Nuclear Materials
Modeling Lab.

Simulation Model of FLiNaK Molten Salt Corrosion With Nickel Alloy Using COMSOL

2023.10.25.

Contents

4th gen nuclear reactor

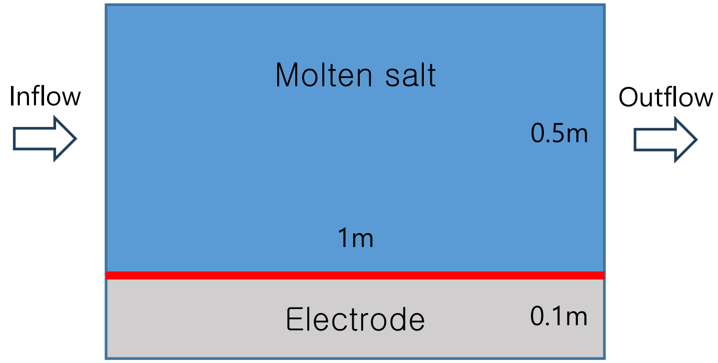
- SFR : Sodium cooled Fast Reactor
- VHTR : Very High Temperature Reactor
- LFR : Lead cooled Fast Reactor
- GFR : Gas cooled Fast Reactor
- SCWR : Supercritical Water Cooled Reactor
- MSR : Molten salt reactor

Pros
- High thermal efficiency
- Air pressure operation
- High safety (LOCA, high negative feedback)

Cons
- Corrosion

Model Geometry

- Model is 2D geometry.
- Blue area is Molten salt with eutectic FLiNaK molten salt(46.5LiF-11.5NaF-42KF). Grey area is Ni alloy area.
- Flow velocity is 0.5 m/s.
- Red surface is electrode surface. All reaction occur red surface.



<Simple geometry of model>

Model assumption

- We assume alloy element is Cr, Ni, Fe.

- Water is inevitable impurity. If there is water in salt, HF will generate with below reaction.

$$H_2O + 2F^- \rightarrow O^{2-} + 2HF$$

- So we choose 5 anodic reaction, and 4 cathodic reaction.

- Anodic reaction

$$Cr \rightarrow Cr^{2+} + 2e^-$$
$$Fe \rightarrow Fe^{2+} + 2e^-$$
$$Ni \rightarrow Ni^{2+} + 2e^-$$
$$Cr \rightarrow Cr^{3+} + 3e^-$$
$$Fe \rightarrow Fe^{3+} + 3e^-$$

- Cathodic reaction

$$Li^+ + e^- \rightarrow Li$$
$$Na^+ + e^- \rightarrow Na$$
$$K^+ + e^- \rightarrow K$$
$$HF(g) + e^- \rightarrow \frac{1}{2}H_2(g) + F^-$$

Model assumption

- Initial salt species concentrations are in table below.

Species	Concentration	Reference
F^-	59674.26(mol/m^3)	46.5LiF−11.5NaF−42KF salt
Li^+	38342.39(mol/m^3)	46.5LiF−11.5NaF−42KF salt
Na^+	5861.198(mol/m^3)	46.5LiF−11.5NaF−42KF salt
K^+	15470.68(mol/m^3)	46.5LiF−11.5NaF−42KF salt
Cr^{2+}	1E−6(M)	Redox potential reference $a = 10^{-6}$
Cr^{3+}	1E−6(M)	Redox potential reference $a = 10^{-6}$
Fe^{2+}	1E−6(M)	Redox potential reference $a = 10^{-6}$
Fe^{3+}	1E−6(M)	Redox potential reference $a = 10^{-6}$
Ni^{2+}	1E−6(M)	Redox potential reference $a = 10^{-6}$
HF	7.441134(mol/m^3)	Henry constant in FLiBe salt $\log K_{HF} = -6.496 + 1399.3/T$
H_2	1E−6(M)	Estimate small amount

Transport equation

- In COMSOL, governing equation of transport is Nernst-Plank equation.

$$\left(\frac{\partial c_j}{\partial t}\right) + \nabla \cdot J_j + u \cdot \nabla c_j = R_j$$

- c_j is concentration, J_j is flux of species, u is flow velocity, and R_j is generation rate. Species not generate. So R_j is 0. And flux has two term, diffusion term, electromigration term.

$$J_j = -D_j \nabla c_j - z_j u_{m,j} F c_j \nabla \phi_l$$

- D_j is diffusion coefficient, z_z is electron number, $u_{m,j}$ is electric mobility, F is faraday constant and ϕ_l is electrolyte potential. ϕ_l is follow the electrolyte electrochemical potential.

