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A Mechanistic Model for the Passive Dissolution of Ni-Cr-Mo Alloys

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Passivity and Surface Structures for Corrosion Protection Symposium

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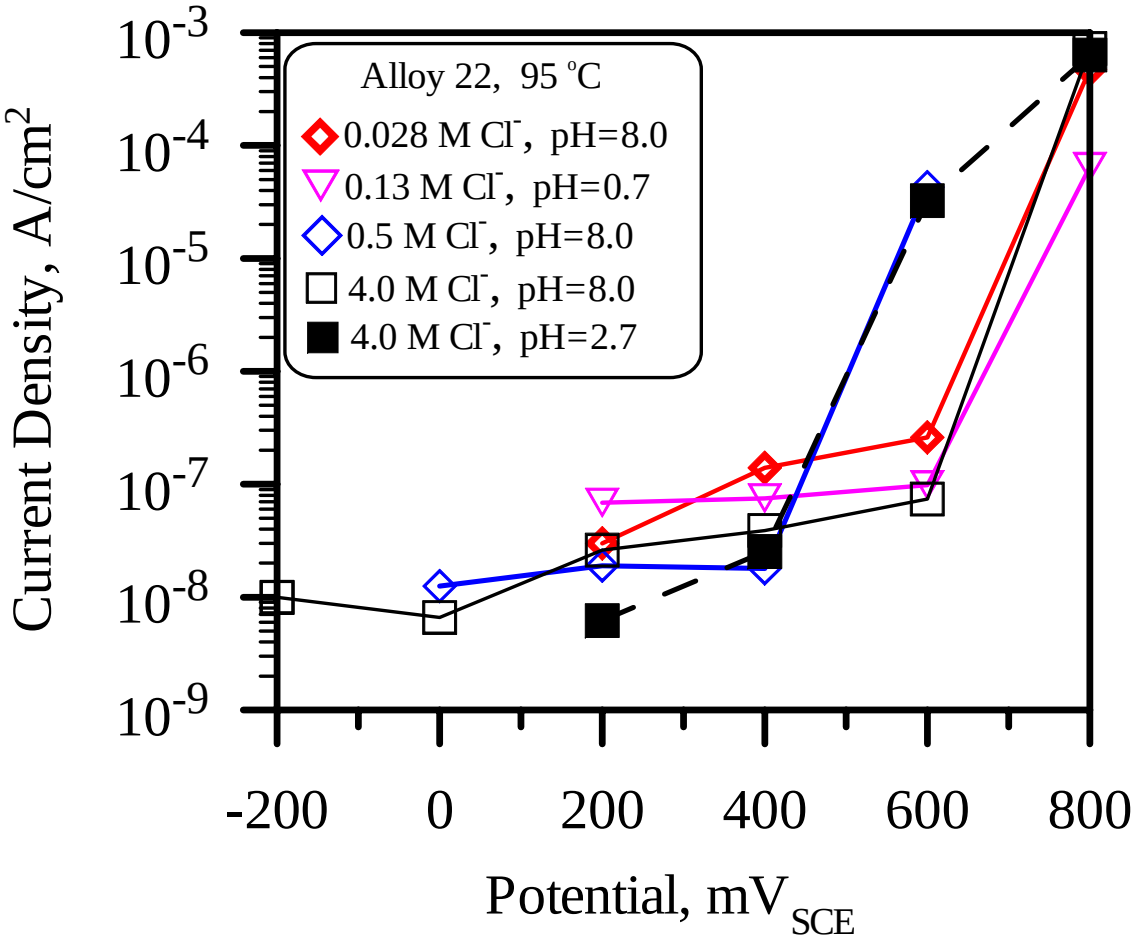
Outline

- Background
- Empirical facts
- Passive dissolution model
- Model results
- Conclusions

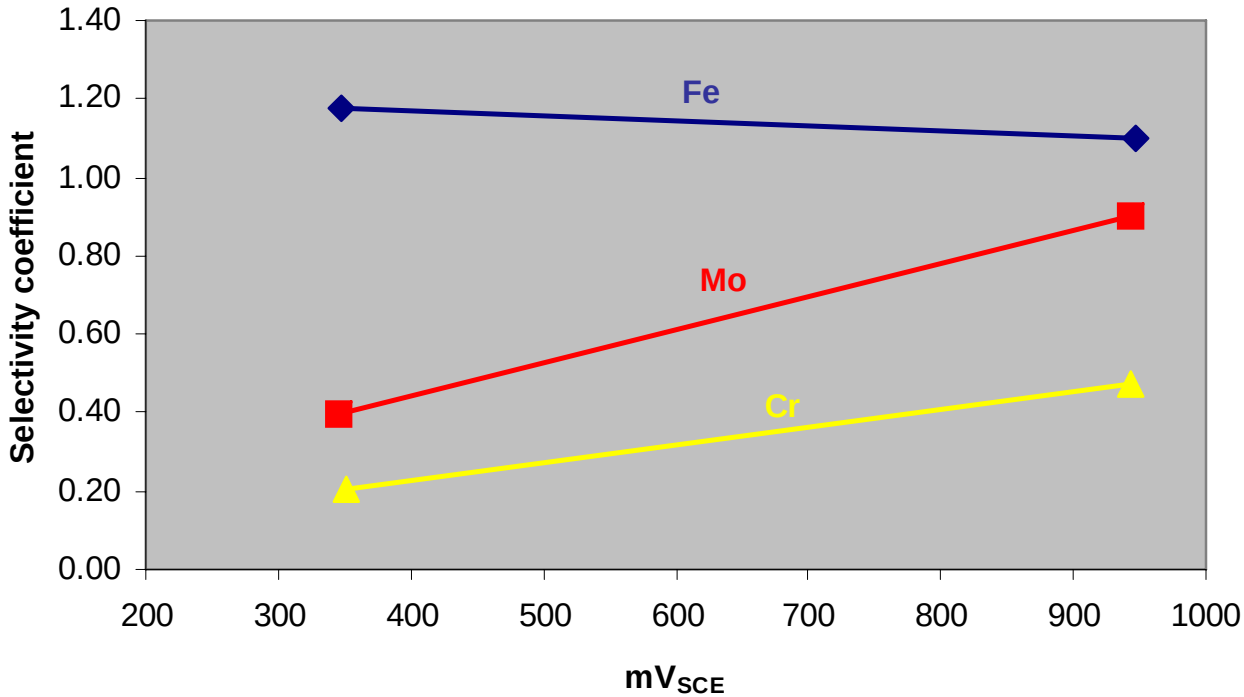
Background

- Alloy 22 (Ni-22Cr-13Mo-3W-4Fe) selected as container material of high-level waste for the proposed repository in the US
- In the absence of conditions leading to localized corrosion, passive dissolution expected to be the predominant corrosion mode
- By extrapolation from short-term experiments, containers estimated to last longer than 10,000 years assuming stability of passive corrosion

