

Long-Term Thermal Aging Behavior of High-Cr Nickel- Base Alloys

Requirements, Review and Statistical Analysis



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Topical Question from CGN

ASME Section III, Non-Mandatory Appendix W3200 lists materials susceptible to thermal embrittlement that require attention during the design stage, including nickel-based alloys, and specifies an iron content limit of 9% as the threshold for susceptibility to thermal embrittlement. It is understood that relevant research is ongoing in the United States. Could you provide details on the specific progress of this research? If the iron content in steam generator tubing or other nickel-based alloy components is below 9% (7%), is there a significant risk of thermal aging failure? Is it necessary to raise the design limit for iron content in corresponding nickel-based alloys to 9%?

ASME 第三卷 非强制性附录 W3200中列举了设计阶段需要关注的热致脆化敏感性材料，其中涉及镍基合金，并给出了铁含量9%的限值作为热致脆化敏感性阈值。据了解美国正在进行相关研究，请介绍具体研究进展情况，如果蒸汽发生器传热管或其他镍基合金部件铁含量低于9%（7%），是否存在明显热老化失效风险？是否有必要将相应镍基合金的铁含量设计限值指标提高至9%。

REFERENCE DOCUMENT

Guidelines for PWR Steam Generator Tubing Specifications and Repair, Volume 2, Revision 1: Guidelines for Procurement of Alloy 690 Steam Generator Tubing, EPRI, Palo Alto, CA: 1999. Report TR-016743-V2R1.

PUBLICLY AVAILABLE ON WWW.EPRI.COM

Background

Revision 0 of the Alloy 690 Guidelines was issued in February 1991 as NP-6743-L, Volume 2. In 1998, Revision 1 to the 1991 Guidelines was begun in response to EPRI utilities' request to reduce the number of anomalous eddy current test (ECT) signals—such as manufacturing burnish marks (MBMs)—that require follow-up during in-service inspections. EPRI members also wanted to control the microstructure to maximize resistance to intergranular attack/ stress corrosion cracking (IGA/SCC) in caustic testing.

Alloy 690 Material Specification Requirements

At the time of publication, the reference report notes:

- Specification contains the requirements for the manufacture, quality assurance, examination, testing, and shipment of seamless nickel-chromium-iron [Alloy 690 \(UNS N06690\)](#) steam generator tubing with [special requirements for chemical composition](#), heat-treatment, microstructure, and quality control.
- Specification incorporates the requirements of ASME SB-163 Alloy N06690 in accordance with ASME III NB-2000, as supplemented by Code Case N-20-3, and incorporates additional requirements. These additional requirements are not in conflict with ASME III NB-2000, Code Case N-20-3, or SB-163.

Alloy 690 Material Specification Requirements

**Chemistry
Requirements from
Table 2-1 of the
Reference Report**

<u>Element</u>	<u>Percent</u>
Nickel (min)	58.0
Chromium	28.5 - 31.0
Iron	9.0 - 11.0
Carbon	0.015 - 0.025
Silicon (max)	0.50
Manganese (max)	0.50
Cobalt	0.014 average for tube bundle with no heat to exceed 0.020%
Copper (max)	0.10
Sulfur (max)	0.003
Phosphorus (max)	0.015
Nitrogen (max)	0.050
Aluminum (max)	0.40
Boron (max)	0.005
Titanium (max)	0.40
Molybdenum (max)	0.2
Niobium (max)	0.1

Element of
interest
from CGN
topical
question

Technical Basis for Fe Requirement

From Section 3 Bases for Alloy 690 Specification of Reference Report:

Iron: The minimum iron was raised from 7.0% to 9.0% to reflect much of industry's practice, and to minimize concerns about possible long range ordering reactions that might possibly lead to embrittlement after long time at temperature. The change also serves to tighten the composition range.

Relevant Research on Thermal Embrittlement of Alloy 690 and Associated Weld Metal

Information as presented at:

**22nd International Conference on Environmental Degradation of Materials in
Nuclear Power Systems – Water Reactors
August 11-14, 2025**

Background

- Long-range ordering (LRO) has been extensively studied
 - EPRI Product ID: 3002013280, 2018
 - EPRI Product ID: 3002018324, 2020
- Well known that LRO causes hardening
- LRO potentially increases PWSCC susceptibility
- There remains several open questions
 - **Is hardening in commercial Alloy 690 attributable to LRO?**
 - And is the hardening statistically significant (small heat-to-heat variability)?
 - **Are there significant parameters that increase susceptibility to hardening?**
 - Composition
 - Thermo-mechanical processing history
 - **What is the engineering significance of hardening in commercial material?**
 - PWSCC susceptibility

Objectives and Methodology

- Review and discuss the results and conclusions made in recent literature pertaining to long-term aging of Alloy 690 and its weld metals
- Pinpoint outliers in the research results and investigate potential reasons behind their atypical behavior
- Analyze the aging phenomena and mechanisms of embrittlement
- Identify open data gaps



Literature Review Summary

- Reviewed 40+ recent (after 2018) investigations involving high-chromium nickel base alloys
 - EPRI 3002013280 covers literature up to 2018
- Multiple studies conclude the potential of LRO formation during plant lifetimes is low
- No study observed LRO forming in aged Alloy 690 and 152
 - However, there were two cases of substantial hardening
- There have been notable additions to help address knowledge gaps
 - Aging studies conducted at lower temperatures (<400°C)
 - Investigations into aging response of low-Fe weld metal variants



Data Analysis

General Linear Model Testing

- Typical ANOVA test
 - Assumes all parameters are independent
 - $X_i' \beta = \beta_0 + \beta_1 X_{i1} + \dots + \beta_{p-1} X_{i,p-1}$
 - Dependent variable is the temperature adjusted aging time
 - $t_{aging} = t_{ref} \cdot \exp \left[-\frac{Q}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T_{aging}} \right) \right]$
 - $Q = 125 \text{ kJ/mol}$
 - $t_{ref} = 325 \text{ }^\circ\text{C}$
- Performed analyses on three compiled databases
 - Model alloys
 - Alloy 690
 - Weld metals (Alloys 52/152 and variants)
- For each independent variable, analysis provides:
 - Statistical significance of dependence
 - Magnitude of dependence

