

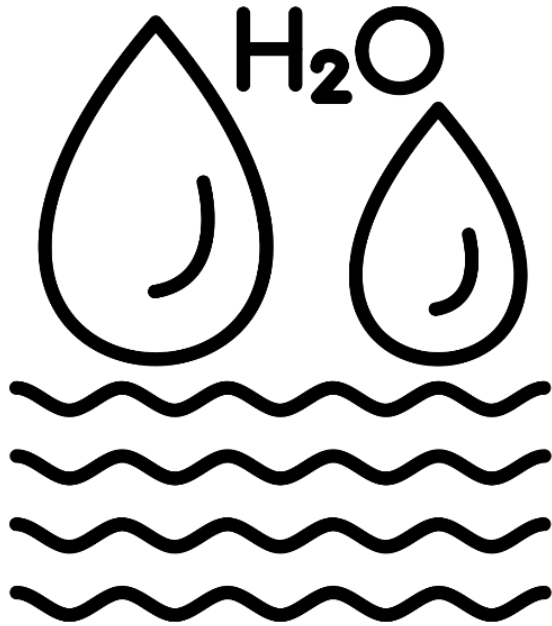
혁신 원자력 시스템의 핵연료 및 원자력 재료 기술 워크숍

용융염 원자로용 구조 소재 부식거동 예측을 위한 다물리 시뮬레이션 전략

이정환, 조매현, 장근옥

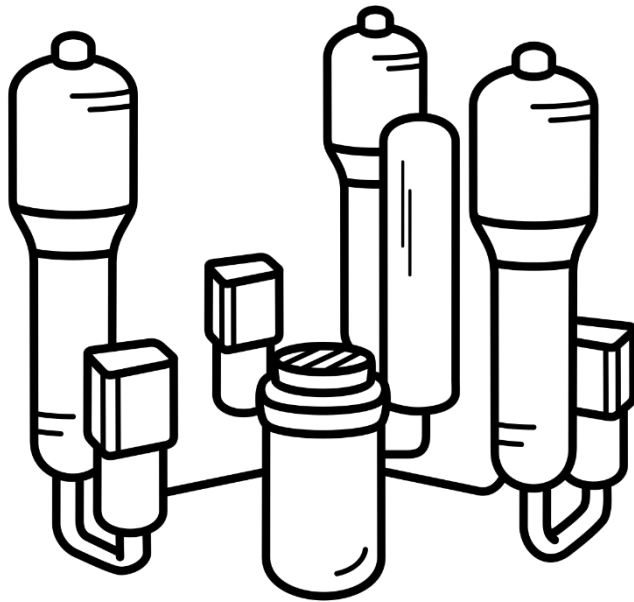
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Water



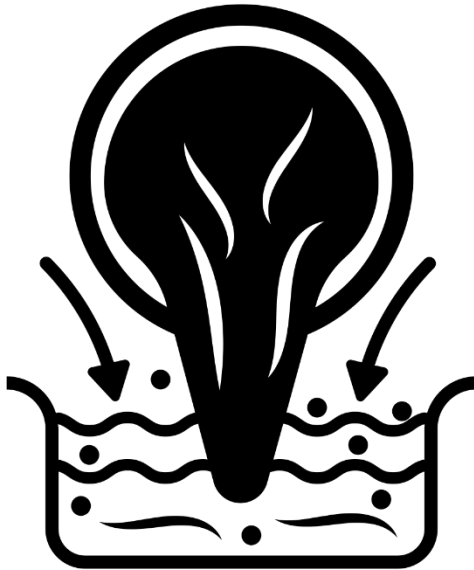
- 흔하다. (문명이 있는 지역에는 물이 있다.)
- 싸다.
- 다루기 쉽다.
- 경험이 많다.
- 통상적으로는 독성이 없다.
- 인체에 무해하다.
- 감속성능이 좋다.
- 화학적 안정성이 뛰어나다.
- 중성자에 의한 activation이 심하지 않다.
- 증기압이 상대적으로 높다.
- 가압이 필요하다.
- 여러 요인을 고려하여, 경수로 가동조건은 290°C , 150기압으로 설정.