Empirical facts: dependence of passive current density on pH and Cl^-

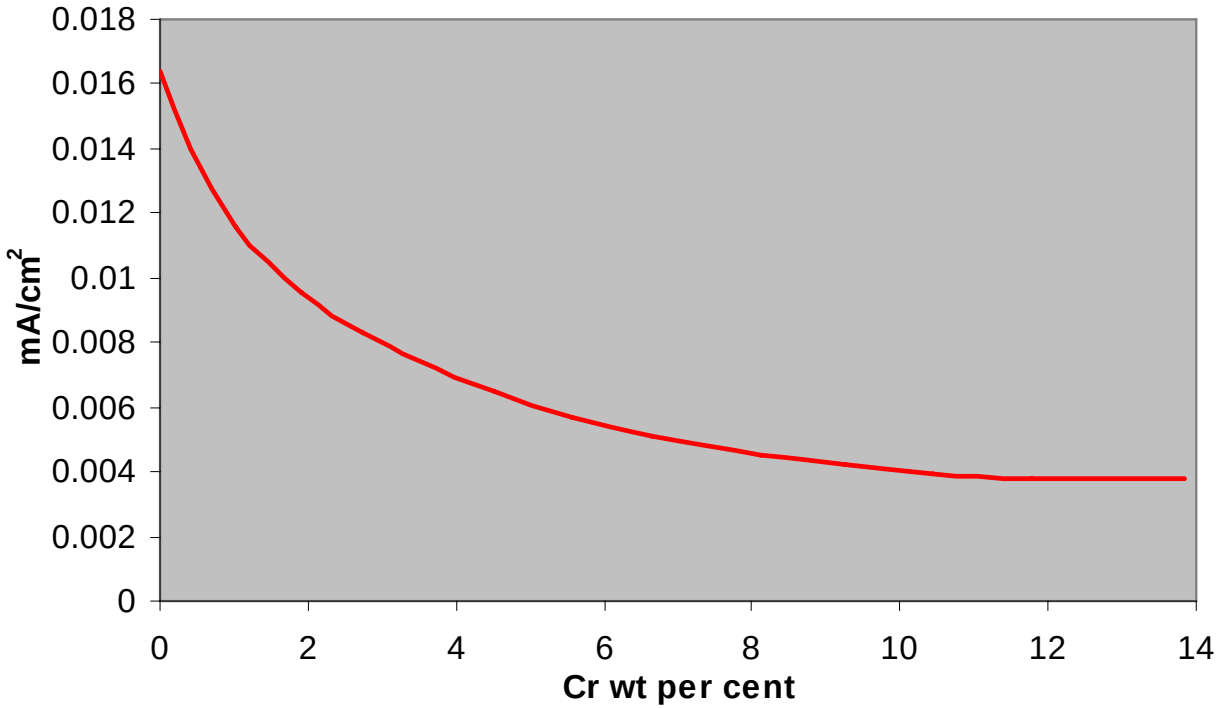


Empirical facts: temporary non-stoichiometric dissolution



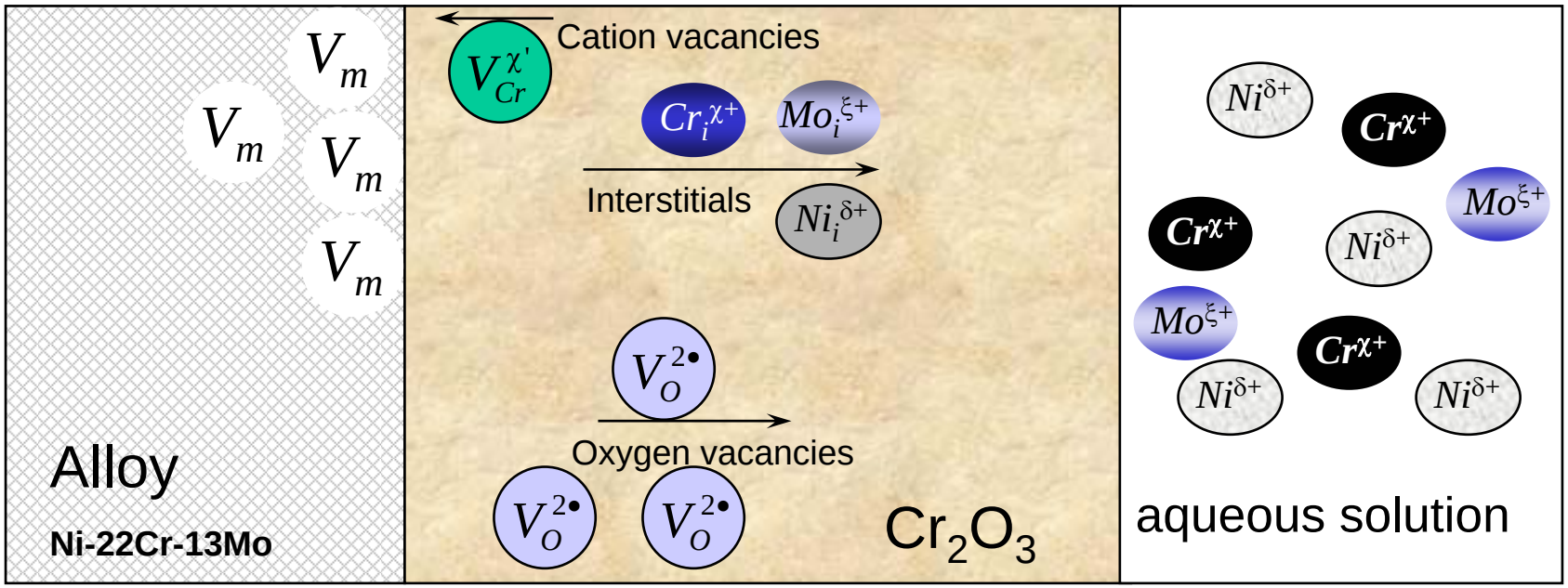
- Temporary non-stoichiometric dissolution in Alloy C-276 (Ni-16Cr-16Mo-4W-5Fe) in 5 N NaCl at 70°C [158°F].
- Data from M. A. Cavanaugh, J. A. Kargol, J. Nickerson, and N. F. Fiore, The anodic dissolution of a Ni-base superalloy, Corrosion-NACE, 39, 144-59 (1983)

