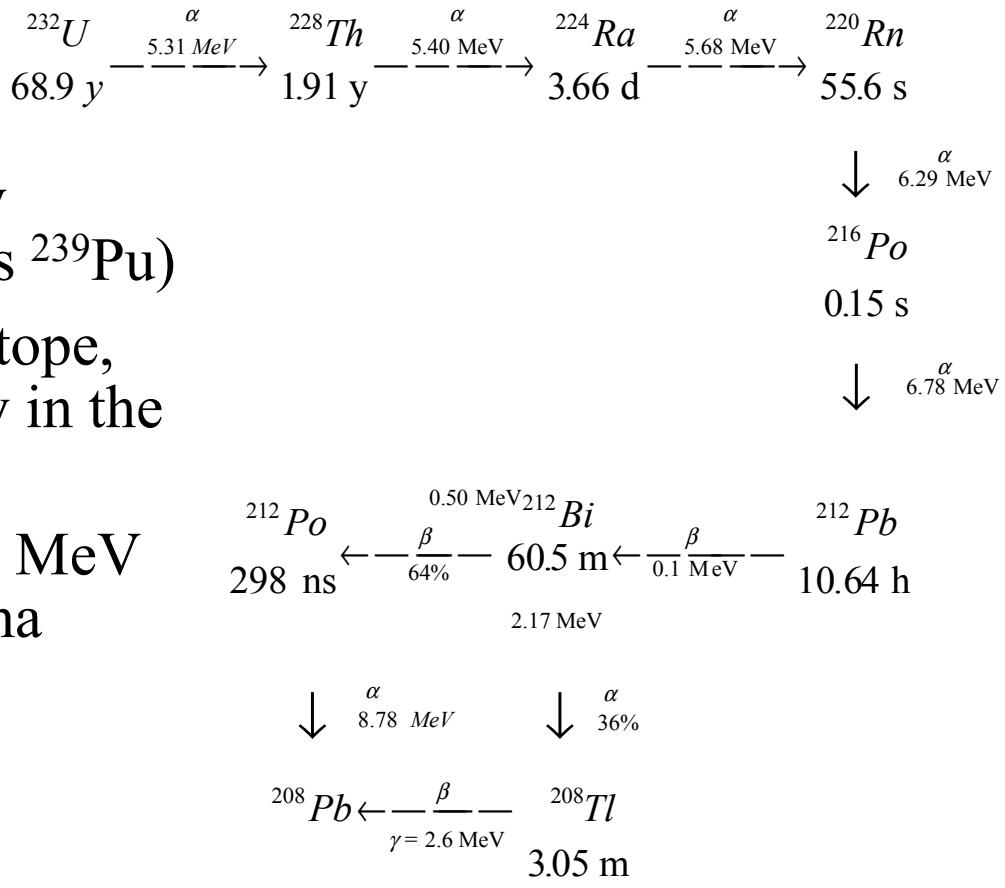
The MSRE was operated from 1965 to 1969 as a test-bed for molten salt reactor technology

- Fuel consisted of LiF-BeF_2-ZrF_4-UF_4
- Initially used ^{235}U, final fuel charge ^{233}U (~ 220 ppm ^{232}U)
- Reactor shut down in December 1969—fuel salt drained into two tanks where it solidified and has remained for more than 30 years
- In 1994 it was discovered that $^{233}UF_6$ had migrated throughout the reactor piping systems, leading to several very dangerous conditions
- A remediation program was initiated to address the hazards and to remove and store the ^{233}U

Simplified overview of the MSRE system



Characteristics of ^{233}U



- Relatively high alpha activity (~5000 times ^{235}U, ~0.2 times ^{239}Pu)
- ^{233}U contains an impurity isotope, ^{232}U (concentrations typically in the range 10-1500 ppm)
- A daughter of ^{232}U (^{208}Tl, 2.6 MeV gamma) results in high gamma radiation fields

