RADIOLYTIC F_2 PRODUCTION FROM MSR RELEVANT FLUORIDE SALTS

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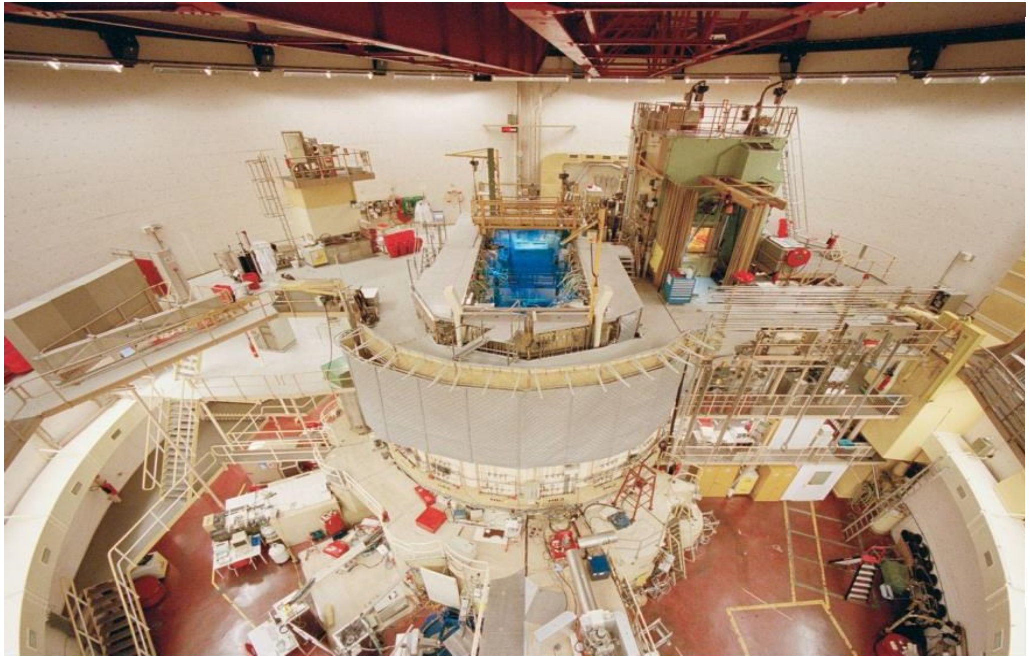
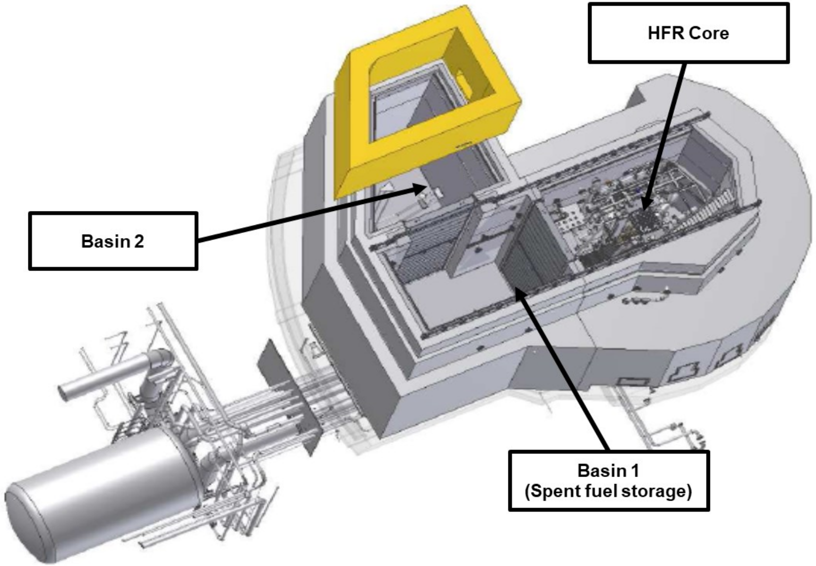
Prepared for:

YMSR Conference, Politecnico di Milano, Lecco campus, June 6 - June 8, 2022

High Flux Reactor (HFR), Petten - NL

Operator: NRG
Power: 45 MW thermal
Applications: Isotope production; Irradiation services; R&D (fuels and materials)
Operation: 30/31 operation days per irradiation cycle; 9 cycles per year





