

**LABORATORY
NOTEBOOK**

GEOSCIENCES & ENGINEERING DIVISION



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Topic #1: Effects of Alloy Sulfur on the Corrosion Resistance of Alloy 22

1. Induction Time Calculation

Based on the observations by Marcus, et al, (Marcus and Talah, 1989) the passive film formed on Ni-based alloys can be broken time after certain induction time if the segregated sulphur concentration is above the critical concentration (i.e., 40 ng/cm²). Assuming all sulfur can present in the alloy accumulates at the metal-film interface, the concentration of sulfur at the interface (θ_s^{interf}) with time was estimated using a Faraday's law.

$$\theta_s^{interf}(t) = \frac{MS}{nF} \int i dt \quad (1)$$

where, M: atomic weight (Ni), S: alloy sulfur concentration (ppm in wt. %), n: number of electron exchanged (2), F: Faraday constant (96485 Coulomb/mol), i: passive current density (A/cm²), t: time (hrs).

The induction time (τ) is the time required to reach a critical concentration of sulfur at the metal-oxide interface ($\theta_{s,max}^{interf}$) above which a breakdown of a passive film occurs.

Assuming that the current density does not change as long as the sample remains passivated, the induction time (t) at a constant passive current density (i) is estimated as

$$\tau = \frac{\theta_{s,max}^{interf} nF}{iMS}$$

where, $\theta_{s,max}^{interf}$ (40 ng/cm²)
 • n (2)
 • F (96485 C/mol) (2)
 • i (C/cm²·yr)
 • M (58.69 g/mol)
 • S (ppm, fraction)

The Eq. 2 is applied to estimate an approximate value of the induction time for Alloy 22 system where i and S are known assuming same or similar mechanisms of sulfur effects in Alloy 22 to Ni or Ni-Fe alloys.

Assumption: The sulfur present in Alloy 22 accumulates at the metal-film interface during passive dissolution and a passive film breakdown can occur above a critical sulfur concentration of 40 ng/cm², the induction time for film breakdown of Alloy 22 under deaerated condition was estimated by utilizing Eq. 2. In these calculations, the passive current density is a temperature dependent Arrhenius function with the activation energy of 44.7 kJ/mol [47.1 Btu/mol] with a reference passive current density of 10⁻⁸ A/cm² [6.5 × 10⁻⁸ A/ft²] at 95 °C [203.25 °F]. These values are consistent with the TPA code (Dunn, et al., 2005). Figure 1 presents the resultant induction time at 10, 50, 100, 200, 1,000 and 2,000 ppm of sulfur concentrations as a function of temperature and summarized values in Table 1 at 25 and 90 °C [77 and 194 °F].

Reference

Dunn, D. S., O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. "Passive and Localized Corrosion of Alloy 22—Modeling and Experiments." CNWRA 2005-02 Revision 1 Center for Nuclear Waste Regulatory Analyses. San Antonio, Texas: CNWRA. 2005.

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Marcus, P. and H. Talah. "The Sulfur Induced Breakdown of the Passive Film and Pitting Studied on Nickel and Nickel Alloys." *Corrosion Science*. Vol. 29, pp. 455 – 463. 1989.

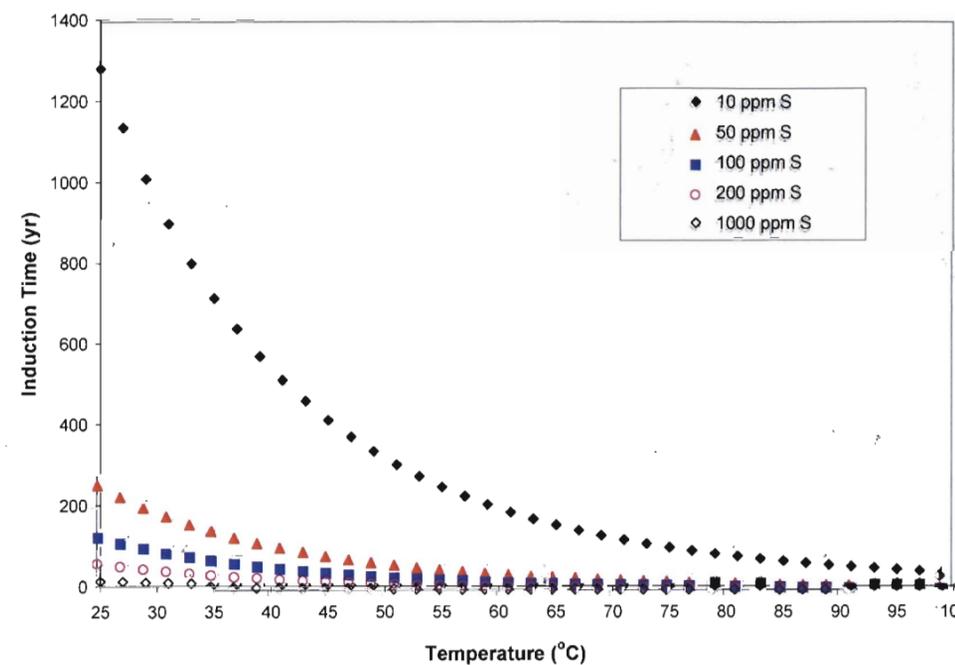


Figure 1. Calculated Induction Time of Alloy 22 as a Function of Temperature.

Table 1. Calculated Induction Time With Various Sulfur Concentrations at 25 and 90 °C [77 and 194 °F].

S Concentration (ppm in weight percent)	Induction Time (years)	
	25 °C [77 °F]	90 °C [194 °F]
10	1,278	50
50	255	10
100	127	5
200	63	2.5
1,000	12	0.5
2,000	6	0.25

Note: Detail calculations are recorded on page 19 as a spreadsheet form. *Jy Akhel*

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As seen in Figure 1 and Table 1, the induction time decreases linearly as the sulfur concentration increases at both temperatures. At 25 °C [77 °F], the induction time for 10 ppm of S is 1,278 yrs, but as S concentration increases to 200 ppm, the induction time decreases to 63 yrs which is about 20 times smaller than 10 ppm of S. The effect of temperature on the induction time is more significant than S concentration. As the temperature increases, the induction time decreases exponentially at a given S concentration. At 90 °C [194 °F], the induction times for 10 ppm and 200 ppm of S are 50 and 2.5 yrs, respectively. In the case of 2,000 ppm of S at 90 °C [194 °F], the resultant induction time is 0.25 yrs (91.25 days). Considering a nominal range of bulk sulfur concentration in Alloy 22 (i.e., less than 0.02 wt.% = 200 ppm in wt.%) and a generally low passive current density {e.g., $< 10^{-8}$ A/cm² [6.5×10^{-8} A/ft²]} in Alloy 22, the calculation result indicates that the film breakdown on Alloy 22 could occur after 2.5 yrs or longer under deaerated condition assuming sulfur in the alloy segregates at the metal-film interface without dissolving into the solution. Note that the calculation is valid under designated conditions as above. The equation 4-2 may need to be further modified if Alloy 22 has a different degradation mechanism of anodic sulfur segregation. For example, if Cr and Mo contents in Alloy 22 can affect significantly to the long-term effects of sulfur related mechanisms, the equation 4-2 is not valid any more. This assumption, however, may be partially validated by the observation of pitting corrosion of Alloy C-4 (Ni-19.4Cr-13.8Mo-2.4Fe) tested in sulfur containing chloride-rich solution at 150 °C. (Smailos, 1993).

Reference

Smailos, E. "Corrosion of High-Level Waste Packaging Materials in Disposal Relevant Brines." Nuclear Technology. Vol. 104. pp. 343-350. 1993.

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2. Thermodynamic stability diagrams of Metal (Ni, Cr, Mo) – S – H₂O systems

2.1. Ni – S – H₂O system

2.1.1 Thermodynamic data

The thermodynamic data used in the calculation are referenced from HSC (database name) as the thermodynamic database.

HSC, "Outokumpu HSC Chemistry for Windows," Version 5.1, Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

Reaction Data	25 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	NiS	-80.22	HSO4-	-755.66
Temperature=	298	K	H2O(l)	-237.14	Ni3S2	-210.45	SO4--	-744.36
Activity of Ni Species=	1E-06	molar	O2(g)	0.00	Ni3S4	-291.99	HS-	12.08
Activity of S Species=	1E-06	molar	H2(g)	0.00	NiSO4	-762.33	S--	85.80
Faradays Constant=	96485.3	C/s	Ni	0.00	Ni(OH)2	-446.93	S	0.00
In to log=	2.303		NiO	-211.58	NiOH+	-227.27	H2S	-28.60
			Ni++	-45.68	Ni(OH)3-	-587.10		

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Reaction Data	90 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	NiS	-84.64	HSO4-	-726.00
Temperature=	388	K	H2O(l)	-231.10	Ni3S2	-209.14	SO4--	-706.10
Activity of Ni Species=	1E-06	molar	O2(g)	0.00	Ni3S4	-289.94	HS-	19.12
Activity of S Species=	1E-06	molar	H2(g)	0.00	NiSO4	-738.18	S--	85.80
Faradays Constant=	96485.3	C/s	Ni	0.00	Ni(OH)2	-428.88	S	0.00
In to log=	2.303		NiO	-205.47	NiOH+	-214.51	H2S	-26.90
			Ni++	-43.62	Ni(OH)3-	-536.75		

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2.2.1. List of Reactions and Corresponding Parameters values.

At 25 °C

No	id	electrode reaction	n	m	dGo	Eo	logK	A value, $Eo - 0.0591/n \cdot \log(a/a)$	pH slope pH value	X1	X2	Y1	Y2
1	Ni++/Ni	Ni++ + 2e -> Ni	2	0	45.680	-0.237	6	-0.414	0.000	0.00	3.29	-0.41	-0.41
2	Ni++/Ni3S2	3Ni++ + 2HS- + 2e -> Ni3S2 + 4H+	2	-4	-16.210	0.084	30	-0.803	0.118	3.29	5.04	-0.41	-0.21
3	Ni++/Ni3S2	3Ni++ + 2HS- + 4e -> Ni3S2 + 2H+	4	-2	-97.570	0.253	30	-0.191	0.030	0.00	14.00	-0.19	0.22
4	Ni++/Ni3S2	3Ni++ + 2HSO4- + 14H+ + 10e -> Ni3S2 + 8H2O	10	14	-459.218	0.476	30	0.299	-0.083	0.00	14.00	0.30	-0.86
5	Ni++/Ni3S2	3Ni++ + 2SO42- + 16H+ + 18e -> Ni3S2 + 8H2O	18	16	-481.818	0.277	30	0.179	-0.053	7.34	9.24	-0.20	-0.28
6	Ni++/Ni3S2	3Ni++ + H2S -> NiS + 2H+	0	-2	-10.944	#DIV/0!	12	#DIV/0!	#DIV/0!	5.04			
7	Ni++/NiS	Ni++ + HS- -> NiS + H+	0	-1	-51.624	#DIV/0!	12	#DIV/0!	#DIV/0!	2.95			
8	Ni++/NiS	Ni++ + HSO4- + 7H+ + 6e -> NiS + 4H2O	6	7	-232.448	0.402	12	0.283	-0.069				
9	Ni++/NiS	Ni++ + SO42- + 8H+ + 8e -> NiS + 4H2O	8	8	-243.748	0.316	12	0.227	-0.059	4.54	7.34	-0.03	-0.20
10	Ni++/Ni3S4	3Ni++ + 4HS- -> Ni3S4 + 8H+ + 2e	-2	-8	-40.550	-0.210	42	1.032	-0.237	5.04	4.49	-0.16	-0.03
11	Ni++/Ni3S4	3Ni++ + 4HS- -> Ni3S4 + 4H+ + 2e	-2	-4	-203.270	-1.053	42	0.189	-0.118				
12	Ni++/Ni3S4	3Ni++ + 4HSO4- + 28H+ + 30e -> Ni3S4 + 16H2O	30	28	-926.566	0.320	42	0.237	-0.055				
13	Ni++/Ni3S4	3Ni++ + SO42- + 32H+ + 30e -> Ni3S4 + 16H2O	30	32	-971.766	0.336	42	0.253	-0.063	4.49	4.54	-0.030	-0.033
14	Ni++/Ni3S2	3Ni + 2H2S -> Ni3S2 + 4H+ + 4e	-4	-4	-153.250	-0.397	12	-0.220	-0.059				
15	Ni++/Ni3S2	3Ni + 2HS- -> Ni3S2 + 2H+ + 4e	-4	-2	-234.610	-0.608	12	-0.430	-0.030				
16	Ni++/Ni3S2	3Ni + 2S- -> Ni3S2 + 4e	-4	0	-382.050	-0.990	12	-0.813	0.000				
17	Ni++/NiS	Ni + H2S -> NiS + 2H+ + 2e	-2	-2	-56.624	-0.293	6	-0.116	-0.059				
18	Ni++/NiS	Ni + HS- -> NiS + H+ + e	-1	-1	-97.304	-1.008	6	-0.654	-0.059				
19	Ni++/NiS	Ni + S- -> NiS + 2e	-2	0	-171.024	-0.886	6	-0.709	0.000				
20	Ni++/Ni3S4	3Ni + 4H2S -> Ni3S4 + 8H+ + 8e	-8	-8	-177.590	-0.230	24	-0.053	-0.059				
21	Ni++/Ni3S4	3Ni + 4HS- -> Ni3S4 + 4H+ + 8e	-8	-4	-340.310	-0.441	24	-0.263	-0.030				
22	Ni++/Ni3S4	3Ni + 4S- -> Ni3S4 + 8e	-8	0	-635.190	-0.823	24	-0.645	0.000				
23	NiO/SO4--Ni3S2	NiO + 2SO4-- + 18H+ + 14e -> Ni3S2 + 9H2O	14	18	-644.419	0.477	12	0.426	-0.076	9.24	11.31	-0.28	-0.43
24	Ni(OH)3/SO4--Ni	3Ni(OH)3- + 2SO4-- + 25H+ + 19e -> Ni3S2 + 17H2O	19	25	-991.827	0.541	30	0.448	-0.078	11.30	14.00	-0.43	-0.64
25	Ni(OH)3/Ni3S2	3Ni + 2H2S -> Ni3S2 + 4H+ + 4e	-4	-4	-153.250	-0.397	12	-0.220	-0.059	3.29	7.13	-0.41	-0.64
26	Ni(OH)3/Ni3S2	3Ni + 2HS- -> Ni3S2 + 2H+ + 4e	-4	-2	-234.610	-0.608	12	-0.430	-0.030	7.13	14.00	-0.64	-0.84
27	Ni(OH)3/NiS	Ni3S2 + H2S -> 3NiS + 2H+ + 2e	-2	-2	-16.622	-0.086	6	0.091	-0.059	5.04	7.13	-0.21	-0.33
28	Ni(OH)3/NiS	Ni3S2 + HS- -> 3NiS + H+ + 2e	-2	-1	-57.302	-0.297	6	-0.120	-0.030	7.13	9.96	-0.33	-0.41
29	Ni(OH)3/Ni3S2	Ni3S2 + SO4-- + 4H+ + 2e -> 3NiS + 2H2O	2	4	224.856	-1.165	6	-1.343	-0.118	9.96	7.34	-0.41	-0.20
30	Ni(OH)3/Ni3S4	3NiS + H2S -> Ni3S4 + 2H+ + 2e	-2	-2	-64.918	-0.336	6	-0.159	-0.059	5.04	7.13	-0.16	-0.28
31	Ni(OH)3/Ni3S4	3NiS + HS- -> Ni3S4 + H+ + 2e	-2	-1	-48.398	-0.251	6	-0.073	-0.030	7.13	8.71	-0.28	-0.33
32	Ni(OH)3/Ni3S4	3NiS + 4S- -> Ni3S4 + 2e -> Ni3S4 + 2H2O	2	4	233.760	-1.211	6	-1.389	-0.118	8.71	4.54	-0.33	-0.03

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No	id	No electron consumption or generation	n	m	dGo	Eo	logK	A value $Eo - 0.0591/n \cdot \log(a/a)$	pH slope pH value	X1	X2	Y1	Y2
17	Ni++/H2S/NiS	Ni++ + H2S -> NiS + 2H+	0	-2	-10.944	#DIV/0!	12	#DIV/0!	5.04	5.04	5.04	-0.20	-0.16
18	Ni++/NiO	Ni++ + H2O -> NiO + 2H+	0	-2	71.241	#DIV/0!	6	#DIV/0!	9.24	9.24	9.24	-0.28	1.00
19	NiO/Ni(OH)3-	NiO + 2H2O -> Ni(OH)3- + H+	0	-1	98.762	#DIV/0!	-6	#DIV/0!	11.31	11.31	11.31	-0.43	1.00
O2	O2/H2O	O2 + 4H+ + 4e -> 2H2O	4	4	-474.282	1.229	0	1.229	-0.059	0.00	14.00	1.23	0.40
H2	H+/H2	2H+ + 2e -> H2	2	2	0	0.000	0	0.000	-0.059	0.00	14.00	0.00	-0.83
S1		HSO4- -> H+ + SO4--	0	-1	11.300	#DIV/0!	0	#DIV/0!	1.98	1.98	1.98	0.14	1.00
S2		H2S -> HS- + H+	0	-1	40.680	#DIV/0!	0	#DIV/0!	7.13	7.13	7.13	-1.60	-0.27
S3		HS- -> S- + H+	0	-1	73.720	#DIV/0!	0	#DIV/0!	12.92	12.92	12.92	-1.60	-0.65
S4		HSO4- + 7H+ + 6e -> S + 4H2O	6	7	-192.904	0.333	6	0.27	-0.069	0.00	1.98	0.27	0.14
S5		SO4-- + 8H+ + 6e -> S + 4H2O	6	8	-204.204	0.353	6	0.29	-0.079	1.98	7.13	0.14	-0.27
S6		SO4-- + 9H+ + 8e -> HS- + 4H2O	8	9	-192.124	0.249	0	0.25	-0.067	7.13	12.92	-0.27	-0.65
S7		SO4-- + 8H+ + 8e -> S- + 4H2O	8	8	-118.404	0.153	0	0.15	-0.059	12.92	14.00	-0.65	-0.72
S8		S + 2H+ + 2e -> H2S	2	2	-28.600	0.148	0	0.15	-0.059	0.00	7.13	0.15	-0.27
S9		S + H+ + 2e -> HS-	2	1	12.080	-0.063	-6	0.11	-0.030	7.13	12.92	-0.27	-0.65

