Development of a Cast Stone Formulation for Hanford Tank Wastes

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The Goal

- Waste Form Validation
- Process and Facility Design
- Environmental Permitting
- Establishment of the Safety Basis

Procedures Employed in CCS Experimental Work

Requirements For Testing (Analytes or Material Parameters)	Testing/ Engineering Analysis Method	Acceptance Criteria	Test Procedures	Used in Activiy Part #
Quick leach	Abbreviated TCLP	None	Informal laboratory procedure developed by J. R. Conner of Conner Technologies used for scoping leachability tests.	1, 6
Compression strength	Compression strength	> 500 psi, 28-day	ASTM C 39/C 39M. Sampling 3 cyl AB	2
Length measurement	Volume reduction	< 5%	ASTM C 174/C 174M. Sampling 3 cyl AB	2
Bleed water after 1 day curing	"Bleed water test"	< 5%	Modified ASTM C 940.	2, 3
Free liquids after 28 days curing	Free liquids test	< 0.5%, pH > 9	ANSI/ANS 55.1, same samples used for bleed water, but at end of 28 day cure period	2, 3
(Tc, U, I, Cs - Rad) NO_3^-, NO_2^-, Cr	ANSI/ANS 16.1	None	ANSI/ANS 16.1, measurement of the leachability of stabilized waste	2, 3
Sb, As, Ba, Be, Cr, Cd, Pb, Hg, Ni, Se, Ag, V, Zn, organics	EPA SW-846, Method 1311 (TCLP)	WAC 173-303 40 CFR 368	EPA SW-846, test methods for evaluating solid waste, physical/chemical methods, Method 1311	2, 3, 6
Peak temperature causing deleterious alterations to microstructure	Maximum curing temperature	Maximum Temperature	Curing at 5 temperatures followed by ANSI/ANS 16.1 immersion and subsequent modified ASTM C 39/C 39M	4
Heat output during cure (1-gal cast stone pour)	Near-adiabatic curing heat evolution	None	CLS-specific procedure to study adiabatic curing heat evolution on a larger cast stone sample. Sampling 1 ea. AB	4
Thermal transmission	Thermal conductivity	None	ASTM C 177. Sampling two 6″ x 6″ x 0.5″ thick plates AB	4
Hardened cast stone permeability	Hydraulic conductivity	None	ASTM D 6527-00. Sampling 3 Cyl AB	4
Heat output during cure (5-gal cast stone pour)	Near-adiabatic curing heat evolution	None	Informal CLS procedure to study adiabatic curing heat evolution on a larger cast stone sample.	4
NH_3, H_2, NO_3^-/NO_2^- ratio, organic load, water	Explosive or toxic gases test (1)	N/A	N/A	5
H_2 rate	Hydrogen gas generation rate test (1)	N/A	N/A	5

Selection of Dry Reagent Formulation

- Chromium leaching can be reduced by adding ferrous sulfate to the formulation.
- Bleed water formation can be avoided by using a formulation that involves adding no more than about 30 to 40 mL of liquid waste, after evaporation or dilution, to 90 g of DRF.