Database Characterization

- Consists of 835 data points categorized by material type
 - Substantial amount of data from EPRI report 3002018324 (373 data points)
 - Additional data added from ten recent publications
- Hardness testing using lower than 25 gf loads (i.e., nanohardness) not included

Condition	Alloy 690	Alloy 52/152	Model Alloys
Thermally Treated	171	0	174
Solution Annealed / As-Welded	29	143	20
Cold Worked	90	0	84
Stress Relief Heat Treatment	20	63	28

Model Alloy Parameter Ranges and ANOVA Results

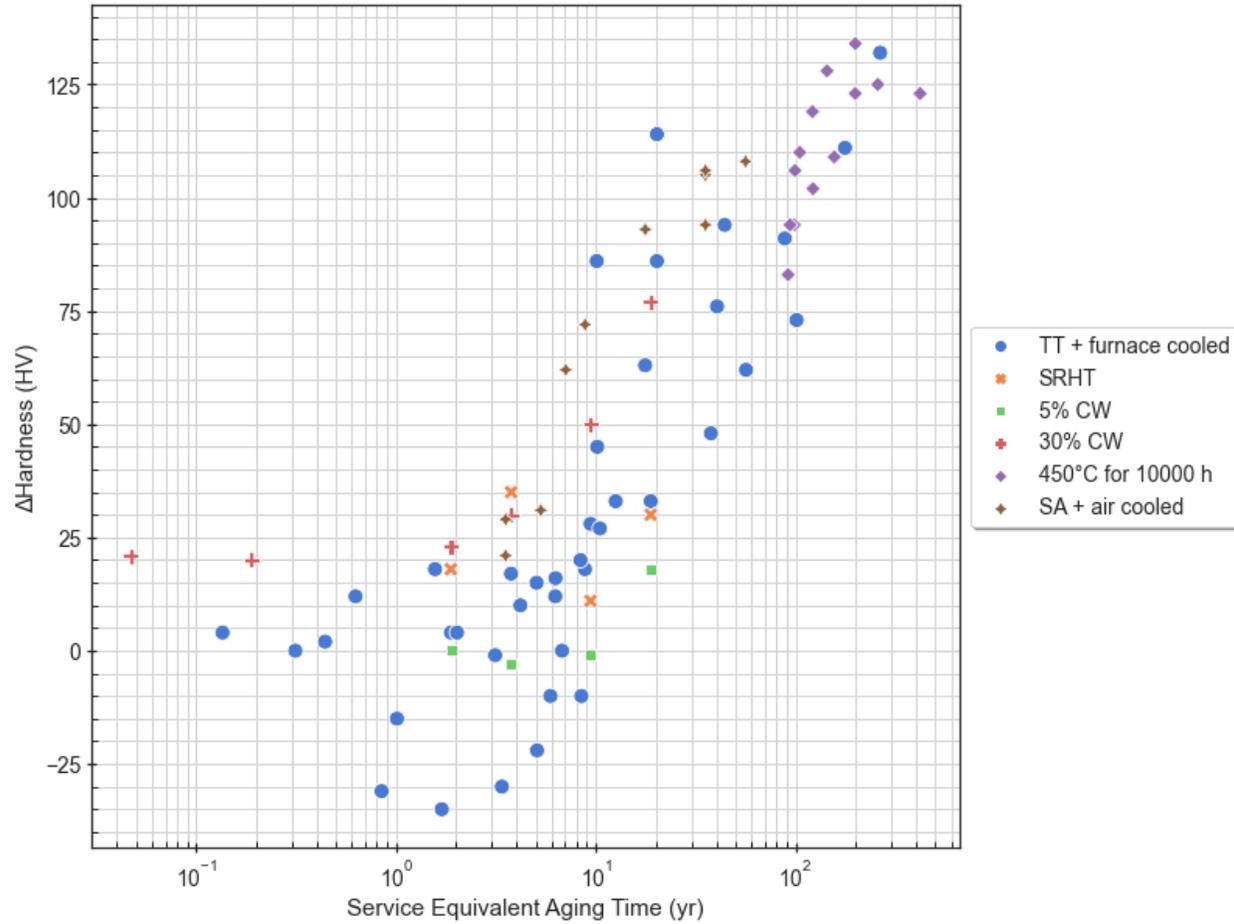
	TT	SA	450°C for 10,000 hours ¹	SRHT	Cold Worked
Cold Work Level (%)	0	0	0	0	5 – 30
Aging Time (hr)	4 – 30,000	200 – 10,000	100 – 3,000	1,000 – 10,000	25 – 10,000
Service Equivalent Aging Time (yr)	0.14 – 264.42	0 – 154.26	91.52 – 418.95	1.88 – 18.80	0.05 – 18.80
Aging Temperature (°C)	350 – 550	330 – 475	500 – 550	400	400
Hardness (HV)	137 – 309	129 – 237	242 – 293	150 – 195	195 – 397
Fe wt.% (%)	0.01 – 10	0 – 10.08	0.01	0.01 – 10	0.01 – 10
Ni wt.% (%)	57.5 – 68.7	60.26 – 69.3	68.7	57.5 – 68.7	57.5 – 68.7
Cr wt.% (%)	27.71 – 31.74	29.6 – 30.7	30.59	27.71 – 31.74	27.71 – 31.74
Ni:Cr Atomic Ratio	1.6 – 2.0	1.8 – 2.0	2.0	1.6 – 2.0	1.6 – 2.0
ΔHardness (HV)	-35 – 132	1 – 108	83 – 134	-11 – 35	-8 – 77

Parameter	Estimated Coefficient	P-Value	Lower Limit	Upper Limit
Cold Work	0.6066	0.000	0	30
Service Equivalent Aging Time	0.3497	0.000	0	418.95
Ni:Cr Atomic Ratio	24.5436	0.000	1.6	2.0
Carbon	-115.1327	0.297	0	0.049
Silicon	-709.6718	0.000	0	0.05
Aluminum	-45.6154	0.000	0	0.45
Iron	-2.6189	0.000	0	10.08