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At 90 °C

No	id	electrode reaction	n	m	dGo	Eo	logK	A value Eo- 0.0591n*log(ka)	pH slope	pH value	X1	X2	Y1	Y2
1	Ni+/Ni	Ni++ + 2e -> Ni	2	0	43,618	-0.226	6	-0.457	0.000		0.00	3.71	-0.46	-0.46
2	Ni+/Ni3S2	3Ni++ + 2HS- + 2e -> Ni3S2 + 4H+	2	-4	-24,481	0.127	30	-1.028	0.154		3.71	5.05	-0.46	-0.25
	Ni+/Ni3S2	3Ni++ + 2HS- + 4e -> Ni3S2 + 2H+	4	-2	-116,520	0.302	30	-0.276	0.038					
	Ni+/Ni3S2	3Ni++ + 2HSO4- + 14H+ + 10e -> Ni3S2 + 8H2O	10	14	-474,297	0.492	30	0.261	-0.108					
6	Ni+/Ni3S2	3Ni++ + 2SO42- + 16H+ + 18e -> Ni3S2 + 8H2O	18	16	-514,095	0.296	30	0.168	-0.068		6.11	7.65	-0.25	-0.33
	Ni+/NiS	Ni++ + H2S -> NiS + 2H+	0	-2	-14,117	#DIV/0!	12	#DIV/0!	#DIV/0!	4.76				
	Ni+/NiS	Ni++ + HS- -> NiS + H+	0	-1	-60,137	#DIV/0!	12	#DIV/0!	#DIV/0!	1.46				
	Ni+/NiS	Ni++ + HSO4- + 7H+ + 6e -> NiS + 4H2O	6	7	-239,025	0.413	12	0.259	-0.090					
5	Ni+/NiS	Ni++ + SO42- + 8H+ + 8e -> NiS + 4H2O	8	8	-258,924	0.335	12	0.220	-0.077		4.89	6.11	-0.15	-0.25
3	Ni+/Ni3S4	3Ni++ + 4HS- -> Ni3S4 + 4H+ + 2e	-2	-4	-235,555	-1.221	42	0.396	-0.154					
	Ni+/Ni3S4	3Ni++ + 4HSO4- + 28H+ + 30e -> Ni3S4 + 16H2	30	28	-951,108	0.329	42	0.221	-0.072		5.05	4.88	-0.21	-0.15
4	Ni+/Ni3S4	3Ni++ + 4SO42- + 32H+ + 30e -> Ni3S4 + 16H2O	32	32	-1,030,704	0.356	42	0.248	-0.082		4.88	4.89	-0.15	-0.15
	Ni+/Ni3S2	3Ni + 2H2S -> Ni3S2 + 4H+ + 4e	-4	-4	-155,335	-0.402	12	-0.171	-0.077					
	Ni+/Ni3S2	3Ni + 2HS- -> Ni3S2 + 2H+ + 4e	-4	-2	-247,375	-0.641	12	-0.410	-0.038					
	Ni+/Ni3S2	3Ni + 2S- -> Ni3S2 + 4e	-4	0	-407,181	-1.055	12	-0.824	0.000					
	Ni+/NiS	Ni + H2S -> NiS + 2H+ + 2e	-2	-2	-57,735	-0.299	6	-0.068	-0.077					
	Ni+/NiS	Ni + HS- -> NiS + H+ + e	-1	-1	-103,755	-1.075	6	-0.613	-0.077					
	Ni+/NiS	Ni + S- -> NiS + 2e	-2	0	-183,658	-0.952	6	-0.721	0.000					
	Ni+/Ni3S4	3Ni + 4H2S -> Ni3S4 + 8H+ + 8e	-8	-8	-182,330	-0.236	24	-0.005	-0.077					
	Ni+/Ni3S4	3Ni + 4HS- -> Ni3S4 + 4H+ + 8e	-8	-4	-366,410	-0.475	24	-0.244	-0.038					
	Ni+/Ni3S4	3Ni + 4S- -> Ni3S4 + 8e	-8	0	-686,023	-0.889	24	-0.658	0.000					
7	NiO/SO4-Ni	NiO + 2SO4- + 18H+ + 14e -> Ni3S2 + 9H2O	14	18	-670,482	0.496	12	0.430	-0.099		7.65	11.60	-0.33	-0.72
8	Ni(OH)3/SO4	3Ni(OH)3 + 2SO4- + 25H+ + 19e -> Ni3S2 + 11H2O	19	25	-1,113,691	0.608	30	0.486	-0.101		11.60	14.00	-0.72	-0.96
9	Ni(OH)3/Ni3S2	3Ni + 2HS- -> Ni3S2 + 4H+ + 4e	-4	-4	-155,335	-0.402	12	-0.171	-0.077		3.71	6.19	-0.46	-0.65
10	Ni(OH)3/Ni3S2	3Ni + 2HS- -> Ni3S2 + 2H+ + 4e	-4	-2	-247,375	-0.641	12	-0.410	-0.038		6.19	14.00	-0.65	-0.95
11	Ni(OH)3/Ni3S2	3Ni + 2HS- -> Ni3S2 + 2H+ + 2e	-2	-2	-17,870	-0.093	6	0.138	-0.077		5.05	6.19	-0.25	-0.34
12	Ni(OH)3/Ni3S2	3Ni + 2HS- -> Ni3S2 + 2H+ + 2e	-2	-1	-63,890	-0.331	6	-0.100	-0.038		6.19	7.78	-0.34	-0.40
13	Ni(OH)3/SO4-Ni	Ni3S2 + SO4- + 4H+ + 2e -> 3NiS + 2H2O	2	4	199,323	-1.033	6	-1.264	-0.154		7.78	6.19	-0.40	-0.25
14	Ni(OH)3/Ni3S2	3NiS + H2S -> Ni3S4 + 2H+ + 2e	-2	-2	-62,932	-0.326	6	-0.095	-0.077		5.05	6.11	-0.21	-0.29
15	Ni(OH)3/Ni3S2	3NiS + HS- -> Ni3S4 + H+ + 2e	-2	-1	-55,145	-0.286	6	-0.055	-0.038		6.11	6.73	-0.29	-0.31
16	Ni(OH)3/Ni3S2	3NiS + SO4- + 4H+ + 2e -> Ni3S4 + 2H2O	2	4	208,068	-1.078	6	-1.309	-0.154		6.73	4.89	-0.31	-0.15

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Date: 6/16/07

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Date

No	id	No electron consumption or generation	n	m	dGu	Eo	logK	A value Eo- 0.0591n*log(ka)	pH slope	pH value	X1	X2	Y1	Y2
17	Ni+/H2S/Ni	Ni++ + H2S -> NiS + 2H+	0	-2	-14,117	#DIV/0!	12	#DIV/0!	#DIV/0!	5.05	5.05	5.05	-0.25	-0.21
18	Ni+/NiO	Ni++ + H2O -> NiO + 2H+	0	-2	69,150	#DIV/0!	6	#DIV/0!	#DIV/0!	7.65	7.65	7.65	-0.33	1.00
19	Ni(OH)3/NiO	NiO + 2H2O -> Ni(OH)3 + H+	0	-1	130,715	#DIV/0!	-6	#DIV/0!	#DIV/0!	11.60	11.60	11.60	-0.72	1.00
No	id	Oxygen evolution	n	m	dGo	Eo	logK	A value Eo- 0.0591n*log(ka)	pH slope	pH value	X1	X2	Y1	Y2
O2	O2/H2O	O2 + 4H+ + 4e -> 2H2O	4	4	-462,000	1.197	0	1.197	-0.077		0.00	14.00	1.20	0.37
No	id	Hydrogen evolution	n	m	dGo	Eo	logK	A value Eo- 0.0591n*log(ka)	pH slope	pH value	X1	X2	Y1	Y2
H2	H+/H2	2H+ + 2e -> H2	2	2	0	0.000	0	0.000	-0.077		0.00	14.00	0.00	-0.83
		Sulfur	n	m	dGo	Eo	logK	A value Eo- 0.0591n*log(ka)	pH slope	pH value	X1	X2	Y1	Y2
S1		HSO4- -> H+ + SO4--	0	-1	19,899	#DIV/0!	0	#DIV/0!	#DIV/0!	2.68	2.68	2.68	0.02	1.00
S2		H2S -> HS- + H+	0	-1	46,020	#DIV/0!	0	#DIV/0!	#DIV/0!	6.19	6.19	6.19	-1.60	-0.34
S3		HS- -> S- + H+	0	-1	79,903	#DIV/0!	0	#DIV/0!	#DIV/0!	10.76	10.76	10.76	-1.60	-0.73
		Sulfur	n	m	dGo	Eo	logK	A value Eo- 0.0591n*log(ka)	pH slope	pH value	X1	X2	Y1	Y2
S4		HSO4- + 7H+ + 6e -> S + 4H2O	6	7	-198,005	0.342	6	0.27	-0.090		0.00	2.68	0.27	0.02
S5		SO4-- + 8H+ + 6e -> S + 4H2O	6	8	-217,904	0.376	6	0.30	-0.103		2.68	6.19	0.02	-0.34
S6		SO4-- + 9H+ + 8e -> HS- + 4H2O	8	9	-198,787	0.258	0	0.26	-0.087		6.19	10.76	-0.34	-0.73
S7		SO4-- + 8H+ + 8e -> S- + 4H2O	8	8	-118,884	0.154	0	0.15	-0.077		10.76	14.00	-0.73	-0.98
S8		S + 2H+ + 2e -> H2S	2	2	-26,903	0.139	0	0.14	-0.077		0.00	6.19	0.14	-0.34
S9		S + H+ + 2e -> HS-	2	1	19,117	-0.099	-6	0.13	-0.038		6.19	10.76	-0.34	-0.73

Recorded by: J. M. ...

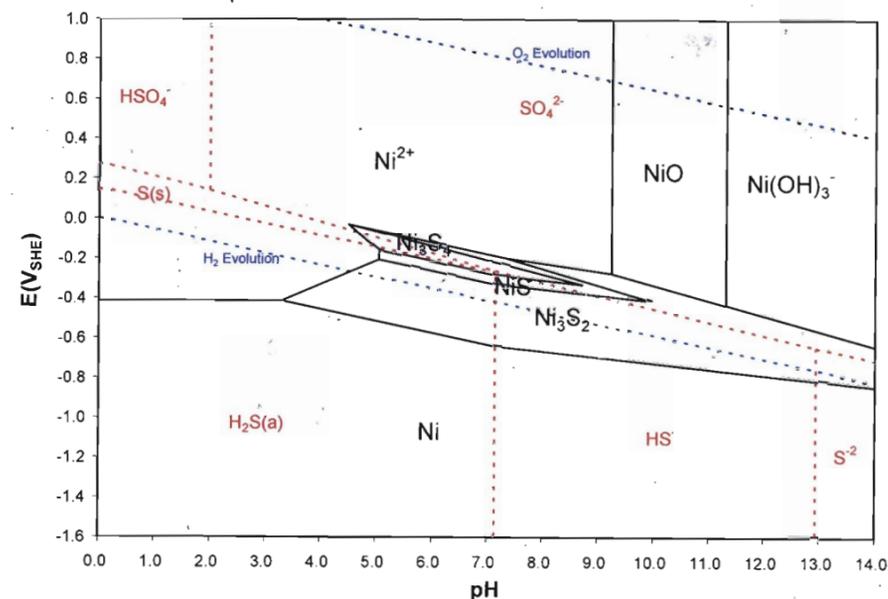
Date: 6/16/07

Verified by:

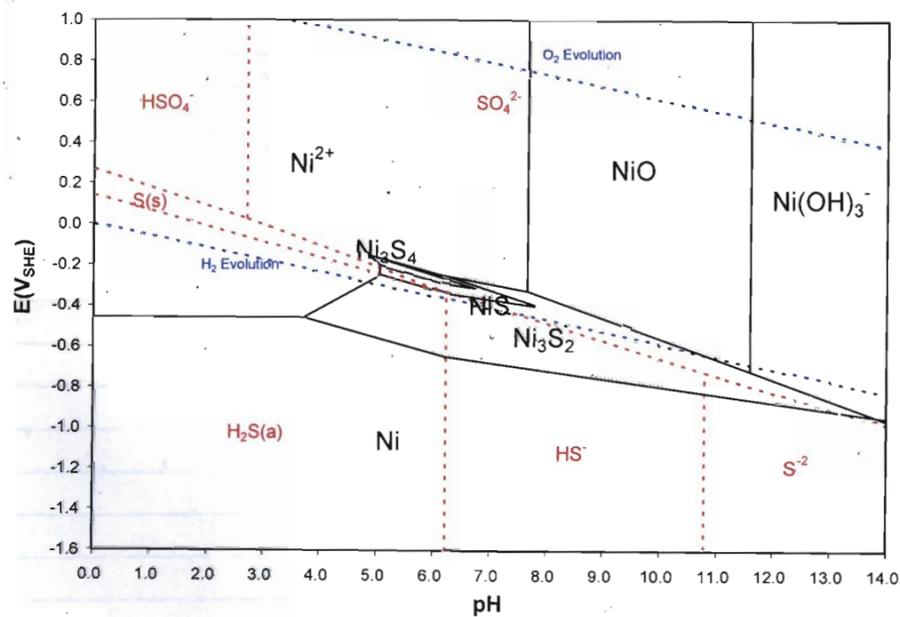
Date

Agua 7/11/07

2.1.3. E-pH diagrams for Ni-S-H₂O system at 25 and 90 °C (Figure 2).



(a)



(b)

Figure 2. E-pH diagrams for Ni-S-H₂O system at (a) 25 °C and (b) 90 °C for 10⁻⁶ M of ions at 1 atm.

Recorded by: *Tytell*

Date: 6/16/09

Verified by:

Date

Entry Date: June 20, 2007

2.2. Cr - S - H₂O system

2.2.1. Thermodynamic data

The thermodynamic data used in the calculation are referenced from HSC (database name) as the thermodynamic database.