Empirical facts: passive current density as a function of Cr content



- Passive current density is a decreasing function of Cr content in Ni-Cr alloys. 1 N H_2SO_4, 25°C [77°F]
- Data from M. H. Tikkanen and O. Hyvärinen, Passivity of nickel-chromium alloys, Acta Polytechnica Scandinavica, Chemistry Incl. Metallurgy Series No. 85, 1-17. Helsinki, 1969.

Passive dissolution model: concept



Passive dissolution model: passive current density and rate constants

- Main charge carriers: cation interstitials and oxygen vacancies:

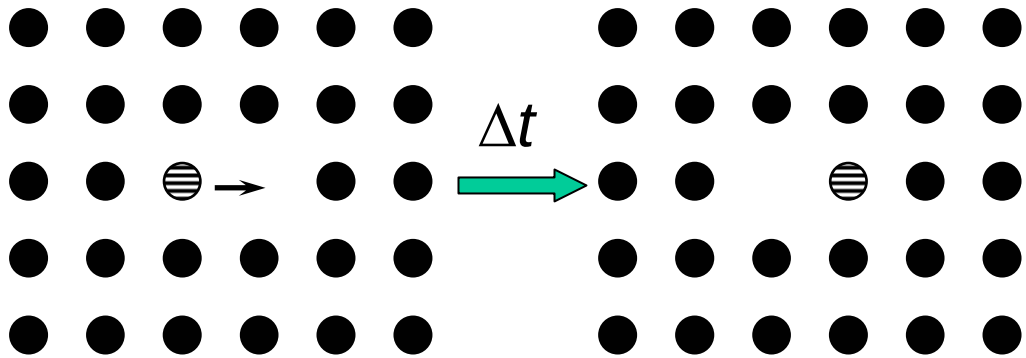
$$I \approx F\left[\chi\, a_{\mathrm{Cr}}\left(k_1^{\mathrm{Cr}} + k_3^{\mathrm{Cr}}\right) + \delta\, a_{\mathrm{Ni}}\left(k_1^{\mathrm{Ni}} + k_3^{\mathrm{Ni}}\right) + \xi\, a_{\mathrm{Mo}}\, k_1^{\mathrm{Mo}}\right]$$

- Current density decreases with increasing Cr content in the alloy:

$$k_1^{\mathrm{Cr}} + k_3^{\mathrm{Cr}} < k_1^{\mathrm{Ni}} + k_3^{\mathrm{Ni}}$$

- If $k_3 \neq 0$, the oxide film would exist in metastable state (continuously forming and dissolving). Situation not likely. Then $k_3 \approx 0$.

Passive dissolution model: mathematical implementation of vacancy transport



$$J_A = -\frac{D_A}{c_v^o}(c_v \nabla c_A - c_A \nabla c_v) = -J_v$$

$$r_v = \frac{1}{c_T}(k_1^{Ni} c_{Ni} + k_1^{Cr} c_{Cr} + k_1^{Mo} c_{Mo})\Big|_{x=0}$$