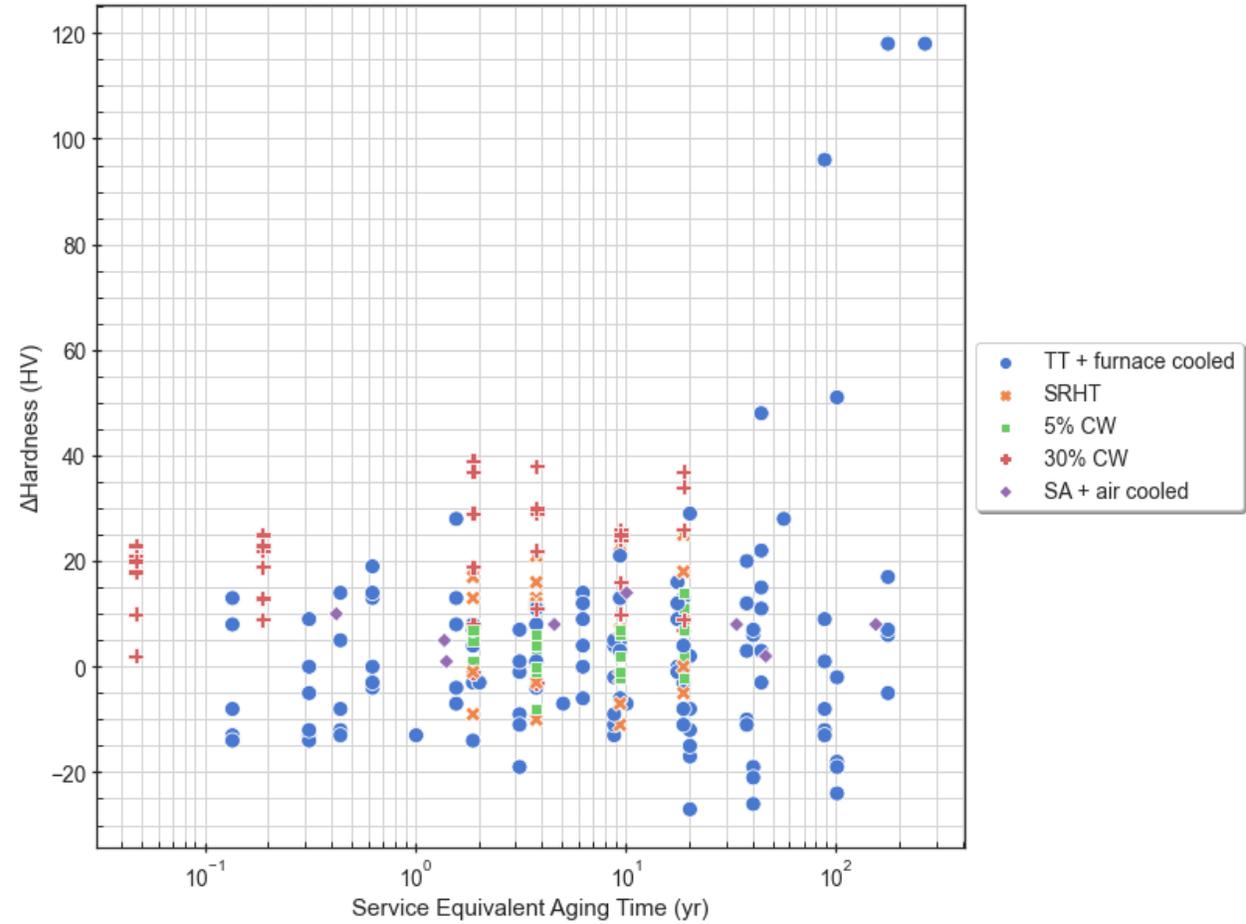
¹Specimens were aged at 450°C and subsequently aged 100-3,000 hours at higher temperatures

Model Alloy Significant Parameters

Ni-Cr Binary Alloys



Ni-Cr-Fe Alloys

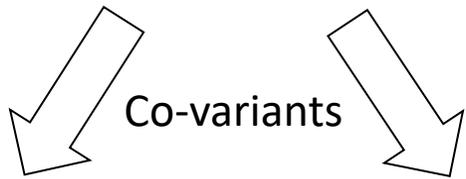


Model Alloy Significant Parameters

■ ANOVA Results

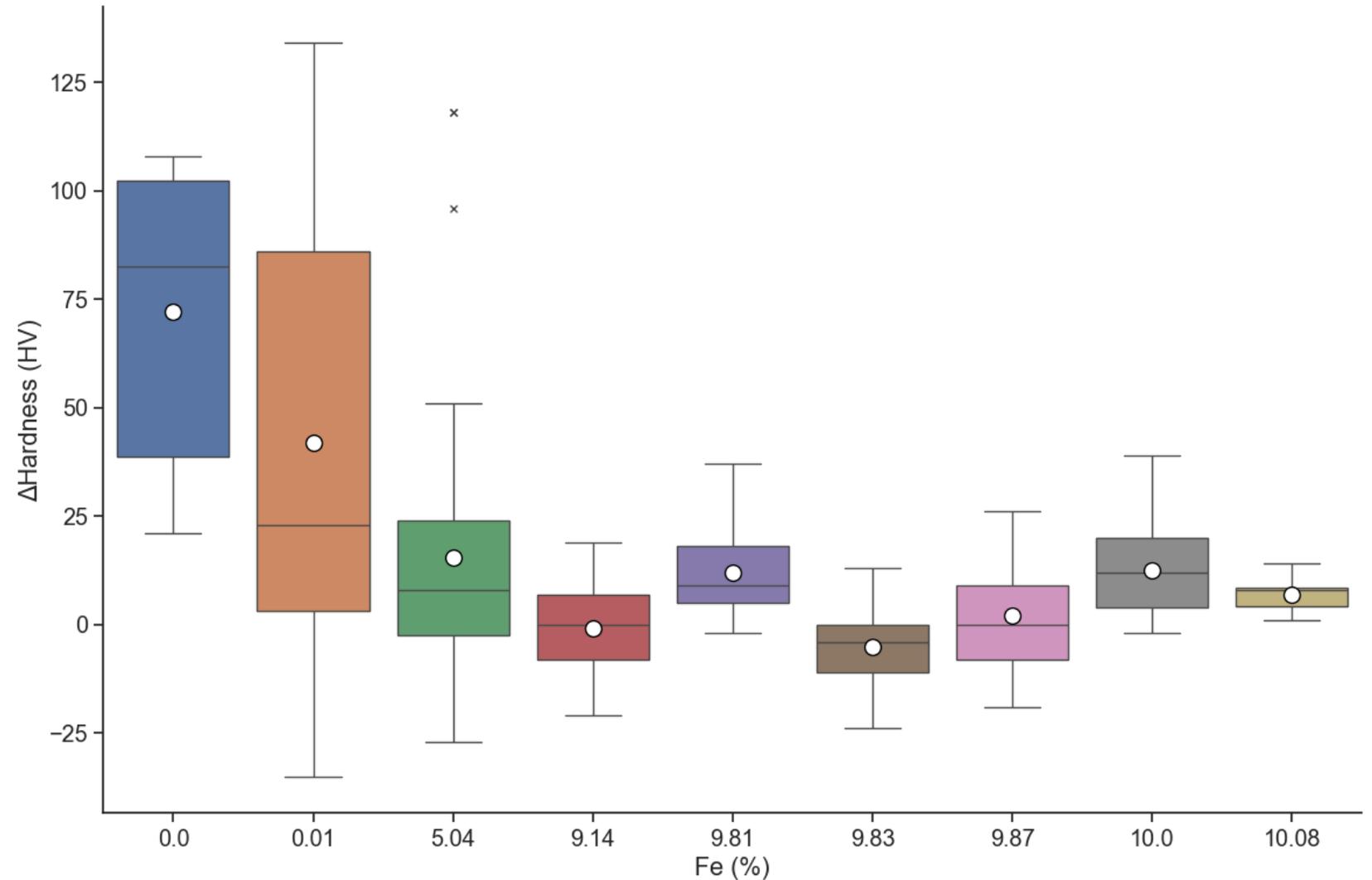
- Iron
- Cold Work
- Aging Time
- Ni:Cr atomic ratio

