GEDEON-PRACTIS WORKSHOP

THE MOLTEN SALT REACTORS (MSR):
PYROCHEMISTRY AND FUEL CYCLES FOR INNOVATIVE NUCLEAR SYSTEMS

June 19th & 20th , 2002

Château de Cadarache

SAINT-PAUL-LEZ-DURANCE, FRANCE

TOPIC: REDOX Control of MSR Fuel

Why? Which Buffer?
How to Measure/Adjust ?

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REDOX Control is Essential to Minimize Corrosion of Container Alloy

Counteracts

- **cation imbalance due to fission (also Te-driven corrosion)**
- **atmospheric oxidants**
- **cyclic corrosion process (maintains low conc. of structural metals)**

Table 7
Chemical consequences of fission in an MSBR

Fission product	Assumed eq. ox. state (Z)	Yield Y	YZ
Br +I	-1	0.015	-0.015
Kr + Xe	0	0.606	0
Rb +Cs	+1	0.004	0.004
Sr +Ba	+2	0.072	0.144
Ln + Y	+3	0.538	1.644
Zr	+4	0.318	1.272
Nb	0	0.014	0
Mo	0	0.201	0
Tc	0	0.059	0
Ru	0	0.126	0
		1.953	3.049

C. F. Baes in *J. Nucl. Mat.* **51** (1974).

More-Reducing Salts will be needed in Next Generation Systems

(1) All Systems:

minimizes the thermodynamic potential for corrosion

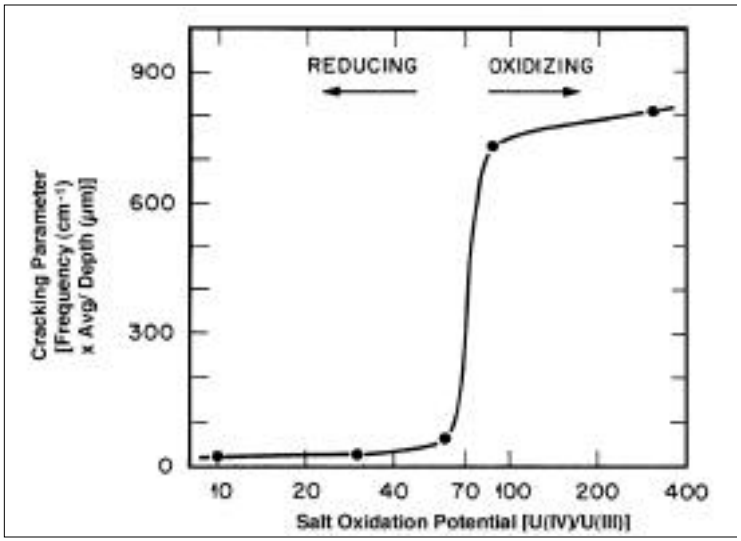
(2) Fluid Fuels:

eliminates Te-attack

compatible with minor actinides

(3) Fusion System:

stripping T_2 from FLiBe



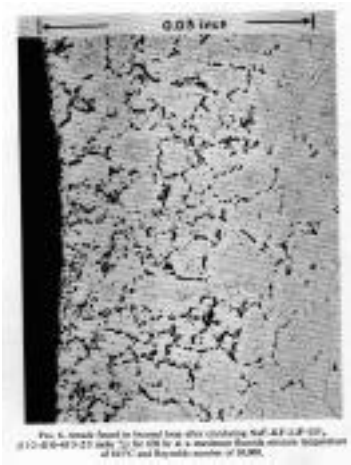
CONTROL OF REDOX STATE IS ESSENTIAL TO ALL APPLICATIONS

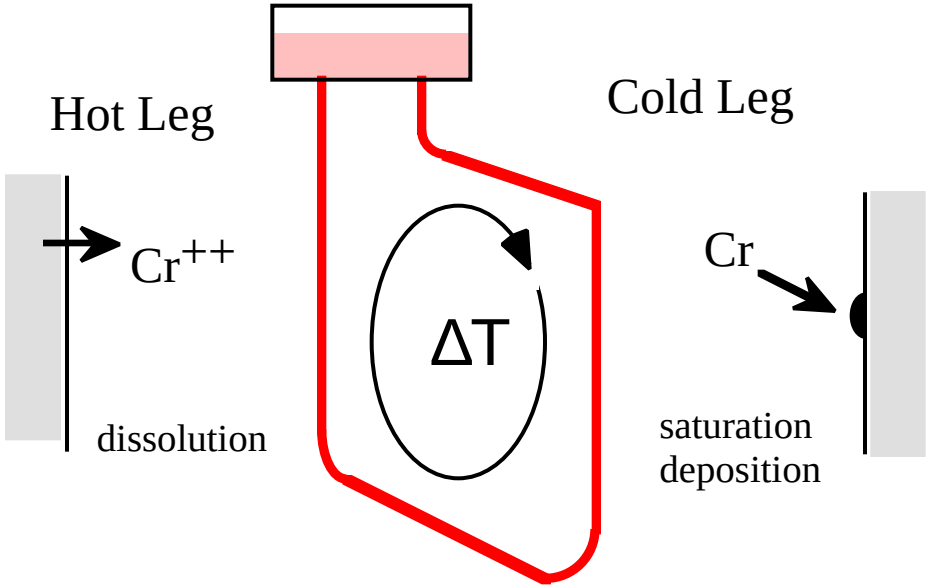
Temperature-Driven Cycle is the Primary Corrosion Path for Molten Salts

