Research on Molten Fluorides as High Temperature Heat Transfer Agents

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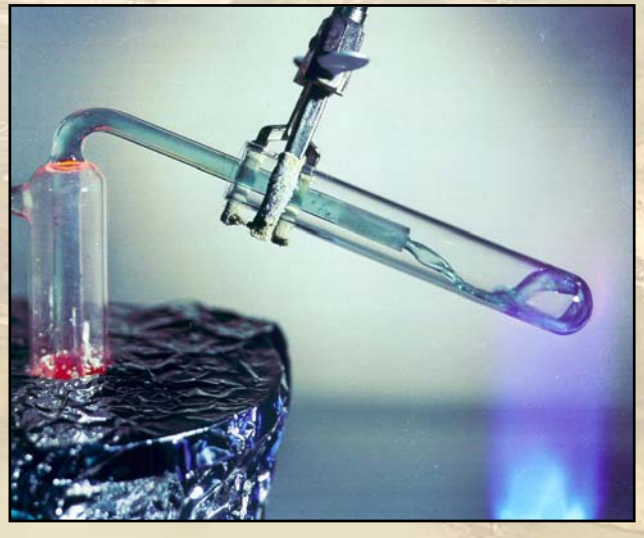

GLOBAL 2003

Session: "Coolant/Material Interactions in Advanced Reactor Systems"

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OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

Talk Outline

1. Background

2. Experimental System

3. Experimental Results

4. Recommendations

Primary Motivation

High Temperature (>800 °C) Motivation:

More attractive Power Generation and Hydrogen Production

Two Salt Coolant Options have been Identified:

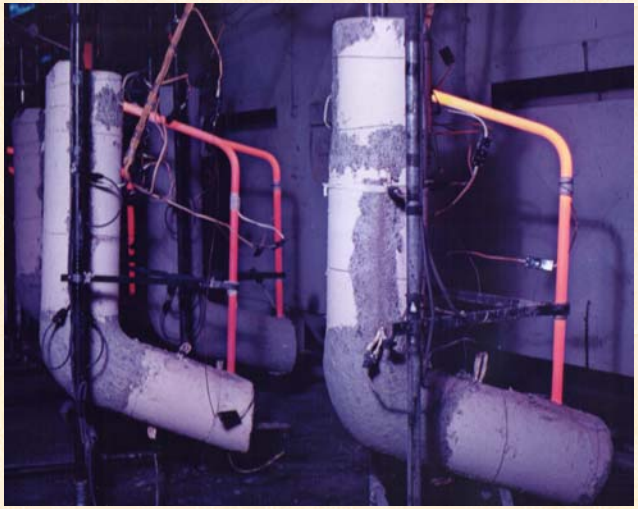
- *Primary coolant for direct cooling of solid fueled Advanced High Temperature Reactor (AHTR)*
- *Secondary coolant for transport of heat to remote Hydrogen Plant*

<u>ORNL LDRD Project was conducted to explore corrosion of high temperature salt coolants</u>

ORNL Explored Fluid-fueled Reactors

	Aircraft Reactor Experiment (1954)	Molten Salt Reactor Experiment (1965-1970)	Molten Salt Breeder Reactor Design (1970-1976)
Length of Operation	1000 h cycle (thermal engine)	Equiv. to 1.5 y at full power	4 year graphite replacement cycle
Peak Temp.	860 C	650 C	705 C
Solid Moderator	BeO	Graphite	Graphite
Fuel Composition (mol %)	$NaF-ZrF_4-UF_4$ (53-41-6)	$^7LiF-BeF_2-ZrF_4-UF_4$ (65-30-5-0.1)	$^7LiF-BeF_2-ThF_4-UF_4$ (72-16-12-0.4)
Secondary Coolant	Na metal	$^7LiF-BeF_2$	$NaF-NaBF_4$
Unique Features	1st molten salt reactor	Xe, Kr removal 1st use of U-233 on-line fuel PuF_3	continuous on-line fuel processing breeding ratio = 1.07

+ numerous loop tests multi-year tests



fuel salt corrosion was much higher

Temperature Driven Cyclic Corrosion Process is the Limiting Corrosion Factor

$$\text{Oxidant} + Cr = \text{Reductant} + CrF_2(d)$$

$$2UF_4(d) + Cr = 2UF_3(d) + CrF_2(d)$$

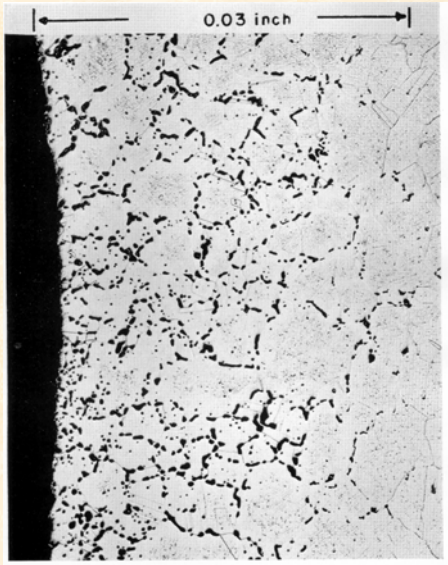
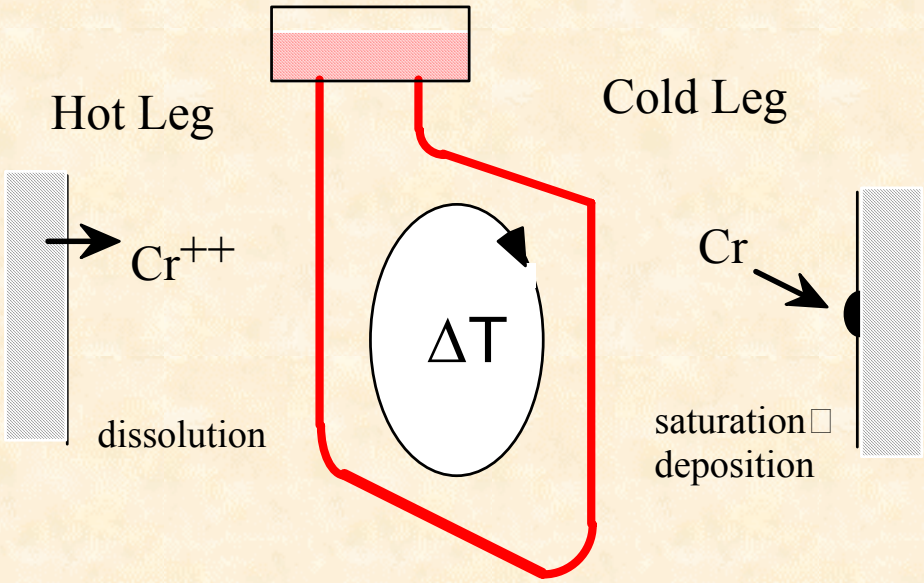


