Evaluation of Thermally Converted Silicotitanate Waste Forms

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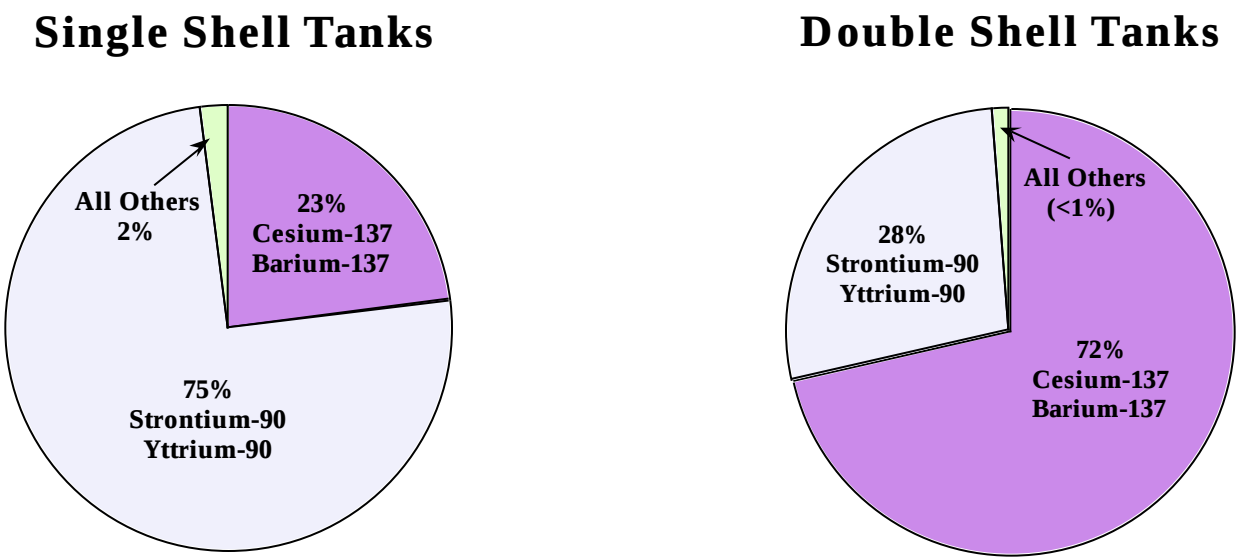
Funded by: Environmental Management Science Program
Office of Energy Management and Office of Environmental Research

Outline

- Background and problem
- Experimental approach
- Durability measurements
- Thermal analysis results
- X-ray diffraction results
- Phase diagram study
- ^{133}Cs NMR results
- Conclusions

Total Radioactive Inventory in Tanks



- 149 SST's → 27 million gallons of waste → 150 million curies
- 28 DST's → 24 million gallons of waste → 92 million curies

Components of Tank Waste Processing

- **The Cs-loaded silicotitanate ion exchanger will be sluiced from the ion exchange column, transferred, mixed with HAW slurry feeds, then dissolved in borosilicate glass.**

Problem

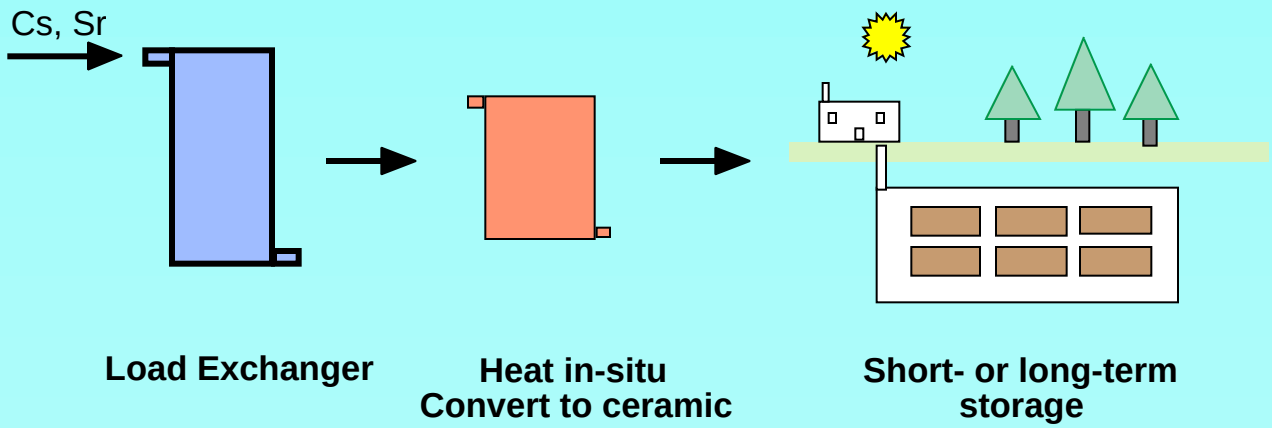
- **Each step in complicated process increases risk of contamination to workers and the environment.**
  - Fines complicate processing and incease risk.
- **Current DWPF borosilicate glass specifications limit TiO_2 content to 1 wt%.**
  - To meet 1 wt% TiO_2, the total Hanford waste volume would increase by 20 %. At ≈ 10,000 total logs, that represents 2,000 glass logs at a cost of 1 million dollars per log!
- **While Cs and Sr have relatively short half lives and short term storage of ion exchangers is likely, no viable process/waste form has been developed.**
  - Short term storage will be necessatated by slow feed into borosilicate glass, limited repository availability, or waste acceptance criteria.
- **Hydrogen generation**

Objectives

- Reduce ion exchanger waste volume by tailoring the waste form composition to the waste feed.
- Reduce cost associated with CST disposal.
- Minimize the risk of contamination during CST processing.
- Provide alternatives for CST disposal.

Approach

- **Determine phase selection, durability, and processability of waste forms that are thermally converted from ion exchange waste.**
- **Predict key waste form properties from an in-depth understanding of waste form structures and thermochemistry.**