HSC, "Outokumpu HSC Chemistry for Windows," Version 5.1, Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

Reaction Data	25 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	CrS	-137.80	HSO4-	-755.66
Temperature=	298	K	H2O(l)	-237.14	Cr2S3	-365.30	SO4--	-744.36
Activity of Ni Species=	1E-06	molar	O2(g)	0.00	Cr3+	-206.41	HS-	12.08
Activity of S Species=	1E-06	molar	H2(g)	0.00	Cr2+	-164.93	S--	85.80
Faradays Constant=	96485.3	C/s	Cr	0.00	CrO2-	-524.46	S	0.00
In to log=	2.303		CrO2	-529.36	CrO4--	-727.81	H2S	-28.60
2.303RT/F=	0.0591		CrO3	-501.23	Cr2O7(-2a)	-1301.35		
			Cr2O3	-1053.11	Cr(OH)2(+a)	-608.78		
			Cr(OH)2	-575.97	H2CrO4(a)	-759.95		
			Cr(OH)3	-846.94	HCrO4(-a)	-764.80		

Reaction Data	90 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	CrS	-138.42	HSO4-	-726.00
Temperature=	388	K	H2O(l)	-231.10	Cr2S3	-365.54	SO4--	-706.10
Activity of Ni Species=	1E-06	molar	O2(g)	0.00	Cr3+	-196.24	HS-	19.12
Activity of S Species=	1E-06	molar	H2(g)	0.00	Cr2+	-165.19	S--	85.80
Faradays Constant=	96485.3	C/s	Cr	0.00	CrO2(-a)	-502.60	S	0.00
In to log=	2.303		CrO2	-517.90	CrO4(-2a)	-692.19	H2S	-26.90
2.303RT/F=	0.0591		CrO3	-483.90	Cr2O7(-2a)	-1258.47		
			Cr2O3	-1035.52	Cr(OH)2(+a)	-582.20		
			Cr(OH)2	-557.34	H2CrO4(a)	-740.70		
			Cr(OH)3	-818.13	HCrO4(-a)	-739.84		

Recorded by: *Tytell*

Date: 06/20/07

Verified by:

Date

2.2.2. List of Reactions and Corresponding Parameters' Values

At 25 °C

No	electrode reaction	n	m	dGo	Eo	logK	A value Eo-0.059/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
1	Cr++ + 2e -> Cr	2	0	164,929	-0.855	6	-1.032	0.000	0.00	7.47	-1.03	-1.03
2	Cr+++ + 3e -> Cr	3	0	206,409	-0.713	6	-0.831	0.000	0.00	4.08	-0.43	-0.43
3	Cr+++ + 4H2O -> HCrO4(-) + 7H+ + 3e	-3	-7	390,176	1.348	0	1.348	-0.138	0.00	4.08	1.35	0.79
4	Cr2O3 + 5H2O -> 2HCrO4(-) + 8H+ + 6e	-6	-8	709,219	1.225	-12	1.107	-0.079	4.08	6.48	0.79	0.60
5	2Cr++ + 3H2O -> Cr2O3 + 6H+ + 2e	-2	-6	-11,827	-0.061	12	0.294	-0.177	4.08	7.47	-0.43	-1.03
6	2Cr + 3H2O -> Cr2O3 + 6H+ + 6e	-6	-6	-341,686	-0.590	0	-0.590	-0.059	7.47	14.00	-1.03	-1.42
7	Cr2O3 + 5H2O -> 2CrO4(2-) + 10H+ + 6e	-6	-10	783,200	1.353	-12	1.235	-0.099	6.48	14.00	0.60	-0.15
No electron consumption or generation												
8	HCrO4(-) -> CrO4(2-) + H+	0	-1	36,991	#DIV/0!	0	#DIV/0!	#DIV/0!	6	6.48	0.60	2.00
9	2Cr+++ + 3H2O -> Cr2O3 + 6H+	0	-6	71,133	#DIV/0!	12	#DIV/0!	#DIV/0!	4	4.08	0.79	-0.43
Oxygen evolution												
O2	O2 + 4H+ + 4e -> 2H2O	4	4	-474,282	1.229	0	1.229	-0.059	0.00	14.00	1.23	0.40
Hydrogen evolution												
H2	2H+ + 2e -> H2	2	2	0	0.000	0	0.000	-0.059	0.00	14.00	0.00	-0.83
Sulfur												
S1	HSO4- -> H+ + SO4--	0	-1	11,300	#DIV/0!	0	#DIV/0!	#DIV/0!	1.98	1.98	0.14	2.00
S2	H2S -> HS- + H+	0	-1	40,680	#DIV/0!	0	#DIV/0!	#DIV/0!	7.13	7.13	-2.00	-0.27
S3	HS- -> S-- + H+	0	-1	73,720	#DIV/0!	0	#DIV/0!	#DIV/0!	12.92	12.92	-2.00	-0.65
Sulfur												
S4	HSO4- + 7H+ + 6e -> S + 4H2O	6	7	-192,904	0.333	6	0.27	-0.069	0.00	1.98	0.27	0.14
S5	SO4-- + 8H+ + 6e -> S + 4H2O	6	8	-204,204	0.353	6	0.29	-0.079	1.98	7.13	0.14	-0.27
S6	SO4- + 9H+ + 8e -> HS- + 4H2O	8	9	-192,124	0.249	0	0.25	-0.067	7.13	12.92	-0.27	-0.65
S7	SO4- + 8H+ + 8e -> S-- + 4H2O	8	8	-118,404	0.153	0	0.15	-0.059	12.92	14.00	-0.65	-0.72
S8	S + 2H+ + 2e -> H2S	2	2	-28,600	0.148	0	0.15	-0.059	0.00	7.13	0.15	-0.27

Recorded by: T. J. Hall

Date: 6/20/07

Verified by:

Date

At 90 °C

No	electrode reaction	n	m	dGo	Eo	logK	A value Eo-0.059/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
1	Cr++ + 2e -> Cr	2	0	165,189	-0.856	6	-1.033	0.000	0.00	8.01	-1.03	-1.03
2	Cr+++ + 3e -> Cr	3	0	196,242	-0.678	6	-0.796	0.000	0.00	4.00	-0.32	-0.32
3	Cr+++ + 4H2O -> HCrO4(-) + 7H+ + 3e	-3	-7	404,966	1.399	0	1.399	-0.138	0.00	4.08	1.40	0.84
4	Cr2O3 + 5H2O -> 2HCrO4(-) + 8H+ + 6e	-6	-8	741,544	1.281	-12	1.163	-0.079	4.08	8.35	0.84	0.50
5	2Cr++ + 3H2O -> Cr2O3 + 6H+ + 2e	-2	-6	6,281	0.033	12	0.387	-0.177	4.00	8.01	-0.32	-1.03
6	2Cr + 3H2O -> Cr2O3 + 6H+ + 6e	-6	-6	-324,096	-0.560	0	-0.560	-0.059	8.01	14.00	-1.03	-1.39
7	Cr2O3 + 5H2O -> 2CrO4(2-) + 10H+ + 6e	-6	-10	836,847	1.446	-12	1.327	-0.099	8.35	14.00	0.50	-0.05
No electron consumption or generation												
8	HCrO4(-) -> CrO4(2-) + H+	0	-1	47,652	#DIV/0!	0	#DIV/0!	#DIV/0!	8	8.35	0.50	2.00
9	2Cr+++ + 3H2O -> Cr2O3 + 6H+	0	-6	68,388	#DIV/0!	12	#DIV/0!	#DIV/0!	4	4.00	0.84	-0.32
Oxygen evolution												
O2	O2 + 4H+ + 4e -> 2H2O	4	4	-474,282	1.229	0	1.229	-0.059	0.00	14.00	1.23	0.40
Hydrogen evolution												
H2	2H+ + 2e -> H2	2	2	0	0.000	0	0.000	-0.059	0.00	14.00	0.00	-0.83
Sulfur												
S1	HSO4- -> H+ + SO4--	0	-1	19,899	#DIV/0!	0	#DIV/0!	#DIV/0!	2.68	2.68	0.02	2.00
S2	H2S -> HS- + H+	0	-1	46,020	#DIV/0!	0	#DIV/0!	#DIV/0!	6.19	6.19	-2.00	-0.34
S3	HS- -> S-- + H+	0	-1	79,903	#DIV/0!	0	#DIV/0!	#DIV/0!	10.76	10.76	-2.00	-0.73
Sulfur												
S4	HSO4- + 7H+ + 6e -> S + 4H2O	6	7	-198,005	0.342	6	0.26	-0.090	0.00	2.68	0.26	0.02
S5	SO4-- + 8H+ + 6e -> S + 4H2O	6	8	-217,904	0.376	6	0.30	-0.103	2.68	6.19	0.02	-0.34
S6	SO4- + 9H+ + 8e -> HS- + 4H2O	8	9	-198,787	0.257	0	0.26	-0.087	6.19	10.76	-0.34	-0.73
S7	SO4- + 8H+ + 8e -> S-- + 4H2O	8	8	-118,884	0.154	0	0.15	-0.077	10.76	14.00	-0.73	-0.98
S8	S + 2H+ + 2e -> H2S	2	2	-26,903	0.139	0	0.14	-0.077	0.00	6.19	0.14	-0.34

Recorded by: T. J. Hall

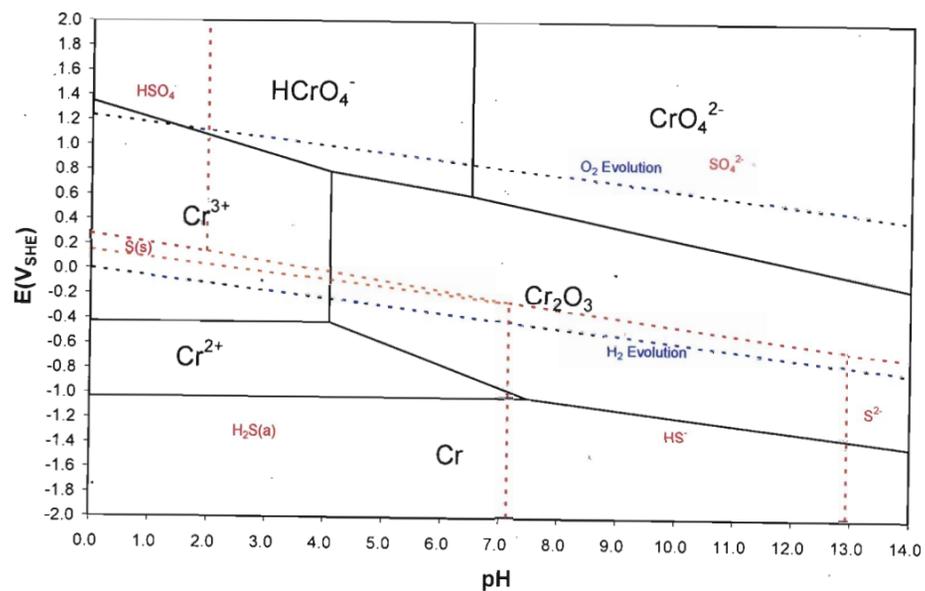
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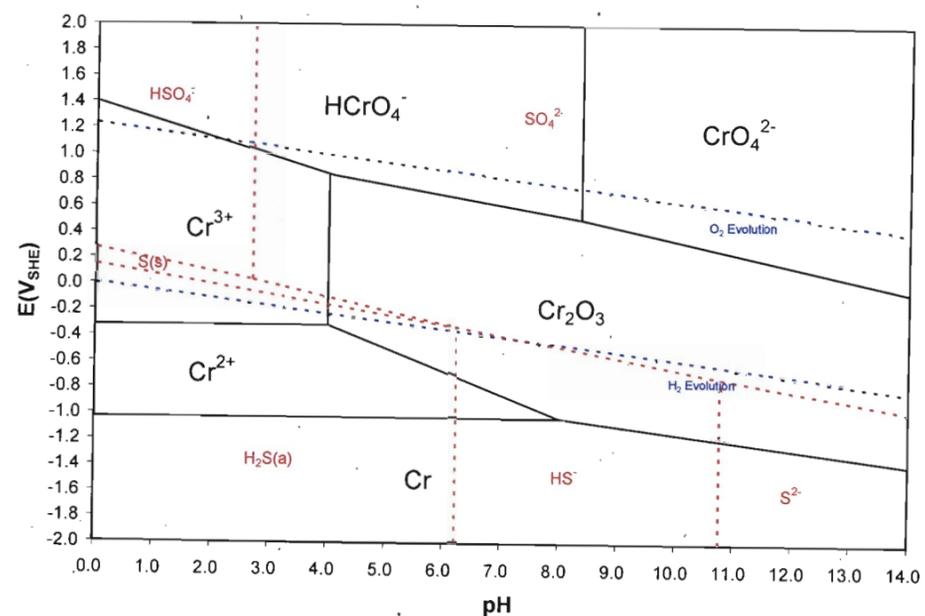
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Md

2.2.3. E-pH diagrams for Cr-S-H₂O system at 25 and 90 °C



(a)



(b)

Figure 3. E-pH diagrams for Cr-S-H₂O system at (a) 25 °C and (b) 90 °C for 10⁻⁶ M of ions at 1 atm.

Recorded by: *Tylal*

Date: 6/7/07

Verified by:

Date

Tylal

Entry Date: June 22, 2007

2.3. Mo - S - H₂O system

2.3.1. Thermodynamic data

The thermodynamic data used in the calculation are referenced from HSC (database name) as the thermodynamic database.

HSC, "Outokumpu HSC Chemistry for Windows," Version 5.1, Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

Reaction Data	25 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	MoS2	-267.17	HSO4-	-755.66
Temperature=	298	K	H2O(l)	-237.14	MoS3	-294.87	SO4--	-744.36
Activity of Ni Species=	1E-06	molar	O2(g)	0.00	Mo2S3	-395.67	HS-	12.08
Activity of S Species=	1E-06	molar	H2(g)	0.00	HMoO4-	-868.62	S--	85.80
Faradays Constant=	96485.3	C/s	Cr	0.00	MoO4--	-836.18	S	0.00
In to log=	2.303		MoO2	-533.49			H2S	-28.60
2.303RT/F=	0.0591							

Reaction Data	90 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	MoS2	-265.18	HSO4-	-726.00
Temperature=	388	K	H2O(l)	-231.10	MoS3	-291.60	SO4--	-706.10
Activity of Ni Species=	1E-06	molar	O2(g)	0.00	Mo2S3	-393.13	HS-	19.12
Activity of S Species=	1E-06	molar	H2(g)	0.00	HMoO4-	-840.39	S--	85.80
Faradays Constant=	96485.3	C/s	Cr	0.00	MoO4--	-806.52	S	0.00
In to log=	2.303		MoO2	-521.35			H2S	-26.90
2.303RT/F=	0.0591							

Recorded by: *Tylal*

Date: 6/22/07

Verified by:

Date

Tylal

2.3.2. List of Reactions and Corresponding Parameters' Values

At 25 °C

No	id	electrode reaction	n	m	dGo	Eo	logK	A value, Eo-0.0591/n *log(a/a)	pH slope pH value	X1	X2	Y1	Y2
1	Mo/MoS2	Mo + 2H2S -> MoS2 + 4H+ + 4e	-4	-4	-209,969	-0.544	12	-0.367	-0.059	0.00	7.13	-0.37	-0.79
2	Mo/MoS2	Mo + 2HS -> MoS2 + 2H+ + 4e	-4	-2	-291,329	-0.755	12	-0.577	-0.030	7.13	14.00	-0.79	-0.99
	Mo/MoS2	Mo + 2SO4- + 16H+ + 12e -> MoS2 + 8H2O	12	16	-675,577	0.583	12	0.524	-0.079				
	Mo/MoS2	Mo + 2e -> MoS2 + 4e	-4	0	-438,769	-1.137	12	-0.959	0.000				
3	MoS2/MoS3	MoS2 + H2S -> MoS3 + 2H+ + 2e	-2	-2	898	0.005	6	0.182	-0.059	0.00	7.13	0.18	-0.24
	MoS2/MoS3	MoS2 + HS -> MoS3 + H+ + 2e	-2	-1	-39,782	-0.206	6	-0.029	-0.030				
4	MoS2/MoS3	MoS2 + SO4- + 8H+ + 6e -> MoS3 + 4H2O	6	8	-231,906	0.401	6	0.341	-0.079	0.00	7.13	0.34	-0.24
5	MoS2/MoS3	MoS2 + 10H2O -> MoO2 + 2SO4- + 20H+ + 16e	-16	-20	616,374	0.399	-12	0.355	-0.074	0.00	8.04	0.35	-0.24
6	MoS2/MoS3	MoO2 + 2H2O -> HMoO4- + 3H+ + 2e	-2	-3	139,148	0.721	-6	0.544	-0.089	0.00	5.68	0.54	0.04
7	MoS2/MoS3	MoO2 + 2H2O -> MoO4- + 4H+ + 2e	-2	-4	171,582	0.889	0	0.889	-0.118	5.68	8.04	0.04	-0.24
8	MoS2/MoS3	MoS2 + 12H2O -> MoO4- + 2SO4- + 24H+ + 2e	-20	-24	787,956	0.408	-12	0.373	-0.071	8.04	11.82	-0.24	-0.51
9	MoS2/MoS3	MoS2 + 4H2O -> MoO4- + 2S- + 8H+ + 2e	-2	-8	551,148	2.856	-12	2.501	-0.237	11.82	14.00	-0.51	-0.93
No	id	No electron consumption or generation	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
10		HMoO4- -> MoO4- + H+	0	-1	32,434	#DIV/0!	0	#DIV/0!	5.68	5.68	5.68	2.00	0.04
No	id	Oxygen evolution	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
O2	O2/H2O	O2 + 4H+ + 4e -> 2H2O	4	4	-474,282	1.229	0	1.229	-0.059	0.00	14.00	1.23	0.40
No	id	Hydrogen evolution	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
H2	H+/H2	2H+ + 2e -> H2	2	2	0	0.000	0	0.000	-0.059	0.00	14.00	0.00	-0.83
		Sulfur	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
S1		HSO4- -> H+ + SO4-	0	-1	11,300	#DIV/0!	0	#DIV/0!	1.98	1.98	1.98	0.14	2.00
S2		H2S -> HS- + H+	0	-1	40,680	#DIV/0!	0	#DIV/0!	7.13	7.13	7.13	-2.00	-0.27
S3		HS- -> S- + H+	0	-1	73,720	#DIV/0!	0	#DIV/0!	12.92	12.92	12.92	-2.00	-0.65
		Sulfur	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
S4		HSO4- + 7H+ + 6e -> S + 4H2O	6	7	-192,904	0.333	6	0.27	-0.069	0.00	1.98	0.27	0.14
S5		SO4- + 8H+ + 6e -> S + 4H2O	6	8	-204,204	0.353	6	0.29	-0.079	1.98	7.13	0.14	-0.27
S6		SO4- + 9H+ + 8e -> HS- + 4H2O	8	9	-192,124	0.249	0	0.25	-0.067	7.13	12.92	-0.27	-0.65
S7		SO4- + 8H+ + 8e -> S- + 4H2O	8	8	-118,404	0.153	0	0.15	-0.059	12.92	14.00	-0.65	-0.72
S8		S + 2H+ + 2e -> H2S	2	2	-28,600	0.148	0	0.15	-0.059	0.00	7.13	0.15	-0.27

Recorded by: Jyhad

Date: 6/20/07

Verified by:

Date

At 90 °C

No	id	electrode reaction	n	m	dGo	Eo	logK	A value, Eo-0.0591/n	pH slope pH value	X1	X2	Y1	Y2
1	Mo/MoS2	Mo + 2H2S -> MoS2 + 4H+ + 4e	-4	-4	-211,376	-0.548	12	-0.317	-0.077	0.00	5.94	-0.33	-0.79
2	Mo/MoS2	Mo + 2HS -> MoS2 + 2H+ + 4e	-4	-2	-303,415	-0.786	12	-0.555	-0.038	5.94	14.00	-0.79	-1.10
	Mo/MoS2	Mo + 2SO4- + 16H+ + 12e -> MoS2 + 8H2O	12	16	-700,990	0.605	12	0.528	-0.103				
	Mo/MoS2	Mo + 2e -> MoS2 + 4e	-4	0	-463,222	-1.200	12	-0.969	0.000				
3	MoS2/MoS3	MoS2 + H2S -> MoS3 + 2H+ + 2e	-2	-2	490	0.003	6	0.234	-0.077	0.00	4.24	0.22	-0.09
	MoS2/MoS3	MoS2 + HS -> MoS3 + H+ + 2e	-2	-1	-45,530	-0.236	6	-0.105	-0.088				
4	MoS2/MoS3	MoS2 + SO4- + 8H+ + 6e -> MoS3 + 4H2O	6	8	-244,318	0.422	6	0.345	-0.103	0.00	4.24	0.29	-0.09
5	MoS2/MoS3	MoS2 + 10H2O -> MoO2 + 2SO4- + 20H+ + 16e	-16	-20	641,638	0.416	-12	0.358	-0.096	0.00	6.68	0.31	-0.27
6	MoS2/MoS3	MoO2 + 2H2O -> HMoO4- + 3H+ + 2e	-2	-3	142,957	0.741	-6	0.510	-0.115	0.00	5.94	0.48	-0.16
7	MoS2/MoS3	MoO2 + 2H2O -> MoO4- + 4H+ + 2e	-2	-4	176,831	0.916	0	0.916	-0.154	5.94	6.68	-0.16	-0.27
8	MoS2/MoS3	MoS2 + 12H2O -> MoO4- + 2SO4- + 24H+ + 2e	-20	-24	818,470	0.424	-12	0.378	-0.092	6.68	9.23	-0.27	-0.51
9	MoS2/MoS3	MoS2 + 4H2O -> MoO4- + 2S- + 8H+ + 2e	-2	-8	580,702	3.009	-12	2.547	-0.308	9.23	14.00	-0.51	-0.93
No	id	No electron consumption or generation	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
10		HMoO4- -> MoO4- + H+	0	-1	33,874	#DIV/0!	0	#DIV/0!	5.94	5.94	5.94	2.00	-0.16
No	id	Oxygen evolution	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
O2	O2/H2O	O2 + 4H+ + 4e -> 2H2O	4	4	-462,000	1.197	0	1.197	-0.077	0.00	14.00	1.20	0.37
No	id	Hydrogen evolution	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
H2	H+/H2	2H+ + 2e -> H2	2	2	0	0.000	0	0.000	-0.077	0.00	14.00	0.00	-0.83
		Sulfur	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
S1		HSO4- -> H+ + SO4-	0	-1	19,899	#DIV/0!	0	#DIV/0!	3.49	3.49	3.49	-0.06	2.00
S2		H2S -> HS- + H+	0	-1	46,020	#DIV/0!	0	#DIV/0!	6.19	6.19	6.19	-2.00	-0.34
S3		HS- -> S- + H+	0	-1	79,903	#DIV/0!	0	#DIV/0!	10.76	10.76	10.76	-2.00	-0.73
		Sulfur	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope pH value	X1	X2	Y1	Y2
S4		HSO4- + 7H+ + 6e -> S + 4H2O	6	7	-198,005	0.342	6	0.27	-0.090	0.00	3.49	0.27	-0.05
S5		SO4- + 8H+ + 6e -> S + 4H2O	6	8	-217,904	0.376	6	0.30	-0.103	3.49	6.19	-0.06	-0.34
S6		SO4- + 9H+ + 8e -> HS- + 4H2O	8	9	-198,787	0.258	0	0.26	-0.087	6.19	10.76	-0.34	-0.73
S7		SO4- + 8H+ + 8e -> S- + 4H2O	8	8	-118,884	0.154	0	0.15	-0.077	10.76	14.00	-0.73	-0.98
S8		S + 2H+ + 2e -> H2S	2	2	-26,903	0.139	0	0.14	-0.077	0.00	6.19	0.14	-0.34

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2.3.3. E-pH diagrams for Mo-S-H₂O system at 25 and 90 °C

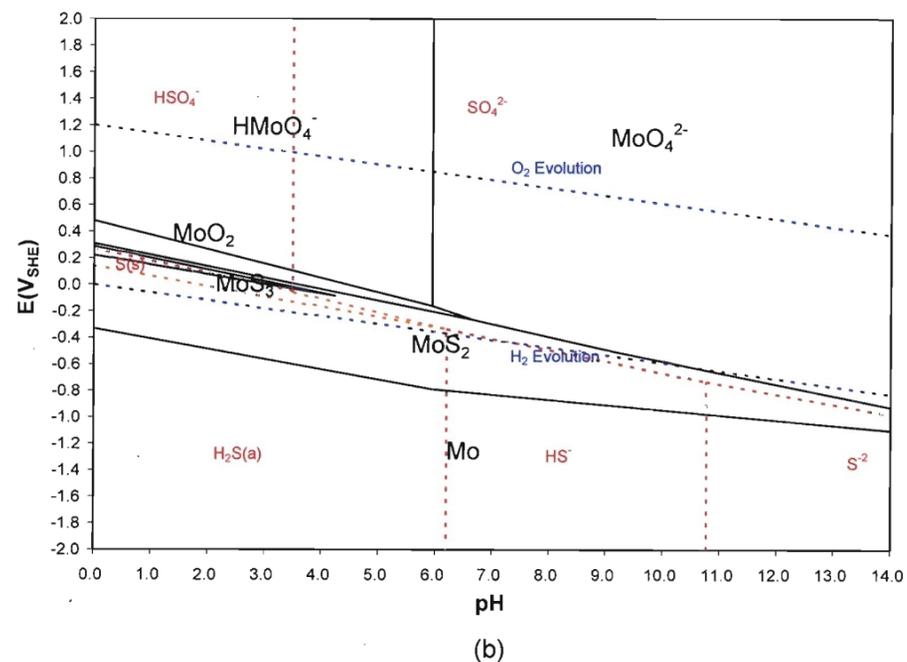
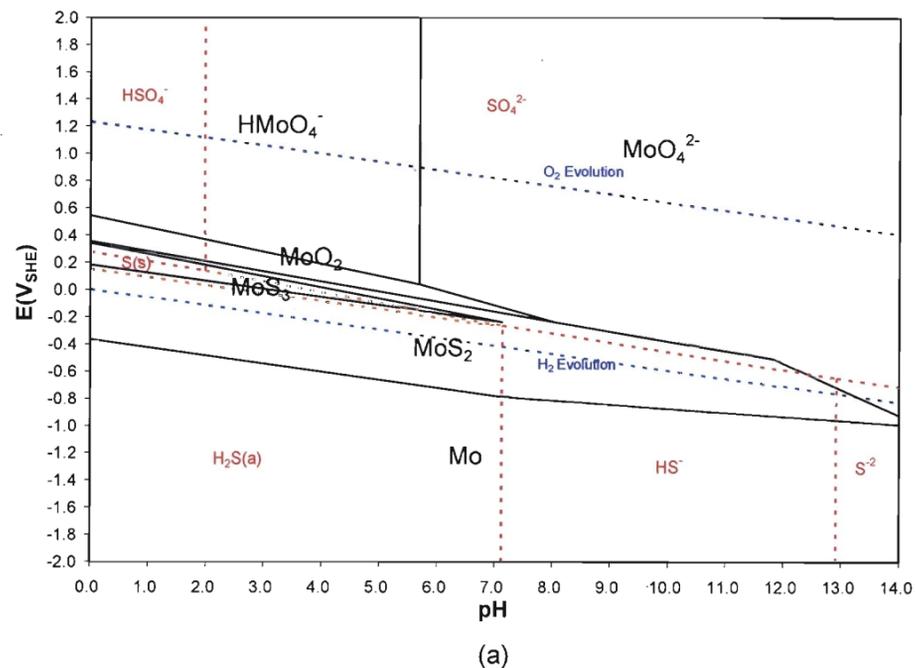


Figure 4. E-pH diagrams for Mo-S-H₂O system at (a) 25 °C and (b) 90 °C for 10⁻⁶ M of ions at 1 atm.

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• Detail calculations for the induction time (spreadsheet is stored in the attached CD.)

i_a^0	E_a^0	T_{ref}^a	R	θ	n	F	M	T increment
0.32 (C/cm ² *yr)	44700 (J/mol)	368.15 (K)	8.3144 (J/mol)	4.00E-08 (g/cm ²)	2.00	96485.00 (C/mol)	58.69 (g/mol)	5 (K)

S (5ppm)	S (10ppm)	S (50ppm)	S (100ppm)	S (200ppm)	S (1000ppm)	S (2000ppm)
0.000005	0.000010	0.000050	0.000100	0.000200	0.001000	0.002000

T (C)	T (K)	i_a (C/cm ² *yr)	i_a (A/cm ²)	Induction Time, τ (years)						
				5 ppm	10 ppm	50 ppm	100 ppm	200 ppm	1000 ppm	2000 ppm
25	298	1.03E-02	3.26E-10	2557.55	1278.77	255.75	127.88	63.94	12.79	6.39
30	303	1.39E-02	4.39E-10	1899.03	949.51	189.90	94.95	47.48	9.50	4.75
35	308	1.85E-02	5.86E-10	1423.76	711.88	142.38	71.19	35.59	7.12	3.56
40	313	2.44E-02	7.74E-10	1077.31	538.65	107.73	53.87	26.93	5.39	2.69
45	318	3.20E-02	1.01E-09	822.34	411.17	82.23	41.12	20.56	4.11	2.06
50	323	4.16E-02	1.32E-09	632.98	316.49	63.30	31.65	15.82	3.16	1.58
55	328	5.36E-02	1.70E-09	491.13	245.57	49.11	24.56	12.28	2.46	1.23
60	333	6.85E-02	2.17E-09	383.98	191.99	38.40	19.20	9.60	1.92	0.96
65	338	8.70E-02	2.76E-09	302.41	151.20	30.24	15.12	7.56	1.51	0.76
70	343	1.10E-01	3.48E-09	239.83	119.91	23.98	11.99	6.00	1.20	0.60
75	348	1.37E-01	4.36E-09	191.47	95.73	19.15	9.57	4.79	0.96	0.48
80	353	1.71E-01	5.42E-09	153.84	76.92	15.38	7.69	3.85	0.77	0.38
85	358	2.12E-01	6.71E-09	124.36	62.18	12.44	6.22	3.11	0.62	0.31
90	363	2.60E-01	8.25E-09	101.12	50.56	10.11	5.06	2.53	0.51	0.25
95	368	3.18E-01	1.01E-08	82.69	41.34	8.27	4.13	2.07	0.41	0.21
100	373	3.87E-01	1.23E-08	67.98	33.99	6.80	3.40	1.70	0.34	0.17
105	378	4.68E-01	1.48E-08	56.18	28.09	5.62	2.81	1.40	0.28	0.14
110	383	5.64E-01	1.79E-08	46.66	23.33	4.67	2.33	1.17	0.23	0.12
115	388	6.75E-01	2.14E-08	38.94	19.47	3.89	1.95	0.97	0.19	0.10
120	393	8.06E-01	2.55E-08	32.65	16.32	3.26	1.63	0.82	0.16	0.08
125	398	9.57E-01	3.03E-08	27.49	13.75	2.75	1.37	0.69	0.14	0.07
130	403	1.13E+00	3.59E-08	23.25	11.62	2.32	1.16	0.58	0.12	0.06
135	408	1.33E+00	4.22E-08	19.74	9.87	1.97	0.99	0.49	0.10	0.05
140	413	1.56E+00	4.96E-08	16.83	8.42	1.68	0.84	0.42	0.08	0.04
145	418	1.83E+00	5.79E-08	14.40	7.20	1.44	0.72	0.36	0.07	0.04
150	423	2.13E+00	6.74E-08	12.37	6.19	1.24	0.62	0.31	0.06	0.03
155	428	2.47E+00	7.82E-08	10.67	5.33	1.07	0.53	0.27	0.05	0.03
160	433	2.85E+00	9.04E-08	9.23	4.61	0.92	0.46	0.23	0.05	0.02
165	438	3.29E+00	1.04E-07	8.01	4.00	0.80	0.40	0.20	0.04	0.02
170	443	3.77E+00	1.20E-07	6.97	3.49	0.70	0.35	0.17	0.03	0.02
175	448	4.32E+00	1.37E-07	6.09	3.04	0.61	0.30	0.15	0.03	0.02
180	453	4.93E+00	1.56E-07	5.33	2.67	0.53	0.27	0.13	0.03	0.01
185	458	5.61E+00	1.78E-07	4.68	2.34	0.47	0.23	0.12	0.02	0.01
190	463	6.37E+00	2.02E-07	4.13	2.06	0.41	0.21	0.10	0.02	0.01
195	468	7.22E+00	2.29E-07	3.65	1.82	0.36	0.18	0.09	0.02	0.01
200	473	8.15E+00	2.58E-07	3.23	1.61	0.32	0.16	0.08	0.02	0.01

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3. The potential-pH diagrams for Metal Sulfides at 150 °CBackground Information

The thermodynamic data used in the calculation are referenced from Roine (2002). In the reference (Roine, 2002), the chemical potentials for each species are estimated at high temperature through the Criss-Cobble based linear ionic heat capacity approximation as suggested by Lewis (Lewis, 1970; Taylor, 1978; Criss and Cobble, 1964a, b) which is very reliable in the temperature range used for this work.

The method used for calculating high temperature Pourbaix diagrams is described in detail elsewhere (Cowan 1971; Taylor 1978). Generally, the standard chemical potential of species i at temperature T , $\mu_{i,T}$, was determined through the use of equation 3-1:

$$\mu_{i,T} = \mu_{i,298} + \int_{298}^T \bar{C}_p dT - T \int_{298}^T \frac{\bar{C}_p}{T} dT - \Delta TS_{298}^0 \quad (3-1)$$

where $\mu_{i,298}$ is the absolute chemical potential of species i at 298 K, \bar{C}_p is the average partial molal heat capacity over the temperature increment $T - 298$ K, and S_{298}^0 is the standard partial molal entropy at 298 K.

The Criss-Cobble ionic entropy correspondence principle is generally used to estimate the average heat capacities for ionic species at high temperatures (Criss, 1964a, b). Cowan and Staehle as well as Taylor have shown that this method is valid up to 573 K (Cowan 1971), (Taylor, 1978). They used the Criss-Cobble theory to calculate standard electrode potentials for the Ag/AgCl H⁺/H₂ cell between 298 and 573 K and compared these results to the experimentally measured values of Greeley (Greeley, 1960). Theoretical values for E^0 were within ~20 % of experimentally determined values as calculated by Cowan and Staehle and within ~10% as calculated by Taylor with smoothed experimental data. Clearly, thermodynamic estimations of this nature will ignore activity changes and partial molal volume changes which undoubtedly result in errors; however Criss and Cobble have shown that these effects can be ignored up to 573 K (Criss and Cobble, 1964b).

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Taylor, D.F. "Thermodynamic properties of metal-water systems at elevated temperatures." Journal of the Electrochemical Society 125, pp. 808-812. 1978.