□ Pressurizer



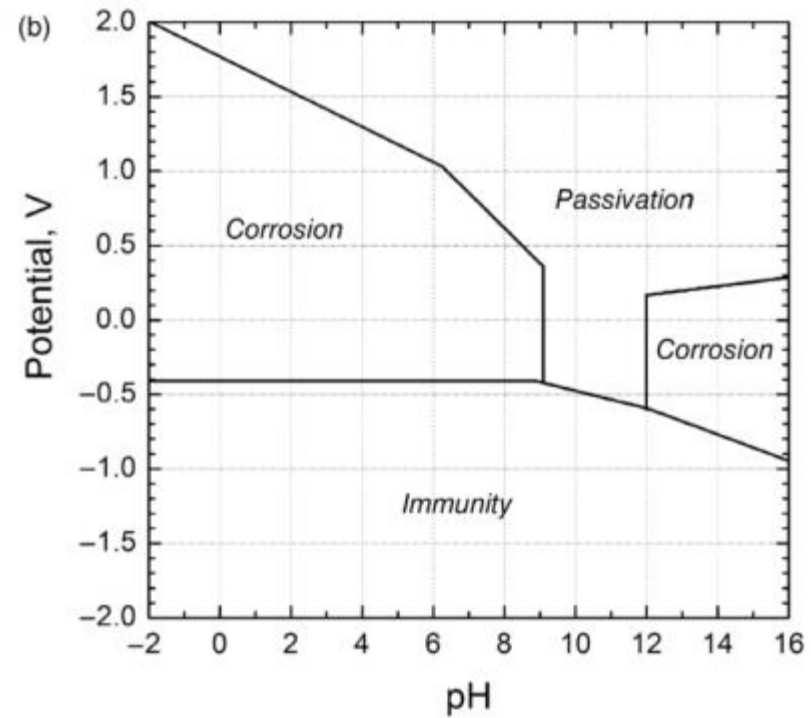
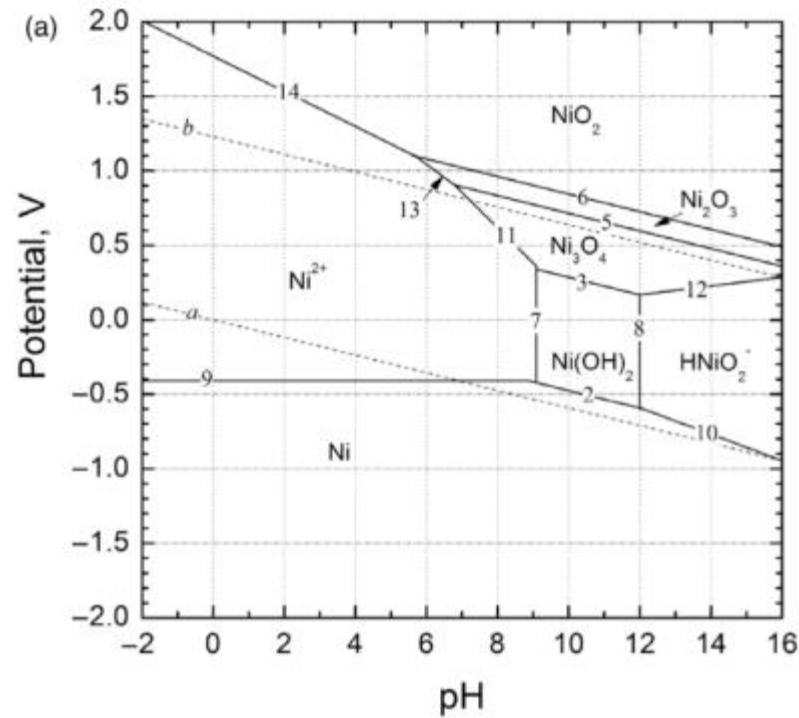
- 에너지가 많이 든다.
- 가압 계통은 비싸다.
- 가압 계통은 통상 가압계통을 위한 냉각 계통이 별도로 존재해야한다.
- 가압하면서 여타 압력경계를 이루는 부품들이 다 비싸지고 만들기가 어려워진다.

□ Molten Salt



- 물보다 증기압이 훨씬 낮다. 융점이 높다.
- 액체 금속과 비교하여 투명하다.
- 용융염의 가격도 저렴한 편이다.
- 가압계통이 필요없고, 매우 단순한 원자로를 만들 수 있다.
- Inherent safety가 우수: 강한 음의
- feedback을 통해 300°C 근처에서 자동으로 정지한다.
- 하지만 저런 문제점을 보완하기 위해 복잡해지기 시작하면 커지고 그러면 메리트가 크게 떨어진다.