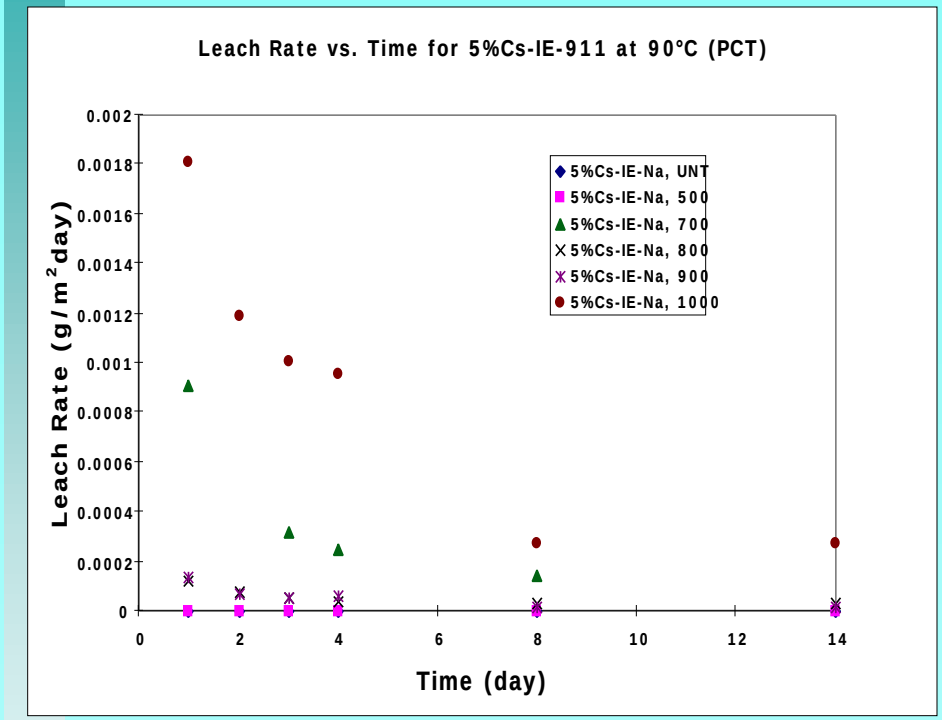
Experimental Procedure

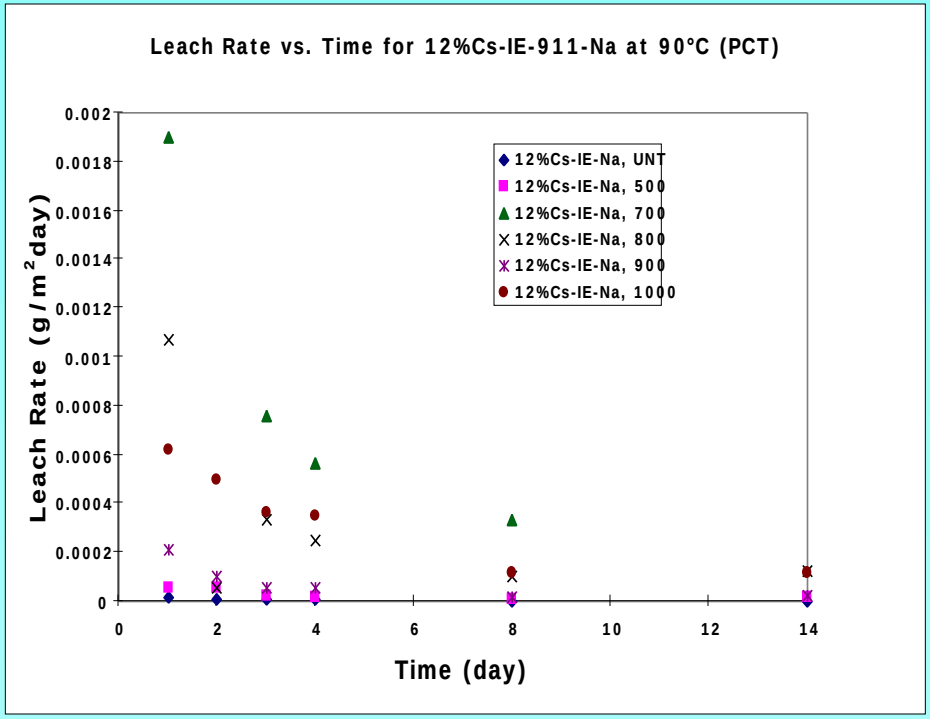
- Load IE-911 with 5 wt% and 12wt% Cs
  - As received
  - UOP specified preparation - Na exchange using NaOH until the pH of the eluting solution is higher than 12.5.
- Heat treat powders from 500-1000°C
- Analyze for durability
  - Aqueous leach rate PCT and MCC-1
- Analyze for phase selection and Cs environment using XRD, TG/DTA, and ^{133}Cs NMR

Leach Test Results

- MCC-1: Pellet suspended in solution. Yields conservative durabilities because solution concentrations of elements are comparatively low and leaching continues during the entire leach period.
  - geometric vs. total surface area
- PCT: Powder in solution. Higher solution concentrations of leached elements can act to reduce dissolution rates and yield higher durabilities.

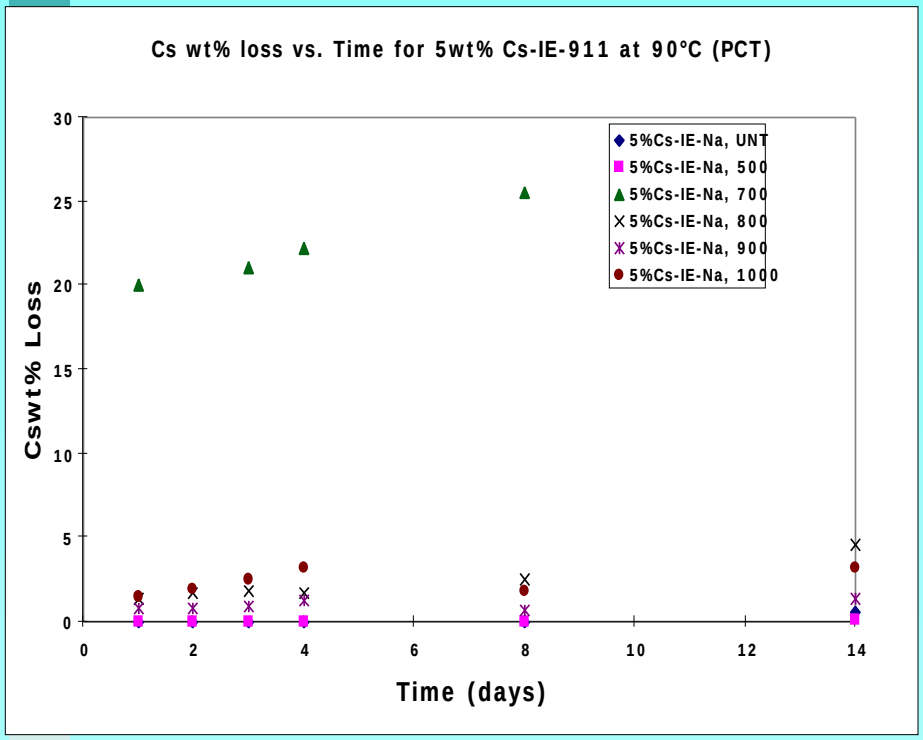
Leach Rate for Na-exchanged IE-911 with 5% and 12% Cs (PCT)

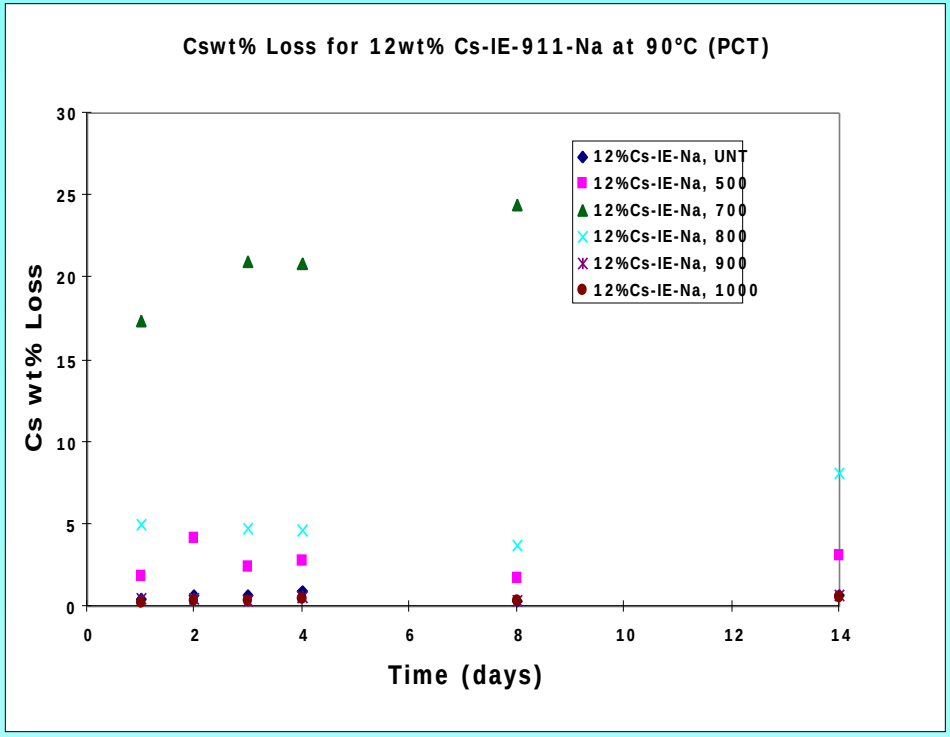




- All leach rates are very low (10^{-8} - 0.002 g/m^2•day)
- Leach rates are lowest for untreated, 500°C, and 900°C samples.