3.1 N-S-water System**3.1.1 Thermodynamic Data**

Reaction Data	150 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K	H+	0.00	NiS	-84.17	HSO4-	-699.98
Temperature=	423	K	H2O(l)	-218.40	Ni3S2	208.20	SO4--	-669.57
Activity of Ni Species=	0.0001	molar	O2(g)	0.00	Ni3S4	288.20	HS-	27.40
Activity of S Species=	1.00E-02	molar	H2(g)	0.00	NiSO4	718.39	S--	114.61
Faradays Constant=	96485.3	C/s	Ni	0.00	Ni(OH)2	413.80	S	0.00
ln to log=	2.303		NiO	-200.63	NiOH+	203.99	H2S	-26.17
2.303RT/F=	0.08394		Ni++	-41.39	Ni(OH)3-	481.80		

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3.1.2. List of Reactions and Corresponding Parameters' Values at 150 °C

No	electrode reaction	n	m	dGo	EO	logK	$\frac{E_o - E_{o,0.05M/0.05M}}{0.05916 \log K}$	pH slope	pH value	X1	X2	Y1	Y2
1	$Ni^{2+} + 2e \rightarrow Ni$	2	0	41,387	-0.214	4	-0.382	0.000	0.00	0.00	0.74	-0.38	-0.38
2	$3Ni^{2+} + 2H_2S + 2e \rightarrow Ni_3S_2 + 4H^+$	2	-4	-31,697	0.164	16	-0.507	0.168	0.74	0.74	1.97	-0.38	-0.18
6	$3Ni^{2+} + 2SO_4^{2-} + 16H^+ + 16e \rightarrow Ni_3S_2 + 8H_2O$	16	16	-492,101	0.293	16	0.209	-0.075	4.50	4.50	5.65	-0.12	-0.21
5	$Ni^{2+} + SO_4^{2-} + 8H^+ + 8e \rightarrow NiS + 4H_2O$	8	8	-246,813	0.320	6	0.257	-0.084	1.09	1.09	4.50	0.18	-0.12
3	$3Ni^{2+} + 4H_2S \rightarrow Ni_3S_4 + 8H^+ + 2e$	-2	-8	-59,354	-0.308	20	0.532	-0.336	1.97	1.97	1.01	-0.13	0.19
4	$3Ni^{2+} + 4SO_4^{2-} + 32H^+ + 30e \rightarrow Ni_3S_4 + 16H_2O$	30	32	-980,162	0.339	20	0.283	-0.090	1.01	1.01	1.09	0.192	0.185
7	$NiO + 2SO_4^{2-} + 16H^+ + 14e \rightarrow Ni_3S_2 + 9H_2O$	14	18	-634,028	0.469	4	0.445	-0.108	5.65	5.65	14.00	-0.21	-0.77
8	$3Ni(OH)_2 + 2SO_4^{2-} + 25H^+ + 19e \rightarrow Ni_3S_2 + 17H_2O$	19	25	-1,136,465	0.620	10	0.576	-0.110	5.65	5.65	14.00	-0.05	-0.97
9	$3Ni + 2H_2S \rightarrow Ni_3S_2 + 4H^+ + 4e$	-4	-4	-155,658	-0.404	4	-0.320	-0.084	0.74	0.74	6.61	-0.38	-0.88
10	$3Ni + 2HS^- \rightarrow Ni_3S_2 + 2H^+ + 4e$	-4	-2	-262,991	-0.681	4	-0.597	-0.042	6.61	6.61	14.00	-0.88	-1.19
11	$Ni_3S_2 + H_2S \rightarrow 3NiS + 2H^+ + 2e$	-2	-2	-18,136	-0.094	2	-0.010	-0.084	1.97	1.97	6.61	-0.18	-0.57
12	$Ni_3S_2 + HS^- \rightarrow 3NiS + H^+ + 2e$	-2	-1	-71,702	-0.372	2	-0.288	-0.042	6.61	6.61	9.79	-0.57	-0.70
13	$Ni_3S_2 + SO_4^{2-} + 4H^+ + 2e \rightarrow 3NiS + 2H_2O$	-2	4	188,462	-0.977	2	-1.061	-0.168	9.79	9.79	4.50	-0.70	-0.12
14	$3NiS + H_2S \rightarrow Ni_3S_4 + 2H^+ + 2e$	-2	-2	-61,862	-0.321	2	-0.237	-0.084	1.97	1.97	6.61	-0.13	-0.52
15	$3NiS + HS^- \rightarrow Ni_3S_4 + H^+ + 2e$	-2	-1	-69,088	-0.327	2	-0.243	-0.042	6.61	6.61	8.94	-0.52	-0.62
16	$3NiS + SO_4^{2-} + 4H^+ + 2e \rightarrow Ni_3S_4 + 2H_2O$	-2	4	197,077	-1.021	2	-1.105	-0.168	8.94	8.94	4.50	-0.62	-0.12
No	No electron consumption or generation	n	m	dGo	EO	logK	$\frac{E_o - E_{o,0.05M/0.05M}}{0.05916 \log K}$	pH slope	pH value	X1	X2	Y1	Y2
17	$Ni^{2+} + H_2S \rightarrow NiS + 2H^+$	0	-2	-16,611	#DIV/0!	6	#DIV/0!	#DIV/0!	1.97	1.97	1.97	-0.13	-0.18
18	$Ni^{2+} + H_2O \rightarrow NiO + 2H^+$	0	-2	59,153	#DIV/0!	4	#DIV/0!	#DIV/0!	5.65	5.65	5.65	-0.21	1.00
19	$NiO + 2H_2O \rightarrow Ni(OH)_2 + H^+$	0	-1	155,635	#DIV/0!	-4	#DIV/0!	#DIV/0!	15.22	15.22	15.22	-0.05	1.00
No	Oxygen evolution	n	m	dGo	EO	logK	$\frac{E_o - E_{o,0.05M/0.05M}}{0.05916 \log K}$	pH slope	pH value	X1	X2	Y1	Y2
O2	$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	4	4	-436,800	1.132	0	1.132	-0.084	0.00	0.00	14.00	1.14	0.31
No	Hydrogen evolution	n	m	dGo	EO	logK	$\frac{E_o - E_{o,0.05M/0.05M}}{0.05916 \log K}$	pH slope	pH value	X1	X2	Y1	Y2
H2	$2H^+ + 2e \rightarrow H_2$	2	2	0	0.000	0	0.000	-0.084	0.00	0.00	14.00	0.00	-0.83
S1	$HSO_4^- \rightarrow H^+ + SO_4^{2-}$	0	-1	30,408	#DIV/0!	0	#DIV/0!	#DIV/0!	3.75	3.75	3.75	-0.10	1.00
S2	$H_2S \rightarrow HS^- + H^+$	0	-1	53,567	#DIV/0!	0	#DIV/0!	#DIV/0!	6.61	6.61	6.61	-1.60	-0.42
S3	$HS^- \rightarrow S^{2-} + H^+$	0	-1	87,217	#DIV/0!	0	#DIV/0!	#DIV/0!	10.77	10.77	10.77	-1.60	-0.81
S4	$HSO_4^- + 7H^+ + 6e \rightarrow S + 4H_2O$	6	7	-173,624	0.300	2	0.27	-0.098	0.00	0.00	3.75	0.27	-0.10
S5	$SO_4^{2-} + 8H^+ + 6e \rightarrow S + 4H_2O$	6	8	-204,032	0.352	2	0.32	-0.112	3.75	3.75	6.61	-0.10	-0.42
S6	$SO_4^{2-} + 9H^+ + 8e \rightarrow HS^- + 4H_2O$	8	9	-176,635	0.229	0	0.23	-0.094	6.61	6.61	10.77	-0.42	-0.81
S7	$SO_4^{2-} + 8H^+ + 8e \rightarrow S^{2-} + 4H_2O$	8	8	-89,418	0.116	0	0.12	-0.084	10.77	10.77	14.00	-0.81	-1.08
S8	$S + 2H^+ + 2e \rightarrow H_2S$	2	2	-26,170	0.136	0	0.14	-0.084	0.00	0.00	6.61	0.14	-0.42
S9	$S + H^+ + 2e \rightarrow HS^-$	2	1	27,397	-0.142	-2	-0.06	-0.042	6.61	6.61	10.77	-0.42	-0.81

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Date: 1/7/2008

Verified by:

Date:

3.1.3. E-pH diagram for Ni-S-water system at 150 °C

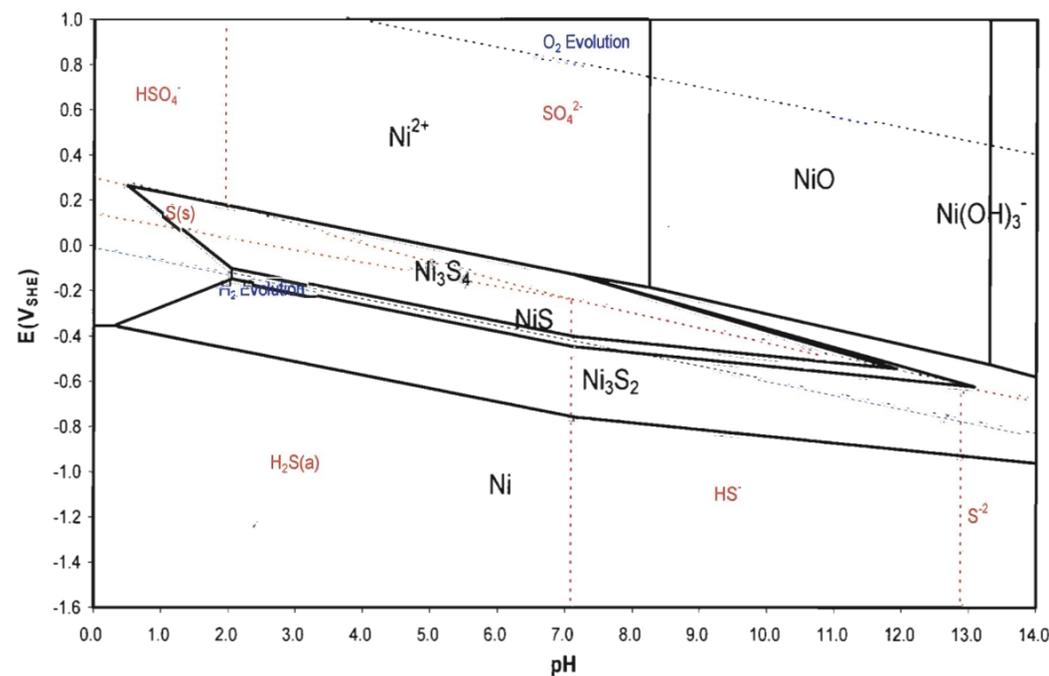


Figure 5. E-pH diagrams for Ni-S-H₂O system at 150 °C for [M] = 10⁻⁴ M and [S] = 10⁻² M at 1 atm.

3.2 Cr-S-water System

3.2.1 Thermodynamic Data

Reaction Data		150 °C		Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314	J/mol*K		H+	0.00	CrS	-138.91	HSO4-	-699.98
Temperature=	423	K		H2O(l)	-218.40	Cr2S3	-364.84	SO4--	-669.57
Activity of Ni Species=	0.000001	molar		O2(g)	0.00	Cr3+	-185.77	HS-	27.40
Activity of S Species=	0.01	molar		H2(g)	0.00	Cr2+	-165.27	S--	114.61
Faradays Constant=	96485.3	C/s		Cr	0.00	CrO2(-a)	-480.74	S	0.00
ln to log=	2.303			CrO2	-507.20	CrO4(-2a)	-655.63	H2S	-26.17
2.303RT/F=	0.083942746			CrO3	-468.19	CrO7(-2a)	-1215.87		
				Cr2O3	-1019.64	Cr(OH)2(+a)	-559.82		
				Cr(OH)2	-539.32	H2CrO4(a)	-720.07		
				Cr(OH)3	-790.36	HCrO4(-a)	-716.30		

Recorded by: Jung Hwaal

Date: 1/8/2008

Verified by:

Date:

3.1.2. List of Reactions and Corresponding Parameters' Values at 150 °C

No	electrode reaction	n	m	dGo	Eo	logK	A value Eo-0.0591/n*log(a/a)	pH slope	pH value	X1	X2	Y1	Y2
1	Cr ³⁺ + 2e → Cr	2	0	165,189	-0.856	6	-1.033	0.000	0.00	0.00	8.01	-1.03	-1.03
2	Cr ³⁺ + 3e → Cr	3	0	196,242	-0.678	6	-0.796	0.000	0.00	0.00	4.00	-0.32	-0.32
3	Cr ³⁺ + 4H ₂ O → HCrO ₄ ⁻ (a) + 7H ⁺ + 3e	-3	-7	404,966	1.399	0	1.399	-0.138	0.00	0.00	4.08	1.40	0.84
4	Cr ₂ O ₃ + 5H ₂ O → 2HCrO ₄ ⁻ (a) + 8H ⁺ + 6e	-6	-8	741,544	1.281	-12	1.163	-0.079	4.08	8.35	8.35	0.84	0.50
5	2Cr ³⁺ + 3H ₂ O → Cr ₂ O ₃ + 6H ⁺ + 2e	-2	-6	6,281	0.033	12	0.387	-0.177	4.00	8.01	8.01	-0.32	-1.03
6	2Cr ³⁺ + 3H ₂ O → Cr ₂ O ₃ + 6H ⁺ + 6e	-6	-6	-324,096	-0.560	0	-0.560	-0.059	8.01	14.00	14.00	-1.03	-1.39
7	2Cr ₂ O ₃ + 5H ₂ O → 2CrO ₄ ²⁻ (a) + 10H ⁺ + 6e	-6	-10	836,847	1.446	-12	1.327	-0.099	8.35	14.00	14.00	0.50	-0.05
No electron consumption or generation													
8	HCrO ₄ ⁻ (a) → CrO ₄ ²⁻ (a) + H ⁺	0	-1	47,662	#DIV/0!	0	#DIV/0!	#DIV/0!	8	8.35	8.35	0.50	2.00
9	2Cr ³⁺ + 3H ₂ O → Cr ₂ O ₃ + 6H ⁺	0	-6	68,388	#DIV/0!	12	#DIV/0!	#DIV/0!	4	4.00	4.00	0.84	-0.32
Oxygen evolution													
O2	O ₂ + 4H ⁺ + 4e → 2H ₂ O	4	4	-474,282	1.229	0	1.229	-0.059	0.00	0.00	14.00	1.23	0.40
Hydrogen evolution													
H2	2H ⁺ + 2e → H ₂	2	2	0	0.000	0	0.000	-0.059	0.00	0.00	14.00	0.00	-0.83
Sulfur													
S1	HSO ₄ ⁻ → H ⁺ + SO ₄ ²⁻	0	-1	19,899	#DIV/0!	0	#DIV/0!	#DIV/0!	2.68	2.68	2.68	0.02	2.00
S2	H ₂ S → HS ⁻ + H ⁺	0	-1	46,020	#DIV/0!	0	#DIV/0!	#DIV/0!	6.19	6.19	6.19	-2.00	-0.34
S3	HS ⁻ → S ²⁻ + H ⁺	0	-1	79,903	#DIV/0!	0	#DIV/0!	#DIV/0!	10.76	10.76	10.76	-2.00	-0.73
Sulfur													
S4	HSO ₄ ⁻ + 7H ⁺ + 6e → S + 4H ₂ O	6	7	-198,005	0.342	6	0.26	-0.090	0.00	0.00	2.68	0.26	0.02
S5	SO ₄ ²⁻ + 8H ⁺ + 6e → S + 4H ₂ O	6	8	-217,904	0.376	6	0.30	-0.103	2.68	6.19	6.19	0.02	-0.34
S6	SO ₄ ²⁻ + 9H ⁺ + 8e → HS ⁻ + 4H ₂ O	8	9	-198,787	0.257	0	0.26	-0.087	6.19	10.76	10.76	-0.34	-0.73
S7	SO ₄ ²⁻ + 8H ⁺ + 8e → S ²⁻ + 4H ₂ O	8	8	-118,884	0.154	0	0.15	-0.077	10.76	14.00	14.00	-0.73	-0.98
S8	S + 2H ⁺ + 2e → H ₂ S	2	2	-26,903	0.139	0	0.14	-0.077	0.00	0.00	6.19	0.14	-0.34
S9	S + H ⁺ + 2e → HS ⁻	2	1	19,117	-0.09905024	-6	0.131905962	-0.038493	6.19	10.76	10.76	-0.34	-0.73

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3.1.3. E-pH diagram for Cr-S-water system at 150 °C

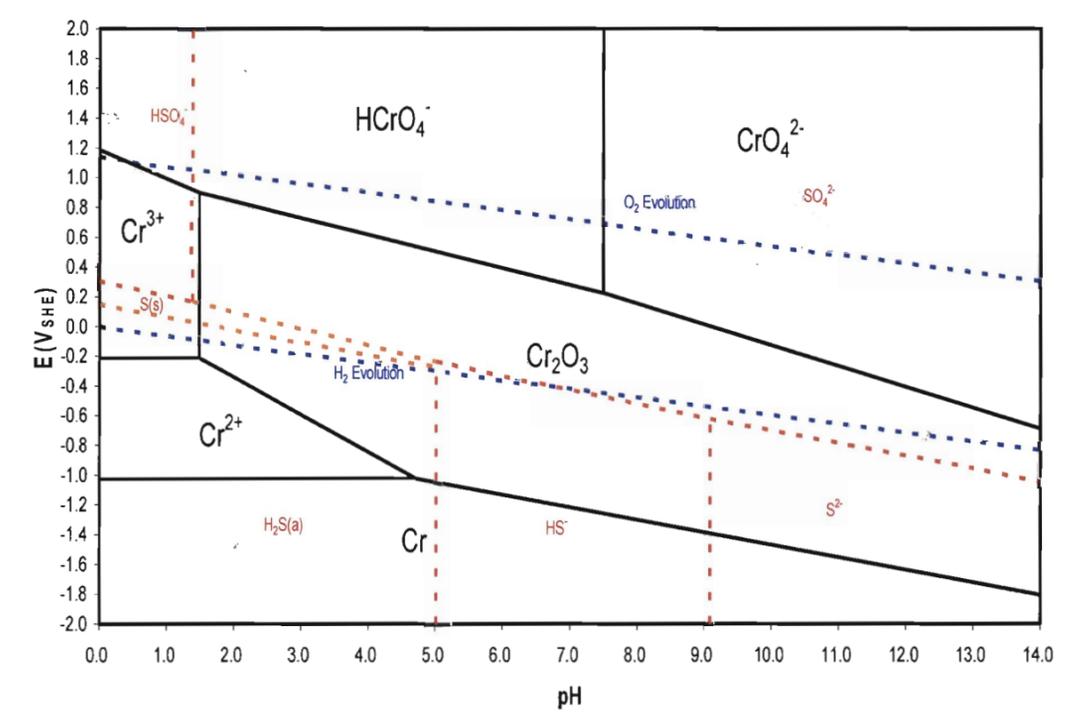


Figure 6. E-pH diagrams for Cr-S-H₂O system at 150 °C for [M] = 10⁻⁴ M and [S] = 10⁻² M at 1 atm.