SAGA Experiment – Background & Aim

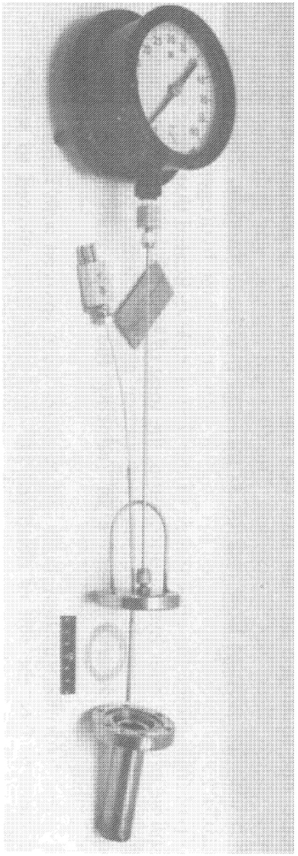
Background:

- Molten Salt Reactor Experiment (MSRE) programme at ORNL - appreciable quantities of fluorine gas production from fluoride salts [1][2].
- Radiolytic production of corrosive fluorine (F_2) gas - operational and long-term safety risk w.r.t. MSR chemical processes.

Objectives/Aims:

NRG has conducted the first phase of the **SA**lt **GA**mma **(SAGA)** experimental project. The main objectives of the SAGA experimental project:

- Determine F_2 production efficiencies (G-values) and saturation levels for several MSR relevant fluoride (and chloride!?) salts
- Quantify suppression of F_2 production with increasing grain size
- Determine rates of F_2 recombination as a function of temperature

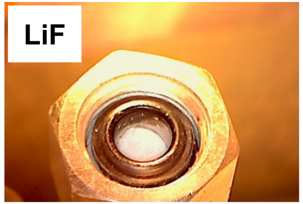


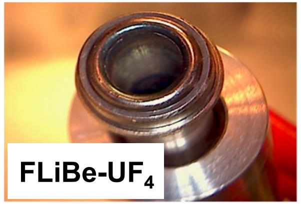
ORNL MSRE Salt gamma irradiation experiment device
(Toth & Felker, 1990) [3]

Salt Samples – Details & Description

- Pre-fluorinated Monel-400 (Ni-Cu) capsules
- Cleaning and rinsing with 0.5% HF solution (elimination of potential oxide layers)
- Fluorination/passivation of capsules at 150 ºC prior to salt loading and capsule sealing
- Inner (1st containment) capsules placed into outer capsule (2nd containment) containing HTC NI-600RP activated catalyst
- Inner capsules connected to pressure sensors via 50 cm minitubes

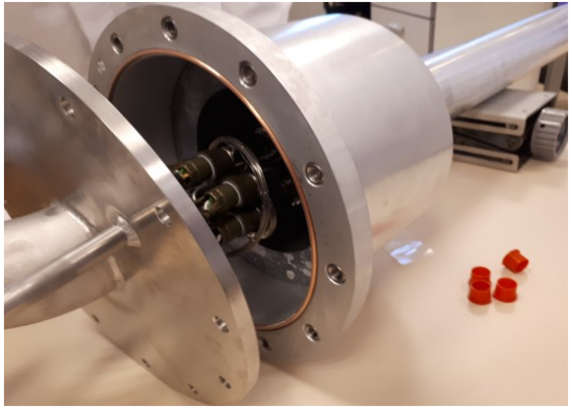
Capsule	Sample	Physical form	Mass (g)
1	BeF_2	Fine powder	6.0 ± 0.1
2	LiF	Fine powder	8.5 ± 0.1
3	He (empty reference)		
4	71.7LiF-16BeF_2-12.3UF_4	Fine powder	13.9 ± 0.1
5	UF_4	Fine powder	14.1 ± 0.1
6	ThF_4	Fine powder	12.4 ± 0.1