During the remediation project, a number of needed radiolysis studies were identified

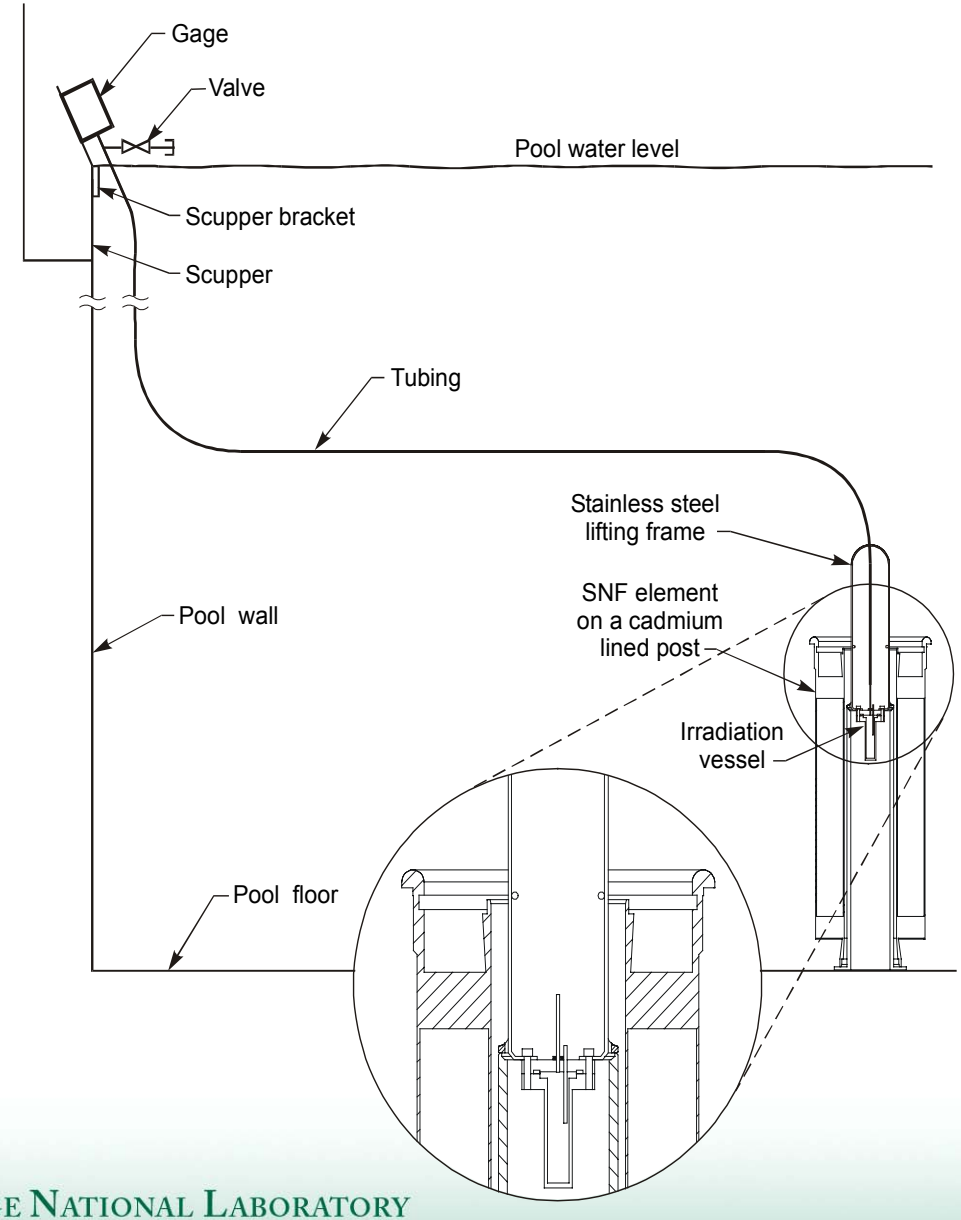
Material Studied	Reason
MSRE fuel salt	Determine cause of UF_6 production
Uranium-laden charcoal	Evaluate potential for production of explosive C_xF compounds
$2NaF \bullet UF_6$	Determine amount of pressurization that could be experienced in storage
Uranium oxides containing residual fluorides and water	Evaluate radiolytic effects for long-term storage of these materials