FIG. 6. Attack found in Inconel loop after circulating NaF–KF–LiF–UF_4. 11·2–41·0–45·3–2·5 mole %) for 630 hr at a maximum fluoride mixture temperature of 815°C and Reynolds number of 10,000.



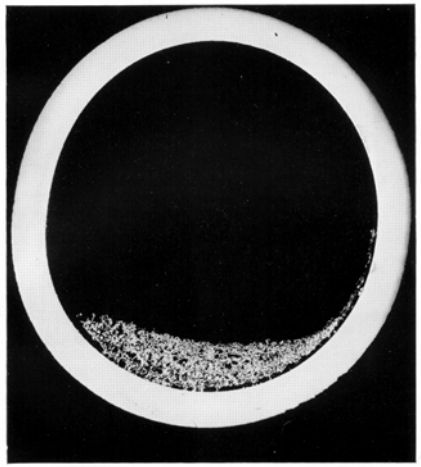
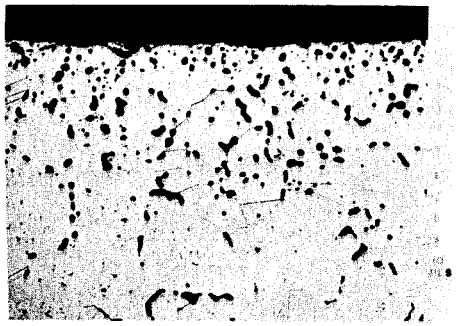


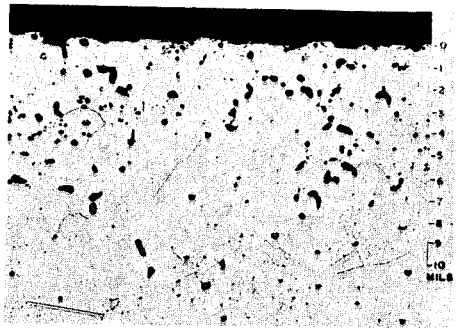
FIG. 7. Chromium deposits found in cold leg of Inconel loop discussed in Fig. 5.

Impurities can mask the fundamental corrosion response



T-4485 250X

FLUORIDE BATCH HIGH IN FE & NI



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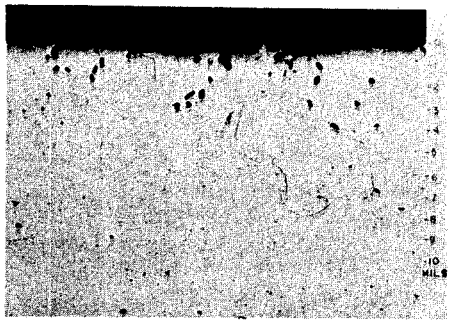
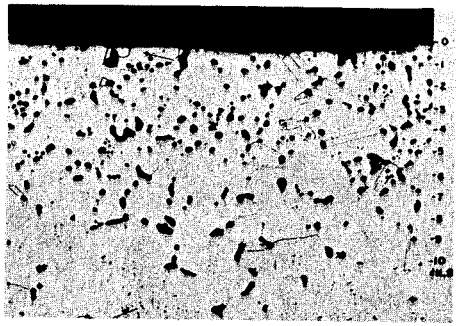
FLUORIDE BATCH MODERATE IN FE & NI