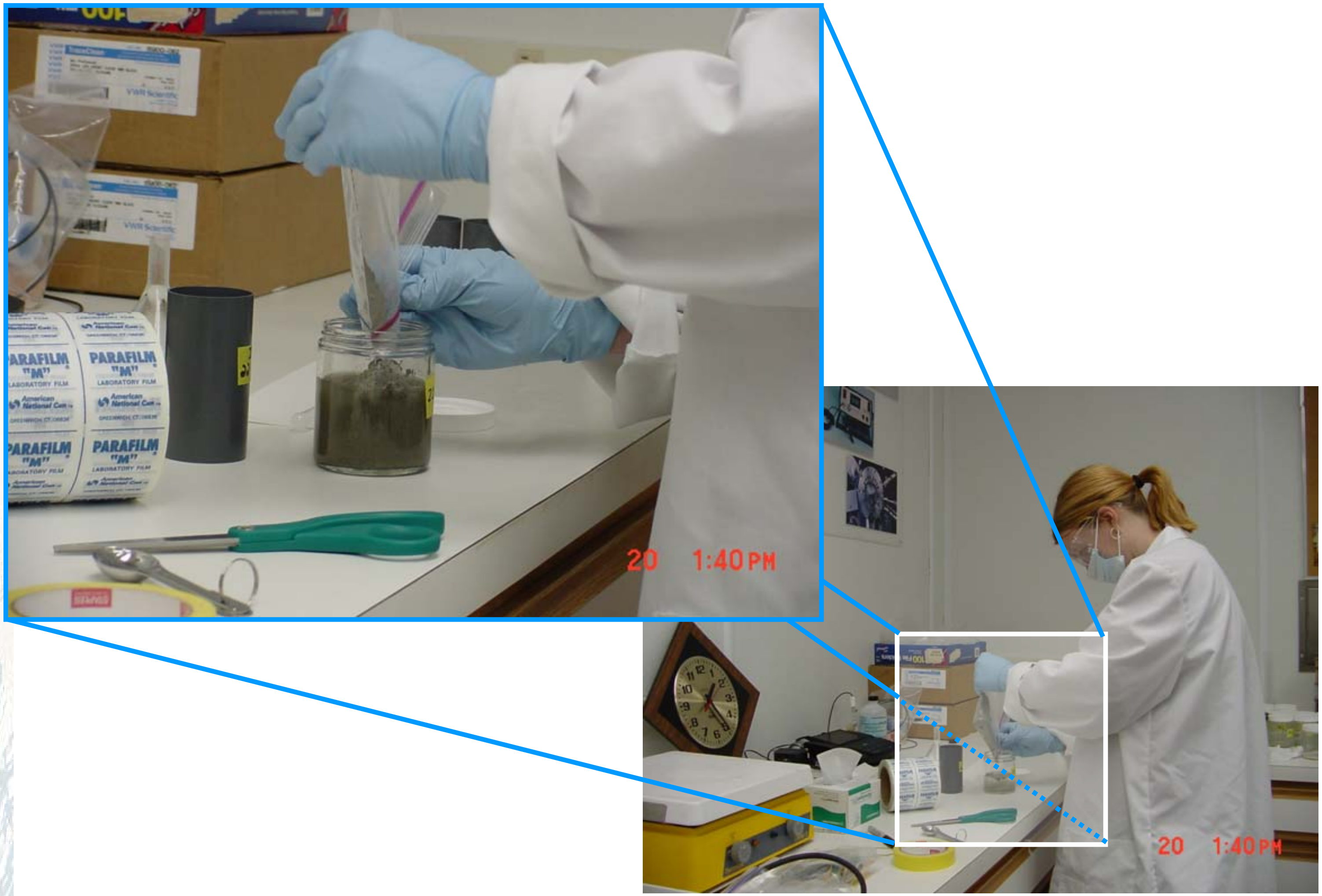
Dry Reagent Tests Performed

- Bleed Water
- Quick Leach

Compositions of Dry Reagent Formulations

Components	DRF1 (wt%)	DRF2 (wt%)	DRF3 (wt%)	DRF4 (wt%)
Portland Cement, Type I,II	44.90	8.16	41.84	20
Fly Ash, Class F	42.86	44.90	39.78	66
Blast Furnace Slag, Grade 120	0	46.94	0	0
Attapulgite Clay	5.10	0	11.22	14
Indian Red Pottery Clay	7.14.	0	7.14	0