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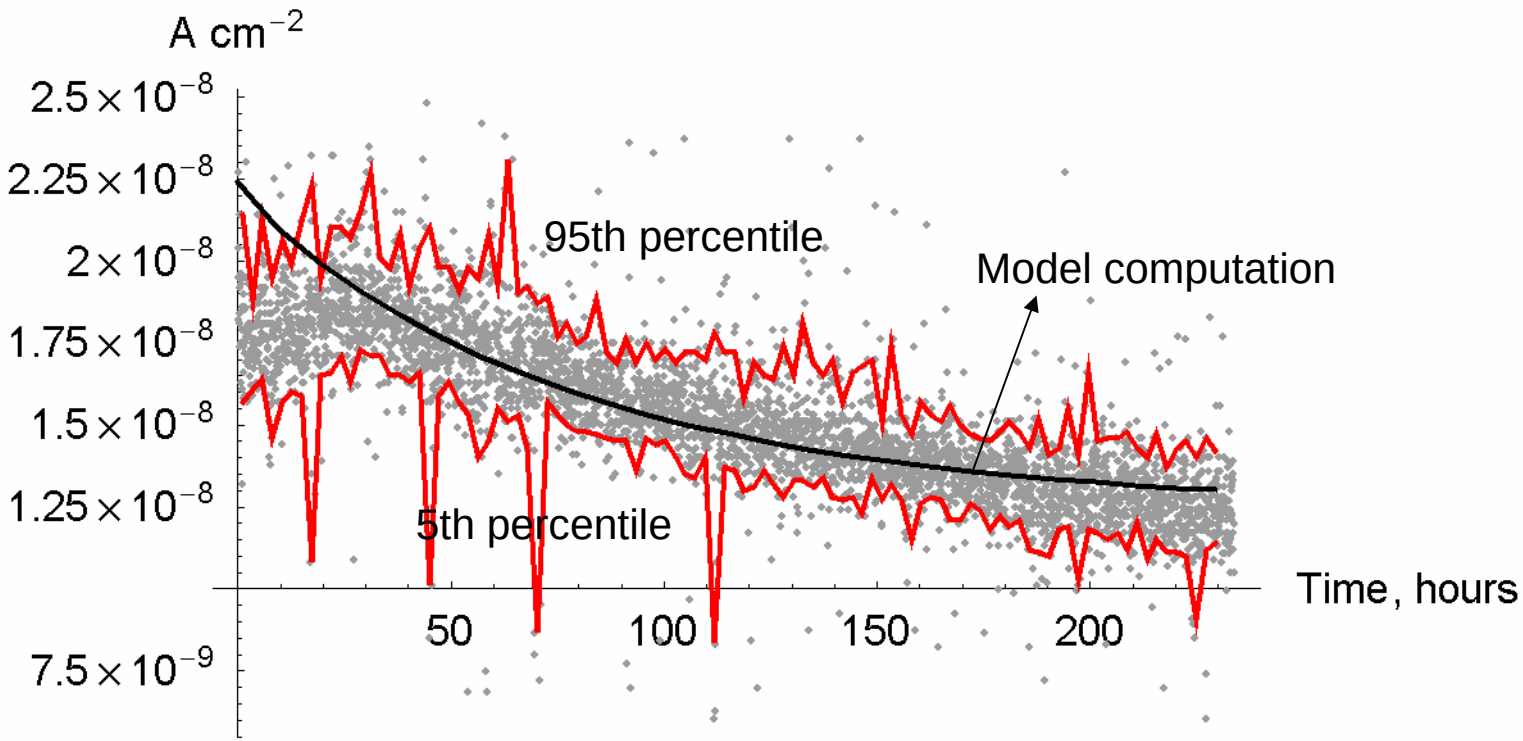
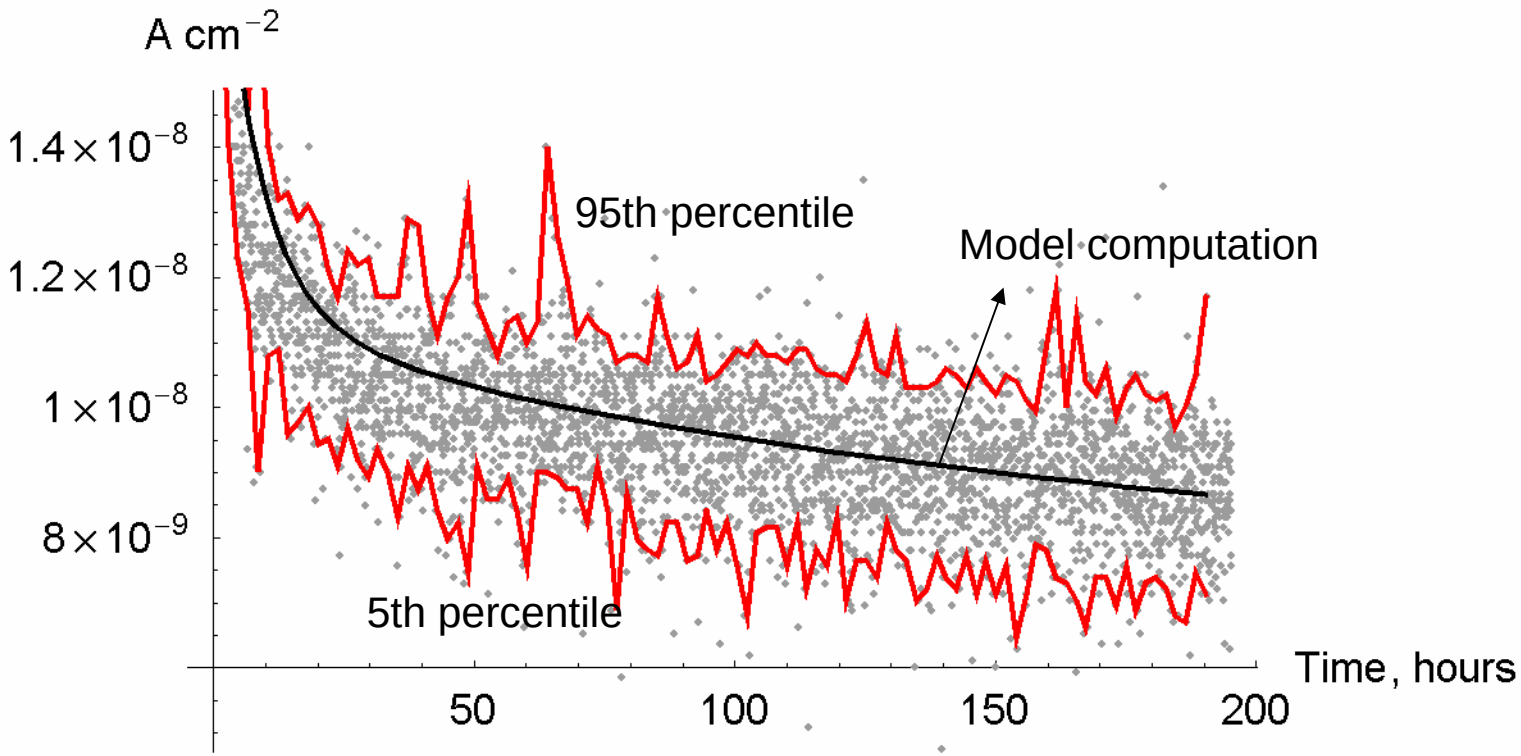
Model results: passive current density versus time