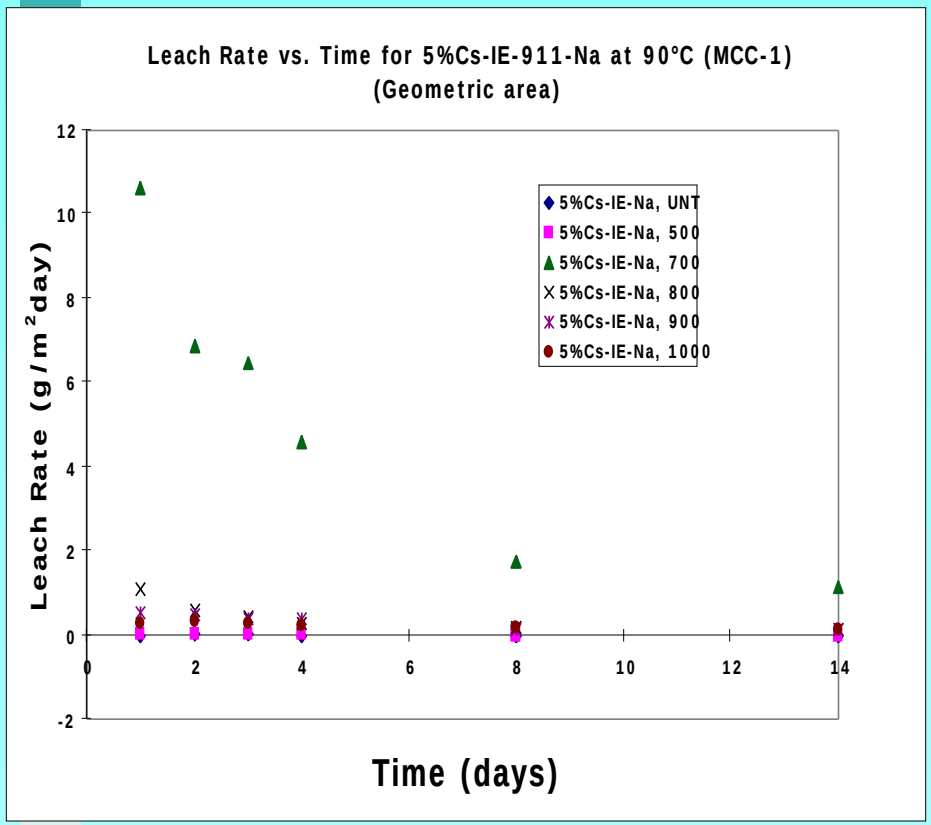
Fractional Cs Release (PCT)

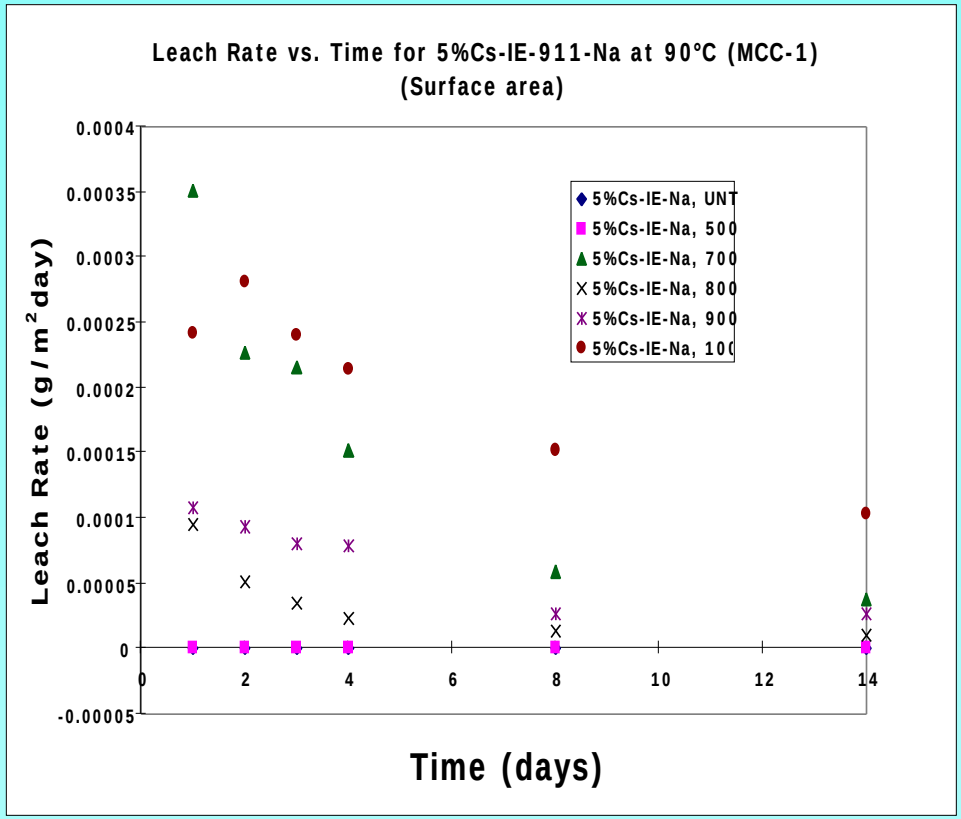




- Less than 1% of total Cs was lost for untreated and 900°C samples.
- Fraction of Cs lost increased with increasing Cs content for untreated, 500°C, 700°C, and 800°C samples.
- Percent total Cs lost decreased for 900°C and 1000°C heat treatments.

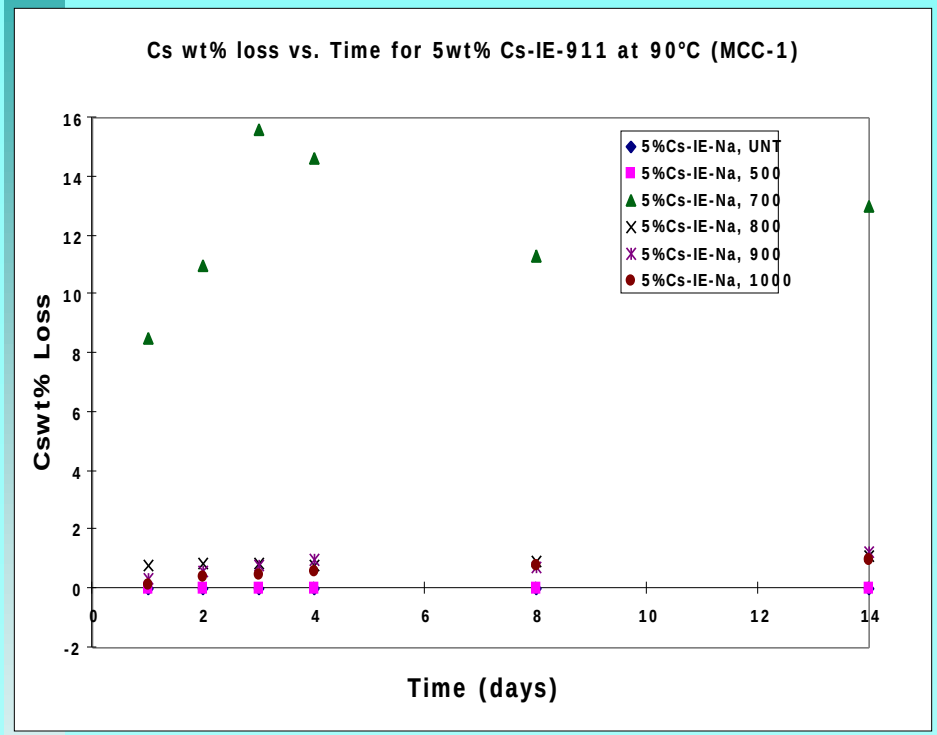
MCC-1 Leach Rate - Geometric and Actual Surface Area