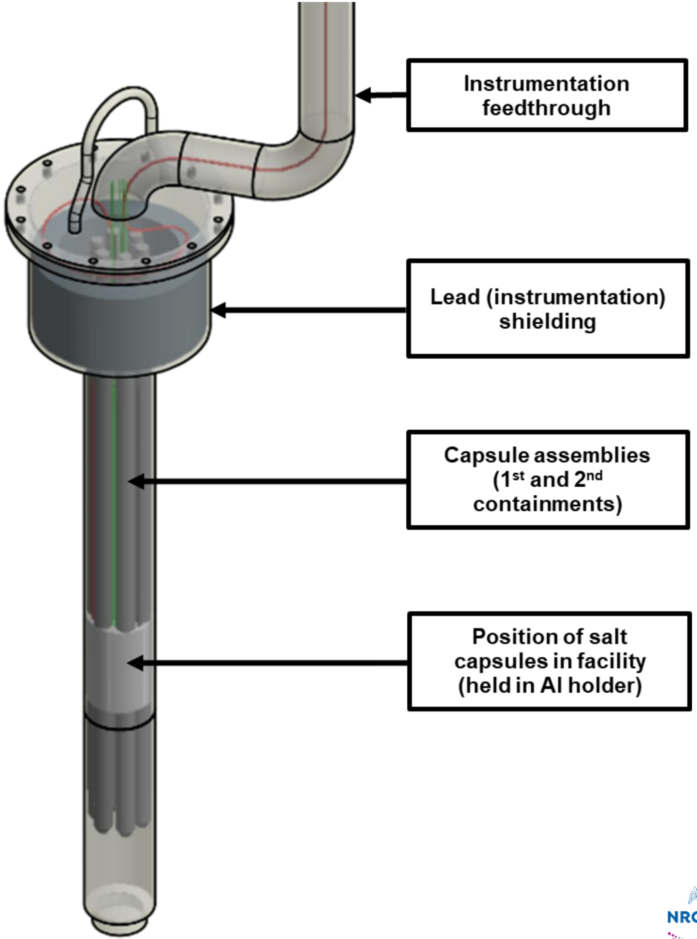




SAGA facility – Assembly

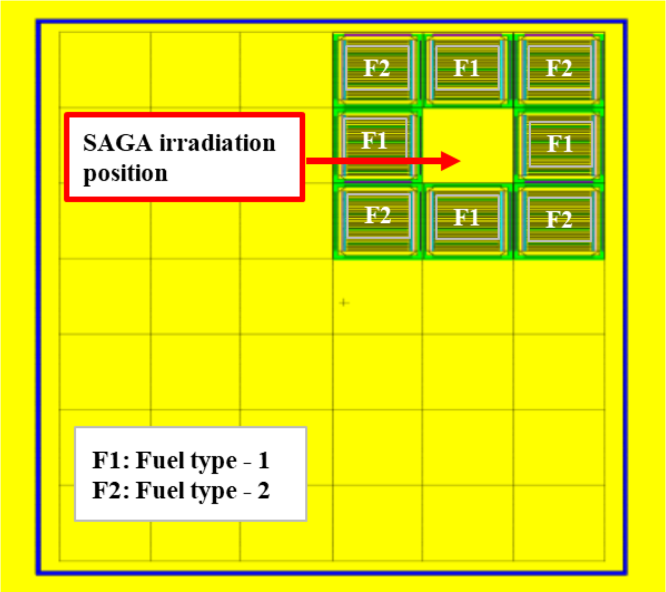
- 6 capsules (1st + 2nd containment) placed in a larger facility providing the 3rd containment
- Lead instrumentation shielding at the head of SAGA facility
- Sample capsules arranged in a cylindrical array and held in position by an aluminium holder