부식 보호 – Passivation



합금 개발 방향 - 스테인리스강

- 스테인리스강
 - 합리적인 가격, 많은 경험
 - 소재표면의 알루미나(Al_2O_3)가 안정된 형태로 존재하며 부동태 역할을 할 수 있다는 보고가 있음. [S.Guo et al. Prog. Mater. Sci. 97 (2018) 448-487]
 - Al의 함량을 높은 스테인리스강 (Fe-16Cr-8Al)의 경우 700°C KCl-NaCl-MgCl₂ 용융 염에서 500시간 부식한 결과에서 Cr 고갈은 거의 발견되지 않았음. [W. Ding et al. Sol. Energ. Mat. Sol. C. 193 (2019) 298-313]
 - 만약 스테인리스강을 쓴다면 높은 air-side 부식저항성과 합리적인 기계적 성질 합리적인 가격대를 기대할 수 있음.

합금 개발 방향 – 니켈 기반 합금

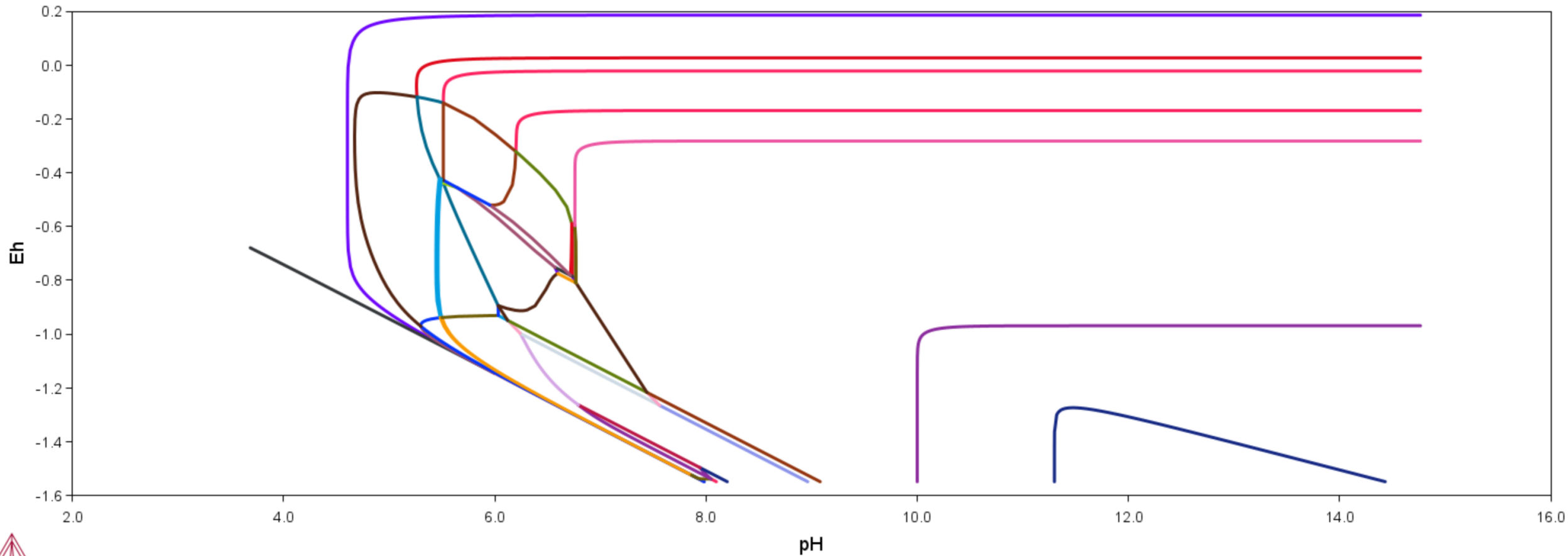
- 니켈기반 합금

- 불화물 환경에서는 내부식 특성이 뛰어난 Hastelloy N이 제안된 바 있음.
- 다만 아직은 실험 결과를 안정적으로 신뢰하기는 어려움.
- 극미량의 수분이나 불순물 등 변수들에 따라 실험 결과가 매우 민감하게 바뀜.
- Ni 가격이 급상승한 것은 최근 발생한 변수.
- 중성자 조사시에 activation이 Fe 대비로 좀 더 많이 되는 것으로 알려져 있음.
- 아무래도 높은 가격대가 가장 큰 도전임.