0.028 M Cl^-, 95°C [203°F]



Model results: passive current density versus time

0.028 M Cl^- and 0.052 M fluoride, 95°C [203°F]



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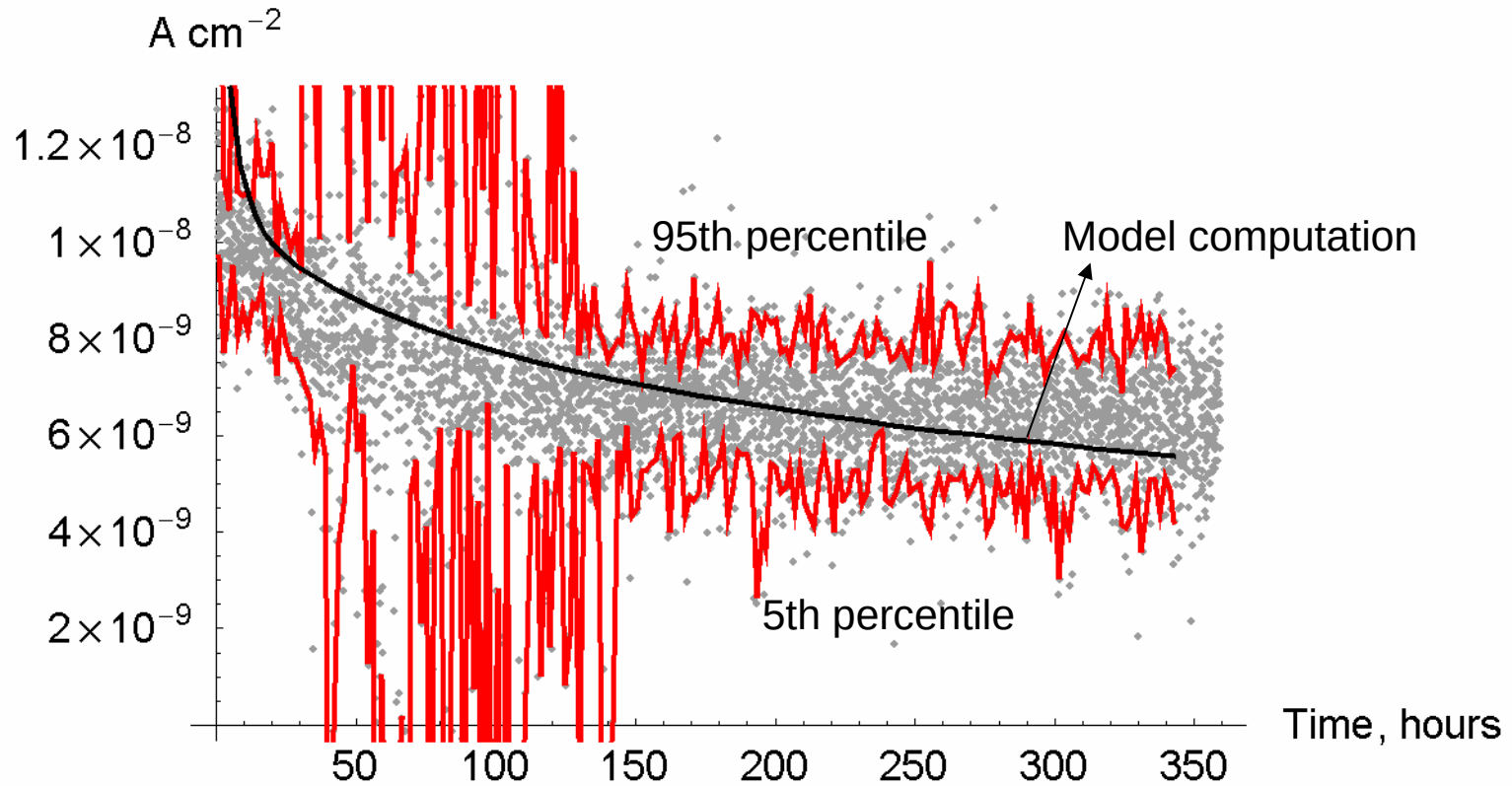
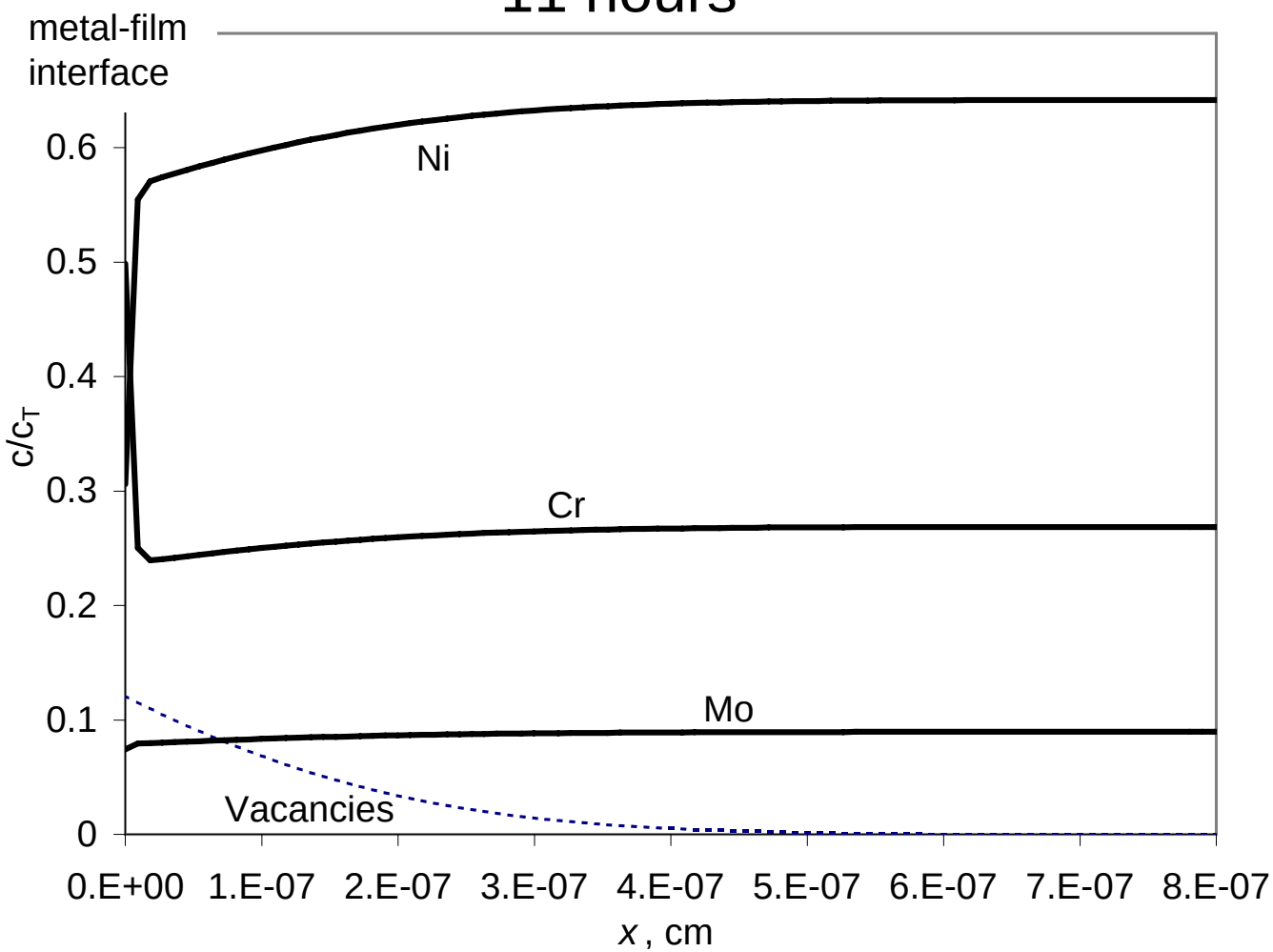
Model results: passive current density versus time