{ ADDITIONAL ANALYSIS }



1.99-2.00 Ni:Cr
has 0% Fe in
data sets

1.6-1.97 Ni:Cr
with Fe in data
sets show no
significant
differences



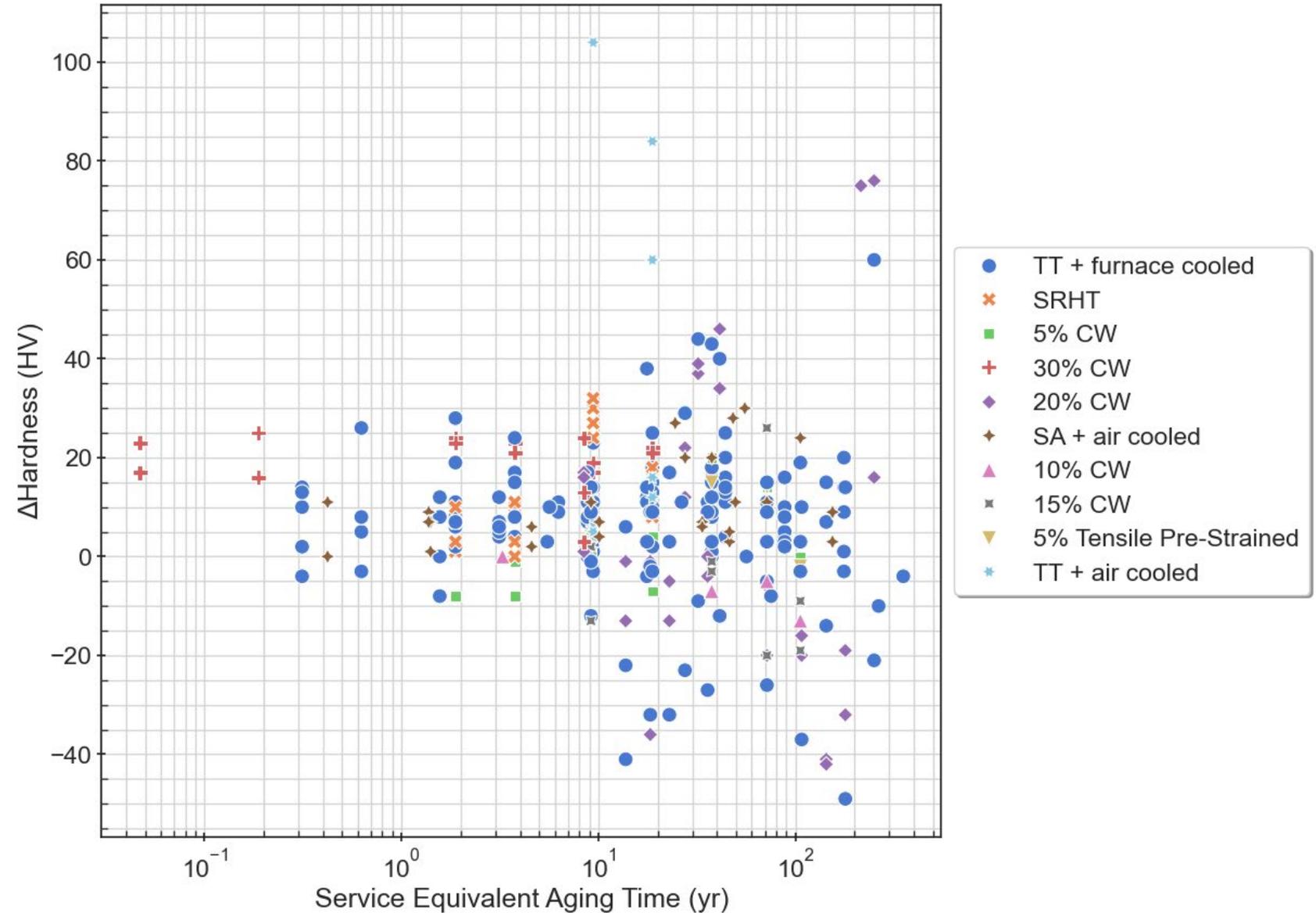
Alloy 690 Parameter Ranges and ANOVA Results