Pourbaix diagram

T = 750°C, P = 100000 Pa
Database = FEDEMO, PAQ2

Fe-12Cr-30Ni in NaCl aqueous



Phase list

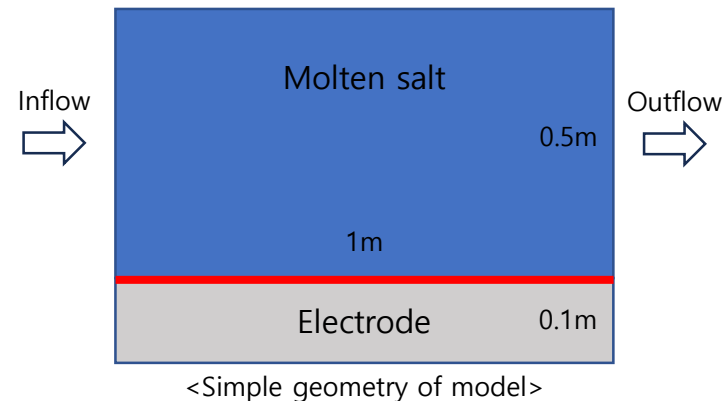
T = 750°C, P = 100000 Pa
Database = FEDEMO, PAQ2

Fe-12Cr-30Ni in NaCl aqueous

— GAS + AQUEOUS + HALITE + NA ₂ FeO ₂ + NIO_S2 + NaOH_S2	— GAS + AQUEOUS + CR ₂ O ₃ + HALITE + NIFE ₂ O ₄ + FECR ₂ O ₄
— GAS + AQUEOUS + HALITE + NA ₂ FeO ₂ + NIO_S2 + NIFE ₂ O ₄	— GAS + AQUEOUS + CR ₂ O ₃ + HALITE + NICKR ₂ O ₄ + NIFE ₂ O ₄ + FECR ₂ O ₄
— GAS + AQUEOUS + HALITE + NIFE ₂ O ₄ + NIO_S2	— GAS + AQUEOUS + HALITE + NICKR ₂ O ₄ + NIFE ₂ O ₄ + FECR ₂ O ₄
— GAS + AQUEOUS + HALITE + NICKR ₂ O ₄ + NIFE ₂ O ₄ + NIO_S2	— GAS + AQUEOUS + HALITE + NICKR ₂ O ₄ + NIFE ₂ O ₄ + CR ₂ O ₃
— GAS + AQUEOUS + FECR ₂ O ₄ + HALITE + NICKR ₂ O ₄ + NIFE ₂ O ₄ + NIO_S2	— GAS + AQUEOUS + HALITE + NIFE ₂ O ₄ + CR ₂ O ₃
— GAS + AQUEOUS + FECR ₂ O ₄ + HALITE + NIFE ₂ O ₄ + NIO_S2	— GAS + AQUEOUS + HALITE + HEMATITE + NIFE ₂ O ₄ + CR ₂ O ₃
— GAS + AQUEOUS + FECR ₂ O ₄ + HALITE + NIO_S2	— GAS + AQUEOUS + HALITE + HEMATITE + CR ₂ O ₃
— GAS + AQUEOUS + FCC_A1 + FECR ₂ O ₄ + HALITE + NIO_S2	— GAS + AQUEOUS + HALITE + CR ₂ O ₃
— GAS + AQUEOUS + FCC_A1 + FECR ₂ O ₄ + HALITE + NIFE ₂ O ₄ + NIO_S2	— GAS + AQUEOUS + FCC_A1 + HALITE + CR ₂ O ₃
— GAS + AQUEOUS + FCC_A1 + HALITE + NIFE ₂ O ₄ + NIO_S2	— GAS + AQUEOUS + HALITE + FCC_A1
— GAS + AQUEOUS + FCC_A1 + HALITE + NIFE ₂ O ₄ + FECR ₂ O ₄	— GAS + AQUEOUS + FCC_A1
— GAS + AQUEOUS + FCC_A1 + HALITE + NIFE ₂ O ₄ + MAGNETITE	— GAS + AQUEOUS + HALITE
— GAS + AQUEOUS + FCC_A1 + FECR ₂ O ₄ + HALITE + NIFE ₂ O ₄ + MAGNETITE	— GAS + AQUEOUS + HALITE + HEMATITE
— GAS + AQUEOUS + FCC_A1 + FECR ₂ O ₄ + HALITE + WUSTITE + MAGNETITE	— GAS + AQUEOUS + HALITE + HEMATITE + NIFE ₂ O ₄
— GAS + AQUEOUS + FCC_A1 + HALITE + WUSTITE + MAGNETITE	— GAS + AQUEOUS + HALITE + NIFE ₂ O ₄ + NICKR ₂ O ₄
— GAS + AQUEOUS + FCC_A1 + HALITE + WUSTITE + FECR ₂ O ₄	— GAS + AQUEOUS + FECR ₂ O ₄ + HALITE + NIFE ₂ O ₄ + HEMATITE
— GAS + AQUEOUS + FCC_A1 + HALITE + FECR ₂ O ₄	— GAS + AQUEOUS + FECR ₂ O ₄ + HALITE + HEMATITE
— GAS + AQUEOUS + CR ₂ O ₃ + FCC_A1 + HALITE + FECR ₂ O ₄	— GAS + AQUEOUS + FECR ₂ O ₄ + HALITE + NIFE ₂ O ₄
— GAS + AQUEOUS + CR ₂ O ₃ + HALITE + FECR ₂ O ₄	— GAS + AQUEOUS + FCC_A1 + HALITE + WUSTITE
— GAS + AQUEOUS + CR ₂ O ₃ + HALITE + HEMATITE + FECR ₂ O ₄	
— GAS + AQUEOUS + CR ₂ O ₃ + HALITE + HEMATITE + NIFE ₂ O ₄ + FECR ₂ O ₄	