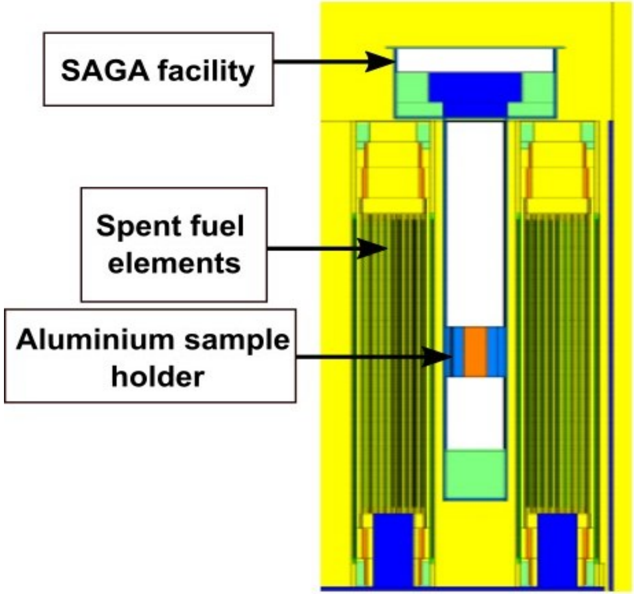


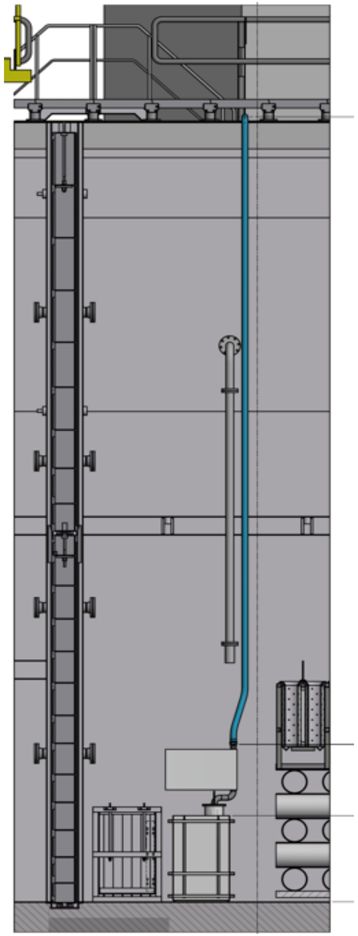


HFR Spent Fuel – Gamma Source

- SAGA facility containing the salt samples irradiated in a central position surrounded by 8 spent fuel elements (FEs) in the HFR spent fuel rack (SFR)
- Maximize dose → Fuel elements with highest burn-up and shortest cooling time
- Type-1 (F1) FE coming from the most recent HFR cycle, Type-2 (F2) FE from the previous HFR cycle.







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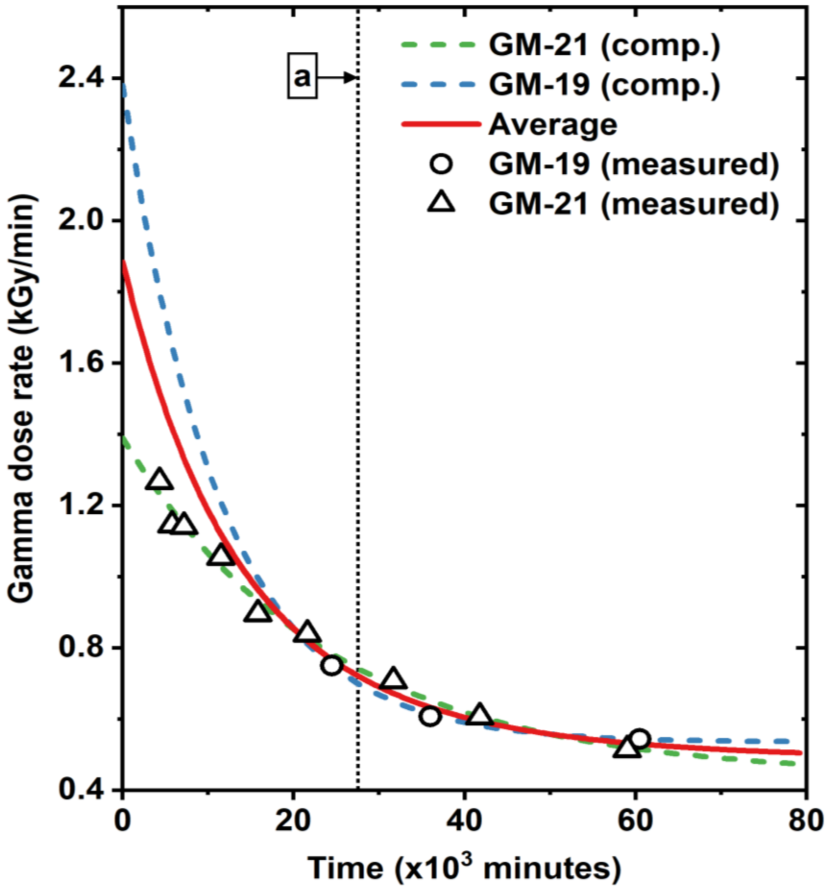
Quantification of gamma field