3.3 Mo-S-water System

3.2.1 Thermodynamic Data

	150 °C	Species	Go (KJ)	Species	Go (KJ)	Species	Go (KJ)
Rate Constant=	8.314 J/mol*K	H ⁺	0.00	MoS ₂	-262.76	HSO ₄ ⁻	-755.66
Temperature=	423 K	H ₂ O(l)	-218.40	MoS ₃	-287.86	SO ₄ ²⁻	-744.36
Activity of Mo Species=	1.00E-04 molar	O ₂ (g)	0.00	Mo ₂ S ₃	-389.95	HS ⁻	12.08
Activity of S Species=	1.00E-02 molar	H ₂ (g)	0.00	HMoO ₄ ⁻	-814.01	S ²⁻	85.80
Faradays Constant=	96485.3 C/s	Mo	0.00	MoO ₄ ²⁻	-761.61	S	0.00
ln to log=	2.303	MoO ₂	-510.03	MoO ₄ ⁻	-544.13	H ₂ S	-28.60
2.303RT/F=	0.083942746						

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3.1.2. List of Reactions and Corresponding Parameters' Values at 150 °C

No	electrode reaction	n	m	dGo	Eo	logK	A value, $E_o - 0.0591/n \log(a/a)$	pH slope	pH value	X1	X2	Y1	Y2
1	Mo + 2H2S → MoS2 + 4H+ + 4e	-4	-4	-205,555	-0.533	4	-0.449	-0.084	0.00	0.00	5.02	-0.45	-0.87
2	Mo + 2HS → MoS2 + 2H+ + 4e	-4	-2	-286,915	-0.743	4	-0.659	-0.042	5.02	5.02	14.00	-0.87	-1.25
3	MoS2 + H2S → MoS3 + 2H+ + 2e	-2	-2	3,496	0.018	2	0.102	-0.084	0.00	0.00	7.13	0.10	-0.50
4	MoS2 + SO4 + 8H+ + 6e → MoS3 + 4H2O	6	8	-154,344	0.287	2	0.239	-0.112	0.00	0.00	7.13	0.24	-0.50
5	MoS2 + 10H2O → MoO2 + 2SO4 + 20H+ + 16e	-16	-20	448,006	0.290	-4	0.269	-0.105	0.00	0.00	6.47	0.27	-0.21
6	MoO2 + 2H2O → HMoO4 + 3H+ + 2e	-2	-3	132,820	0.688	-2	0.604	-0.126	0.00	0.00	6.47	0.60	-0.21
7	MoO2 + 2H2O → MoO4 + 4H+ + 2e	-2	-4	185,216	0.960	0	0.960	-0.168	6.47	6.47	6.47	-0.21	-0.21
8	MoS2 + 12H2O → MoO4 + 2SO4 + 24H+ + 2e	-20	-24	633,222	0.328	-4	0.311	-0.101	6.47	6.47	14.00	-0.21	-0.97
9	MoS2 + 4H2O → MoO4 + 2S + 8H+ + 2e	-2	-8	546,342	2.831	-4	2.663	-0.336	14.00	14.00	14.00	-0.97	-0.93
No	No electron consumption or generation	n	m	dGo	Eo	logK	A value, $E_o - 0.0591/n \log(a/a)$	#DIV/0!	pH slope	X1	X2	Y1	Y2
10	HMoO4 → MoO4 + H+	0	-1	52,396	#DIV/0!	0	#DIV/0!	#DIV/0!	6.47	6.47	6.47	2.00	-0.21
No	Oxygen evolution	n	m	dGo	Eo	logK	A value, $E_o - 0.0591/n \log(a/a)$	#DIV/0!	pH slope	X1	X2	Y1	Y2
O2	O2 + 4H+ + 4e → 2H2O	4	4	-436,800	1.132	0	1.132	-0.084	0.00	0.00	14.00	1.14	0.31
No	Hydrogen evolution	n	m	dGo	Eo	logK	A value, $E_o - 0.0591/n \log(a/a)$	#DIV/0!	pH slope	X1	X2	Y1	Y2
H2	2H+ + 2e → H2	2	2	0	0.000	0	0.000	-0.084	0.00	0.00	14.00	0.00	-0.83
No	Sulfur	n	m	dGo	Eo	logK	A value, $E_o - 0.0591/n \log(a/a)$	#DIV/0!	pH slope	X1	X2	Y1	Y2
S1	HSO4 → H+ + SO4	0	-1	11,300	#DIV/0!	0	0.18	-0.098	1.40	1.40	1.40	0.17	2.00
S2	H2S → HS + H+	0	-1	40,680	#DIV/0!	0	0.20	-0.112	5.02	5.02	5.02	-2.00	-0.24
S3	HS → S + H+	0	-1	73,720	#DIV/0!	0	0.15	-0.094	9.10	9.10	9.10	-2.00	-0.62
No	Sulfur	n	m	dGo	Eo	logK	A value, $E_o - 0.0591/n \log(a/a)$	#DIV/0!	pH slope	X1	X2	Y1	Y2
S4	HSO4 + 7H+ + 6e → S + 4H2O	6	7	-117,940	0.204	2	0.18	-0.098	0.00	0.00	1.40	0.31	0.17
S5	SO4 + 8H+ + 6e → S + 4H2O	6	8	-129,240	0.223	2	0.20	-0.112	1.40	1.40	5.02	0.17	-0.24
S6	SO4 + 9H+ + 8e → HS + 4H2O	8	9	-117,160	0.152	0	0.15	-0.094	5.02	5.02	9.10	-0.24	-0.62
S7	SO4 + 8H+ + 8e → S + 4H2O	8	8	-43,440	0.056	0	0.06	-0.084	9.10	9.10	14.00	-0.62	-1.03
S8	S + 2H+ + 2e → H2S	2	2	-28,600	0.148	0	0.15	-0.084	0.00	0.00	5.02	0.15	-0.27

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3.1.3. E-pH diagram for Mo-S-water system at 150 °C

Figure 7. E-pH diagrams for Mo-S-H2O system at 150 °C for [M] = 10⁻⁴ M and [S] = 10⁻² M at 1 atm.

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Date: 1/8/2008

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1/8/2008

Entry Date: December 12, 2008

Topic #2: Evaluation of DOE general corrosion model in TSPA-LA

This topic section documents the work conducted on the evaluation of model abstraction in TSPA-LA for general corrosion of Alloy 22.

Software used: Microsoft Excel 2003, Mathematica 6.0

1. Overview of DOE general corrosion model

- General corrosion rate of Alloy 22 in TSPA-LA is a temperature dependent and represented by an Arrhenius type equation.

$$R_T \text{ (nm/yr)} = R_o \exp[C_1(1/T-1/T_o)] \quad \text{Eq. 1}$$

where, R_o (nm/yr) is the general corrosion rate at 60 °C; C_1 (K)= E_a/R , E_a (J/mol) is activation energy

- The general corrosion rate of Alloy 22 is assumed constant (i.e., time-independent) at a given temperature and is conservative and DOE consider that the model is conservative because the corrosion rate of Alloy 22 decreases with time.
- Mean general corrosion rate of 7.36 nm/yr at 60 °C was determined from the weight-loss measurements for 5 years long-term corrosion test facility (LTCTF) crevice type coupons tested in aqueous phases of SAW, SDW, and SCW at 60 and 90 °C. (weight-loss type coupons -> 3.15 nm/yr)
- For all 5 years LTCTF samples, no crevice corrosion observed and were covered with surface deposits.
- No significant difference in the corrosion rates for mill-annealed and welded specimens.
- No clear dependence of the corrosion rates on temperature was found except weight-loss type coupons in SCW (i.e., corrosion rate at 90 °C was higher than 60 °C in aqueous phase SCW).
- Therefore, temperature dependence of the general corrosion rate was determined in separate tests using a short term polarization resistance techniques in a mixture of 1 to 9 m NaCl and 0.05 to 3 m KNO_3 solutions at three different temperatures (60, 80, and 100 °C) and the apparent activation energy of Alloy 22 was estimated to be 40.75 ± 11.75 kJ/mol (± 1 standard deviation).

2. Uncertainty Analysis of Weight-loss Data for 5 years Crevice Samples

- Total 58 corrosion rates were analyzed and fitted with a Weibull distribution
- Represented two parameters, scale (b) and shape (c) factors with three uncertainty levels (i.e., low, medium, and high): $R_o = b[\ln(1/1-p)]^{1/c}$
- Represent the Alloy 22 general corrosion rate WPOB at 60 °C

The parameters used in the general corrosion model (Eq. 1) are given in Table 1.

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Table 1. Parameters used in the general corrosion model to determine Ro values

Uncertainty Level	Scale factor (b)	Shape factor (c)
Low	6.628	1.380
Medium	8.134	1.476
High	9.774	1.578

Table 2. Raw data used in the general corrosion model

Sample #	measured data (nm/yr)	measured data (nm/yr)	CDF
1	9.4	0.41	0.077458
2	8.22	0.41	0.077458
3	8.63	0.81	0.090046
4	6.36	0.82	0.090379
5	9.75	1.25	0.10558
6	22.52	2	0.136361
7	12.04	2.01	0.136809
8	17.29	2.03	0.137708
9	15.75	2.08	0.139974
10	5.76	2.74	0.172253
11	8.3	2.85	0.178062
12	6.4	3.06	0.18949
13	3.06	3.1	0.191717
14	3.1	3.11	0.192276
15	4.19	3.54	0.217256
16	9.52	4.19	0.258362
17	7.23	4.29	0.265026
18	14.71	4.32	0.267042
19	5.81	4.71	0.293933
20	11.6	5.24	0.332358
21	5.77	5.28	0.335338
22	3.11	5.69	0.36645
23	10.56	5.76	0.371858
24	10.91	5.77	0.372632
25	4.71	5.81	0.375736
26	3.54	5.84	0.378069
27	2.74	5.89	0.381967
28	6.27	5.92	0.384312
29	5.89	6.27	0.411958
30	8.27	6.36	0.419144
31	0.82	6.4	0.422347
32	0.81	6.89	0.461933
33	8.4	6.94	0.466001
34	5.24	7.23	0.48965
35	5.28	7.88	0.542662
36	10.24	8.22	0.570152
37	6.94	8.27	0.574169
38	5.84	8.3	0.576576
39	6.89	8.4	0.584577
40	16.07	8.63	0.602842

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41	14.51	9.05	0.635594
42	4.29	9.4	0.662162
43	5.92	9.52	0.671096
44	2	9.75	0.687946
45	7.88	10.24	0.722527
46	19.58	10.56	0.744052
47	13.61	10.86	0.76341
48	4.32	10.91	0.766556
49	2.01	11.6	0.807531
50	9.05	12.04	0.831202
51	10.86	13.61	0.899796
52	2.85	14.51	0.928494
53	2.03	14.71	0.933918
54	5.69	15.75	0.957153
55	0.41	16.07	0.962795
56	2.08	17.29	0.979019
57	1.25	19.58	0.993839
58	0.41	22.52	0.999048

Results:

The model was implemented in Excel 2003. Detailed calculation spreadsheet is stored in the attached CD (file name: SN #835_Weibull distribution.xls).

The cumulative function of general corrosion rates using Weibull distribution is presented Figure 1.

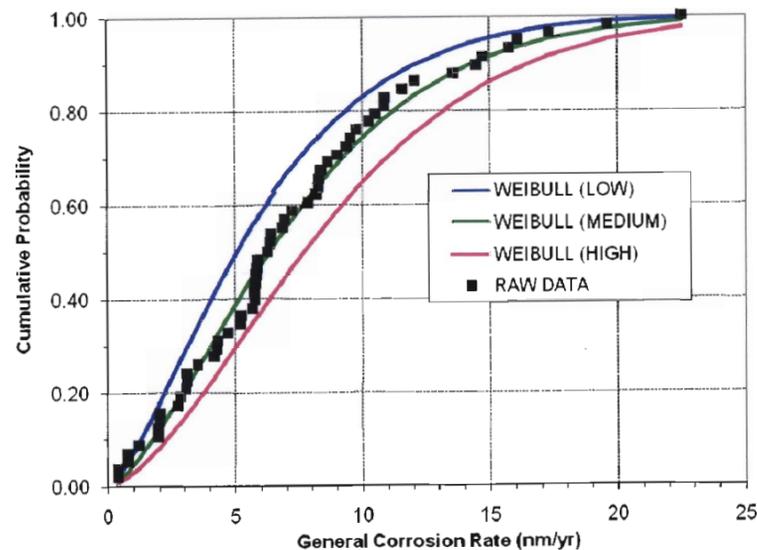


Figure 1. General corrosion rate distributions using Weibull distribution resulting from fitting of 5-year long-term crevice-type corrosion test facilities.

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The other fitting methods such as normal and log normal distributions are implemented and the results are compared to the Weibull distribution fitting (Figure 2).

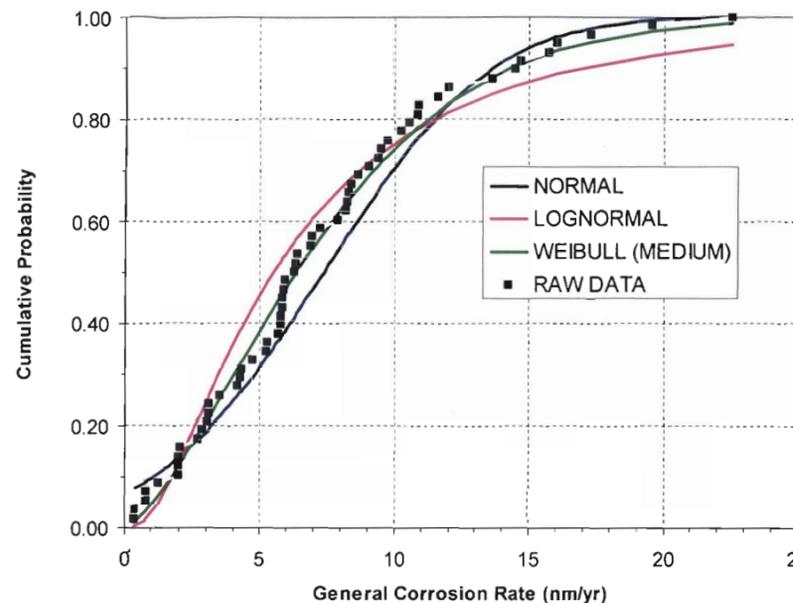


Figure 2. General corrosion rate distributions fitted by normal, lognormal and Weibull distributions

In an actual TSPA implementation for general corrosion of the waste package outer barrier, the waste package surface is divided into subareas (referred to as patches). Each patch has a surface area of 231.5 cm² [35.9 in²] which is four times the area of crevice geometry sample size. DOE has stated that this dividing is to simulate variability of general corrosion across the waste package surface. To account for such a change in scale (i.e., four times patch area to the crevice coupon size), in the TSPA, the general corrosion rate is adjusted in a manner that uses the highest of four sampled general corrosion rates for each patch. For each TSPA realization, a single general corrosion rate (i.e., the highest) is applied to each patch term on the waste package outer barrier (Sandia National Laboratories, 2008, p 6.3.5-9).

Sandia National Laboratories. "Total System Performance Assessment Model/Analysis for the License Application." MDL-WIS-PA-000005. Rev. 00. Las Vegas, Nevada: Sandia National Laboratories. 2008.

Figure 3 represents the resultant distributions for low, medium, and high level uncertainties after applying size factor of 4.

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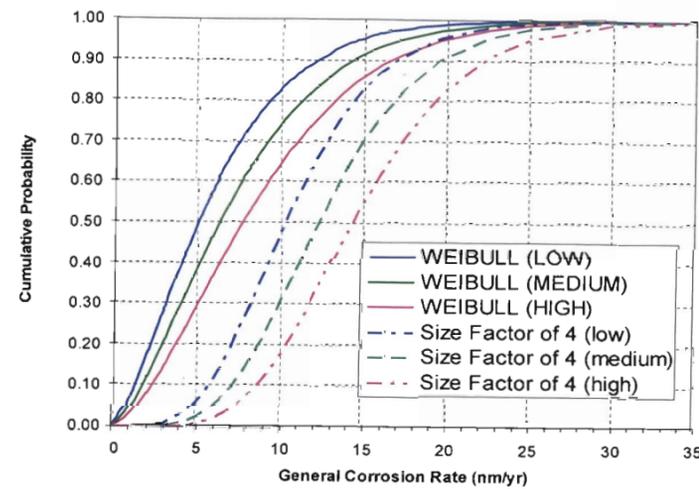


Figure 3. General corrosion rate distributions after applying size factor of 4

3. Calculated Model Outputs of Base-case Temperature-Dependent Corrosion Rate

- Total 58 corrosion rates were analyzed and fitted with a Weibull distribution and Figure 4 shows the calculation results.
- The median general corrosion rates (P=0.5) at a mean apparent activation energy (40.78 kJ/mol) are 0.33 to 6.2 nm/yr at 25 °C and 9.2 to 7430 nm/yr at 200 °C. (conversion: 1 nm/yr = 10⁻³ mm/yr = 10⁻⁶ mm/yr = 10⁻⁹ m/yr)
- Activation energy values were truncated between +2σ (7731K, 65.54kJ/mol) and -3σ (666K, 5.54kJ/mol).