Gamma radiation sources

ORNL ^{60}Co irradiator
~10^5 rad/h

High Flux Isotope Reactor
spent nuclear fuel element
~10^7– 10^8 rad/h

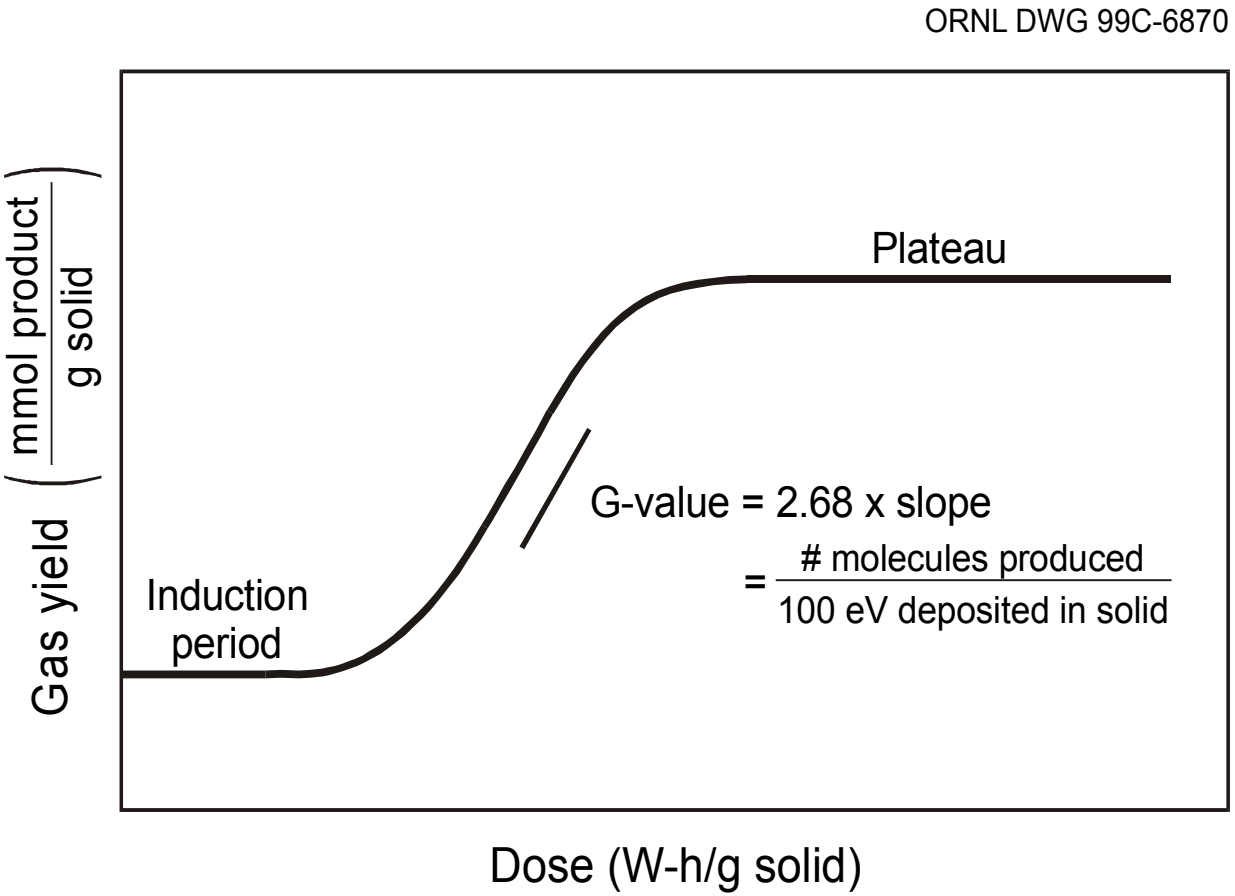
ORNL DWG 99C-487



HFIR SNF irradiation configuration

Typical gas-yield curve for radiolysis experiments

Not all characteristics may be seen



MSRE Fuel Salt