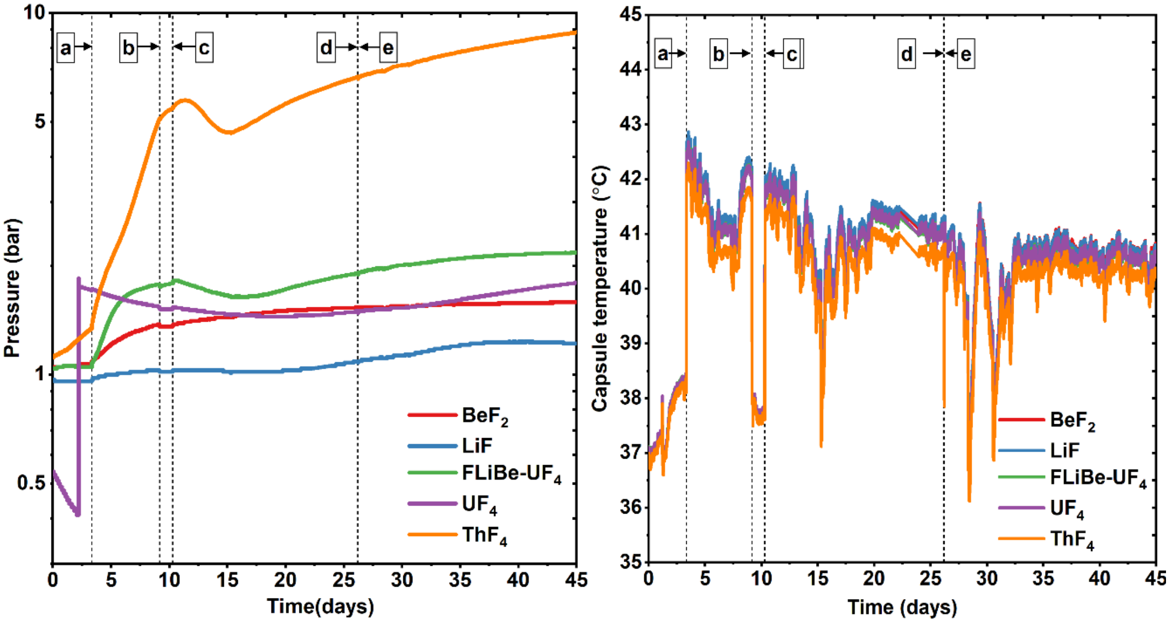
- ➢ Gamma dose rate measurements:
  - Air-filled gamma ionization chamber
  - Measurement along the height of the SAGA irradiation position
- ➢ Two dose rate measurement campaigns:
  - In 2019 (GM-19) – 3 measurements. <u>Poor statistics!</u>
  - In 2021 (GM-21) – 9 measurements. Better statistics.
- ➢ Dose rate to samples → integration over sample height → time evolved dose rate profile/curves
- ➢ GM-19 and GM-21 curves → curve fitting → linear interpolation to produce average decay curve (max. uncertainty 3.5%)



*Point **a** – start of SAGA irradiation*

Pressure & Temperature measurements

- Slight pressure increase before start of irradiation – low level gamma field
- UF_4 ‘anomalous’ pressure profile (Not assessed further.
- First removal period (b – c) resulted in a F_2 pressure decrease and recovery
- Capsule irradiation temperature range, 40 – 42 ºC. Salt temperatures predicted to be < 9 ºC higher than capsule temperature - significant recombination not expected!



- Data recording resolution – 1 minutes
- SAGA irradiation interrupted on two occasions for gamma dose measurements; Points b – c and d – e.

*Point **a** – start of SAGA irradiation*
*Point **b** – SAGA removal*
*Point **c** –SAGA insertion*
*Point **d** – SAGA removal*
*Point **e** – SAGA insertion*

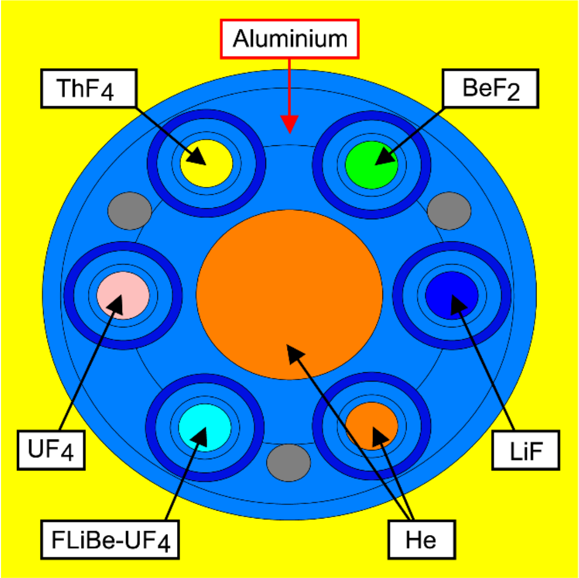
Data processing – F_2 production & dose absorbed