- If there is no flow, J_j is main transport term. But there is flow, $u \cdot \nabla c_j$ is main.

Kinetic equation of charge transport

- Governing equation of corrosion reaction is Butler-Volmer equation or Tafel equation.

- Butler-Volmer Eq.

$$i_{loc} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT} \right) - \exp\left(-\frac{\alpha_c F \eta}{RT} \right) \right)$$

- In this Eq., overpotential η is very important parameter.

$$\eta = \phi_s - \phi_l - E_{eq}$$

- ϕ_s is electrode potential and E_{eq} is equilibrium potential of reaction. In corrosion reaction, there is no external electric potential. So $\phi_s = 0$. So E_{eq} is important to predict corrosion.

Kinetic equation of charge transport

- Equilibrium potential E_{eq} is redox potential. And calculated by Nernst equation.

$$E_{eq} = E_{eq,ref} - \frac{RT}{nF} \ln \prod_i \left(\frac{c_i}{c_{i,ref}} \right)^{v_i}$$

- Important parameter is equilibrium potential E_{eq}, exchange current density i_0

Exchange current density i_0

- In Butler-Volmer equation, Exchange current density i_0 and transfer coefficient a is key parameter to calculate corrosion current density.

$$a_c = n - a_a$$

- i_0 and a_a was used with some reference.

Reaction	i_0 (mA/m^2)	a_a
$Cr \rightarrow Cr^{2+} + 2e^-$	0.88[1)]	0.22[1)]
$Cr \rightarrow Cr^{3+} + 3e^-$	0.88[1)]	0.22[1)]
$Fe \rightarrow Fe^{2+} + 2e^-$	6.15[1)]	0.11[1)]
$Fe \rightarrow Fe^{3+} + 3e^-$	6.15[1)]	0.11[1)]
$Ni \rightarrow Ni^{2+} + 2e^-$	0.88[1)]	0.22[1)]
$Li^+ + e^- \rightarrow Li$	0.05[2)]	0.5[2)]
$Na^+ + e^- \rightarrow Na$	0.05[2)]	0.5[2)]
$K^+ + e^- \rightarrow K$	0.05[2)]	0.5[2)]
$HF(g) + e^- \rightarrow \frac{1}{2}H_2(g) + F^-$	6.15[3)]	0.5[2)]

1) Wei Wu, Shaoqiang Guo and Jinsuo Zhang, Exchange Current Densities and Charge-Transfer Coefficients of Chromium and Iron Dissolution in Molten LiF-NaF-KF Eutectic, *J. Electrochem. Soc.* 164 C840(2017)
2) Default value of COMSOL
3) For convergence

Equilibrium potential

- Right graph is redox potential for various redox couple in molten salt.

- With this curve, we choose E_{eq} at 750℃

Reaction	Equilibrium potential
$Cr \rightarrow Cr^{2+} + 2e^-$	−3.9
$Cr \rightarrow Cr^{3+} + 3e^-$	−3.55
$Fe \rightarrow Fe^{2+} + 2e^-$	−3.5
$Fe \rightarrow Fe^{3+} + 3e^-$	−3.1
$Ni \rightarrow Ni^{2+} + 2e^-$	−3.05
$Li^+ + e^- \rightarrow Li$	−5.45
$Na^+ + e^- \rightarrow Na$	−5.1
$K^+ + e^- \rightarrow K$	−4.9
$HF(g) + e^- \rightarrow \frac{1}{2}H_2(g) + F^-$	−2.89