	TT	SA	SRHT	Cold Worked
Cold Work Level (%)	0	0	0	5 – 30
Aging Time (hr)	1,000 – 90,000	3,000 – 74,808	1,000 – 10,000	25 – 90,000
Service Equivalent Aging Time (yr)	0.31 – 352.56	0.42 – 262.25	1.88 – 18.80	0.05 – 250.81
Aging Temperature (°C)	350 – 475	330 – 475	400	360 – 475
Hardness (HV)	153 – 273	166 – 203	170 – 235	193 – 391
Fe wt.% (%)	7.17 – 11.19	8.53 – 10.48	8.7 – 11.19	7.2 – 10.4
Ni wt.% (%)	57.6 – 61	59.41 – 59.67	57.6 – 61	59.55 – 61
Cr wt.% (%)	27.08 – 30.92	29.42 – 30.82	27.08 – 29.98	27.08 – 30.7
Ni:Cr Atomic Ratio	1.7 – 2	1.72 – 1.79	1.7 – 2.0	1.74 – 2
ΔHardness (HV)	-49 – 104	0 – 30	0 – 32	-42 – 76

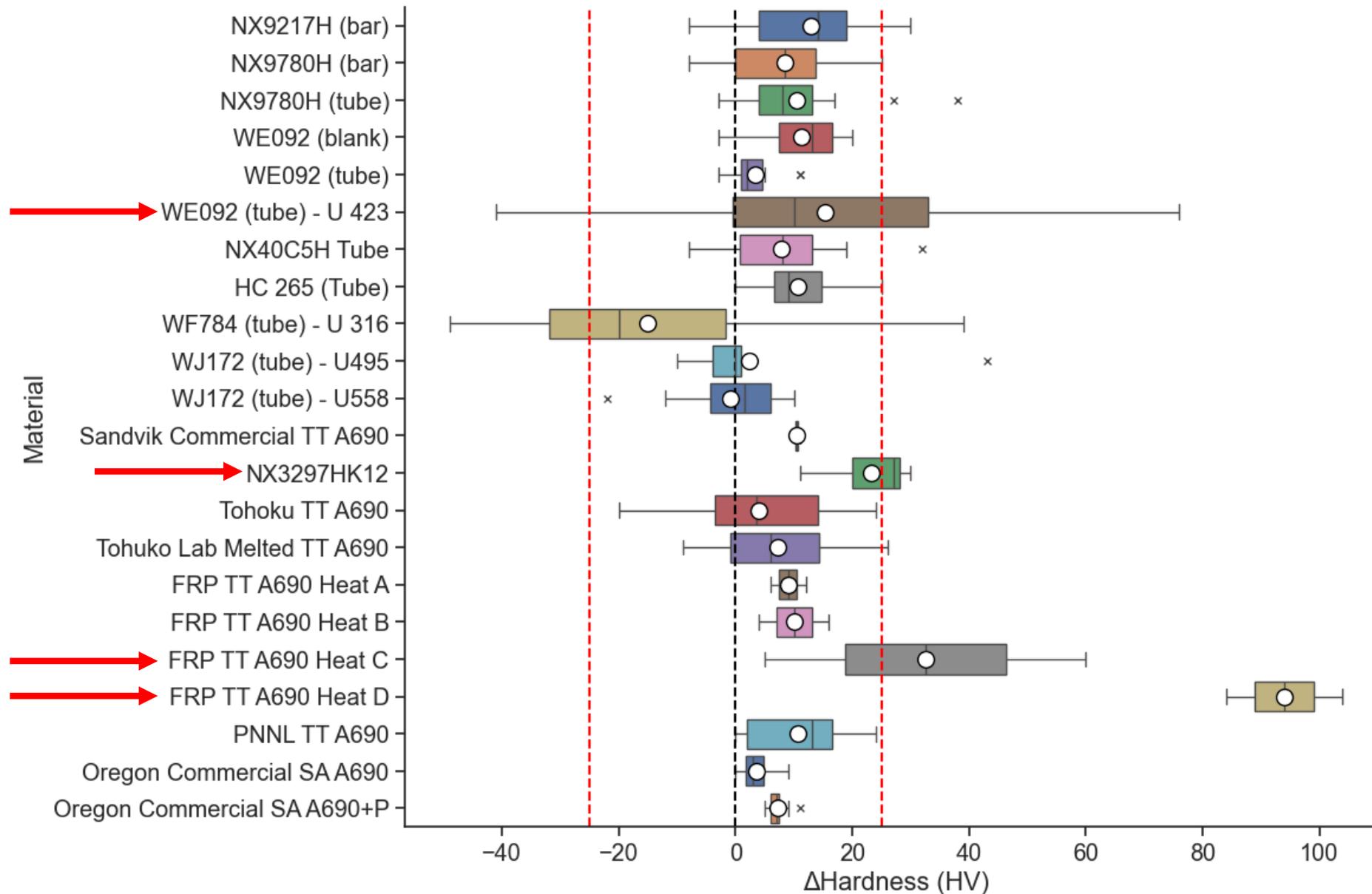
Parameter	Estimated Coefficients	P-Value	Lower Limit	Upper Limit
Cold Work	0.1027	0.363	0	30
Service Equivalent Aging Time	0.0101	0.581	0.05	352.56
Ni:Cr Atomic Ratio	-9.9777	0.685	1.7	2.0
Carbon	275.6972	0.426	0.012	0.041
Silicon	1.1548	0.947	0.02	0.5
Sulfur	7340.0216	0.028	0	0.002
Phosphorous	-1039.5286	0.089	0.001	0.02
Manganese	-22.4921	0.085	0.031	0.48
Copper	10.0030	0.835	0.006	0.19
Titanium	12.2221	0.515	0.14	0.49
Aluminum	-23.8112	0.175	0.08	0.35
Iron	-0.0430	0.988	7.17	11.19
Molybdenum	40.2133	0.098	0.004	0.5
Cobalt	435.1569	0.090	0.01	0.03