T-4410 250X

FLUORIDE BATCH LOW IN FE & NI



T-3920 250X

FLUORIDE BATCH HIGH IN HF

INCONEL THERMAL CONVECTION LOOPS - 500 HRS. AT 1500°F

(T-4544) EFFECT OF FLUORIDE BATCH PURITY

Salt Corrosion Studies have a Characteristic Pattern

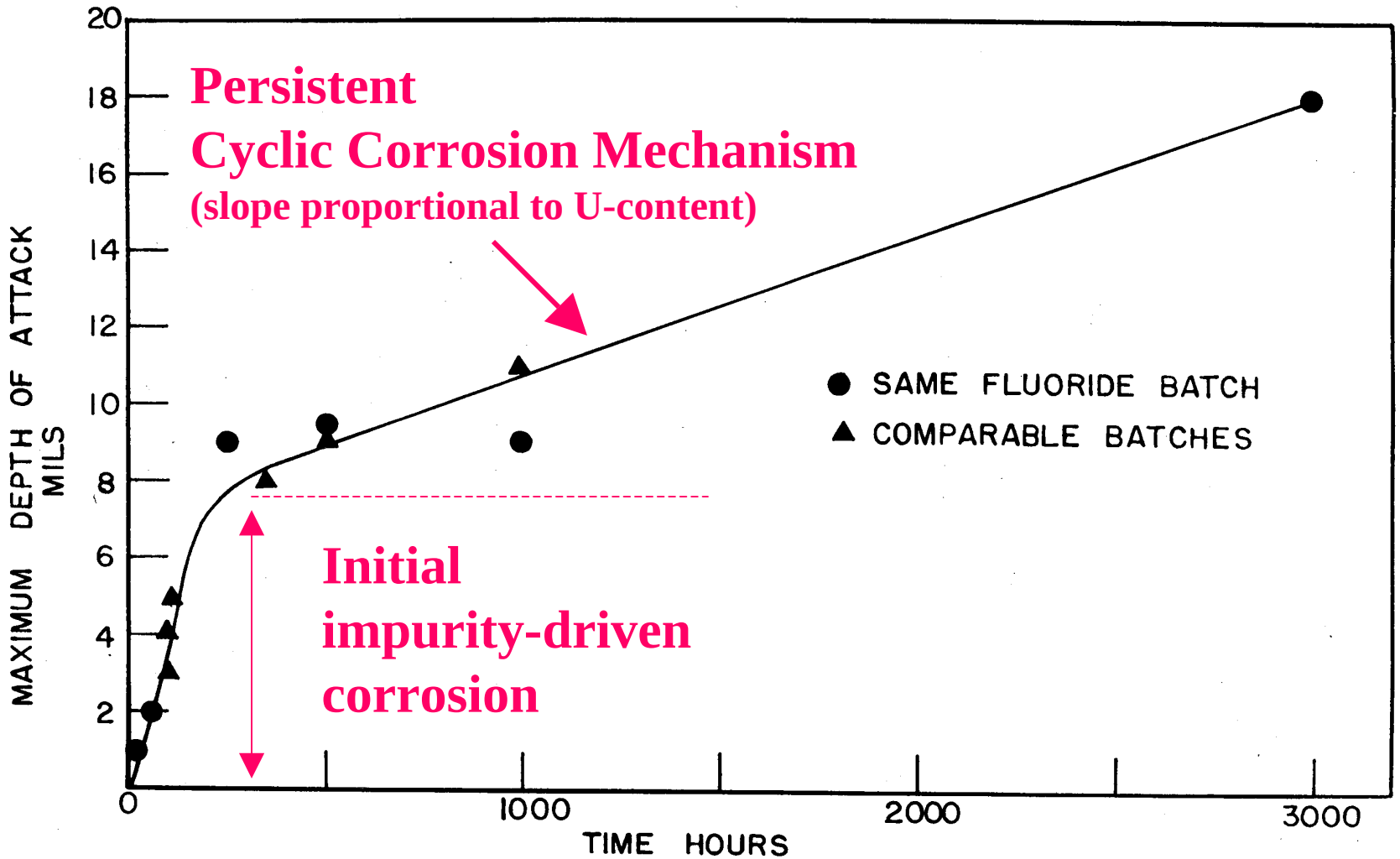
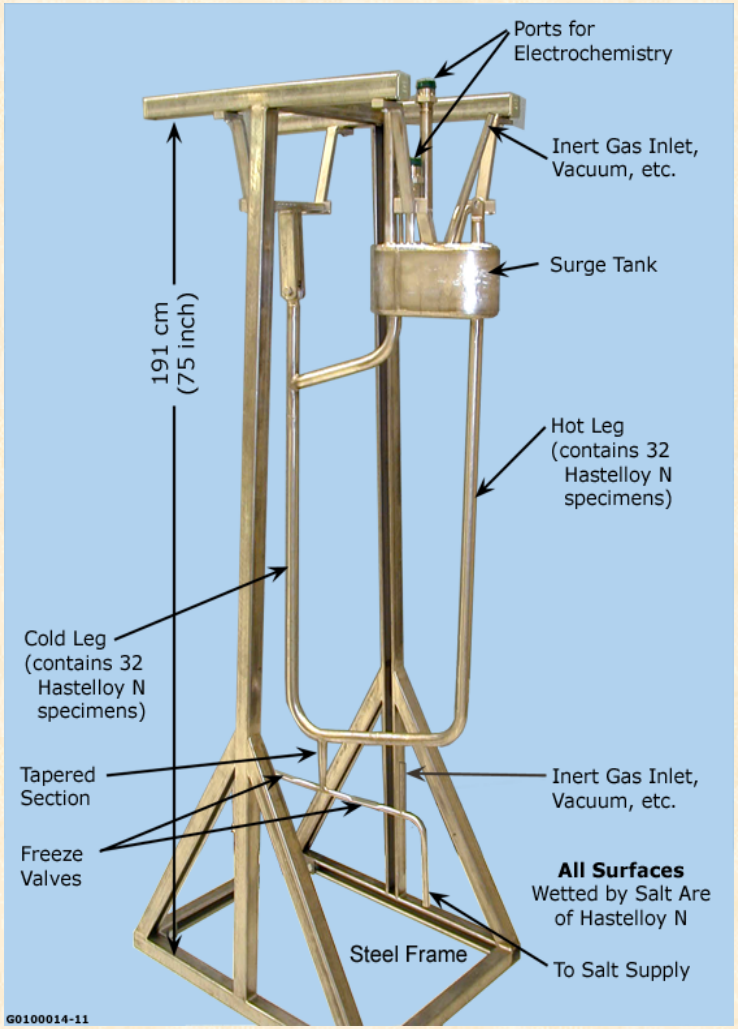
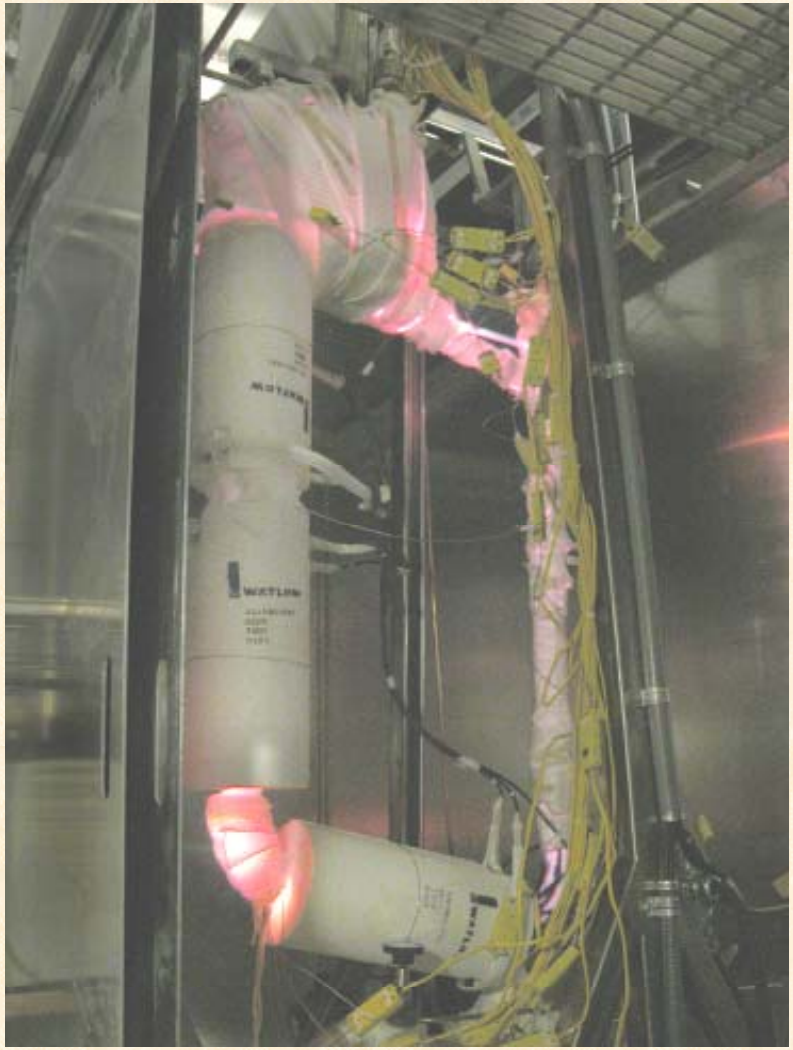