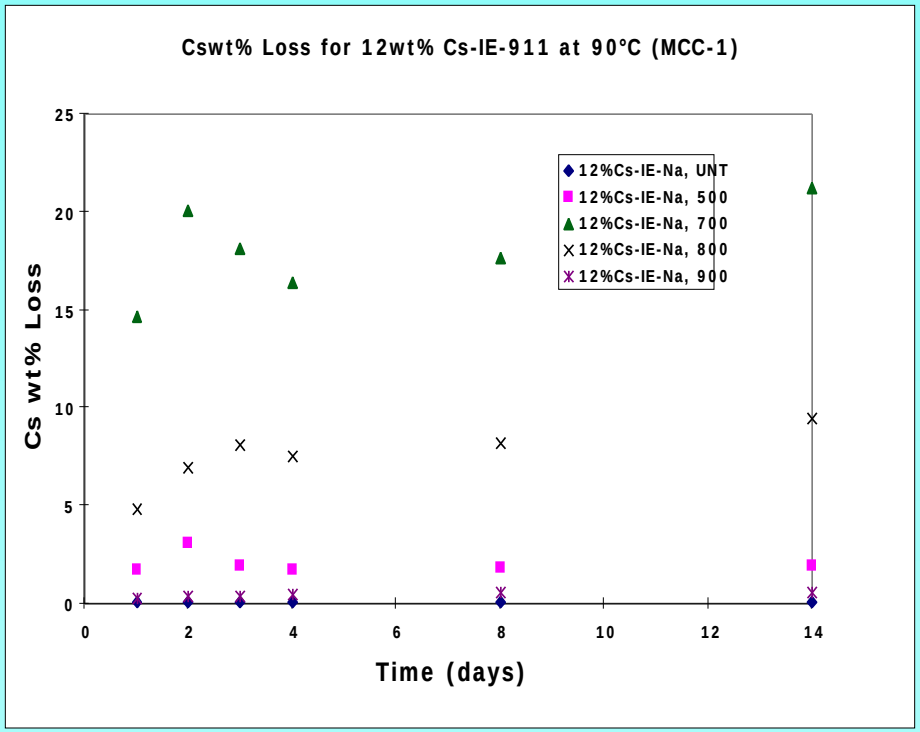




- Samples do not significantly densify at heat treatment temperatures less than 900°C.
- 700°C and 1000°C heat treated samples have the highest Cs leach rates.

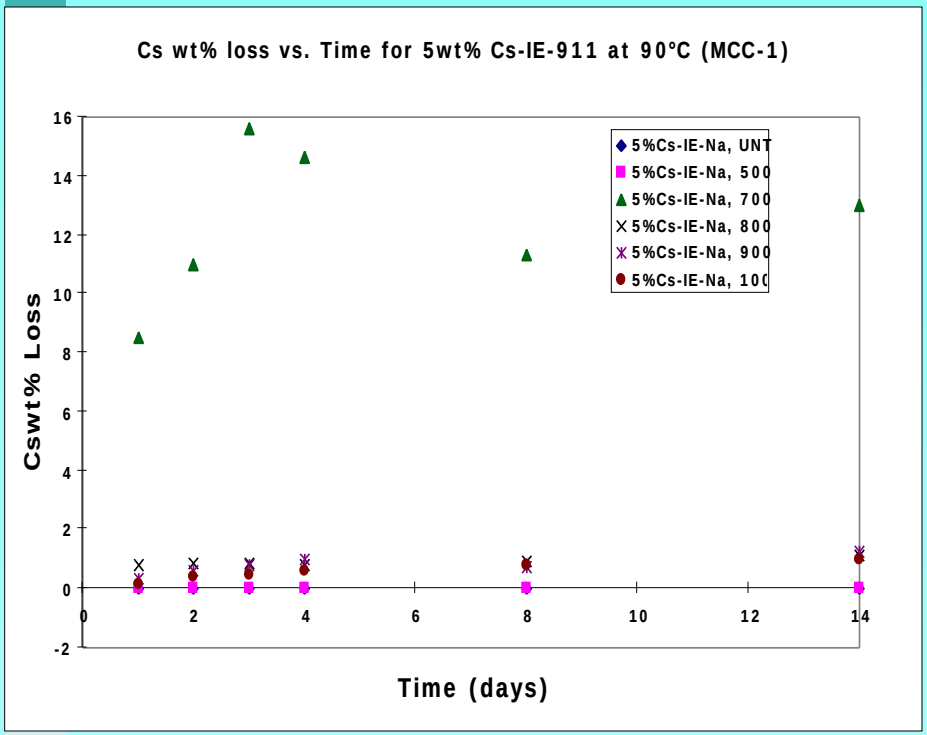
Fractional Cs Release (MCC-1)