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

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

W. D. Manly in
Geneva Conf. 1958





W. D. Manly in
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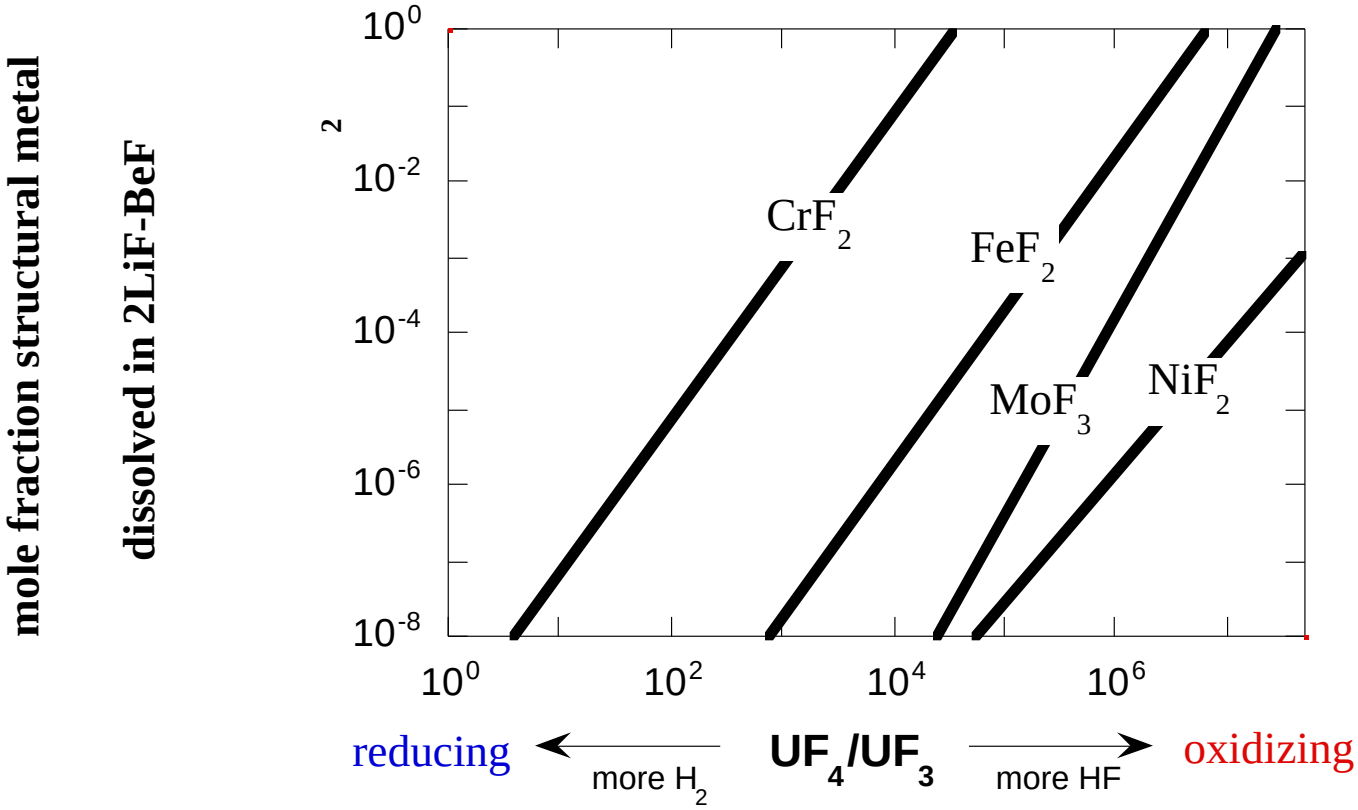
reductant
inhibits dissolution