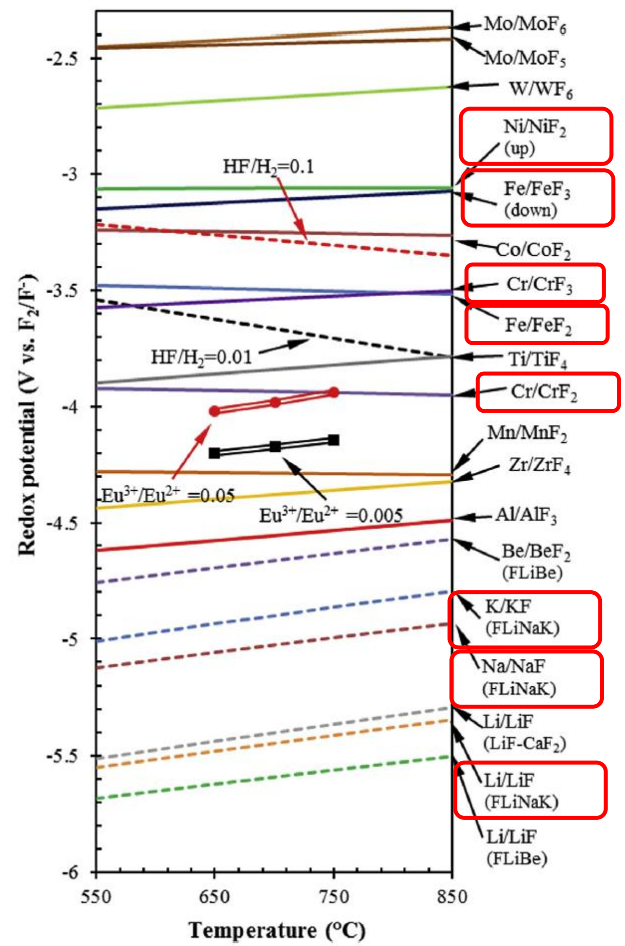


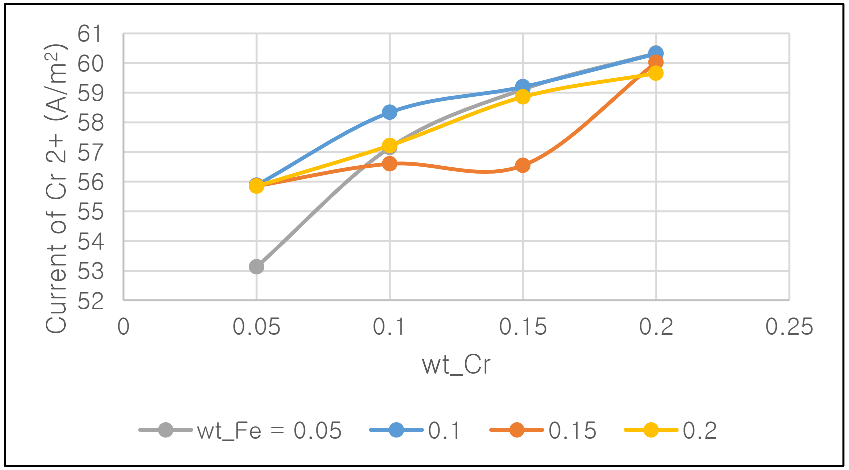
Fig. 8. Redox potential versus temperature for various redox couples in FLiNaK and FLiBe salts. Solid line: metal dissolution at limit activity of 10^{-6}; Dotted line: reduction of oxidants. HF/H_2 = 0.1: a mole ratio of HF/H_2 = 0.1 at 1 atm total pressure. Double solid line: redox potential calculated based on the measured formal potentials.

Result

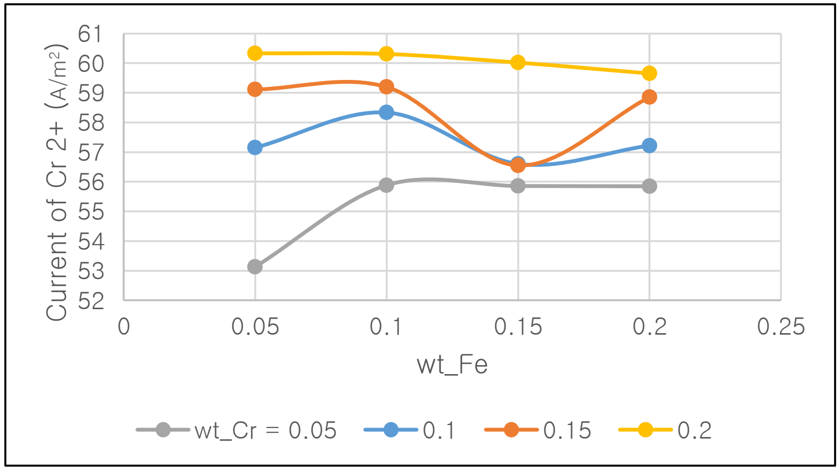
- We measured the current of each chemical species from the cases of different composition of Ni-Cr-Fe alloy. The Positive value means that the oxidation reaction occurs.