Pressure to F_2 production:

- Ideal gas law applied to – (1) Normalize pressure deviations due to temperatures by dividing recorded pressures by recorded temperatures for each salt capsule, and (2) obtain F_2 quantity in moles

Dose absorbed by salt (absorption factors):

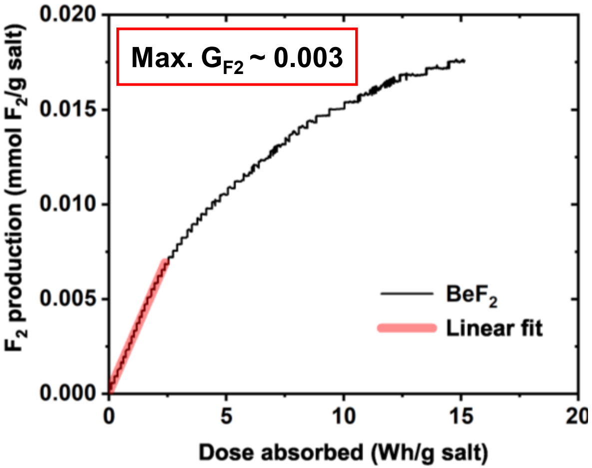
- FEs gamma emission spectrum - MCNP and FISPACT depletion calculations.
- Emission spectrum → MCNP simulation of sample array → dose rates in the salts and He/air
- Dose absorption factor ~ $\frac{\text{Computed salt dose rate}}{\text{Air (reference) dose rate}}$

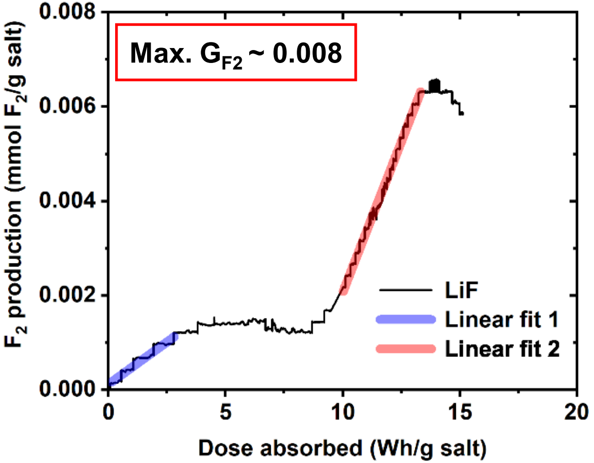


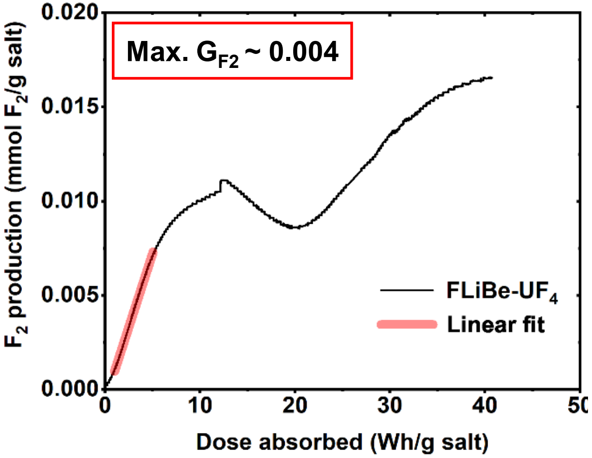
Capsule	Sample	Dose absorption factor
1	BeF_2	0.93
2	LiF	0.93
3	*He (empty reference)*	**1.00**
4	71.7LiF-16BeF_2-12.3UF_4	2.50
5	UF_4	3.43
6	ThF_4	3.43