Fig. 6 (T-3844) EFFECT OF TIME ON CORROSION DEPTH FLUORIDE IN INCONEL

Our System:
FLiNaK at 815°C for 3000h in INOR-8



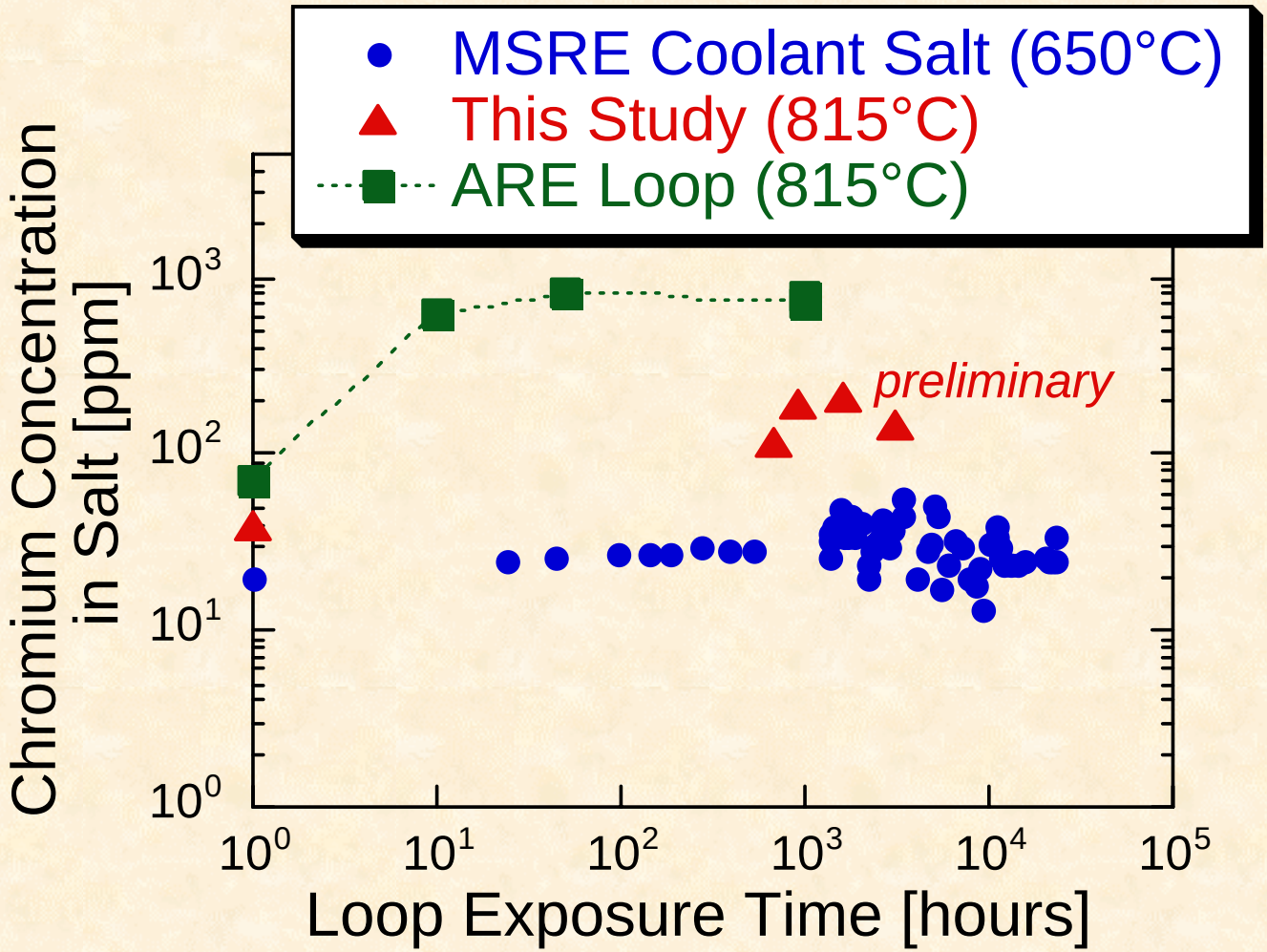


Experimental Results

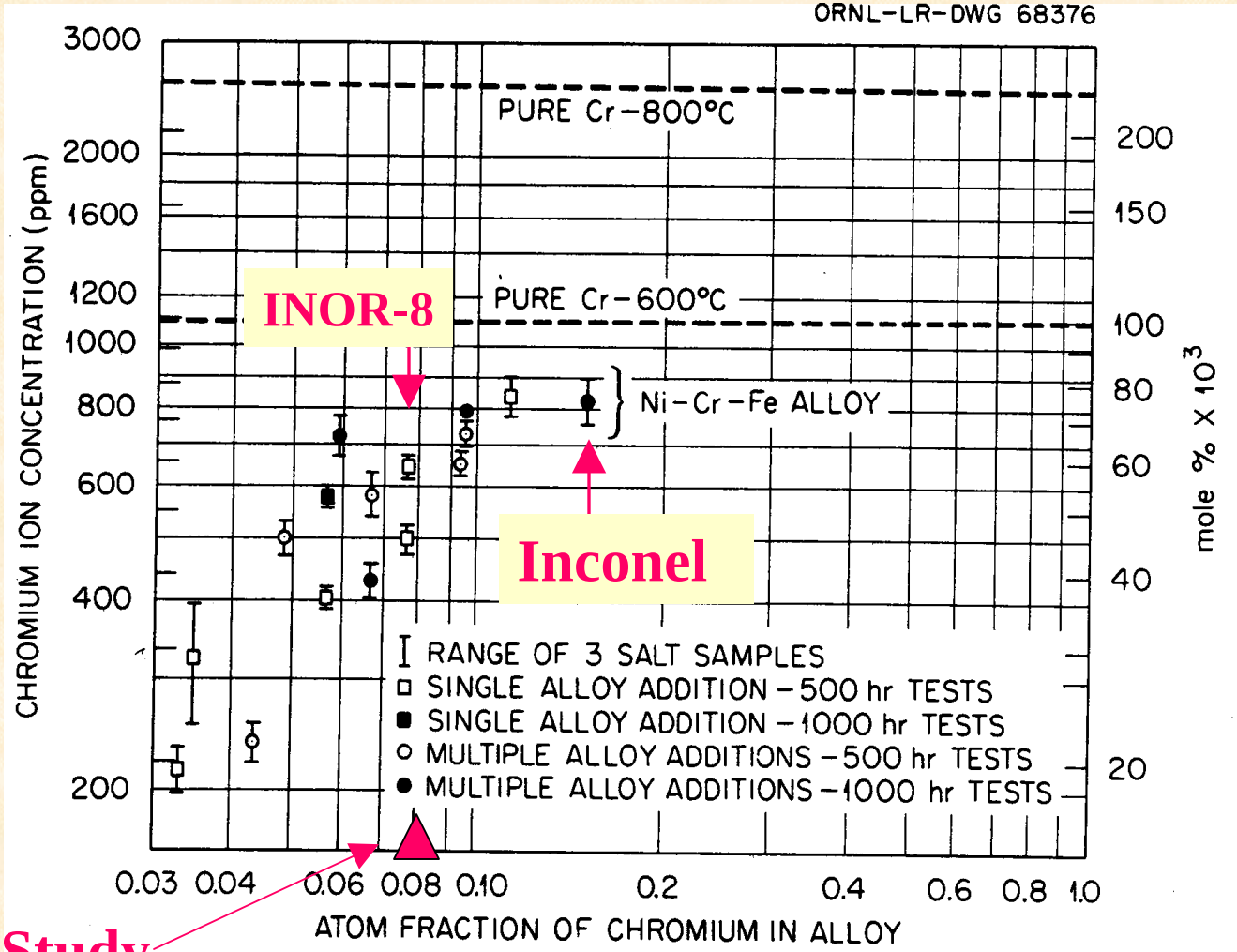
1. **Metal Fluorides (Cr) dissolved in the Salt**