also depends on
salt identity
(coord. chemistry)

Properly Buffered System Inhibits Corrosion

(from Baes in Nuclear Metallurgy, v. 15, p.632)



$$2\ MF_{x+1}(d) + Cr = 2MF_x\ (d) + CrF_2$$

Corrosion Inhibition ← reducing conditions high (MF_x / MF_{X+1})

Alternate REDOX Buffers are Needed

U(IV)/U(III) was used for the MSRE (very dilute: 0.1–1 mol% U)

New buffer systems are needed for:

- **Systems with no uranium**
- **Molten salt–cooled concepts**
- **Fusion blankets**
- **More reducing conditions**

ORNL is Exploring REDOX Buffers for New Molten Salt Applications

Part of an internally funded activity: http://www.ornl.gov/ldrd/

see: Forsberg: September 2001 Nuclear News / ANS 2001 RENO:

13th INTERNATIONAL SYMPOSIUM ON MOLTEN SALTS: May, 2002

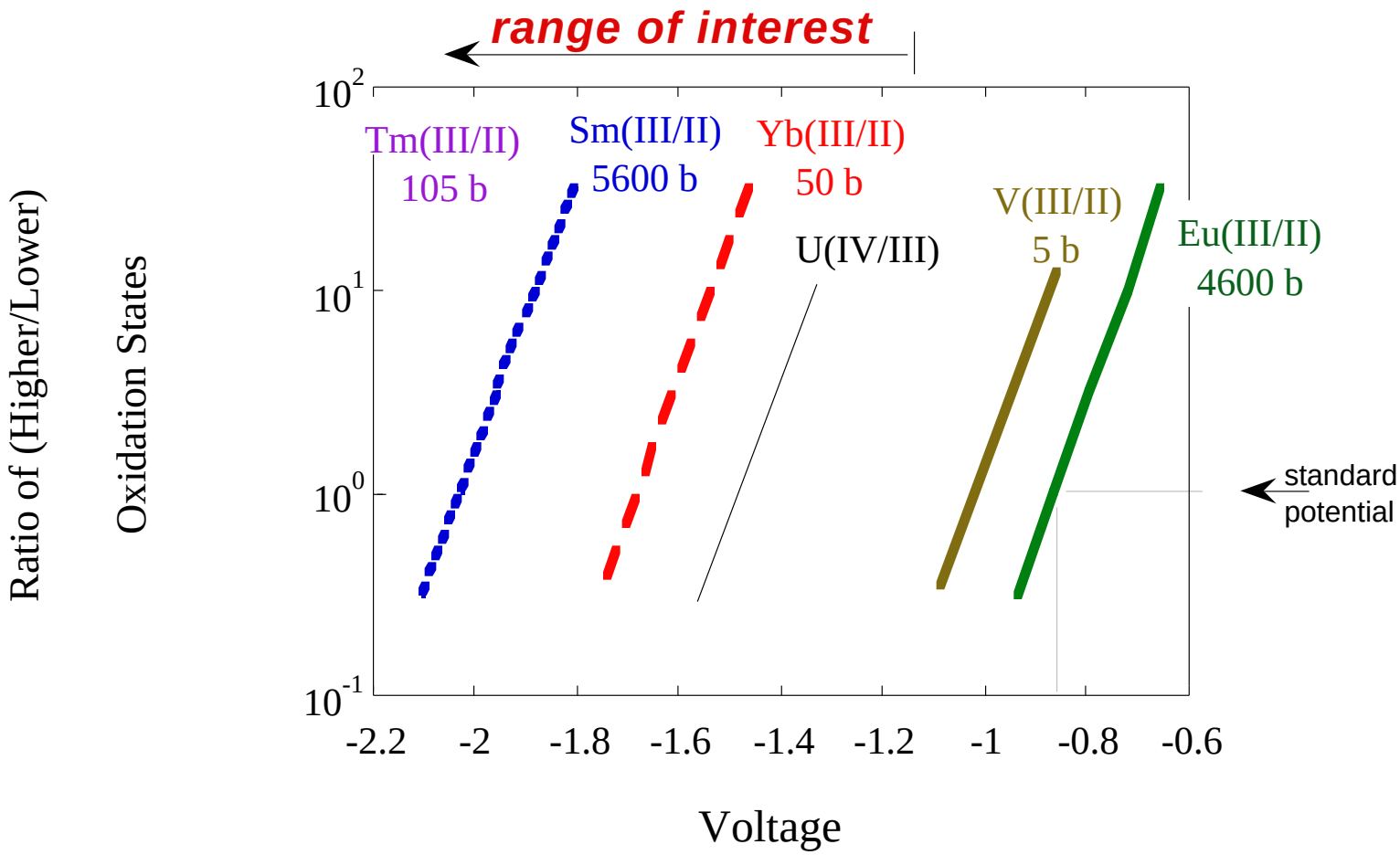
Candidate systems selected:

- **redox-active lanthanides (Yb, Tm, Sm, Eu)**
- **electropositive redox-active transition metals (V)**
- **possibility for Np in fueled systems**

Electrochemistry and neutronic screening this year

Convection loop work planned for next year

Chloride Electrochemistry supports choices for Candidate Fluoride REDOX Buffers



Improved Cyclic Voltammetry Apparatus was Assembled for Molten Fluorides

Electrode design: Adapted from C. G. Kontoyannis, ***Electrochimica Acta***, **40**, 2547,1995