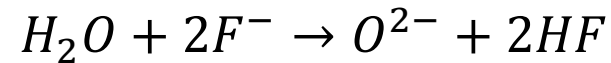
Model Geometry

- 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.



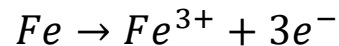
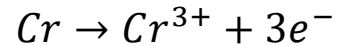
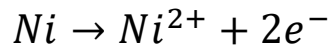
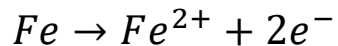
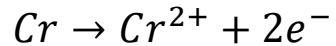
Model Assumptions

- We assume alloy element is Cr, Ni, Fe.
- Water is inevitable impurity. If there is water in salt, HF will generate with below reaction.

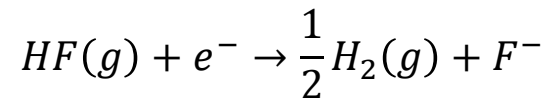
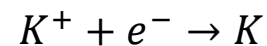
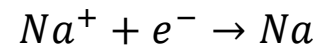
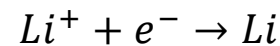


- Therefore, we choose 5 anodic reaction, and 4 cathodic reaction.

- Anodic reaction



- Cathodic reaction



Initial concentration

- 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-Planck 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.

Equilibrium potential

- Right graph is redox potential for various redox couple in molten salt.
- With this curve, we choose E_{eq} at 750°C