wt_Cr	wt_Fe	Current of Cr^{2+} (A/m²)	Current of Cr^{3+} (A/m²)	Current of Fe^{2+} (A/m²)	Current of Fe^{3+} (A/m²)	Current of Ni^{2+} (A/m²)	Current of HF (A/m²)	Total Current(A/m²)
0.05	0.05	53.13	3.41	0.4441	−1.0232	−0.02991	−55.935	−0.00449
0.05	0.1	55.885	3.6093	0.60537	−0.88375	−0.04255	−59.176	−0.00335
0.05	0.15	55.858	3.5874	0.75168	−0.80881	−0.05279	−59.337	−0.00182
0.05	0.2	55.848	3.5401	0.88076	−0.75634	−0.06213	−59.449	0.001223
0.1	0.05	57.149	3.924	0.37999	−1.1531	−0.03204	−60.275	−0.0068
0.1	0.1	58.335	3.9579	0.52912	−0.9909	−0.0463	−61.791	−0.00585
0.1	0.15	56.603	3.9598	0.64181	−0.90565	−0.05782	−60.245	−0.00383
0.1	0.2	57.221	3.8964	0.7587	−0.8475	−0.06835	−60.966	−0.0057
0.15	0.05	59.112	4.2615	0.36363	−1.2395	−0.03389	−62.468	−0.00438
0.15	0.1	59.196	4.1682	0.49056	−1.0611	−0.0496	−62.75	−0.00576
0.15	0.15	56.55	3.9692	0.60777	−0.96847	−0.06224	−60.102	−0.00613
0.15	0.2	58.857	4.1191	0.69959	−0.90445	−0.07393	−62.7	−0.00297
0.2	0.05	60.332	4.4038	0.34893	−1.3066	−0.03586	−63.746	−0.00437
0.2	0.1	60.31	4.3057	0.46584	−1.1146	−0.05291	−63.92	−0.00645
0.2	0.15	60.019	4.3059	0.56863	−1.0149	−0.06669	−63.815	−0.00262
0.2	0.2	59.654	4.2631	0.65891	−0.94739	−0.07969	−63.552	−0.00281

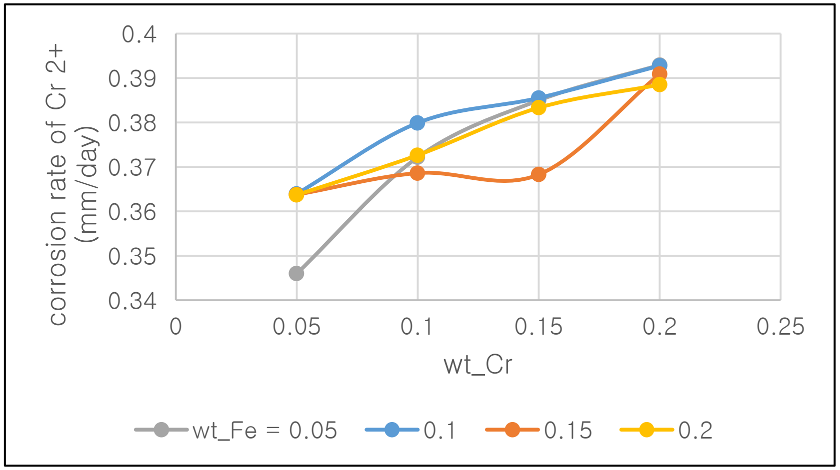
Result



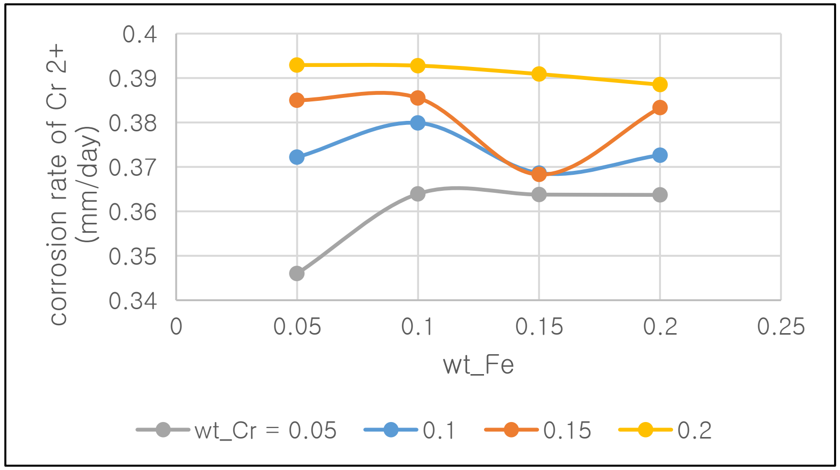
Current of Cr 2+ (A/m²)
61 60 59 58 57 56 55 54 53 52
0 0.05 0.1 0.15 0.2 0.25
wt_Cr
wt_Fe = 0.05
0.1
0.15
0.2