Alloy 690 Significant Parameters

- ANOVA Results
 - Sulfur
- Some concerning outliers

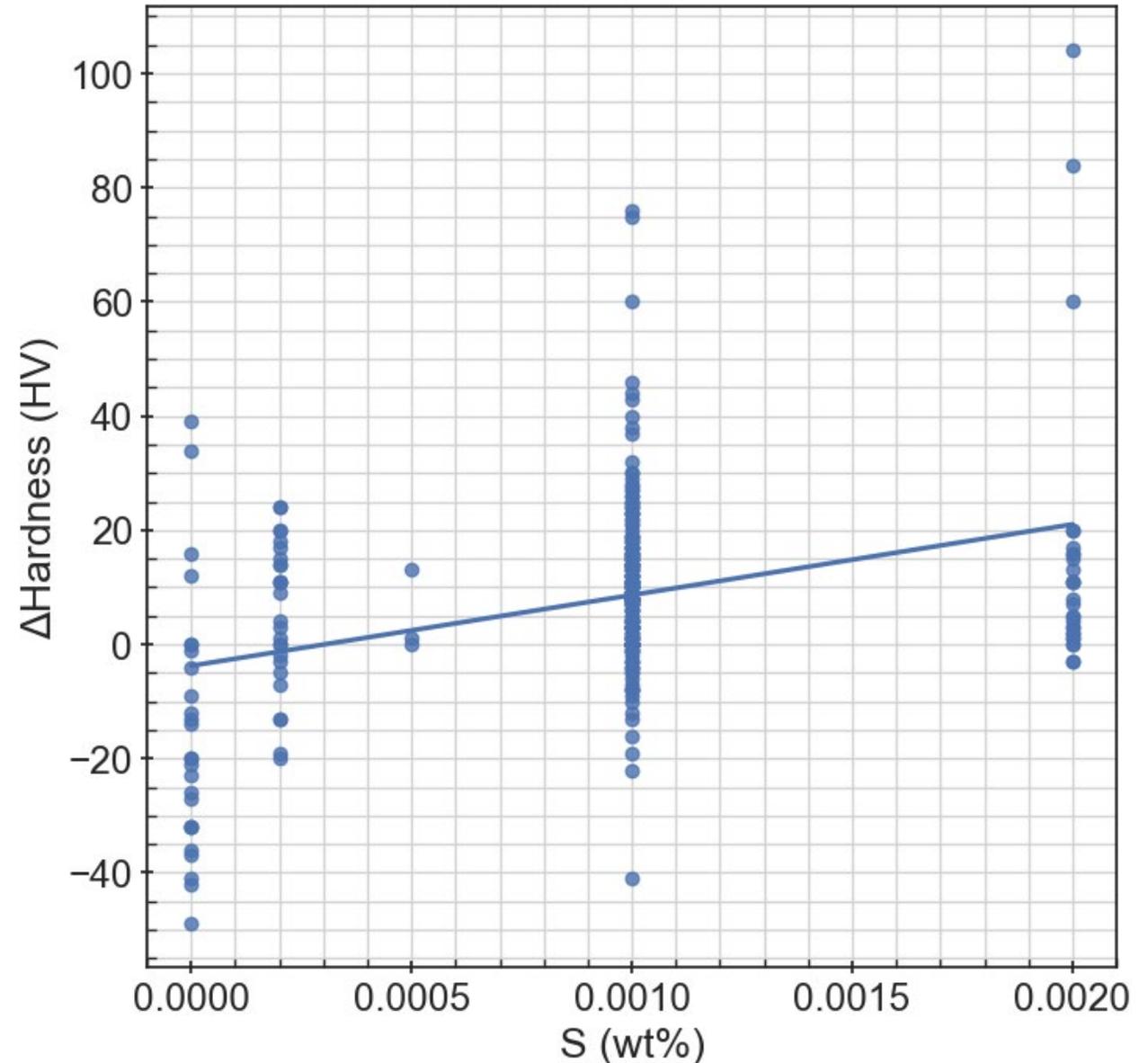


Alloy 690 Heats with Significant Hardening



Alloy 690 Significant Parameters

- Sulfur exhibits slight positive correlation with change in hardness
- Outlier data from VTT study strongly affecting the correlation