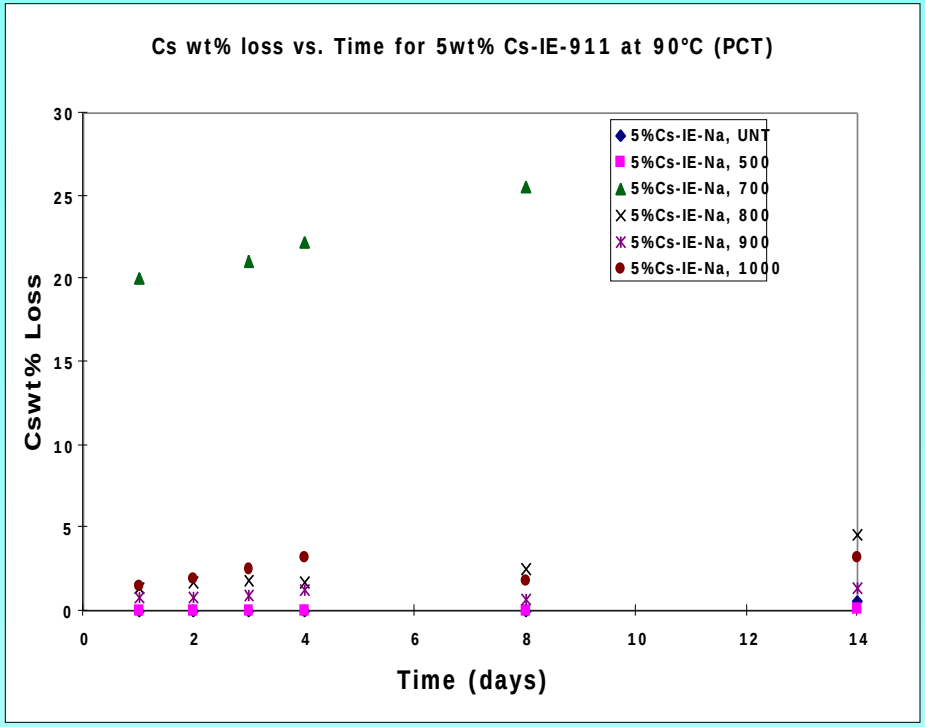




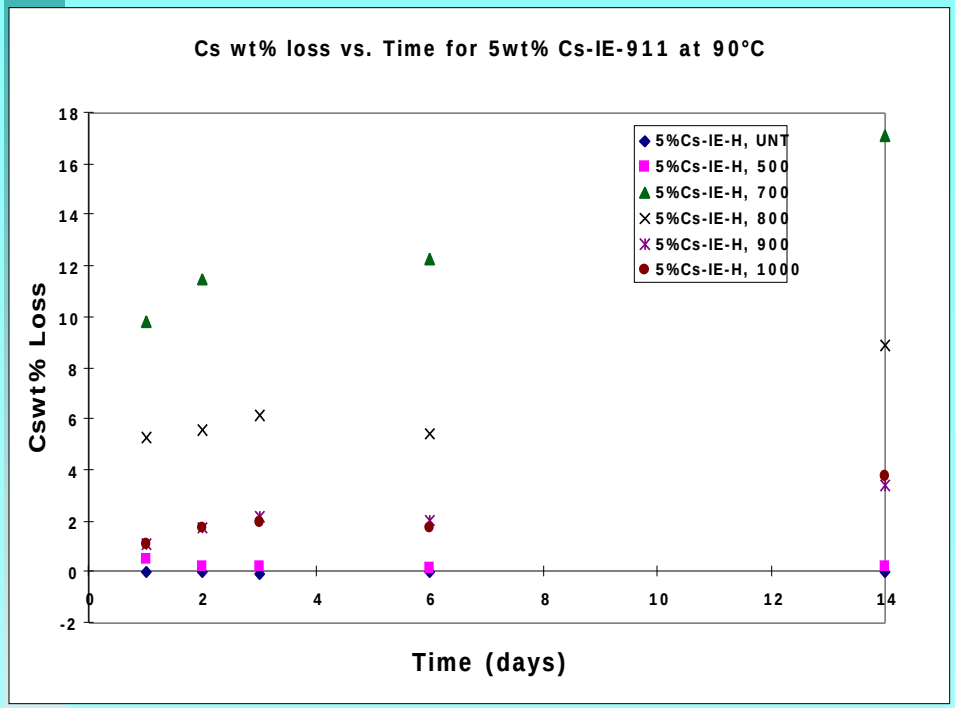
- Fraction of Cs lost increased with increasing Cs loading for all samples except those heated to 900°

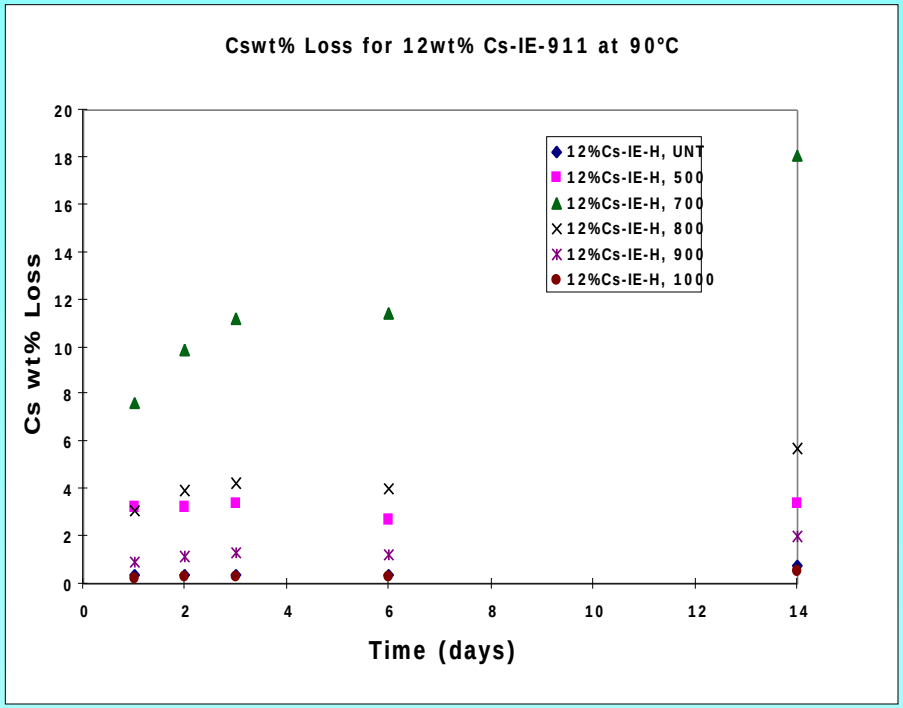
Comparison of MCC-1 and PCT test Results





As Received (no Na Exchange) Fractional Cs Release



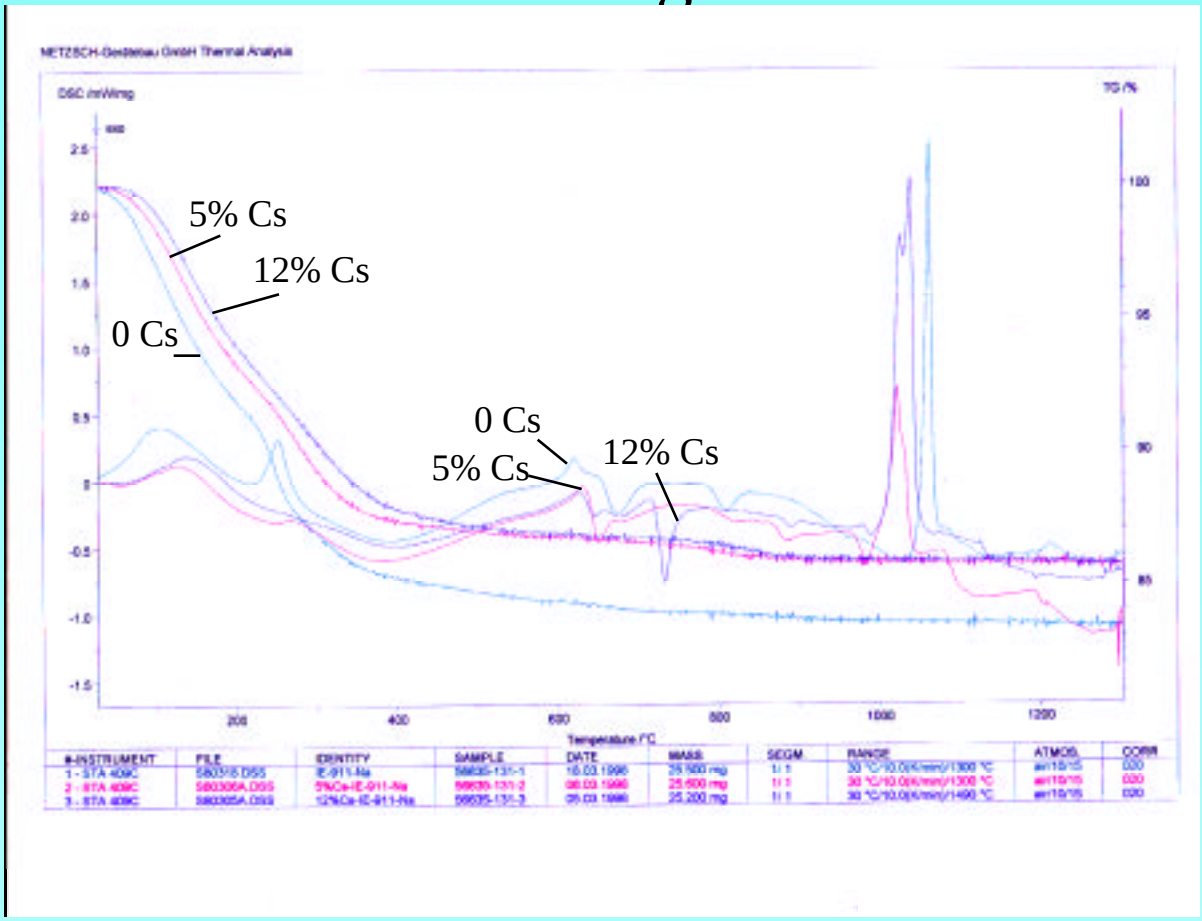


- Similar to Na-exchanged form.
- Leach rates low for all samples (10^{-9} - 0.0002 g/m^2•day).
- Leached fraction increases with increasing Cs content up to 700°C, decreases for 800-1000°C heat treatments.