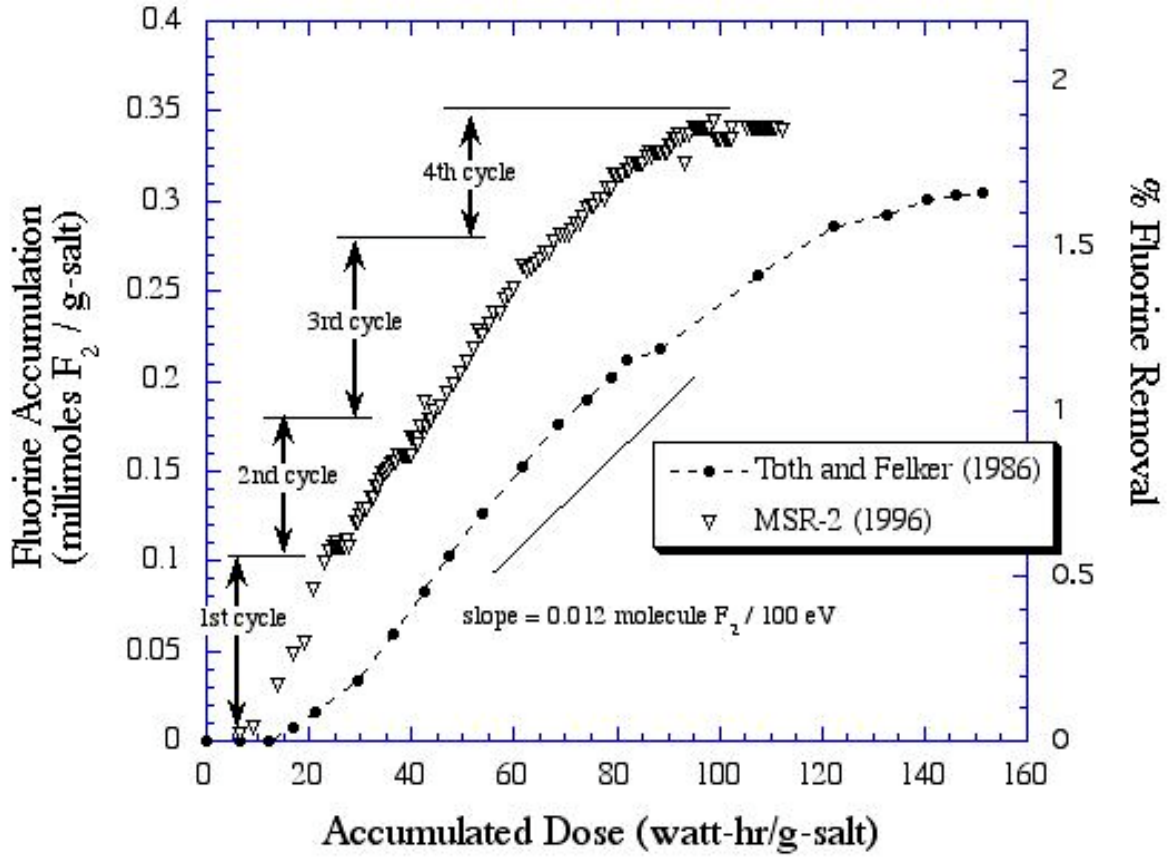
- $LiF\text{-}BeF_2\text{-}ZrF_4\text{-}^{238}UF_4$ (64.5, 30.3, 5.0, 0.13 mol%) irradiated in HFIR SNF elements
- Pressure monitoring and gas sampling used to quantify radiolytic yields and gas composition
- Measured $G_(F_2) = 0.012–0.02$ molecules F_2/100 eV, example reactions:

$$LiF + (\longrightarrow Li\cdot + F\cdot$$

$$F\cdot + F\cdot \longrightarrow F_2$$

- Induction period observed (i.e., no gas was produced) and maximum damage limit (~2%) demonstrated at high total dose
- Periodic heating of the salt, combined with the presence of F_2 produced the volatile UF_6 at MSRE: $UF_4 + F_2 \longrightarrow UF_6$

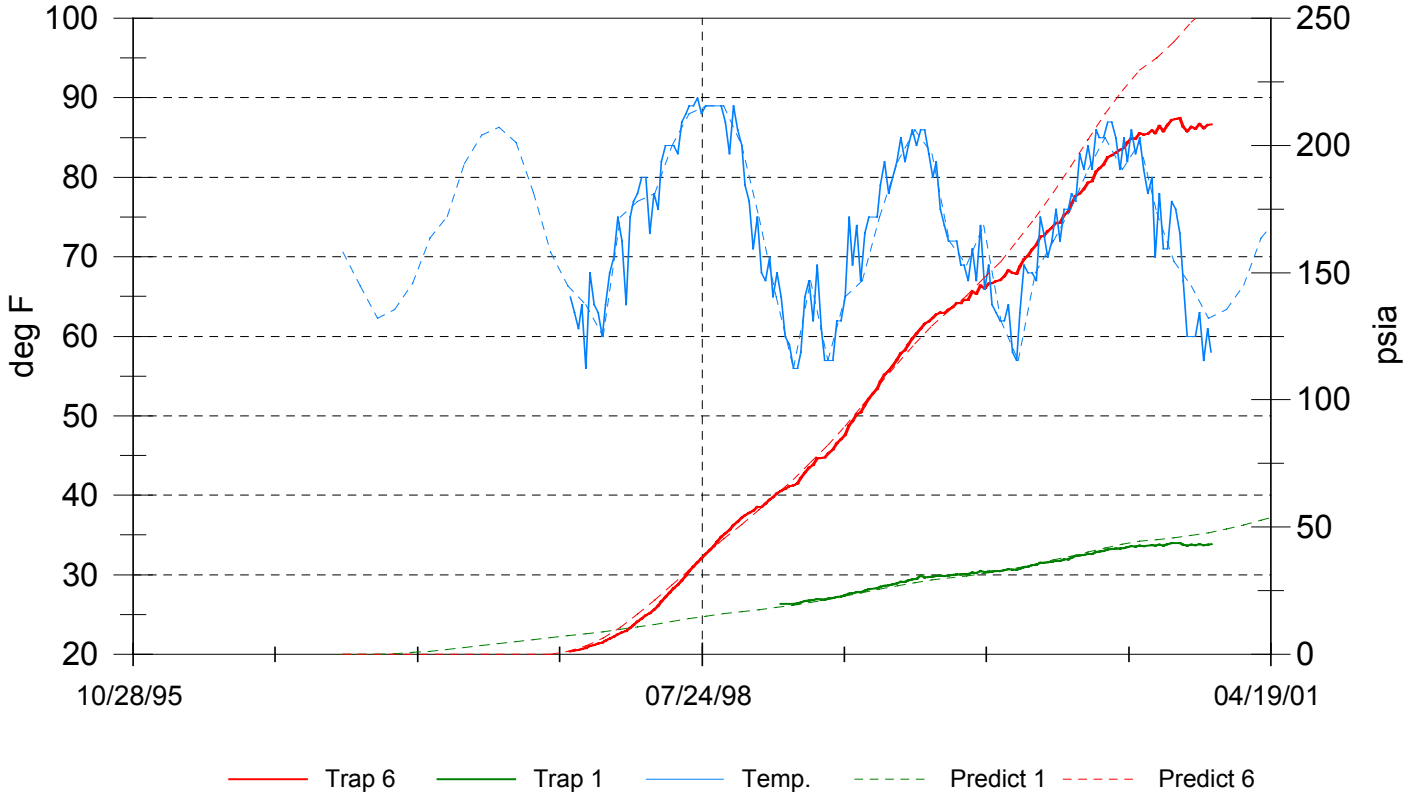
Gamma radiolysis of MSRE surrogate fuel salt (LiF-BeF_2-ZrF_4-$^{238}UF_4$) in HFIR SNF elements