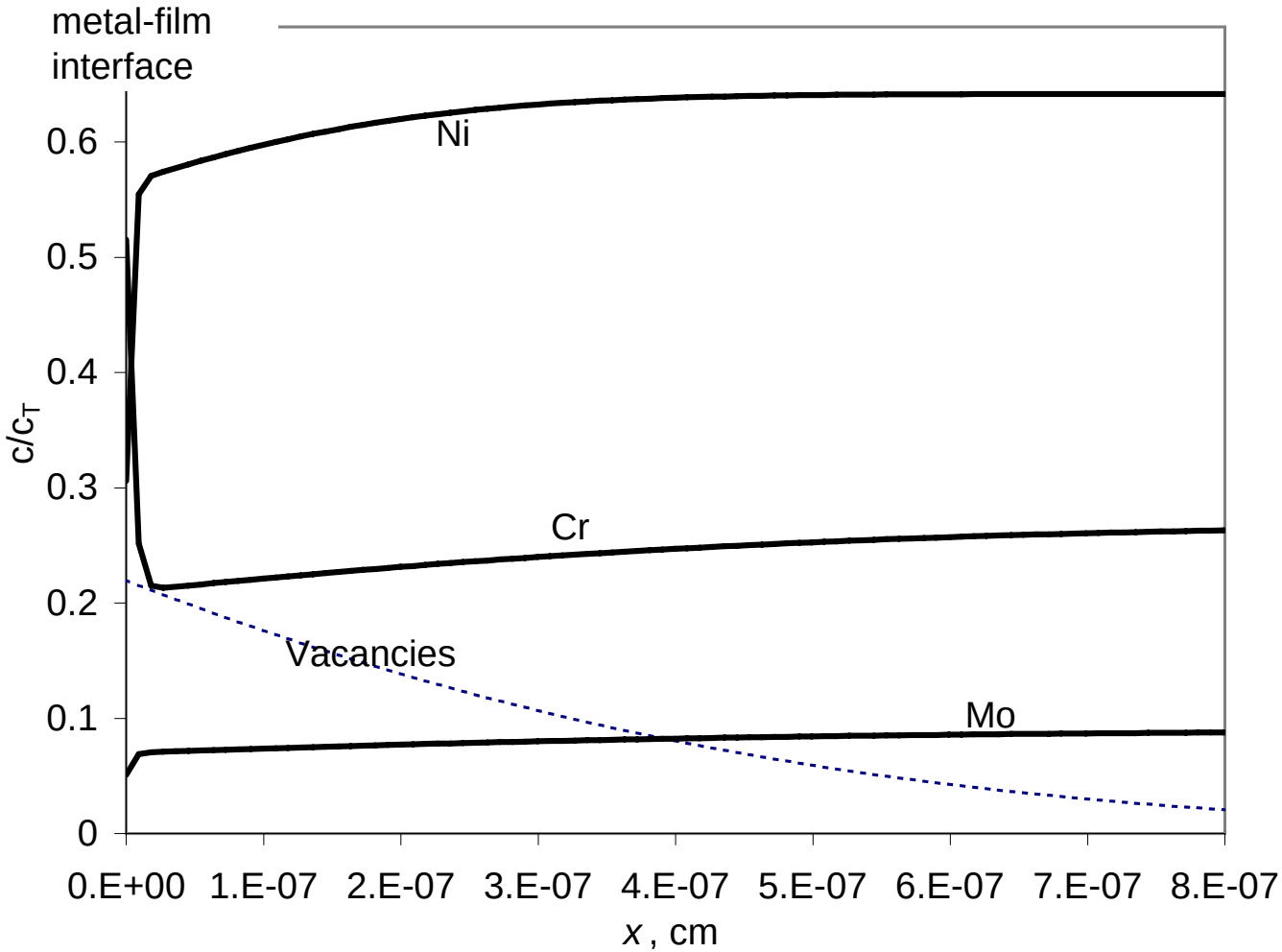
1,000 ppm Cl^- + 1,000 ppm SO_4^{2-}, 95°C [203°F]