Comparison to Borosilicate Glass

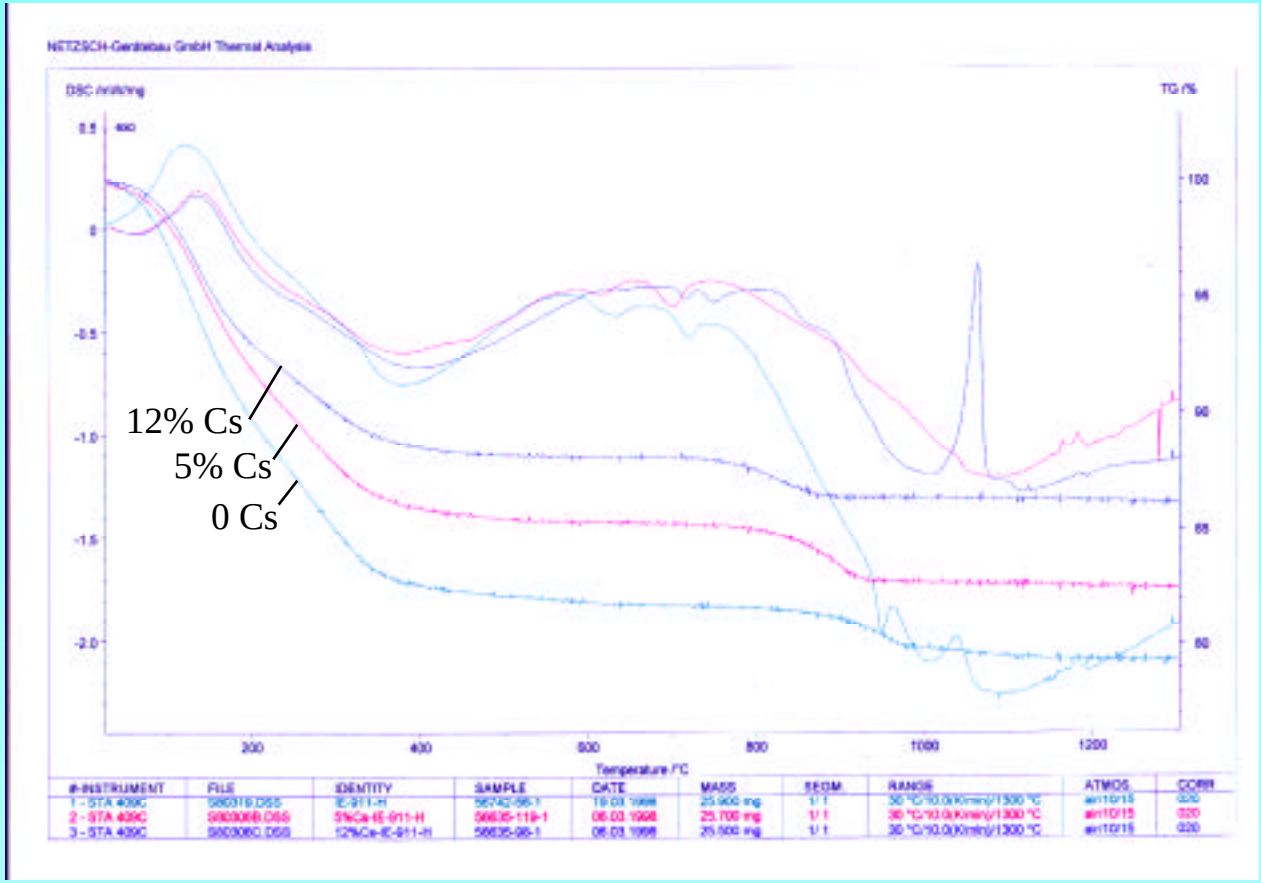
- R7T7 glass with 1.42 wt% Cs and total alkali content of 13.26 wt% has a leach rate of 0.16 $g/m^2 \cdot day$.
- Engineering assessment (EA) glass shows 7 day leached concentration of 13.3 g/L Na. *(WSRC-TR-97-00320 Ferrara, Andrews et al.)*
- IE-911 heat treated to 900°C shows a leached concentration after 7 days of 0.008 g/L Cs (0.175 g/L worst case 700°C heat treatment).

TGA/DTA of Na-Exchanged Cs-Loaded IE-911



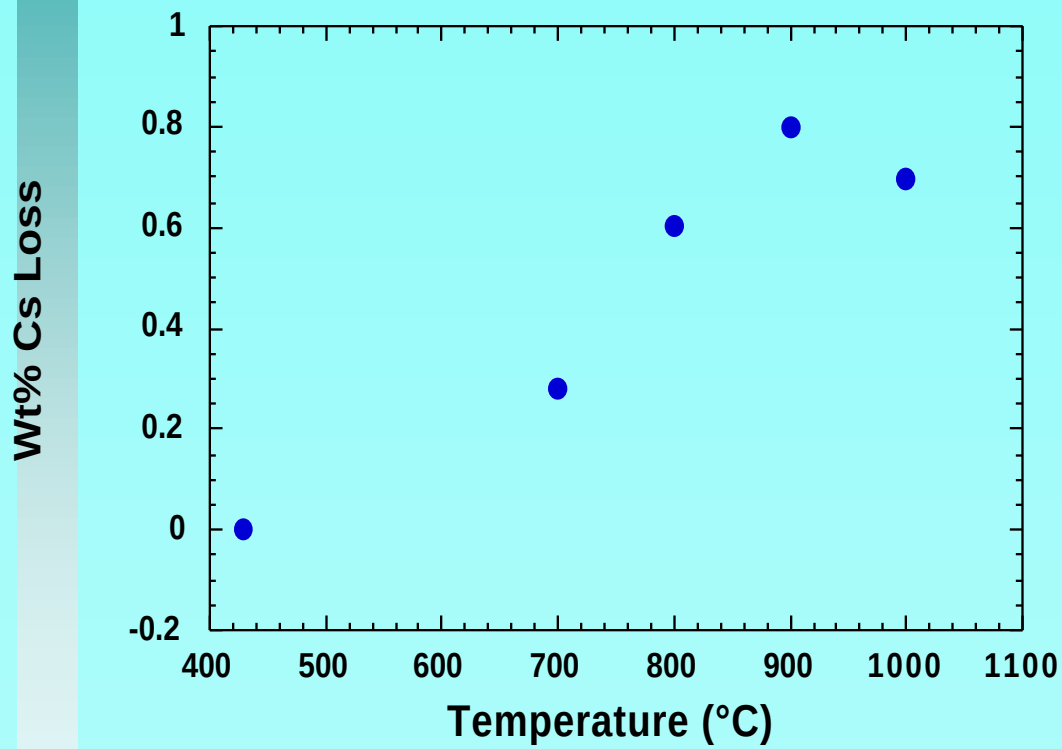
- Majority weight loss < 400°C : Total weight loss is 14-16.5 wt%.
- Crystallization events similar for 0, 5, and 12 wt% Cs loadings.
- Melting temperature decreases with Cs addition.

TGA/DTA of Cs-Loaded IE-911 (no Na exchange)



- Majority weight loss < 400°C : Total weight loss 14-21 wt%.
- Weight loss at 900°C likely due to dehydroxylation.
- Crystallization events similar to Na exchanged form.