$2NaF \cdot UF_6$ complex

- ^{233}U sorbed on NaF pellets forming $2NaF \cdot UF_6$
- Containers of $2NaF \cdot UF_6$ referred to as "NaF traps"
- Two of the traps have been instrumented with pressure transducers
- Pressure rise observed for these traps
  - $UF_6 + (",\$,() \longrightarrow UF_5 + 1/2F_2$
  - uranium may be reduced further
- Estimated G-values
  - $G_{"}(F_2) \sim 0.44$ molecules F_2/100 eV
  - $G_{\$,(}(F_2) \sim 0.02$ molecules F_2/100 eV (based on work with other fluoride salts, i.e., LiF, BeF_2)

Pressure monitoring data for two NaF traps



Pressure in NaF/UF_6 traps in Bldg 3019, ORNL

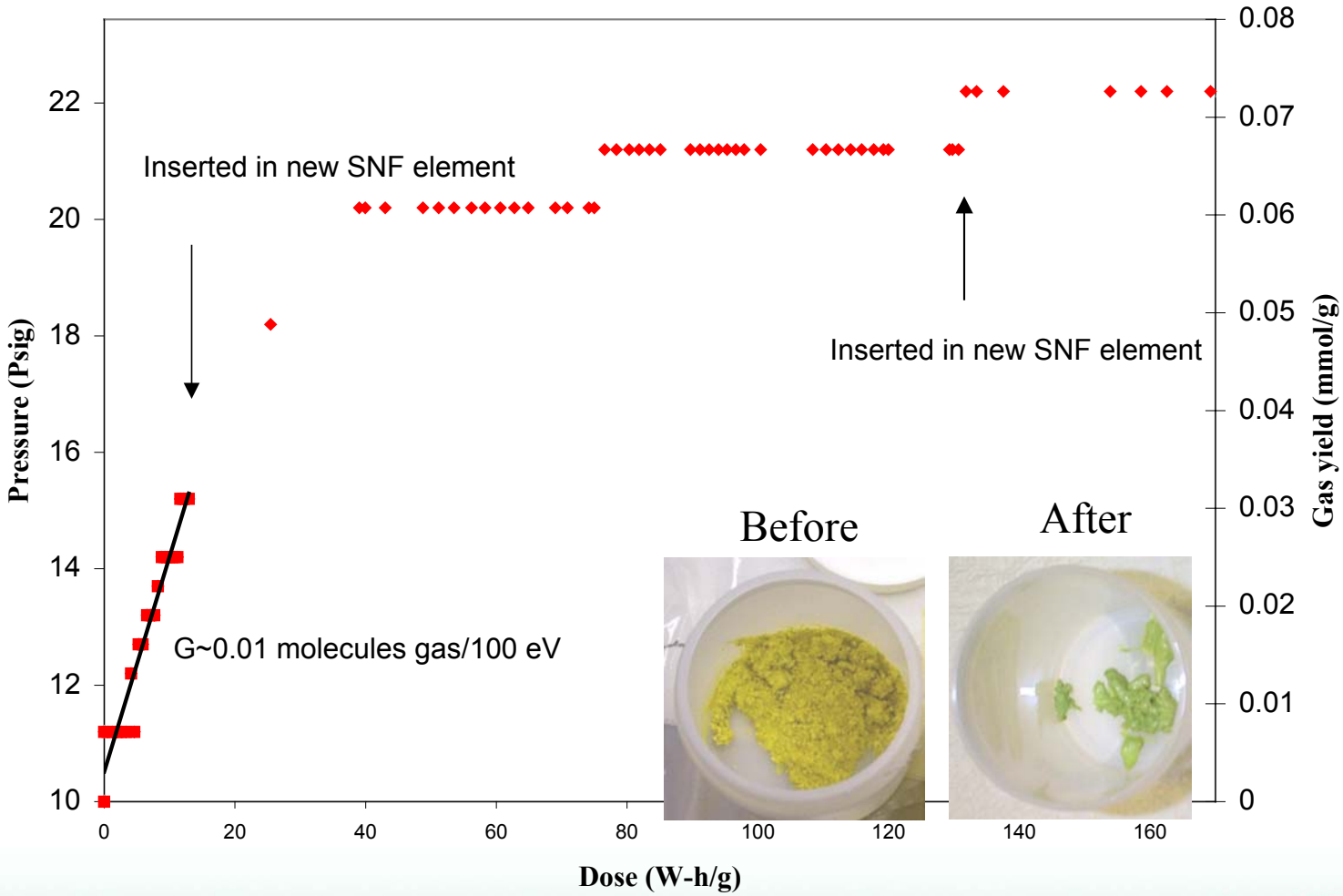
Radiolysis of NH_3-treated $C_{2.6}F$

- Fluorinated charcoal in the charcoal bed at MSRE treated with NH_3 to remove explosive potential and forming NH_4F
- Radiolysis of NH_4F can lead to reformation of C_xF
- ^{60}Co irradiation resulted in $G_{(}$(gas) ~ 0.24 molecules/100 eV
- Gas analyses of the treated charcoal bed revealed products consistent with the reported results for the decomposition of NH_4F (i.e., production of H_2 and N_2). The material in the charcoal bed was irradiated by both alpha and gamma radiation.
- Results of these analyses used to establish the frequency of retreatment of the charcoal bed with NH_3

Gamma radiolysis of $UO_2F_2 \cdot xH_2O$

- $UO_2F_2 \cdot xH_2O$ is an intermediate compound formed in the conversion of UF_6 to U_3O_8
- $UO_2F_2 \cdot xH_2O$ irradiated in both the ^{60}Co source and in HFIR SNF elements (x varied from 0.4 to 1.7)