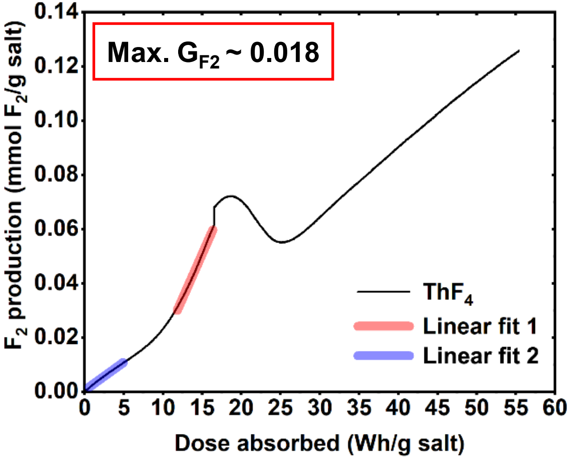
Results - Radiolytic F_2 production

- F_2 production efficiency (*in molecules F_2 per 100 eV*) or <u>G-value</u>, is obtained by measuring the slope of the F_2 production vs dose absorbed plot.
- SAGA irradiation interruption → marked effect on F_2 production curves (except BeF_2) - does not invalidate max. G-values.
- Minimal to no induction period noted
- No production-recombination equilibria (saturation) observed









Results - Radiolytic F_2 production (cont.)

	This work	Similar work/Literature			
Salt type	G-Value [molecules F_2/100 eV]	G-Value [molecules F_2/100 eV]	Salt type (form)	Radiation source (dose rate)	Conducted by
BeF_2	~ 0.008				
LiF	~ 0.003	0	LiF (?)	Soft X-rays (0.3 kGy/hr)	MSRE, ORNL [4]
71.7LiF-16BeF_2-12.3UF_4 (FLiBe-UF_4)	~ 0.004	0.005 – 0.031	65LiF-29BeF_2-5ZrF_4-0.66UF_4 (solid plug)	Post-irradiation decay (varying)	MSRE, ORNL [4]
		0.045	65LiF-29BeF_2-5ZrF_4-0.66UF_4 (solid plug)	^{60}Co gamma source (6.3 kGy/hr)	MSRE, ORNL [2]
		0.012	65LiF-29BeF_2-5ZrF_4-0.66UF_4 (powder)	HFIR Spent fuel (175 kGy/hr)	MSRE, ORNL [5]
		0.006	71.7LiF-16BeF_2-12ThF_4-0.3UF_4 (solid)	In-core test (??)	NRCKI [6]
		0.01	66LiF-33BeF_2-1UF_4 (solid)	In-core test (??)	NRCKI [6]
		0.005– 0.04	65LiF-29BeF_2-5ZrF_4-0.66UF_4 (fine powder, < 50 μm)	Soft X-rays (1.26 kGy/hr)	MSRE, ORNL [4]
ThF_4	~ 0.018	0.003 – 0.008	ThF_4 (?)	Soft X-rays (2.9 kGy/hr)	MSRE, ORNL [4]

Conclusions & Recommendations

Conclusions:

- SAGA-01 successfully executed by NRG
- Radiolytic F_2 production efficiencies (G-values) for tested MSR salt matrices appears to be within the bounds of expectation

Recommendations:

A follow-up SAGA irradiation campaign (SAGA-02) to be conducted in order to verify and refine the G-values reported for these fluoride salts and the factors which influence it. The following changes are made to the experiment to improve measurements and scope:

- SAGA facility should not be disturbed during the irradiation period
- Salt sample particle size characterization to be conducted
- The irradiation period will be extended in order to verify the existence of equilibria between production and adsorption/recombination
- Inclusion of one or more chloride salts will be added to the experiment to obtain information on chloride radiolysis (NaCl, KCl and/or a heavy chloride)

Acknowledgements

NRG

<u>P.R. Hania</u>

D.A. Boomstra

D.J. Rossouw

F.F. Charpin-Jacobs

CVŘ Centrum výzkumu Řež

J. Uhlir

M. Marecek

Freie Universität Berlin

H. Beckers

S. Riedel

This work is supported by the Dutch Ministry of Economic Affairs

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[1] M. Rosenthal, R. Briggs, and P. Kasten, “Molten-salt reactor program semiannual progress report for period ending February 28, 1969.” Tech. Rep. ORNL-4396. (Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States).

[2] P. Haubenreich, “Fluorine production and recombination in frozen msr salts after reactor operation.” Tech. Rep. ORNL TM-3144 (Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States), 1970.