Cs Volatility

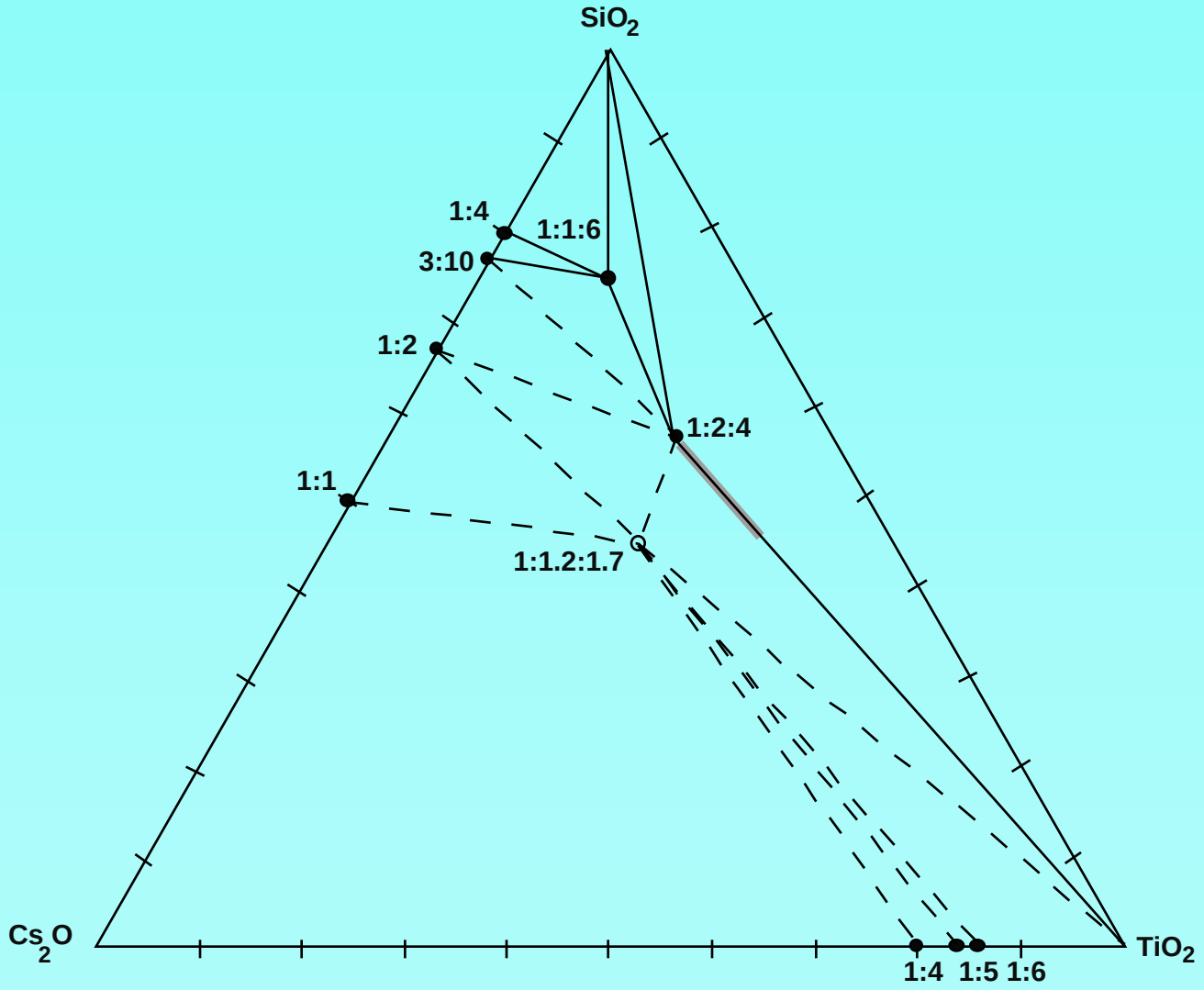


- Cs-loaded powder heat treated in a Pt container with a cold finger.
- Pt container acid washed and solution analyzed for Cs.

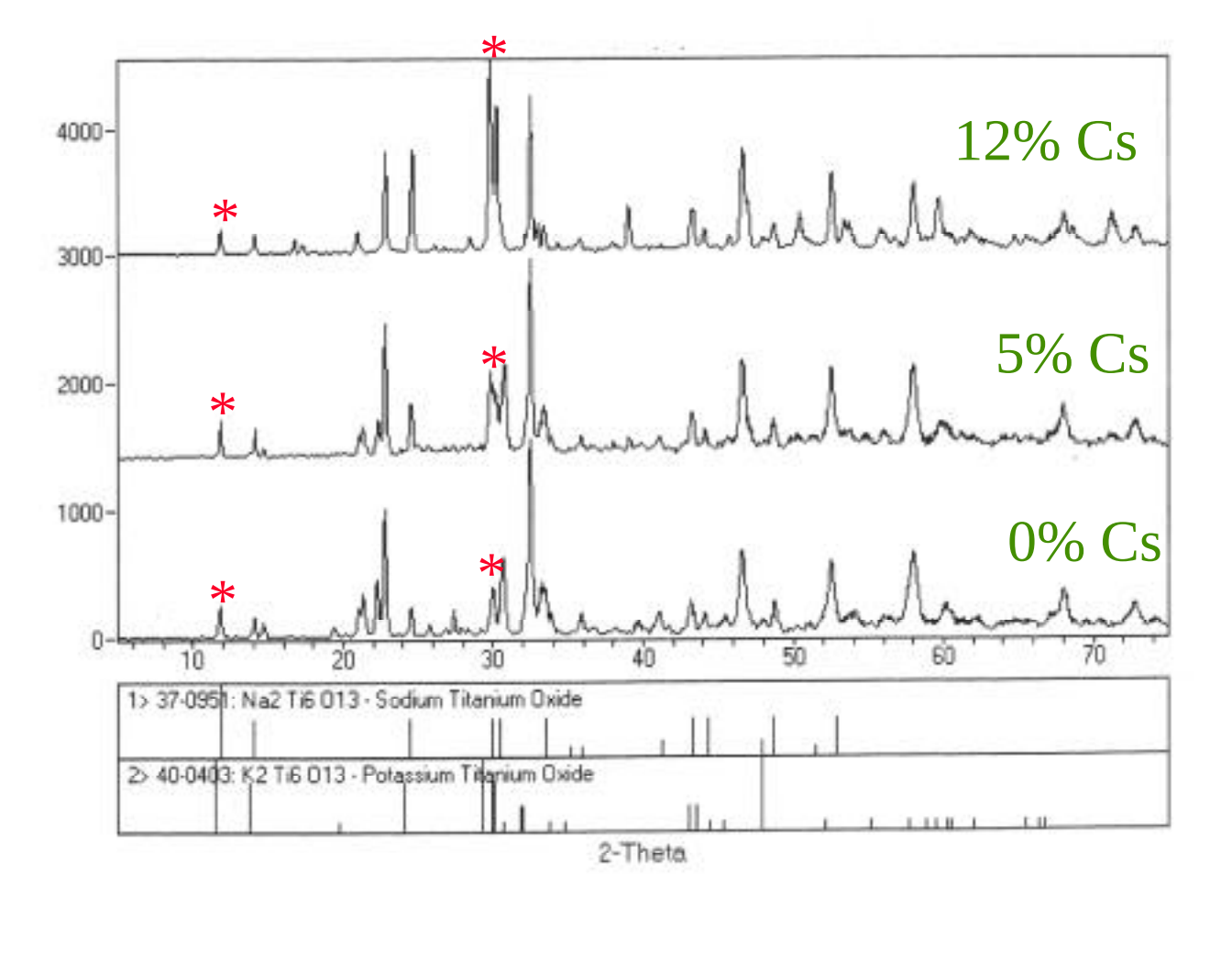
X-ray Diffraction Analysis

- XRD does not reveal any obvious Cs-containing phases.
  - Cs in solid solution in a crystalline phase
  - Cs in an amorphous phase
- Unidentified, potentially new phases exist.