Weld Metal Parameter Ranges and ANOVA Results

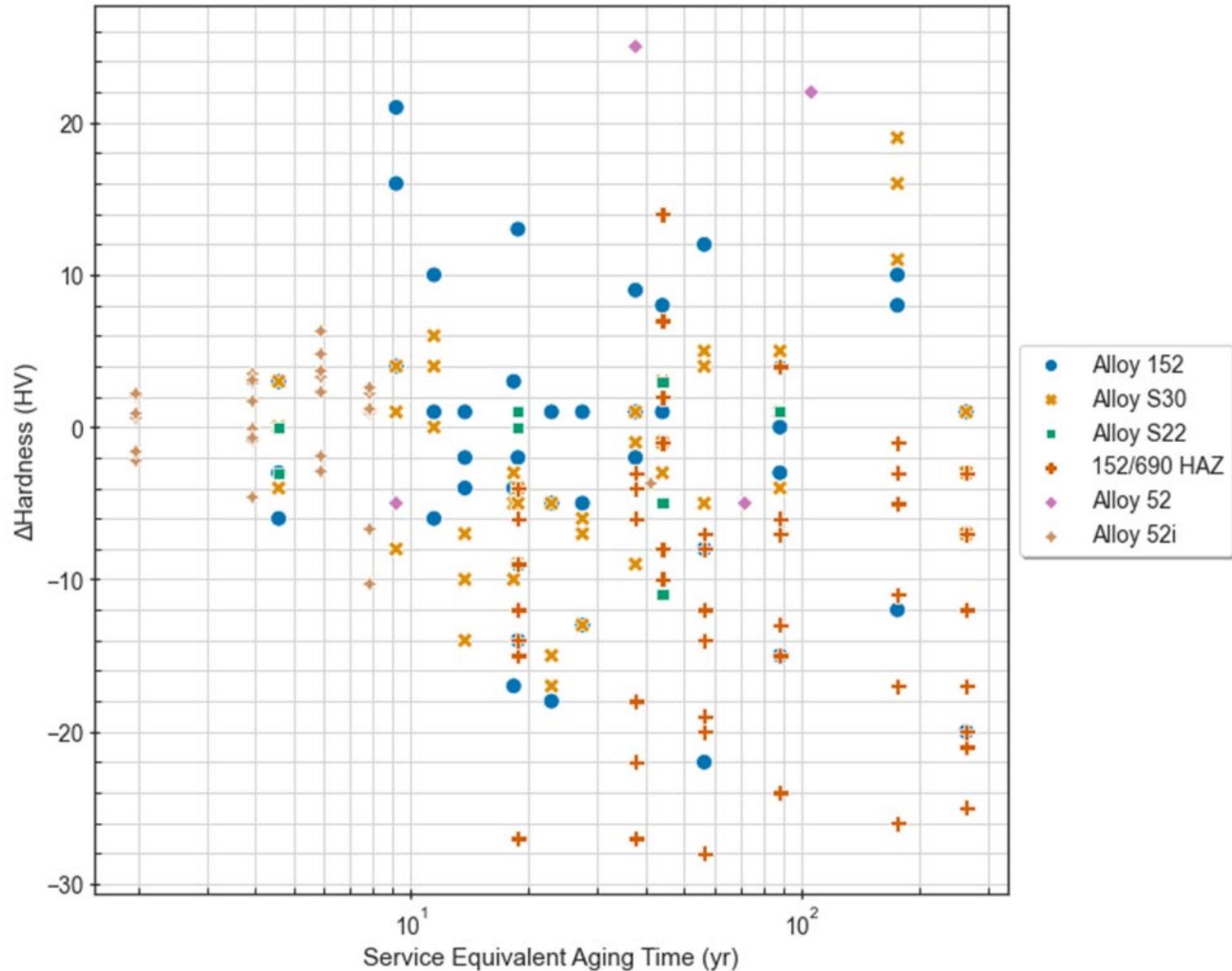
	Alloy 152	Alloy 52	Alloy 52i	Alloy S22	Alloy S30	Alloy 690/152 HAZ
Aging Time (hr)	5,000 – 60,000	6,000 – 20,000	2,081 – 8,264	5,000 – 10,000	5,000 – 60,000	5,000 – 30,000
Service Equivalent Aging Time (yr)	4.58 – 264.42	9.17 – 105.36	1.97 – 7.84	4.58 – 88.14	4.58 – 264.42	18.80 – 264.42
Aging Temperature (°C)	360 – 450	360 – 475	380	360 – 450	360 – 450	400 – 450
Hardness (HV)	204 – 247	236 – 266	NA ^a	195 – 212	198 – 236	189 – 244
Fe wt.% (%)	9.625	9.32	1 – 7.2	4.85	10.375	9.625
Ni wt.% (%)	55	59.59	63.6 – 74.5	66.85	52.95	55
Cr wt.% (%)	28.8	29.43	22.2 – 30.7	21.75	29.8	28.8
Ni:Cr Atomic Ratio	1.69	1.79	1.90 – 2.97	2.72	1.57	1.69
ΔHardness (HV)	-22 – 21	-5 – 25	-10.3 – 6.3	-11 – 4	-17 – 19	-28 – 14

Parameter	Estimated Coefficients	P-Value	Upper Limit	Lower Limit
Service Equivalent Aging Time	-0.0154	0.083	264.42	0
Ni:Cr Atomic Ratio	0.7806	0.873	2.97	1.57
Carbon	2.0090	0.592	0.0445	0
Silicon	14.6539	0.600	0.515	0
Sulfur	-0.0156	0.675	0.0045	0
Phosphorous	0.0169	0.447	0.0045	0
Manganese	-0.5646	0.813	4.305	0
Titanium	0.5572	0.936	0.54	0
Aluminum	5.6379	0.345	0.67	0
Iron	0.2633	0.691	10.375	1
Molybdenum	9.381	0.622	0.2	0
Niobium	0.0569	0.962	4.5	0
Nitrogen	-0.0247	0.036	550 ^a	0
Oxygen	-0.2623	0.609	0.081	0

^aReported in parts per million (ppm).