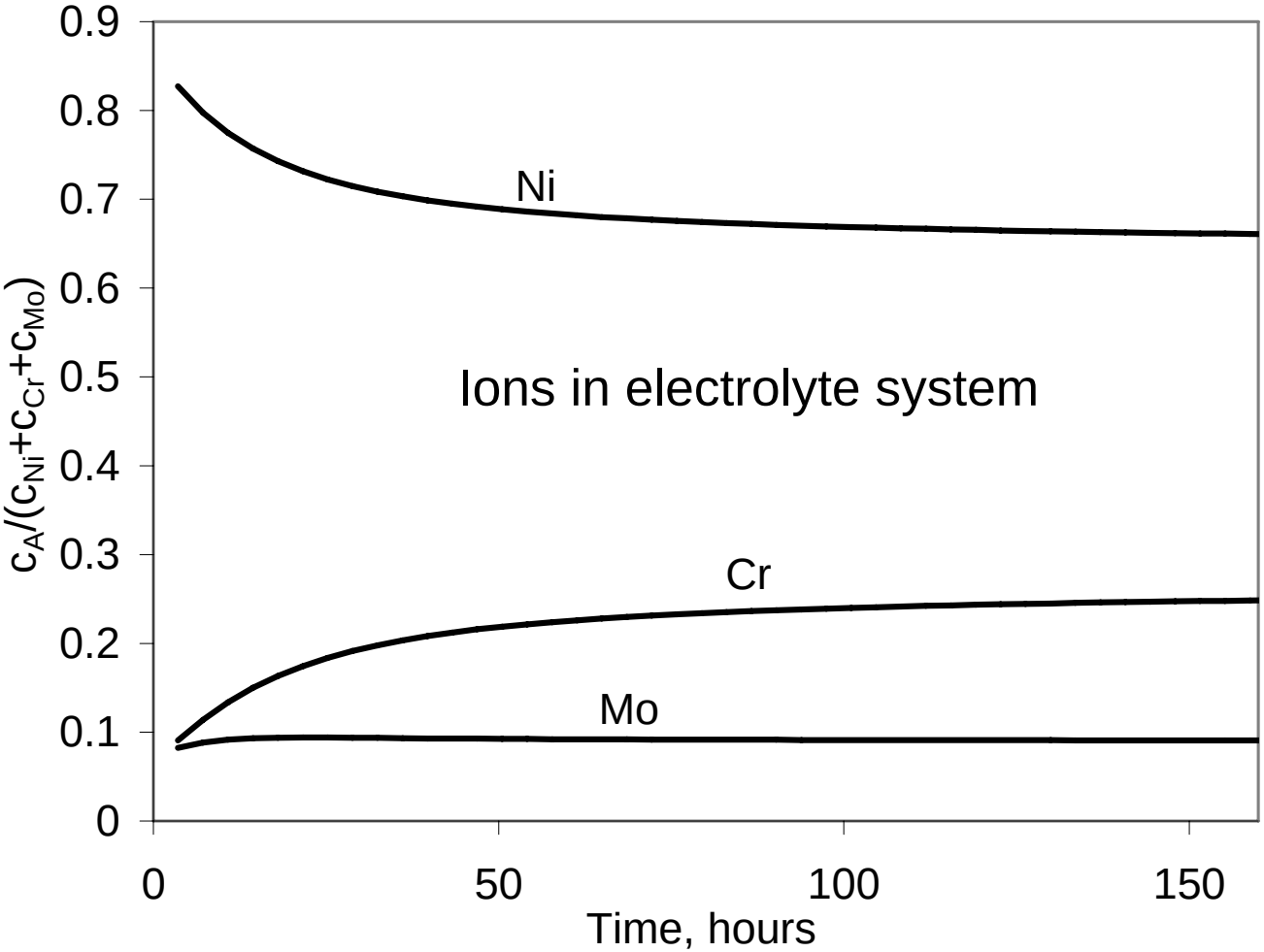
Model results: concentration profile in the metal 11 hours



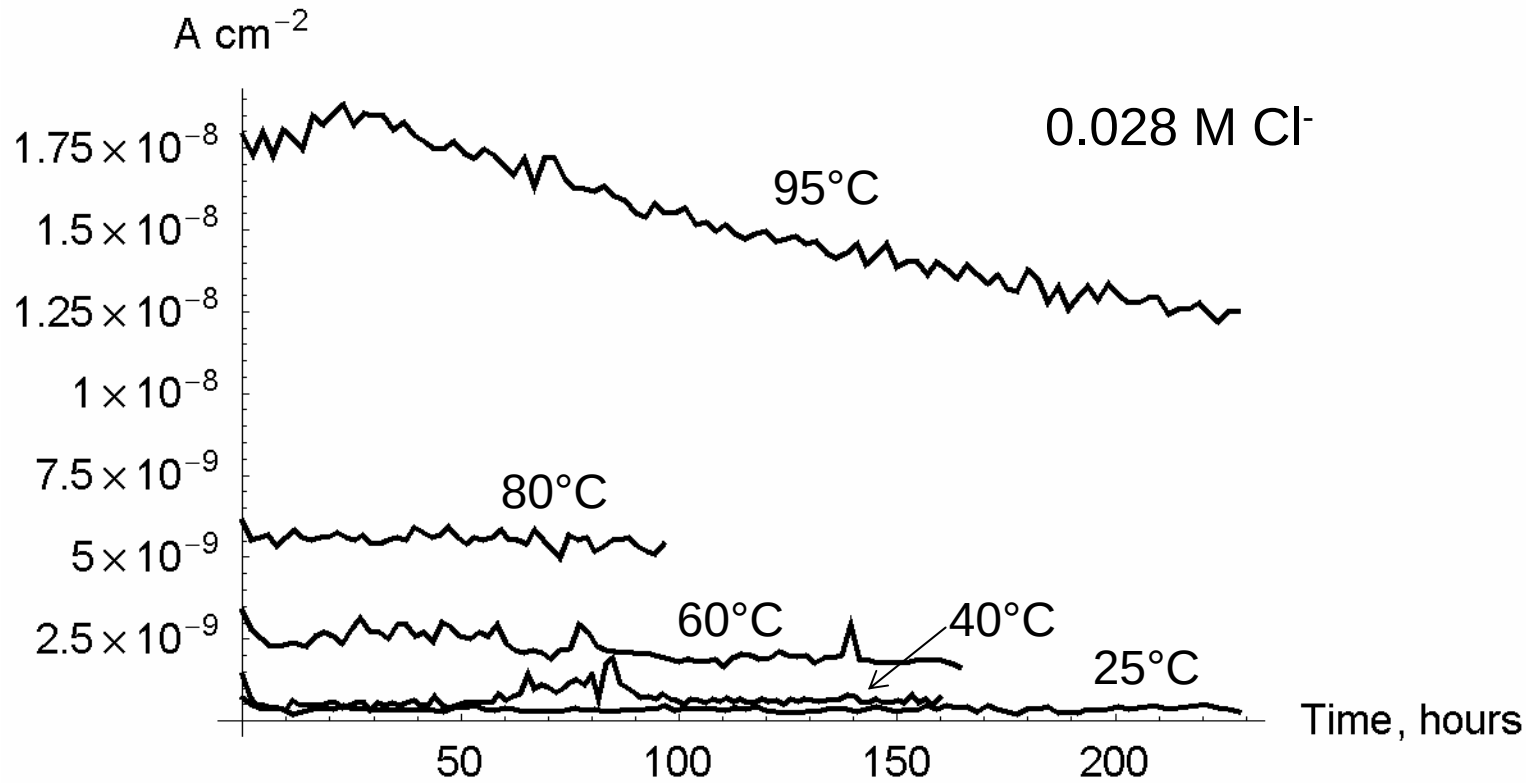
Model results: concentration profile in the metal 65 hours