[3] L. Toth and L. Felker, “Fluorine generation by gamma radiolysis of a fluoride salt mixture,” Radiation Effects and Defects in Solids 112, 201–210 (1990).

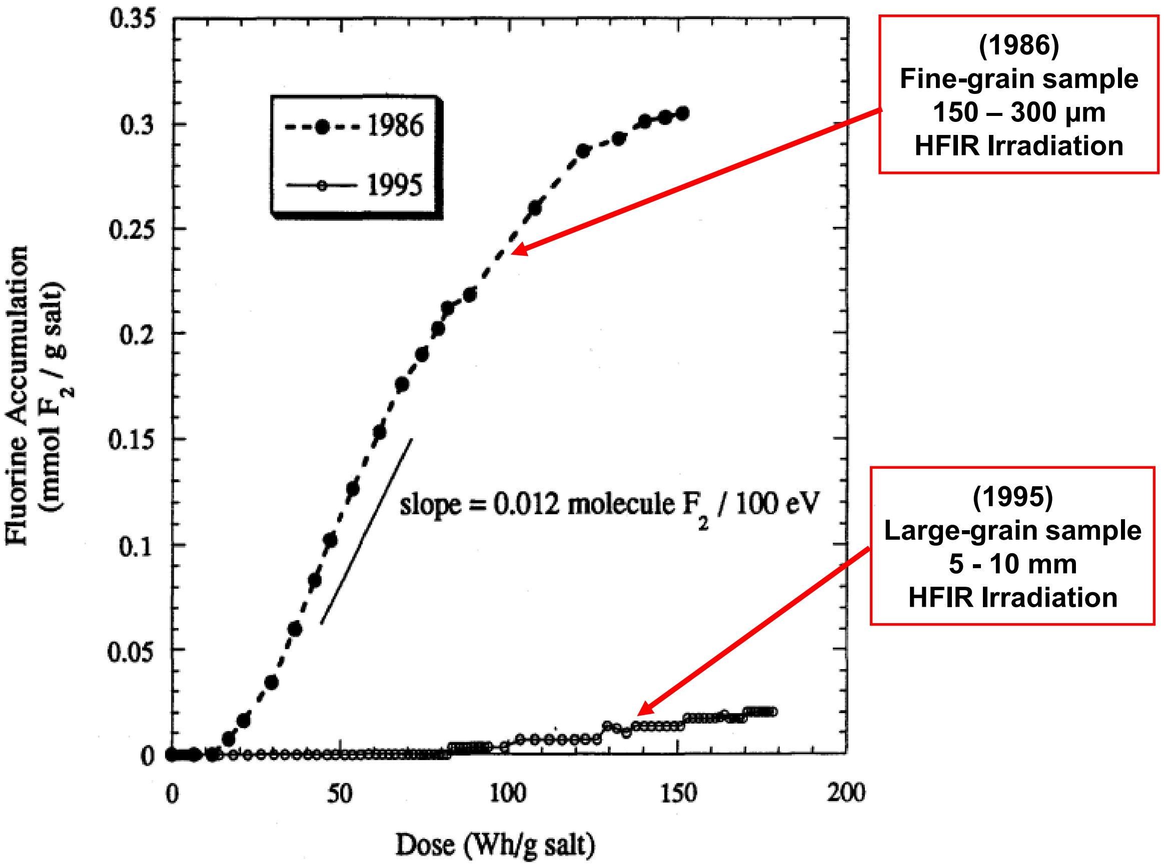
[4] R. Briggs, “Molten-salt reactor program semiannual progress report for period ending july 31, 1964,” Tech. Rep. Oak Ridge National Lab., Tenn., 1964.

[5] D. Williams, G. D. Cul, and L. Toth, “A descriptive model of the molten salt reactor experiment after shutdown: Review of fy 1995 progress,” 1996.

[6] V. Ignatiev, “Molten salts characteristics under irradiation in fission related systems,” IAEA TECDOC SERIES, 70 (2020).

Appendix A: Effect of salt size on F_2 production [5]

- Comparison of 1986 and 1995 HFIR irradiations
- Same salt type (i.e. MSRE salt) – difference particle size
- Postulated that large salt particles experience higher heating which may drive the recombination back-reaction



Appendix B: ORNL ^{60}Co gamma irradiation experiment [2]