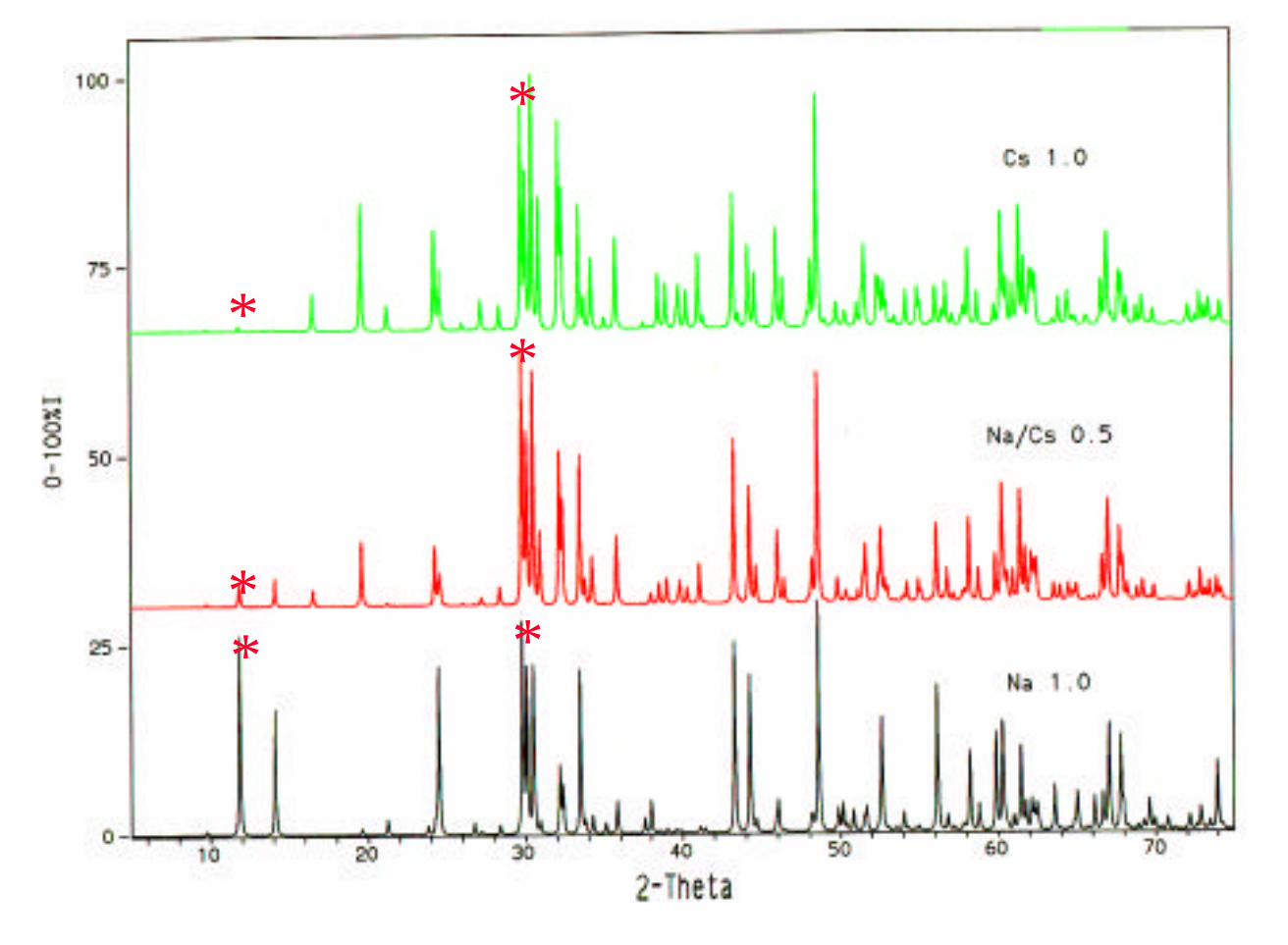
Ternary Cs_2O-TiO_2-SiO_2 Phase Diagram



Na-exchanged Cs-loaded 1000°C Heat Treatment

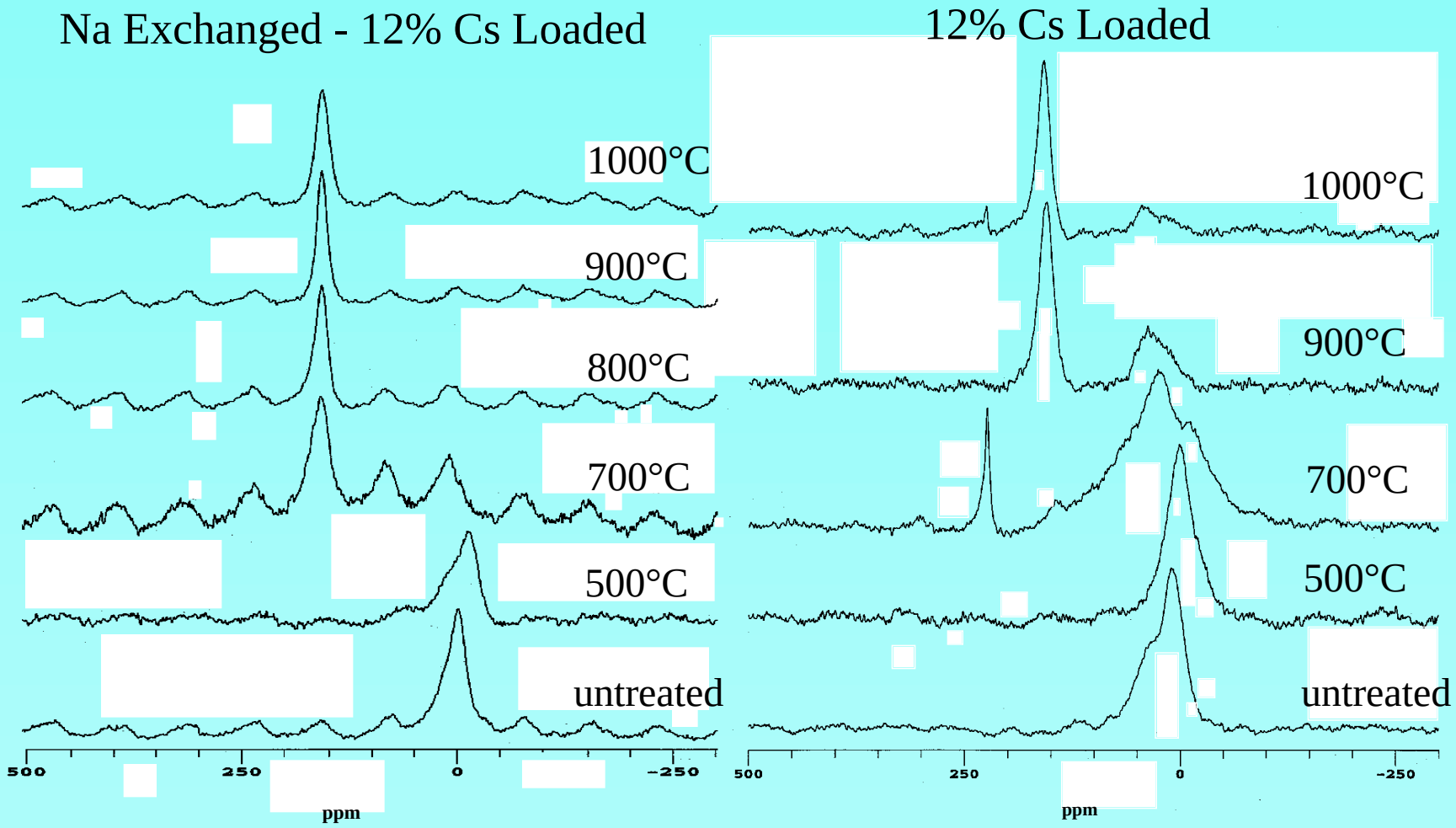


Simulated $Na_2Ti_6O_{13}$ with Cs Substitution



S. Andersson and A.D. Wadsley, Acta. Cryst., 15, 194, 1962

^{133}Cs NMR for Na-exchanged and As Received Heat Treated IE-911



Conclusions

- Heat treated IE-911 **with no additives** is a viable waste form and is more Cs leach resistant than baseline borosilicate glass formulations.
- Water of hydration and hydoxyls are removed during heat treatment eliminating the possibility of hydrogen generation during short term storage.
- Coarsening during heat treatment eliminates fines.
- Heat treated IE-911 is multi-phase. Cs appears to reside either in an amorphous silicate or in solid solution with sodium titanate.