- Color change, CO_2/O_2 production, and U(IV) increase provide evidence that gamma radiation releases oxygen from the UO_2F_2 matrix: $UO_2F_2 + \gamma \rightarrow UOF_2 + O$
- Oxygen radicals react with other oxygen radicals or carbon impurities, producing O_2 and CO_2
- $G(O_2)$ = 0.007–0.03 molecules O_2/100 eV
- A steady state was reached in HFIR SNF elements providing a measure of the damage limit to $UO_2F_2 \cdot xH_2O$
- Damage measured by amount of U(IV): 7–9 wt% at 10^8 rad/h

HFIR SNF element radiolysis of $UO_2F_2 \cdot 0.4\ H_2O$ (loaded in helium, dose rate 10^7–10^8 rad/h)



Summary of results for gamma radiolysis experiments for uranium oxides with sorbed water

- Samples of U_3O_8 and $UO_3 \cdot xH_2O$ with water contents up to 10 wt% were irradiated
- In general, little or no pressure increase observed
- Sample pressure decreased for some experiments
- Little hydrogen produced
- Oxygen depleted for many samples

Follow-on alpha radiolysis experiments on uranium oxides with water and fluoride impurities are being conducted

- Samples are doped with ^{244}Cm
- Samples are designed for long-term pressure monitoring and for periodic gas sampling

Summary

- A number of radiolysis experiments have been conducted in support of the MSRE remediation program

- Results from these studies were used to establish criteria for the intermediate and long-term storage of materials removed from the MSRE