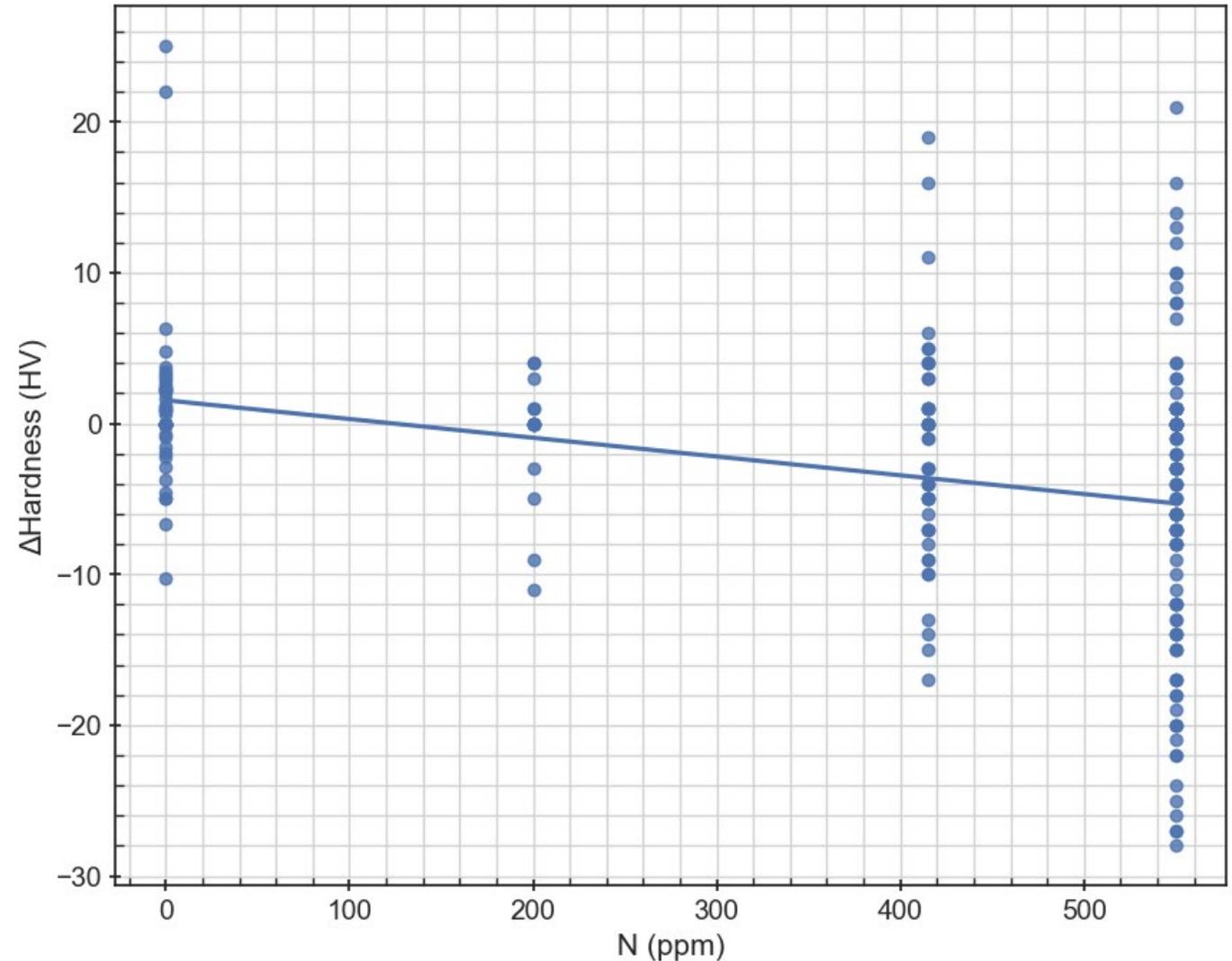
Weld Metal Significant Parameters

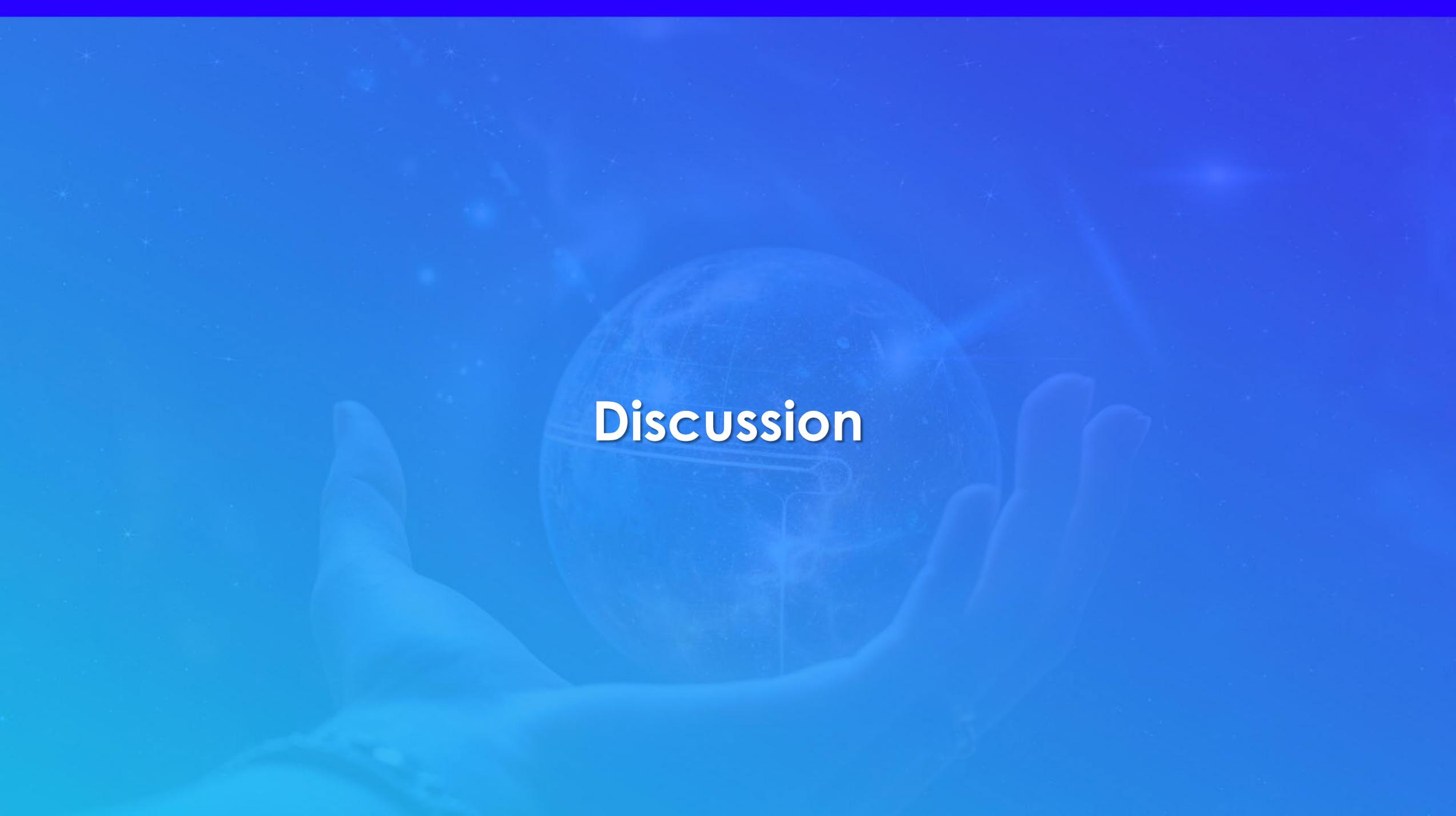
- ANOVA Results
 - Nitrogen
- No outliers identified
- Softening attributable to stress relief in HAZ and as-welded material



Weld Metal Significant Parameters

- No significant difference in the average hardening response of samples with nitrogen contents of 200-550 ppm
- Unlikely that there is a detrimental effect due to nitrogen





Discussion

Alternative Aging Mechanisms

- Other potential culprits
 - Carbide precipitation/coarsening
 - Other secondary phases
 - SRO
 - Shown to impact nanohardness but limited impact on microhardness





Conclusions and Recommendations

Conclusions and Recommendations

- Aging studies of weld metal variants may still be warranted for low-Fe compositions
 - Example: Alloy 52i (2.5 wt.% Fe)
- Determining the hardening mechanisms of observed outliers
 - May involve assessing the likelihood of other hardening mechanisms
 - Findings could help inform preventative measures during material sourcing (i.e., compositional and thermo-mechanical processing constraints)
- If available, additional CGR testing of aged material with hardness increases should be performed
- Detailed results are documented in EPRI IMR-107

The literature reviewed and the analyses conducted suggest that LRO is **unlikely** to form in Alloy 690 during plant lifetimes



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