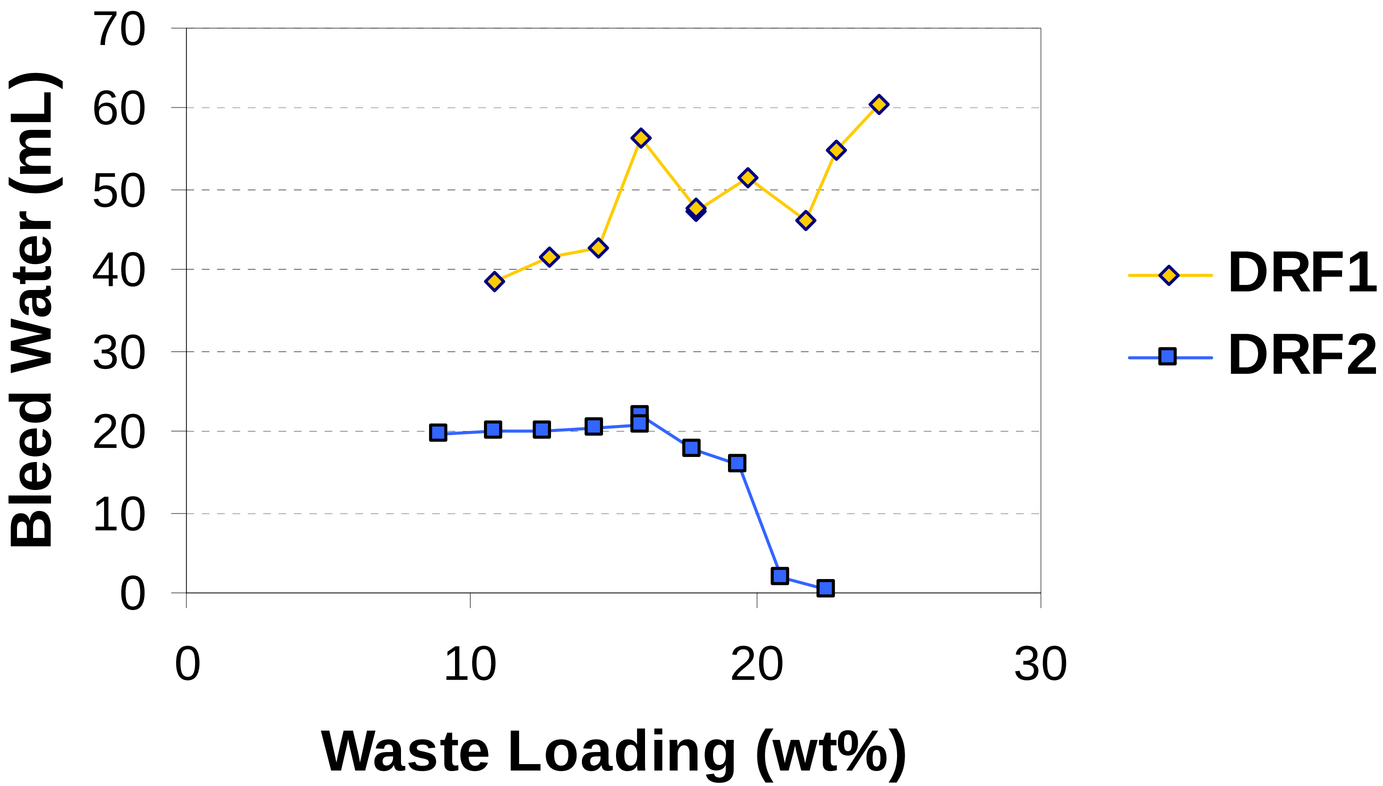
Mixing DRFs



Mixing DRFs


actually become stronger and more insoluble over time.
Unlike other techniques such as vitrification and encapsulation, S/S does not rely on the physical structure alone. Even when the structure is deliberately destroyed, as in the EPA Toxicity Characteristic Leaching Procedure (TCLP) test, the chemical form of heavy metals in the S/S treated waste minimizes leaching to better than the most stringent regulatory levels.
Part 1 Testing
Formulation Development
DELL