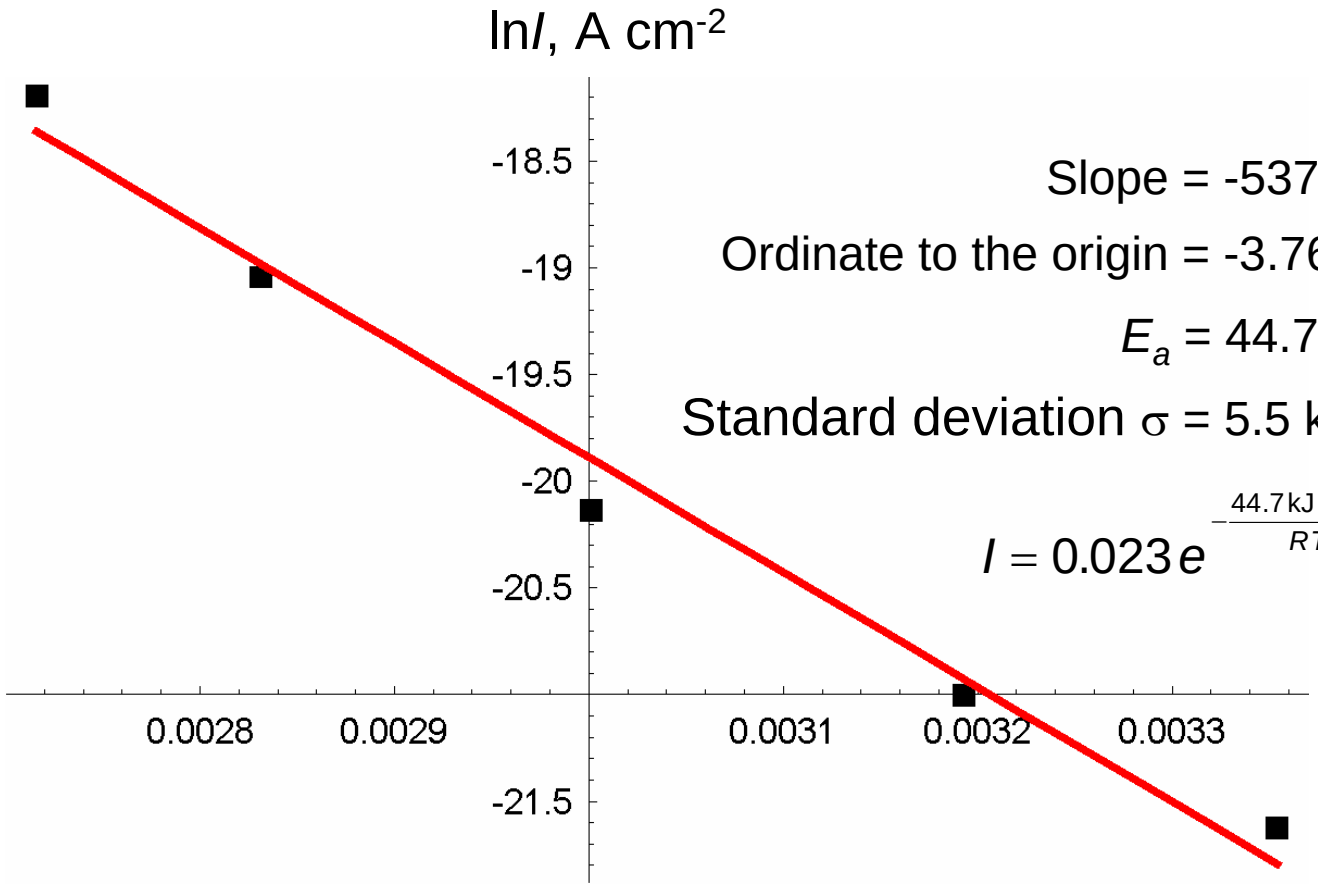
Model results: evolution of ion distribution



Experimental results: effect of temperature



Experimental results: effect of temperature



Slope = -5377 K

Ordinate to the origin = -3.76

E_a = 44.7 kJ/mol

Standard deviation σ = 5.5 kJ/mol

$$I = 0.023\, e^{-\frac{44.7\,\mathrm{kJ\ mol^{-1}}}{RT}}\ \mathrm{A\,cm^{-2}}$$

Conclusions

- Charge conducted through the oxide in the form of interstitials
- Accumulation of vacancies at metal/film interface causes decrease in the current density
- Dissolution is stoichiometric and regulated by solid state diffusion
- Passive dissolution is envisioned to prevail for extended periods (if film spalling occurs, Cr_2O_3 is expected to form again immediately)

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Disclaimer

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- This work is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.