2. **Weight Change on Alloy Specimens**
3. **Depth of Corrosion/micrographs**

Compare with previous studies

Much less Chromium is in the Salt - (1)



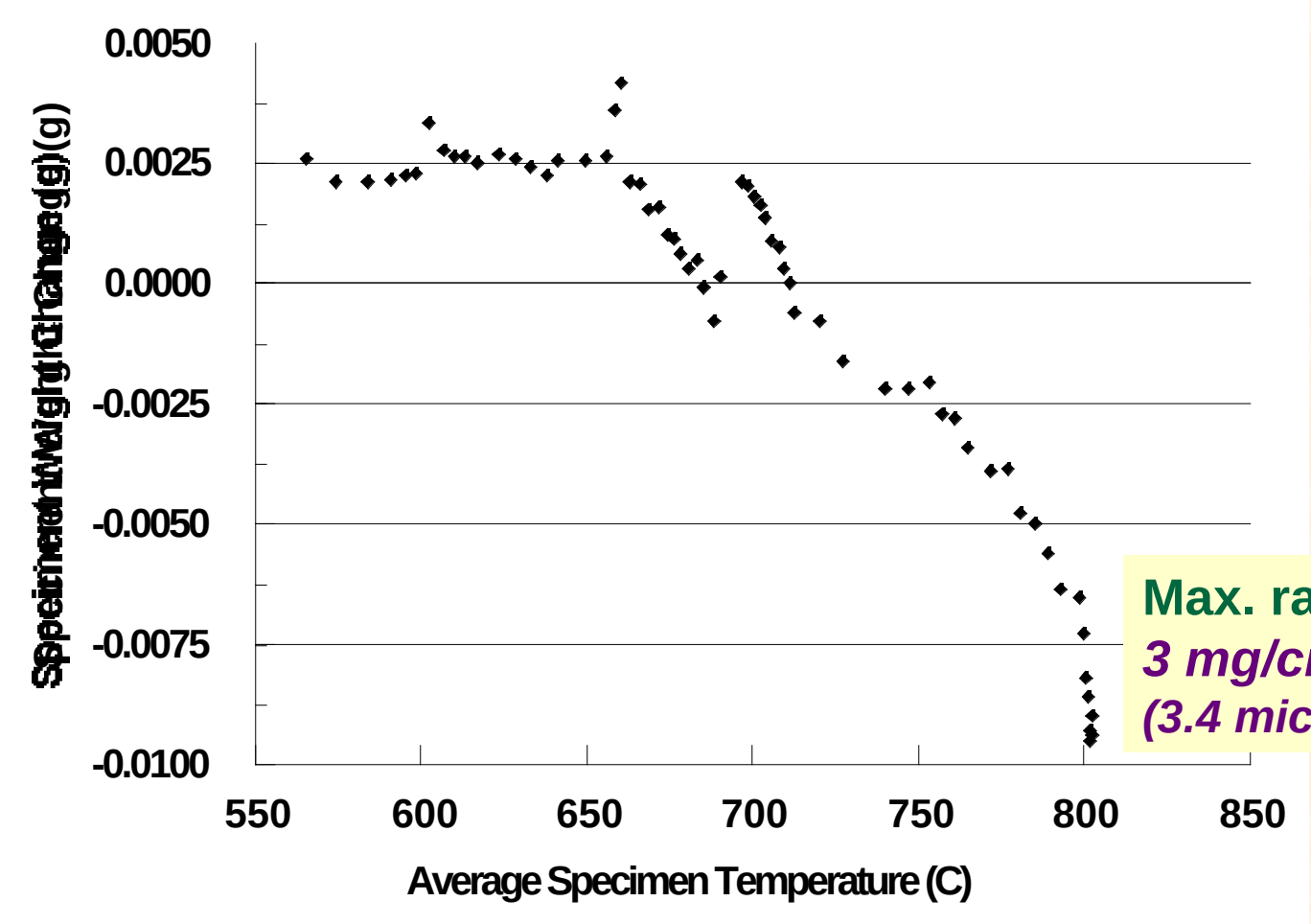
Much less Chromium is in the Salt - (2)