Initial (24 Hr) Bleed Water Measurements



Sample Prep for Quick Leach

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Simulant Tests Performed

- Density
- Bleed Water
- Compressive Strength
- Volume Change
- Toxicity Characteristic Leaching Procedure (TCLP)
- ANSI/ANS 16.1 Leaching

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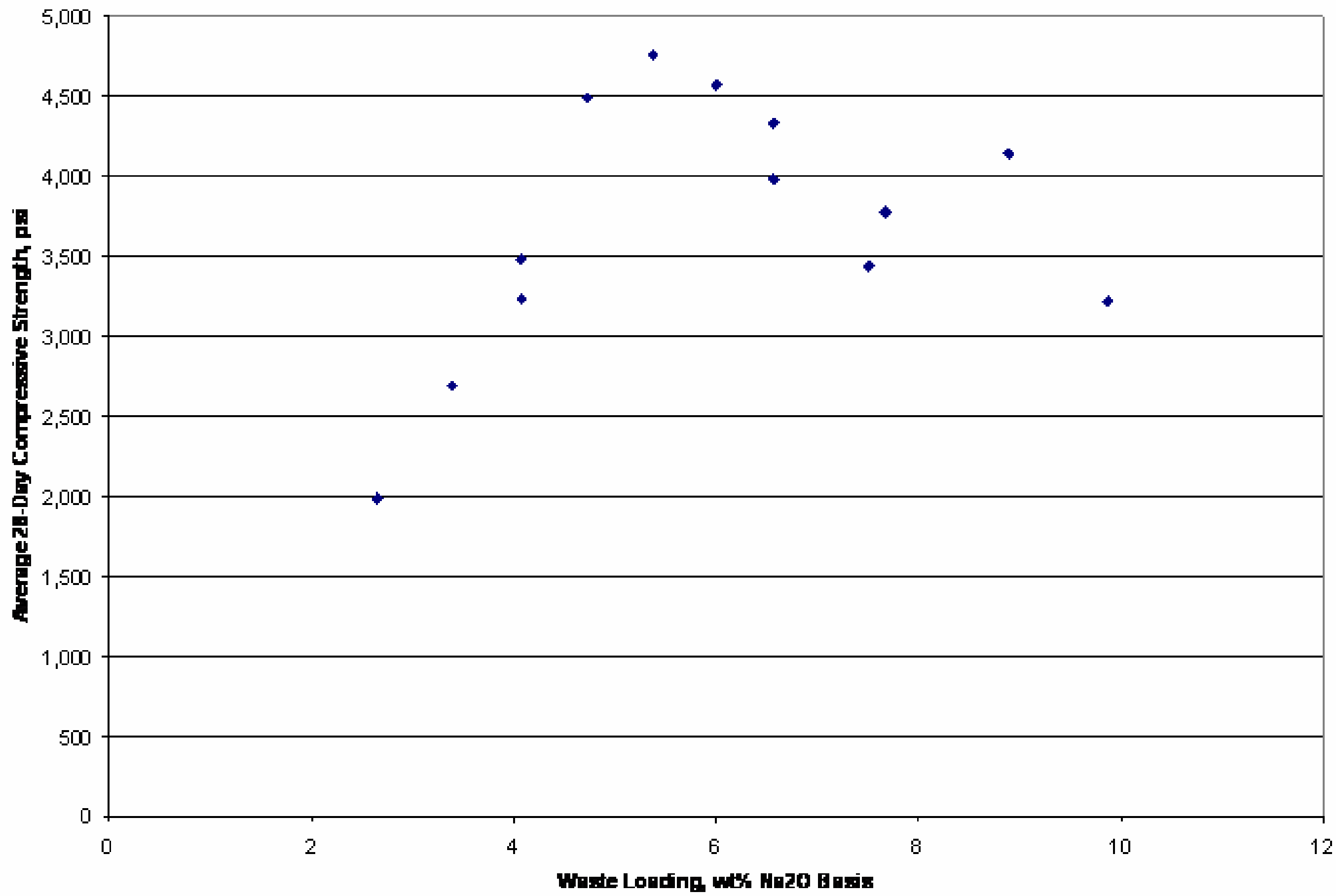
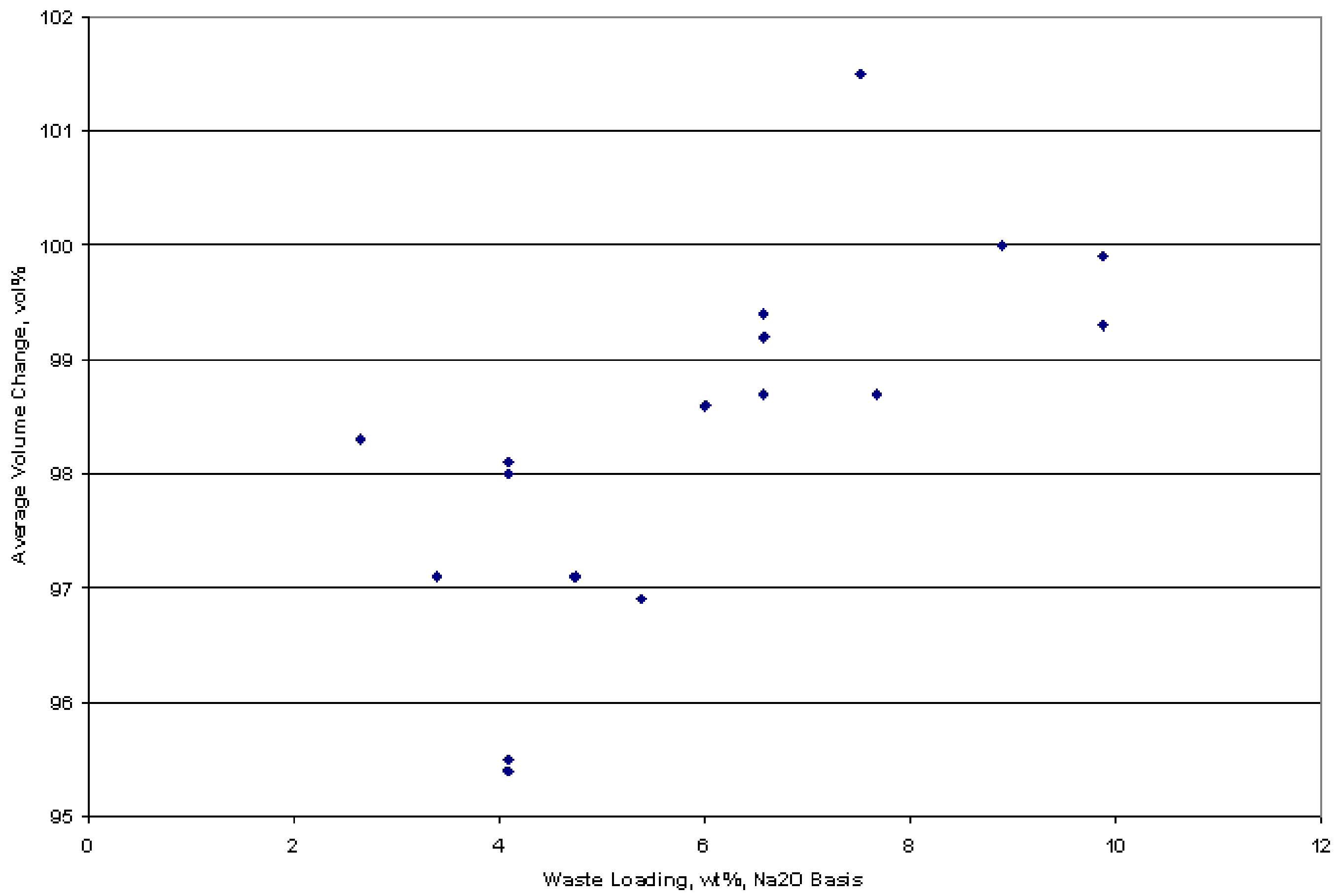
28-Day Compressive Strength vs. Waste Loading