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

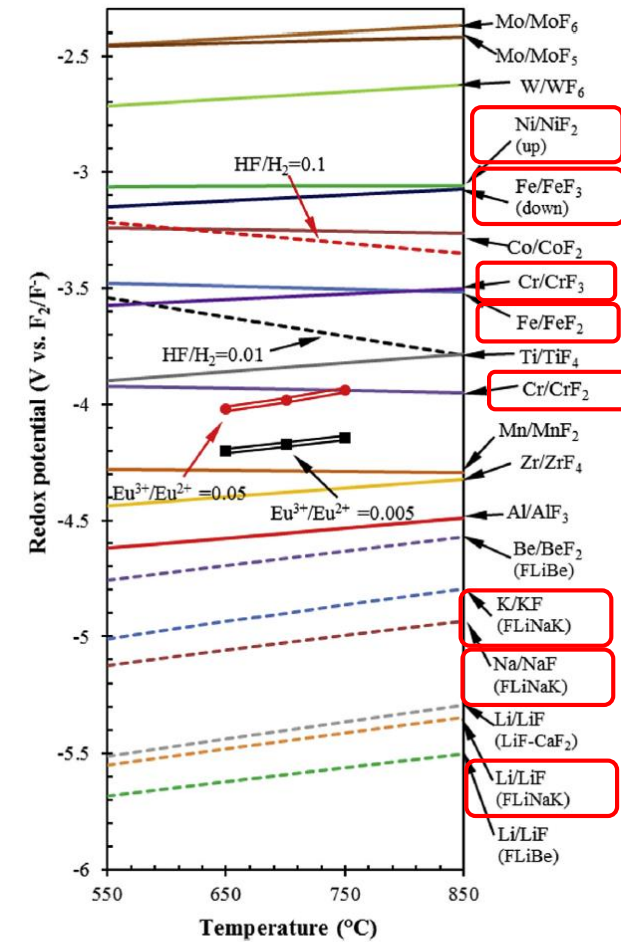


Fig. 8. Redox potential versus temperature for various redox couples in FLiNaK and FLiBe salts. Solid line: metal dissolution at limit activity of 10^{-6} ; Dotted line: reduction of oxidants. $HF/H_2 = 0.1$: a mole ratio of $HF/H_2 = 0.1$ at 1 atm total pressure. Double solid line: redox potential calculated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

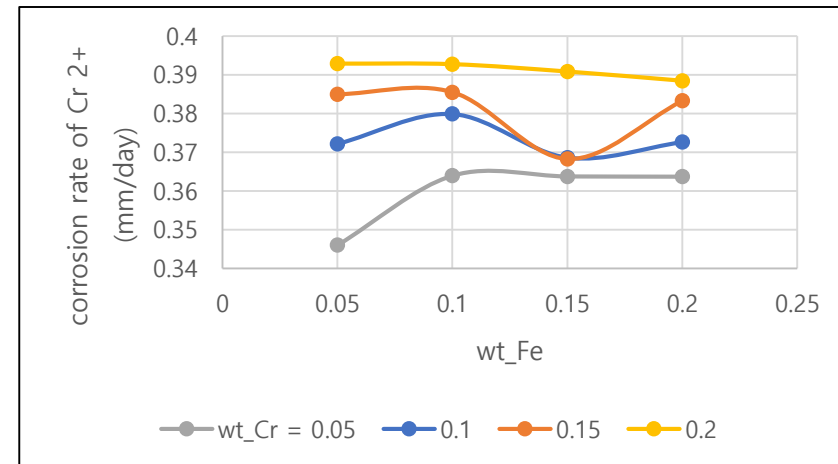
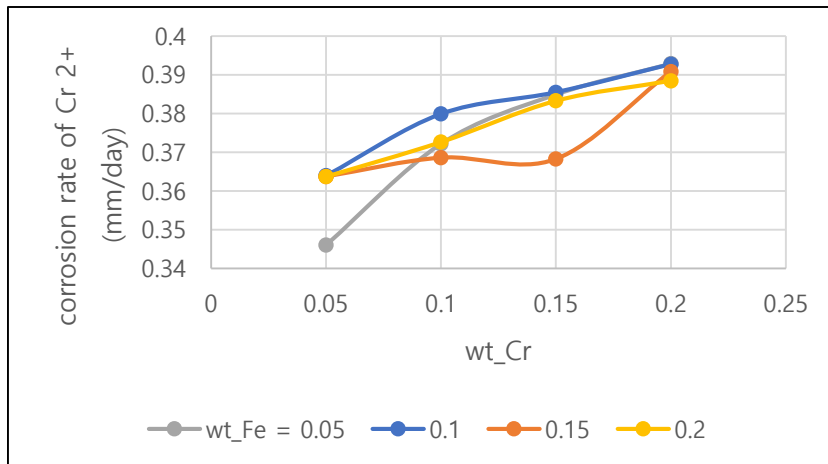
Result

- We measured the current of each chemical species from the cases of different composition of Ni-Cr-Fe alloy.

wt_Cr	wt_Fe	Current of Cr ²⁺ (A/m ²)	Current of Cr ³⁺ (A/m ²)	Current of Fe ²⁺ (A/m ²)	Current of Fe ³⁺ (A/m ²)	Current of Ni ²⁺ (A/m ²)	Current of HF (A/m ²)	Total Current(A/m ²)
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

- It is not straightforward to correlate the composition of materials to corrosion rate directly. The activity data is not good enough in terms of accuracy and data volume. We estimated the rate in very primitive way with assumption of ideal solution model. The positive value means that the oxidation reaction occurs.



THANK YOU!