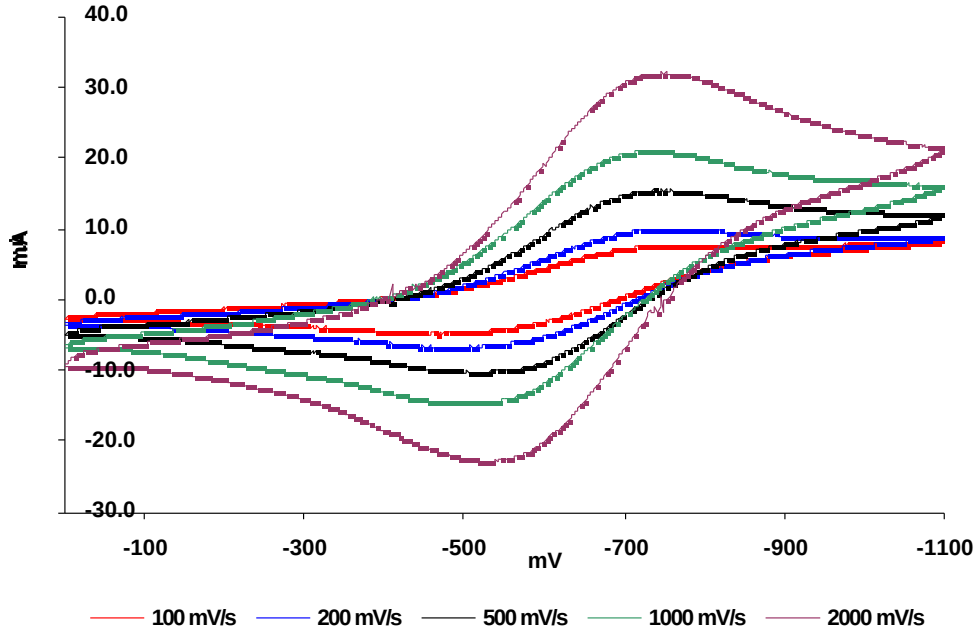
Ni/NiF_2 reference electrode

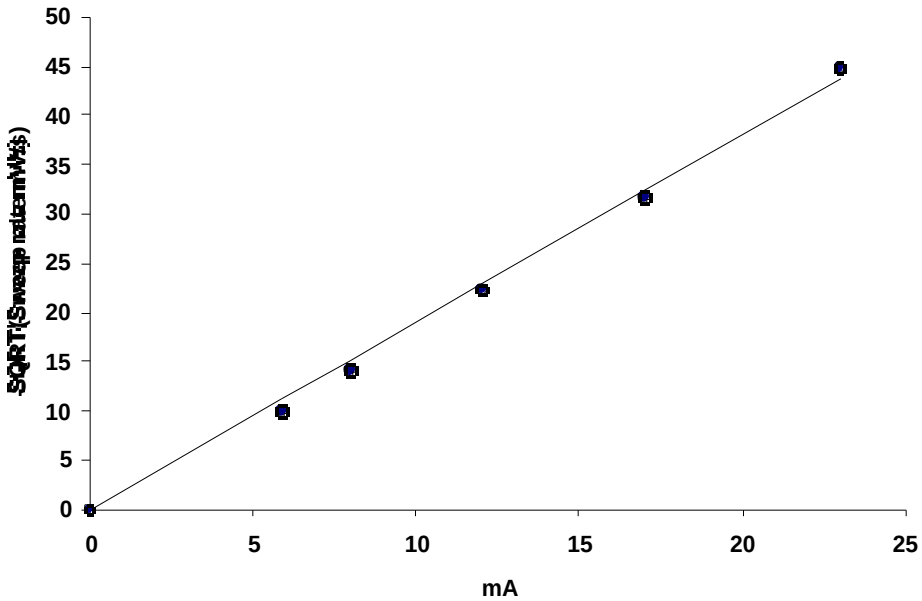
Materials: graphite: UCAR ATJ grade and Ringdorff R6300

Pyrolytic boron nitride coating by Advanced Ceramics

Ir wire working- and counter-electrodes

Eu(III/II) was found to be reversible at 610°C in FLINAK





Preliminary results also obtained for U, V, and Yb

Preliminary Assignment of Standard Potentials for Fluoride Couples in FLINAK

Redox Couple	Standard Reduction Potential (V)	
	LiCl-KCl 450°C Ref. Cl_2/Cl^-	FLINAK 610°C Ref. Ni/NiF_2
Sm(III)/Sm(II)	-2.035	
Yb(III)/Yb(II)	-1.68	-1.45
U(IV)/U(III)	-1.55	-1.2
V(III)/V(II)	-1.07	-0.9
Eu(III)/Eu(II)	-0.86	-0.64

Measurement and Adjustment of REDOX "The Practical Problem"

Measurement by

transpiration (exhaust gas analysis of H_2/HF)
electrochemistry
spectroscopy

indicator (Cr^{2+}, Nb valence)

Adjustment by

Gas treatment (H_2/HF)
Metal treatment (Be, Zr)
electrochemistry

Very reliable and simple approaches needed for a power plant

Summary

More-reducing REDOX buffers will be necessary in the future to

minimize corrosion,
increase service temperature.

Promising buffer systems for more reducing systems have been identified and are being explored

Measurement and adjustment of REDOX are possible by many methods. Very simple and practical methods need to be developed for industrial systems.