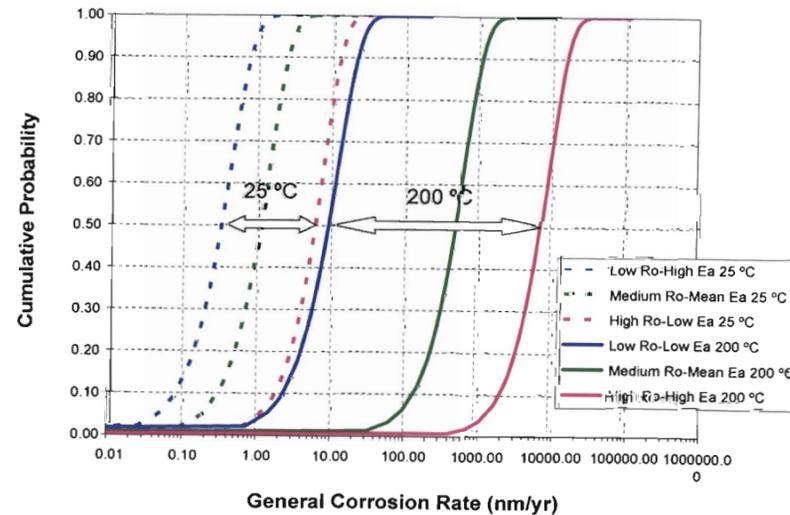


Figure 4. Calculated model outputs of the base-case temperature dependent general corrosion model with uncertainty levels and apparent activation energies at 25 and 200 °C.

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4. General Corrosion Rate at P=0.5 (median) At Different Temperature

The model was implemented in Excel 2003. Detailed calculation spreadsheet is stored in the attached CD (file name: SN #835_DOE general corrosion model.xls).

- General corrosion rates at P=0.5 (median) were compared at different temperatures with uncertainty levels and apparent activation energies as shown in Figure 5.
- At high T, the calculated corrosion rate shows broad distribution of corrosion rate and high activation energy resulted in high general corrosion rate.
- At low T, low activation energy leads to higher corrosion rate than high activation energy.

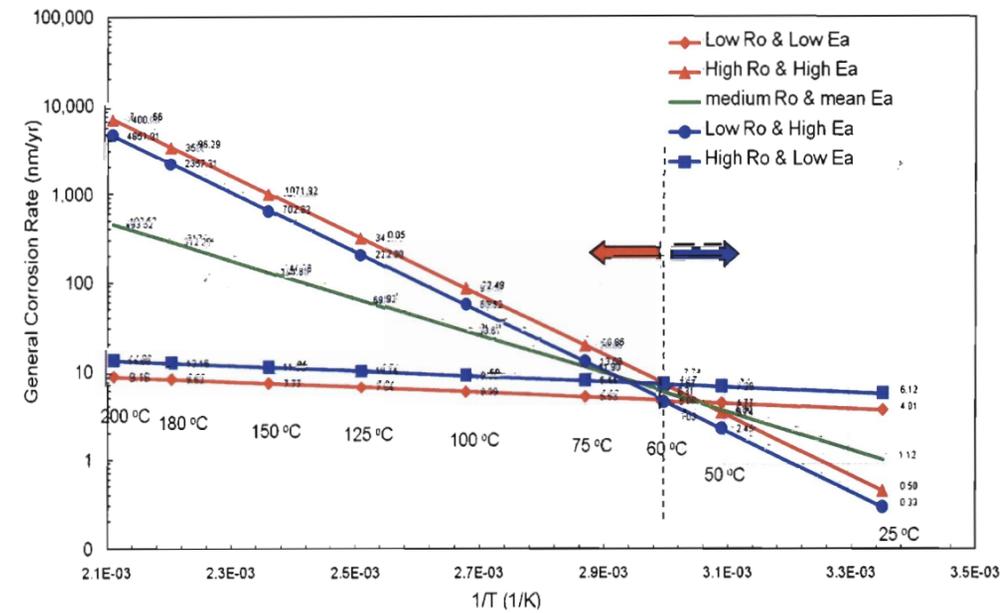


Figure 5. General corrosion rates as a function temperature with uncertainty levels and apparent activation energies (P=0.5)

5. WPOB (waste package outer barrier) Penetrated Depth

- Penetrated depth of WPOB can be calculated using Eq. 2 and result is shown in Figure 6.
- $$\text{Penetrated Depth (mm)} = \text{Corrosion Rate (mm/year)} \times \text{Duration (year)} \quad \text{Eq. 2}$$
- In the DOE model in TSPA-LA, the mean general corrosion rate at 25 °C is 1.12 nm/yr.

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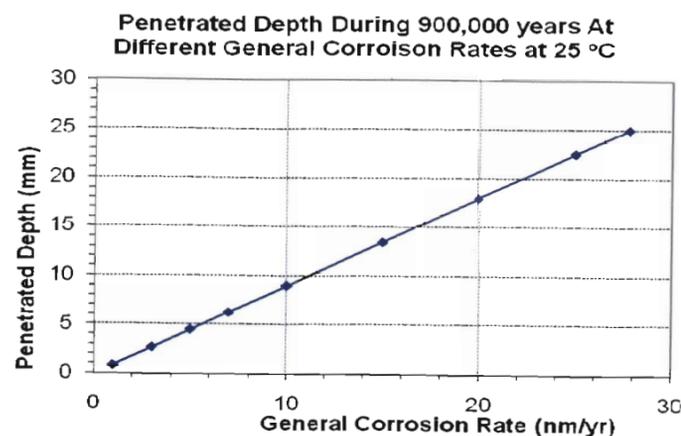


Figure 6. Penetrated depth of waste package outer barrier during 900,000 years at different general corrosion rate at 25 °C

6. Uncertainties in Activation Energy

- In the literature, the apparent mean activation energy ranged from 19 to 44.7 kJ/mol as seen in Table 3.

Table 3. Activation energies for Alloy 22 and C-4 in TSPA, TPA, and literature

Source, Material	Method(duration)	Activation energy	Solution	Temperature
TSPA-LA, Alloy 22	Polarization (24 hrs)	40.78 kJ/mol	1 to 6 M NaCl + 0.05 to 3 M KNO ₃	60, 80, 100 °C
TSPA (in previous versions), Alloy 22	Polarization (24 hrs)	26 kJ/mol	1 to 9 M NaCl or CaCl ₂ + 0.0125 to 0.5 M Ca(NO ₃) ₂	45 to 170 °C
TPA, Alloy 22	Passive current (2 days)	44.7 kJ/mol	0.028 M NaCl	25 to 95 °C
	EIS (1 day)	41.8 kJ/mol	4 M NaCl	40 to 150 °C
Hua and Gordon (2004), Alloy 22	Weight-loss (8 weeks)	25.3 kJ/mol	BSW	60 to 105 °C
EPR (2002), Alloy C-4	Weight-loss (3 to 5 years)	19 kJ/mol	Saturated Mg ²⁺ -dominated brines	90 to 200 °C
Lloyd et al. (2003), Alloy 22	Passive current (10 to 12 hours)	32 kJ/mol	1 M NaCl + 0.1 M H ₂ SO ₄	25 to 85 °C

Hua, F. and G. Gordon. "Corrosion Behavior of Alloy 22 and Ti Grade 7 in a Nuclear Waste Repository Environment." Corrosion. Vol. 60, No. 8. pp. 764-777. 2004.

Lloyd, A.C., J.J. Noël, S. McIntyre, and D.W. Shoesmith. "Cr, Mo and W alloying additions in Ni and Their Effect on Passivity." Electrochimica Acta. Vol. 49. pp. 3,015-3,027. 2004.

Recorded by: Juyatual

Date: 1/12/08

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Date: 2/24/09

7. General Corrosion Rate Distribution At Two Different Activation Energies At 25 °C

The model was implemented in Mathematica 6.0. Detailed information for calculation and coding is stored in the attached CD (file name: CorrSampling.nb).

- Mean activation energy, $E_a = 40.75$ or 25.3 kJ/mol (normal distribution without truncation)
- Mean general corrosion rate at 60 °C, $R_o = 6.35$ nm/yr

Table 4. Calculated mean general rates at 25 °C and estimated waste package failure by general corrosion at 1 million year in nominal case results

Activation Energy	Mean general corrosion rate at 25 °C	WP failure by general corrosion at 1 M year
40.75 kJ/mol	~3.5 nm/yr*	~ 9 % (from the TSPA result)
25.3 kJ/mol	~6.8 nm/yr*	~ 40 %

* After applying size factor of 4 and MIC enhancement factor (1 to 2)

- Assuming that WP is failed when the general corrosion rate is higher than ~ 7 nm/yr at 25 °C under same failure mechanisms, it is possible that the mean fraction of failed WP could increase to ~ 40% when the activation energy is 25.3 kJ/mol.
- The current high activation energy in TSPA-LA may underestimate the general corrosion rate at low temperature (e.g., 25 °C) and result in less WPOB lifetime.
- No experimental general corrosion data at low temperatures (e.g., 25 °C) are given to support the model.
- DOE has a long-term corrosion test plan using simulated water from 30 °C to build up better confidence for the current model.

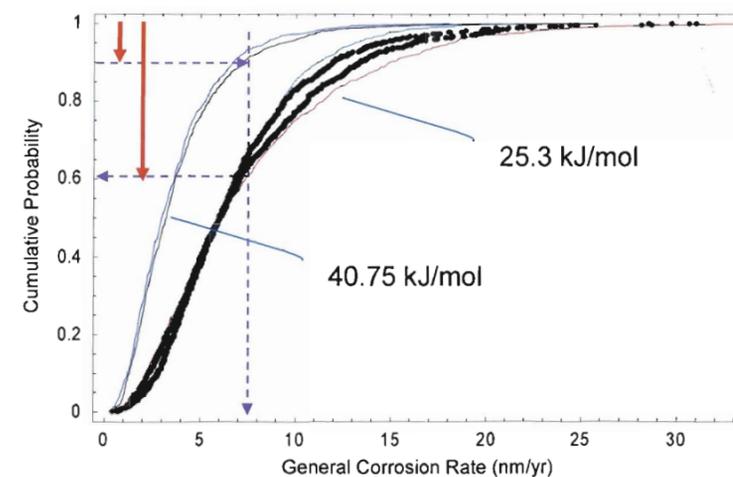


Figure 7. General corrosion rates at two different activation energies (25.3 and 40.75 kJ/mol)

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Date: 1/12/08

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Date: 2/24/09

CALCULATION VERIFICATION WORKSHEET

Associated Document or Activity: **Verification of Calculated values featured in SAR**

Project Number: **14002.01.351**

Assigned Verifier: **O. Pensado** Manager: **K. Axler** Required Completion Date: **3-5-09**

Location of Calculation(s): **Scientific Notebook # 835** Page Number(s): **28-35**

Location of Corresponding Data in Document (Table or Page #, When Applicable):

Identify the Calculation Tools Used and Over Checks Needed.	Document the Calculation Verification: Which Calculations Were Checked; How They Were Checked, Software Used for the Original Calculation (When Applicable), and Conclusions.
Controlled Software: Check input for accuracy and output for reasonableness.	
Uncontrolled Software: Check inputs, perform check calculations (copy of code shall be attached for QA records).	
Commercial Off-the-Shelf Software: Check inputs and outputs, check formulae.	<i>I checked the functional form of the Weibull distribution on p. 28 and it is accurate. The confidence bounds in Figure 1 on page 30 are consistent with DOE data. The trends in Figures 3 and 4 on p. 32 are consistent with physical intuition (corrosion rates should be higher with higher size factors, and at higher temperatures). I read the Mathematica notebook for Sampling.hb and the equations and the sampling approach were properly implemented.</i>
Other Calculation(s): Check inputs and perform check calculations.	
Verification By: Oswaldo Pensado Date: 2/24/2009	

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Entry Date: August 14, 2009

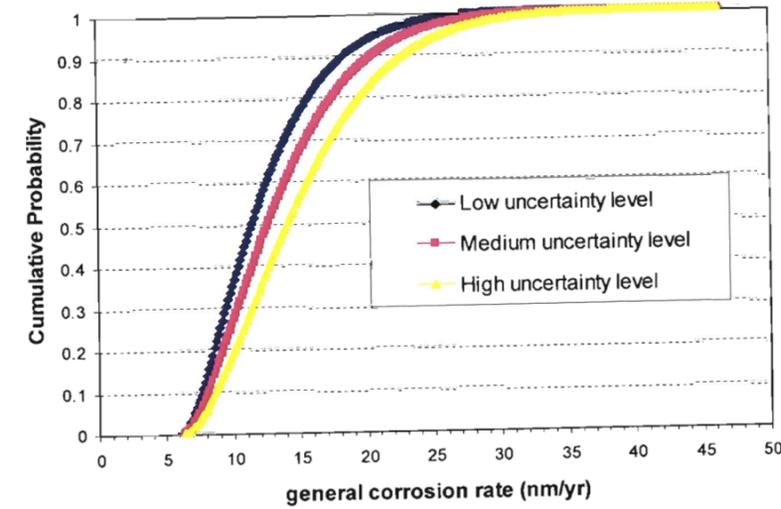
Continue for topic #2 (Evaluation of DOE general corrosion model in TSPA-LA)

This topic section documents the work conducted on the evaluation of model abstraction in TSPA-LA for general corrosion of Alloy 22.

Software used: Microsoft Excel 2003, Mathematica 6.0, GoldSim

8. Confirmatory calculation of the mean total dose as a function of Ro and C1 values using TSPA GoldSim model

- Mean total dose was calculated as a function two parameters, Ro and C1 using GoldSim. The input values for two parameters were developed by Hundal (Andy) Jung at CNWRA. Using these values, Christopher T. Markley in NRC conducted TSPA implementation using GoldSim models.
- The input data are listed in the following table and the original source is saved to the file name of parameters_GCM.xls in the attached CD.
- In the case of 2x Ro,

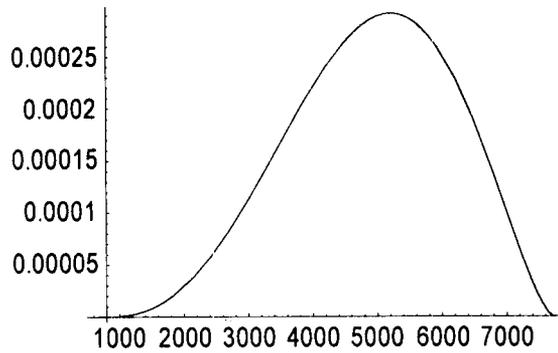


- For C1,

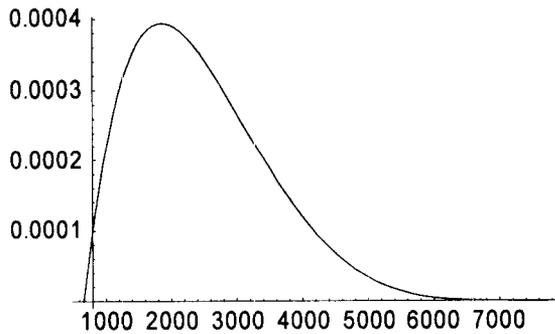
	mean Ea (KJ/mol)	mean C1 (K)	standard deviation (K)	a	b
basecase	40.7	4905	1250.01	4	2.66667
low Ea	20.4	2452.5	1028.8	2	5.90932
high Ea	48.9	5886	1113.53	5	1.76724

Recorded by: **Justin Hall** Date: **8/14/09** Verified by: _____ Date: _____

(i) basecase



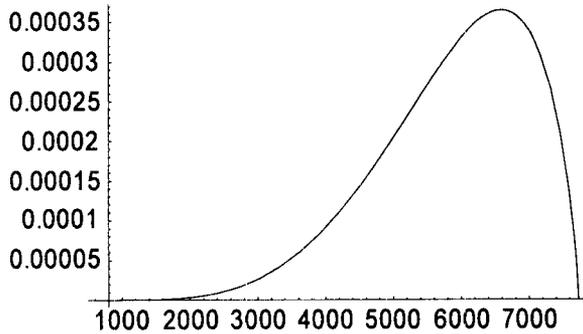
(ii) low Ea



75

75

(iii) high Ea



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8/14/09

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Date

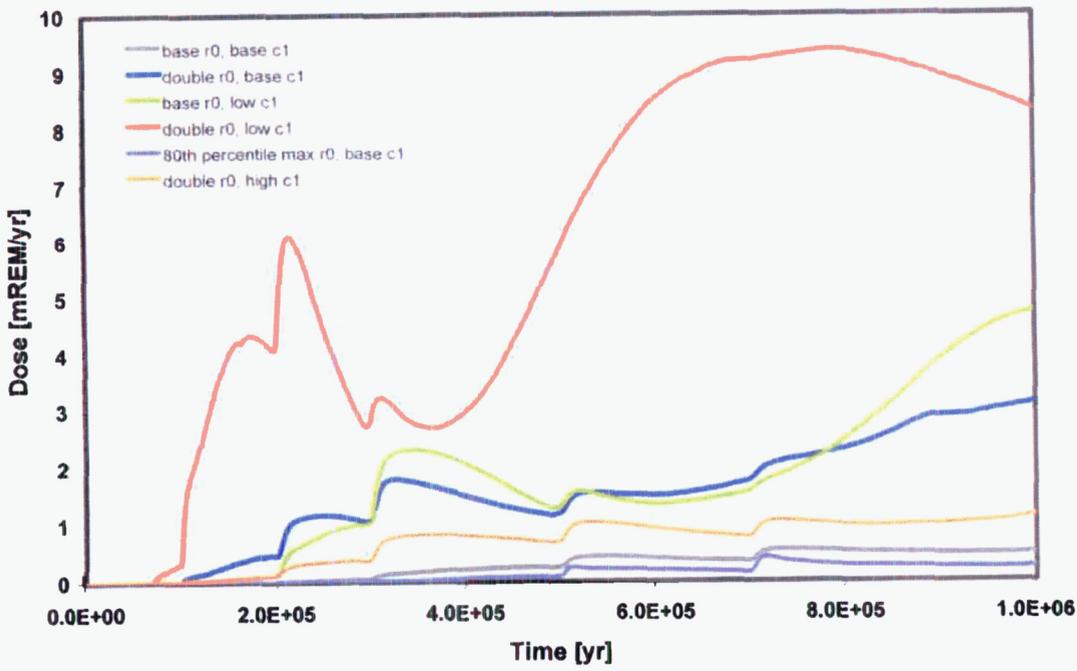
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• TSPA GoldSim model running

Chris Markley in NRC conducted a set of GoldSim implementation depending on Ro and C1 values. No difference between weighted and unweighted in the nominal modeling case.