This Study

Fig. 2. Chromium Concentration of Fluoride Salt Circulated in Thermal-Convection Loops as a Function of Chromium Content of the Loop. Salt mixture: $NaF-LiF-KF-UF_4$ (11.2-45.3-41.0-2.5 mole %). Loop temperature: hot leg, 815°C; cold leg, 650°C.

Relatively Small Specimen Weight Changes Occurred

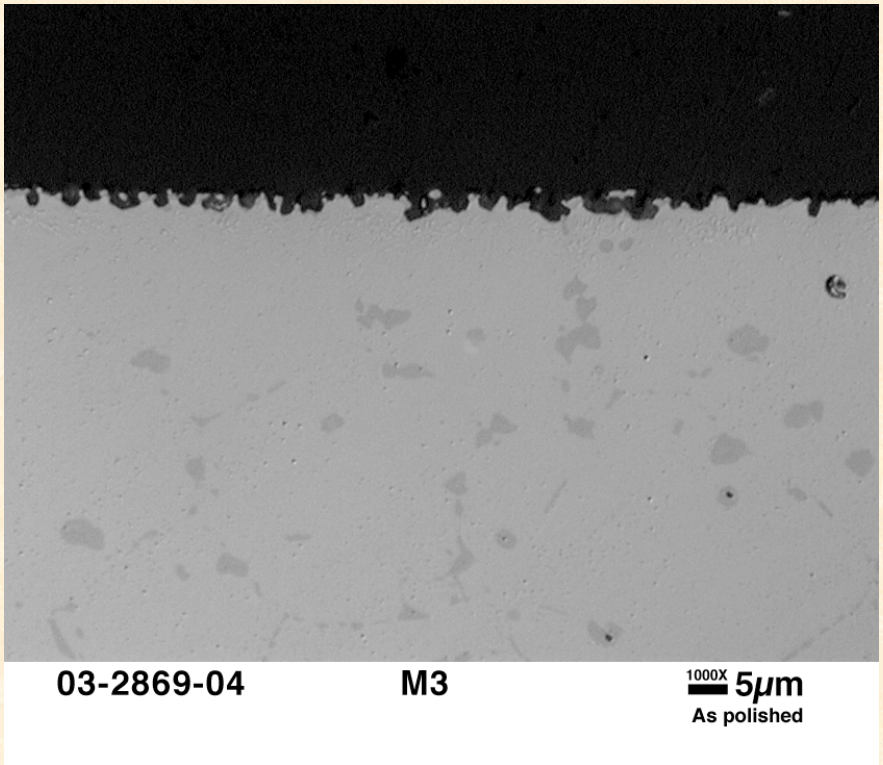


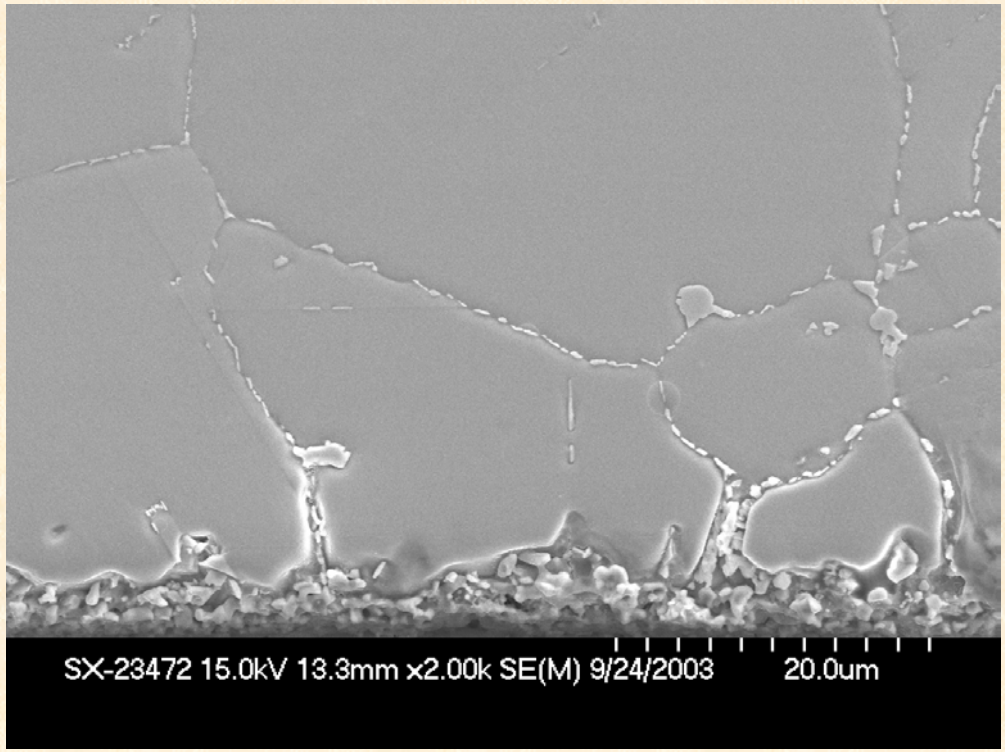
Comparable rates with Fuel Salt at 815°C:

16 mg/cm^2-yr
(18 microns)

Max. rate =
3 mg/cm^2-yr
(3.4 microns)

Micrographs of specimens reveal no sub-surface Cr-removal

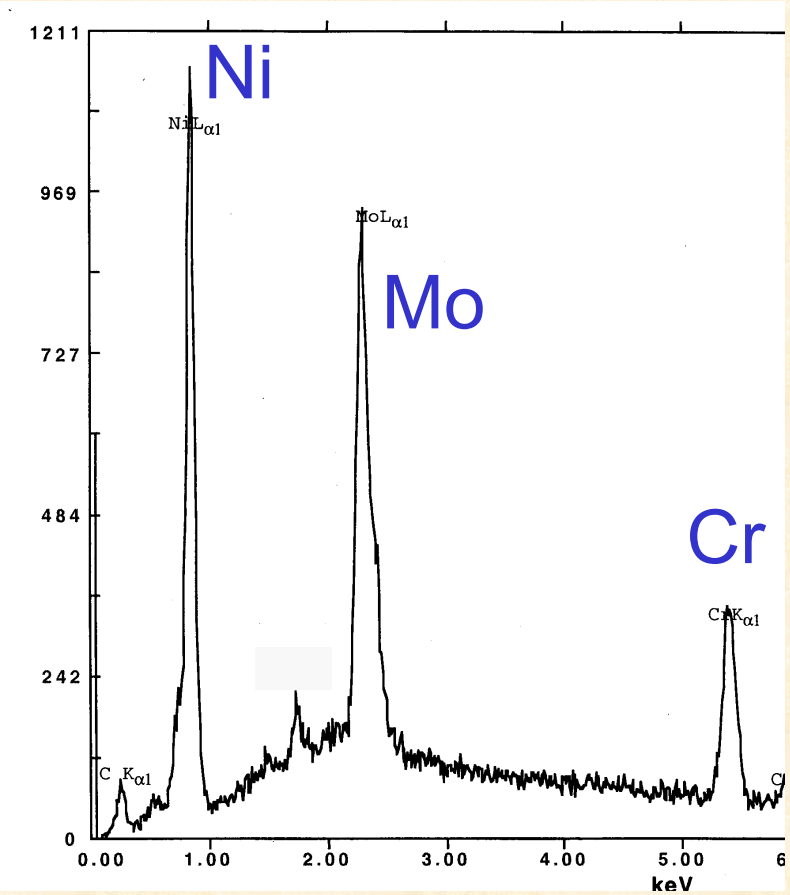




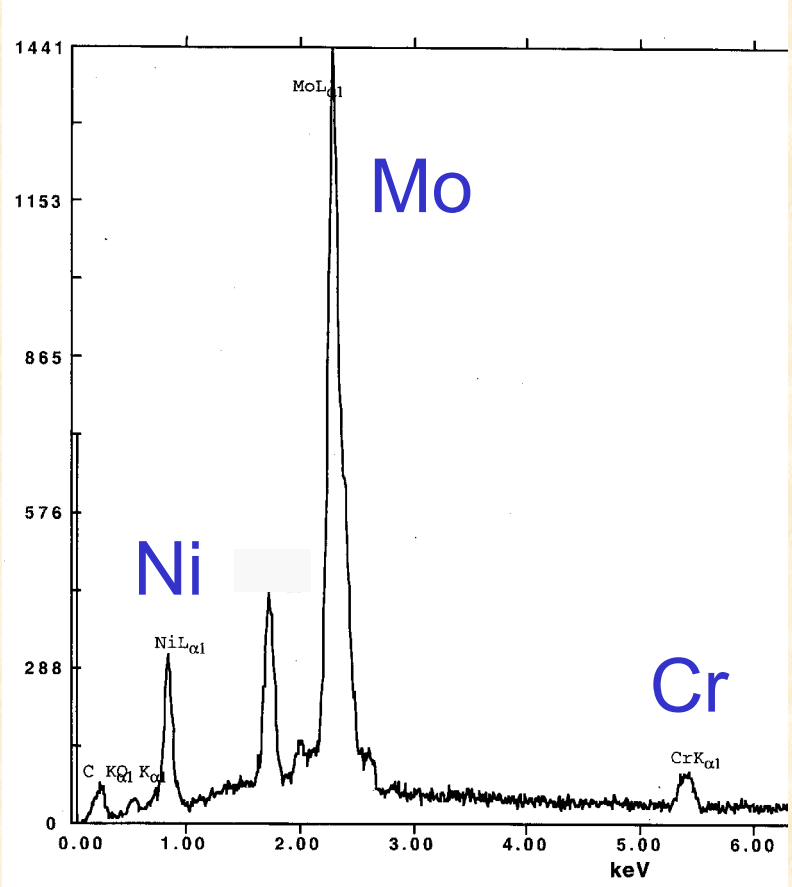
802°C hot-leg specimen

660 °C cold-leg specimen

Unexpected Surface Layer is Molybdenum Rich

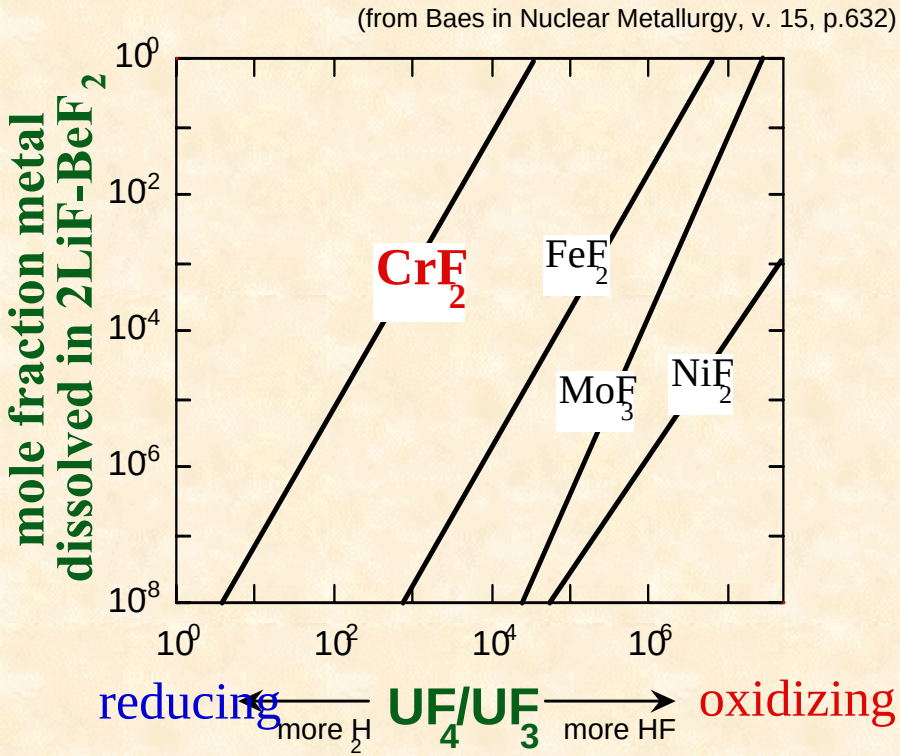


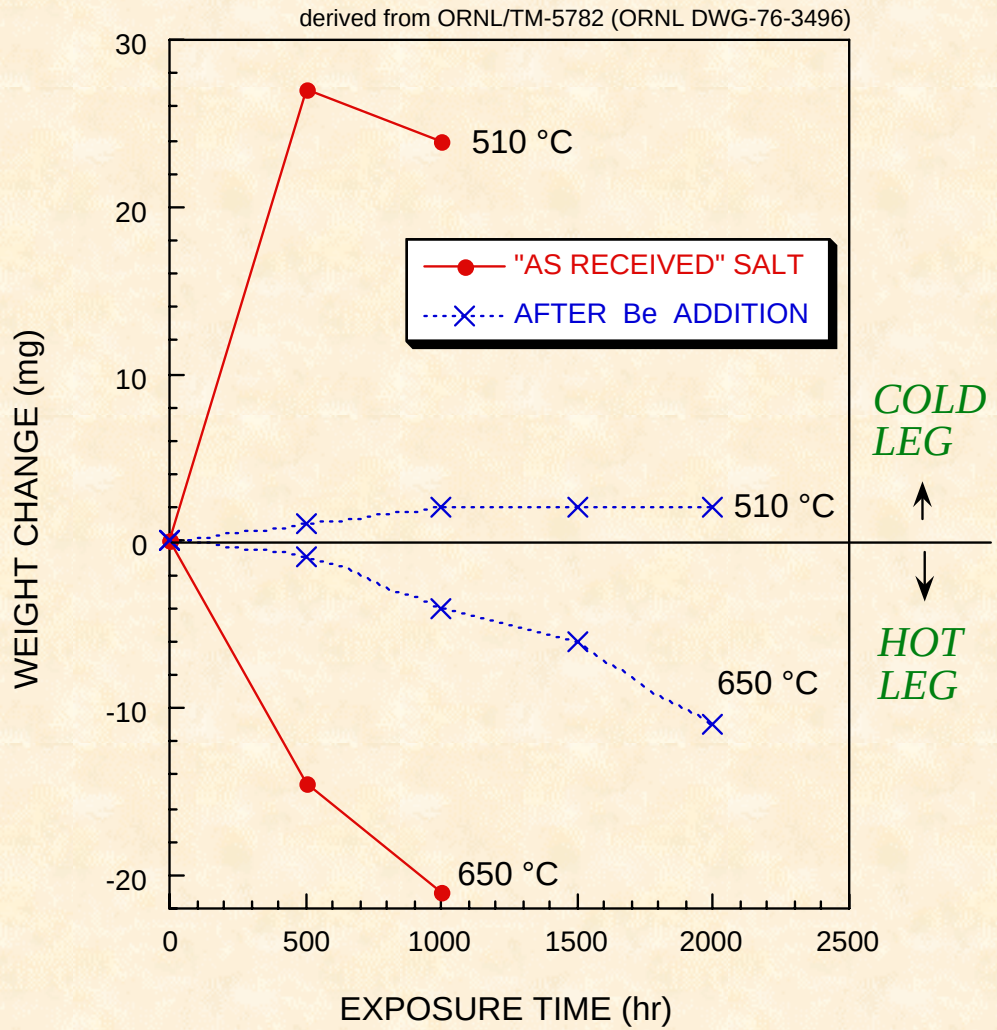
INOR-8 base alloy



Surface deposit

The Original Plan Called for a Reducing Chemistry Comparison





Recommendations for Future Work

Completion of this Phase of Study (LDRD):

- *Continue analysis of specimens, refine impurity analysis*

A New Phase of Investigation is Proposed:

- ***Expand Efforts above 1-person-year level***
  - *periodic specimen removal and analysis*
  - *operate INOR-8 loop in a reducing environment*
  - *operate at higher temperatures:*
    - *use a higher temperature alloy (Hastelloy-X)*
    - *refine choice of salts to small set of candidates (capsule tests)*
  - *refine electrochemical analysis*