Current of Cr 2+ (A/m²)
61 60 59 58 57 56 55 54 53 52
0 0.05 0.1 0.15 0.2 0.25
wt_Fe
wt_Cr = 0.05
0.1
0.15
0.2



corrosion rate of Cr 2+ (mm/day)
0.4 0.39 0.38 0.37 0.36 0.35 0.34
0 0.05 0.1 0.15 0.2 0.25
wt_Cr
wt_Fe = 0.05
0.1
0.15
0.2

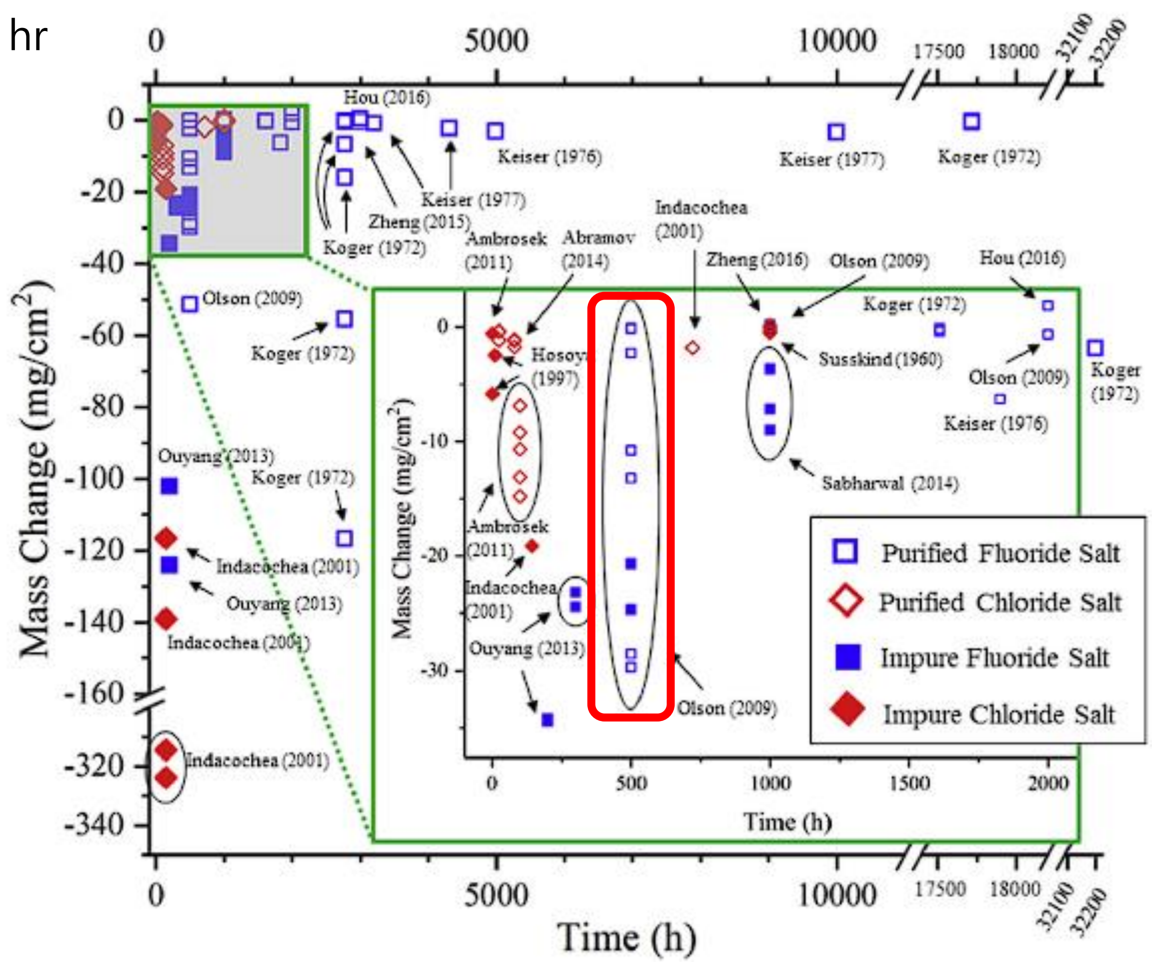


corrosion rate of Cr 2+ (mm/day)
0.4 0.39 0.38 0.37 0.36 0.35 0.34
0 0.05 0.1 0.15 0.2 0.25
wt_Fe
wt_Cr = 0.05
0.1
0.15
0.2

Conclusion

- 0.35mm/day with 500 hr
- 5.15 g/cm^2

S.S. Raiman, S. Lee / Journal of Nuclear Materials 511 (2018) 523–535



Conclusion

- We assume impurity HF was maximum value using Henry constant.
- We assume alloy was ideal solution.
- Result was not linear. If we optimize this system, we can find minimum point and composition of alloy.