- 500 realizations for each case
- For Ro, used the data treated by Weibull distribution
- For C1, used a normal distribution without truncation

Unweighted Mean Total Dose



73

76

• Main findings

The mean total dose increases with increasing Ro and C1, which is more significant after about 100,000 years.

At 1 M years, the mean total dose depends on the different combinations of Ro and C1 values.

Mean total doses at 1 M years:

(i) base r0, base c1 -> ~0.49 mrem

(ii) double r0, low c1 -> ~8 mrem

Recorded by: Trey Auwiler

Date: 8/14/09

Verified by:

Date

Entry Date: September 15, 2009

9. Simplified Computations to check failure times by general corrosion of the WP and DS

The objective was exploring whether failure times can be approximated with simplified computations. Osvaldo Pensado in CNWRA is an originator for the associated computation files. All files were compressed as a zip file named "PensadoContributionToJungSciNotebook.zip".

Reference

SNL. 2007a. "General Corrosion and Localized Corrosion of Waste Package Outer Barrier." ANL-EBS-MD-000003. Rev. 03. ACN 01, ERD 01. Las Vegas, Nevada: Sandia National Laboratories.

Approach

1. Power of 4 assumed to account for differences in sample size versus patch size
2. MIC enhancing factor, uniform(1,2), implemented
3. Assumed 1400 patches (Actual count: 1430 for CSNF, 1408 for CDSP: GoldSim parameters Num_WP_Patches_CS NF; Num_WP_Patches_CDSP)
4. If $CDF_r(r)$ is the cumulative corrosion rate distribution, then the distribution for the maximum corrosion rate, $CDF_m(r)$, of a sample of N elements (N = number of patches) is $CDF_m(r) = [CDF_r(r)]^N$
5. Sampled the reference corrosion rate from the Weibull distribution, modified by the power N , corrected by the MIC factor.
6. The distribution of extreme corrosion rates were adjusted by the activation energy (sampled from a truncated normal distribution) and the temperature dependence
7. A temperature of 25 °C was considered, because this is the dominant temperature in the long-term
8. The approach to sample an extreme corrosion rate is only an approximation. A more accurate approach would require creating a corrosion rate sample with N elements; adjust by the MIC factor; adjust by the temperature; and then select the maximum (after the MIC and temperature corrections) of the sample. However, the simplified approach consider should suffice to derive rough estimates
9. A bound for the failure time distributions and the WP surface fraction compromised by general corrosion was derived by considering an increase in the corrosion rate by a factor of 2, to account for corrosion from the inside-out. Clearly, this factor of 2 would lead to shorter failure times than the DOE model. In the TSPA model, this corrosion rate enhancement only applies when the WP is damaged by any mechanism. In this simplified approach, the factor of 2 is applied at time=0.
10. A low bound was derived by not considering the factor 2.
11. The fraction of WPs failed by GC versus time is equivalent to the cumulative distribution function of the failure time (failure time computed with the extreme corrosion rate from a sample of N elements)
12. The fraction of the WP surface compromised by GC versus time is equivalent to the cumulative distribution function of the PATCH failure time (failure time computed with the whole, uncorrected by the power N , distribution of corrosion rates)

Recorded by: Jung Anell

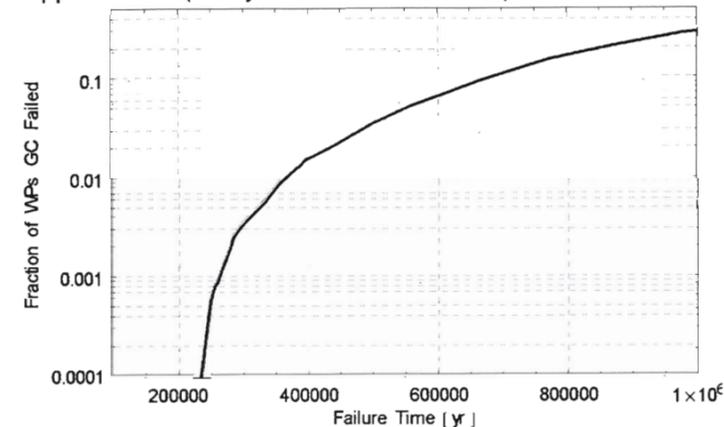
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Results

Upper Bound (always inside-out corrosion)



Lower bound (never inside-out corrosion)

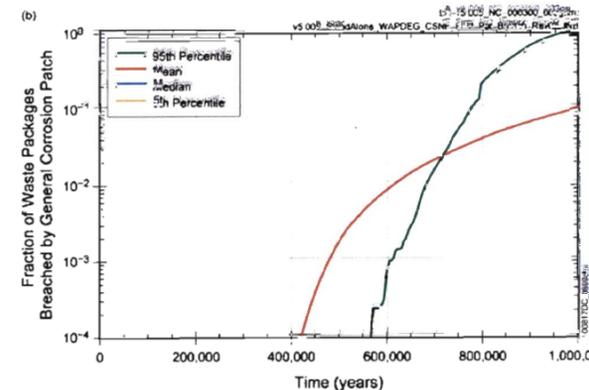
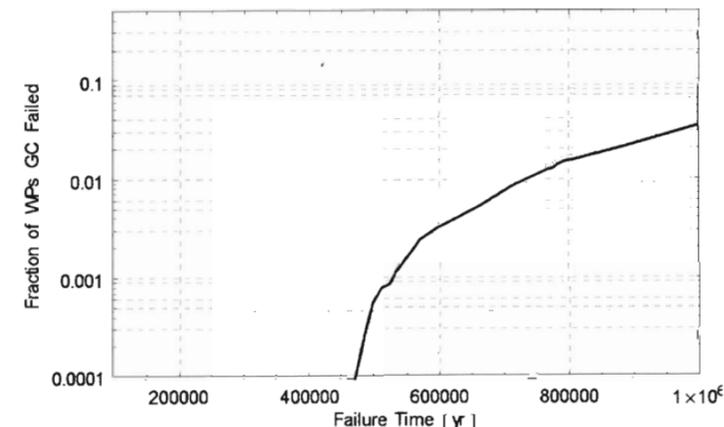


Figure 2.1-10. Summary Statistics for Fraction of Commercial SNF Waste Packages (a) Breached by Stress Corrosion Cracking and (b) Breached by General Corrosion Patches for the Nominal Modeling Case as a Function of Time

Source: SNL 2008d, Figure 8.3-6(a).

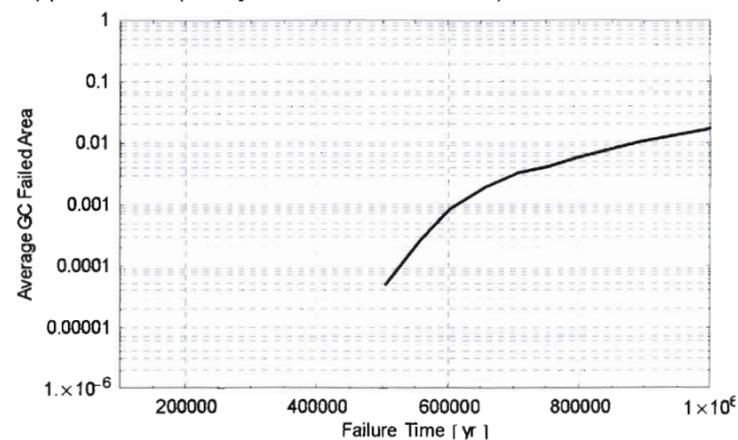
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Upper Bound (always inside-out corrosion)



Lower bound (never inside-out corrosion)

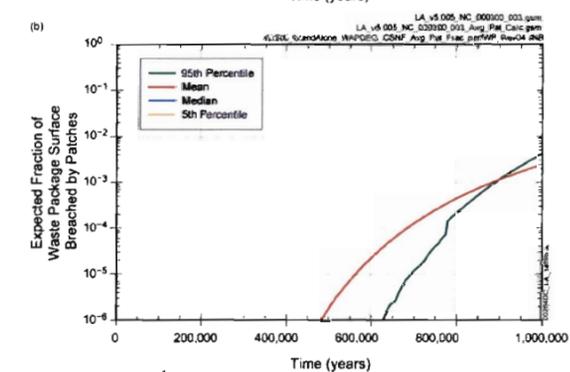
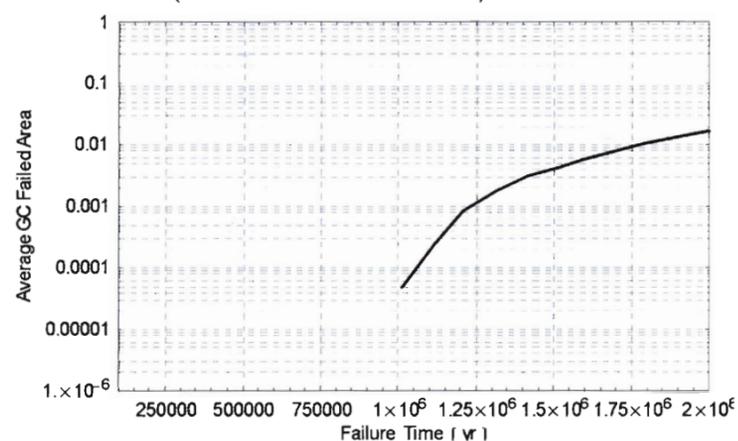


Figure 2.1-16. Summary Statistics for Fraction of Commercial SNF Waste Package Surface Breached by Patches per Breached Waste Package for (a) the Seismic Ground Motion Modeling Case and (b) the Nominal Modeling Case, as a Function of Time

Source: SNL 2008d, Figure 8.3-11(a)

Conclusions

The simplified approach produces results that are consistent with the TSPA results.

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DS Failure by General Corrosion

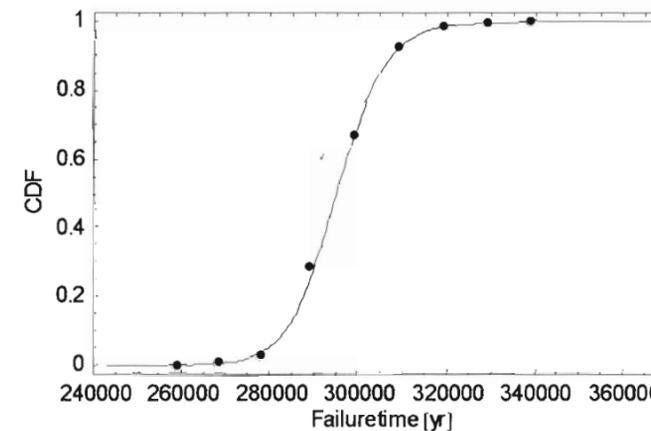
In this case the TSPA model is relatively simple. I accurately reproduced the failure time from sampling two DS corrosion rates, r_a and r_b , from two distributions:

$$t = \frac{r_a - r_m}{\frac{\sigma}{\sqrt{6}}}$$

t follows a Student-t distribution with 5 degrees of freedom. $r_m = 4.61 \times 10^{-5}$ mm/yr (GoldSim TSPA parameter WDDSAggrGC_Uncert_Mean), $\sigma = 2.9 \times 10^{-5}$ mm/yr (GoldSim TSPA parameter WDDSAggrGC_Uncert_SD)

On the other hand, r_b follows a normal distribution with mean = 5.15×10^{-6} mm/yr (GoldSim TSPA parameters WDDSBenignGC_Mean_a or WDDSBenignGC_a) and standard deviation = 8.31×10^{-7} mm/yr.

The total corrosion rate equals $r = r_a + r_b$.



The dots were scanned from SAR Figure 2.1-8

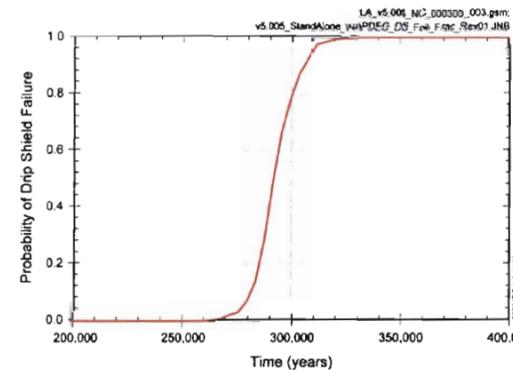


Figure 2.1-8. Probability of Drip Shield Failure by General Corrosion for the Nominal Modeling Case Based on 300 Epistemic Realizations of Drip Shield General Corrosion Rates

Source: SNL 2008d, Figure 8.3-4(a)

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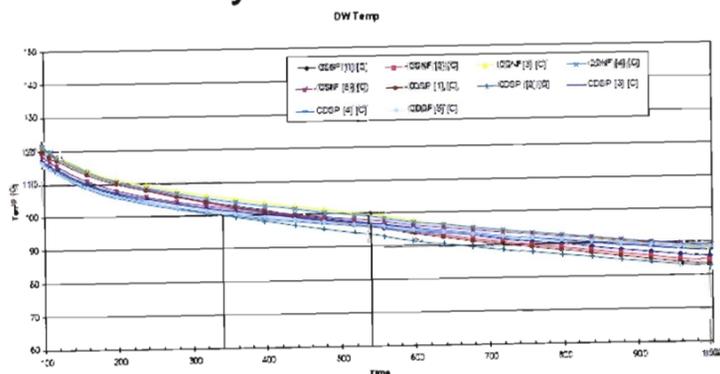
Reasonable ranges of waste package temperature and its corresponded relative humidity for potential dripping condition

This topic section documents the work conducted on the estimating reasonable ranges of waste package temperature and its corresponded relative humidity as a function of the repository time in which there is a potential seepage water dripping with evaporation process. The range of temperature and relative humidity was obtained from the GoldSim models in the TSPA-LA.

Software used: Microsoft Excel 2003
Chandrika Manepally in CNWRA is an originator for the associated computation files. All files were compressed as a zip file named "ChandrikaContributionToJungSciNotebook#899.zip".

Temperature/RH Considerations

- Start Time – when the DW temperature is below boiling
- TSPA average results
- Note – breaching of the boiling isotherm neglected
- Range – 350 – 550 years



Recorded by: *Jyosthna*

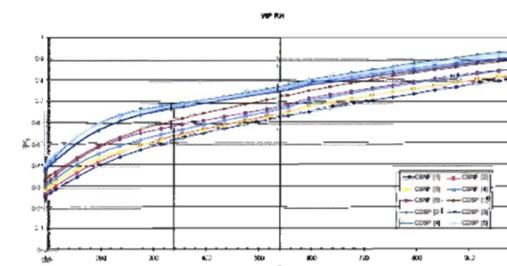
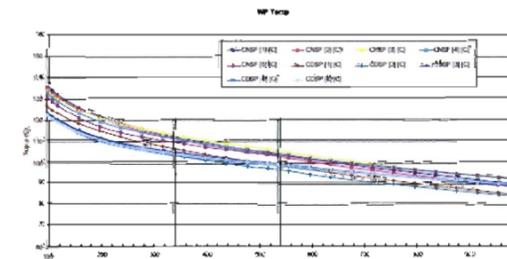
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Temperature/ RH Considerations

- Start time 350-550 years
- In this period
 - WP Temperature Range: ~ 96 – 112 °C
 - WP RH Range : ~ 50 – 80%



Temperature/ RH Considerations

- End time – continuous aqueous film forms on the WP surface
- Formation of the continuous aqueous film is dependent on the
 - Evaporation and condensation rate on WP surface
 - RH at DW and WP surface (assumed well-mixed conditions)
- WP surface RH approach > 95% values around 2000-4000 years (depending on the WP type).
 - WP surface temperature < 60 C
 - Implies conditions suitable for formation of aqueous film could occur around this time

Recorded by: *Jyosthna*

Date: 9/21/10

Verified by:

Date

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 835

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