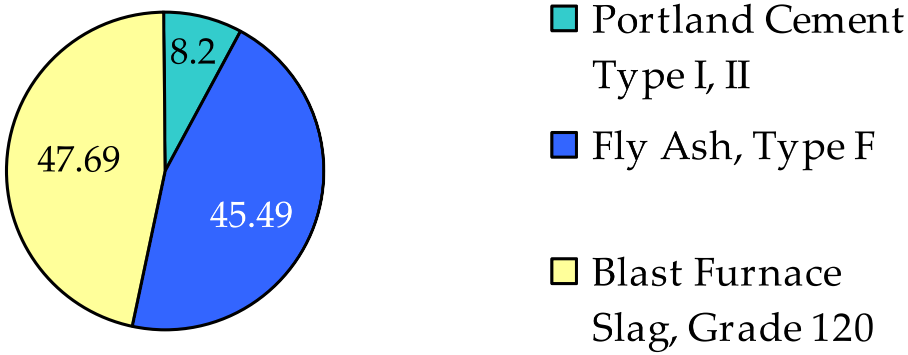


Cured Cast Stone Volume Change vs. Waste Loading

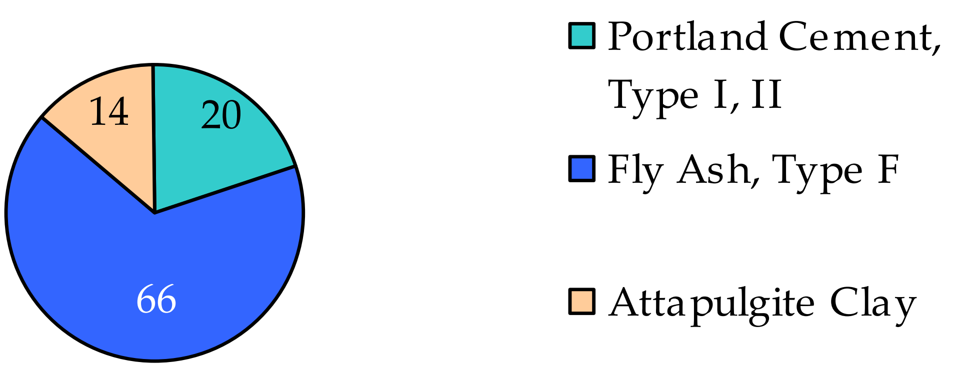


Dry Reagent Formulations Selected for Further Evaluation (wt% basis)

DRF2



DRF4



Waste Form Performance Testing with Simulant

- The use of DRF2 results in cast stone with compressive strengths well above the requirement of 500 psi
- For most conditions studied, a slight reduction in volume can be expected during the curing of the cast stone samples
- A formulation condition with a waste loading of 18.8 wt% (TDS basis), or 7.67 wt% (Na_2O basis), provides satisfactory waste form testing results

Waste Form Performance Testing with Simulant (leaching)

- For samples prepared from DRF2 and simulant ANSI/ANS 16.1 leaching indices are between 7.1 to 8.5 for nitrate, 7.0 to 8.4 for nitrite, and greater than about 10 to 11 for chromium

Radioactive Sample Tests Performed

- ANSI/ANS 16.1
- TCLP
- Bleed Water
- Total Organic Volatiles
- Semivolatile Organic Analysis (SVOA)

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Validation Tests Performed

- Maximum Curing Temperature
- Curing Heat Evolution and Modeling
- Thermal Conductivity
- Hydraulic Conductivity

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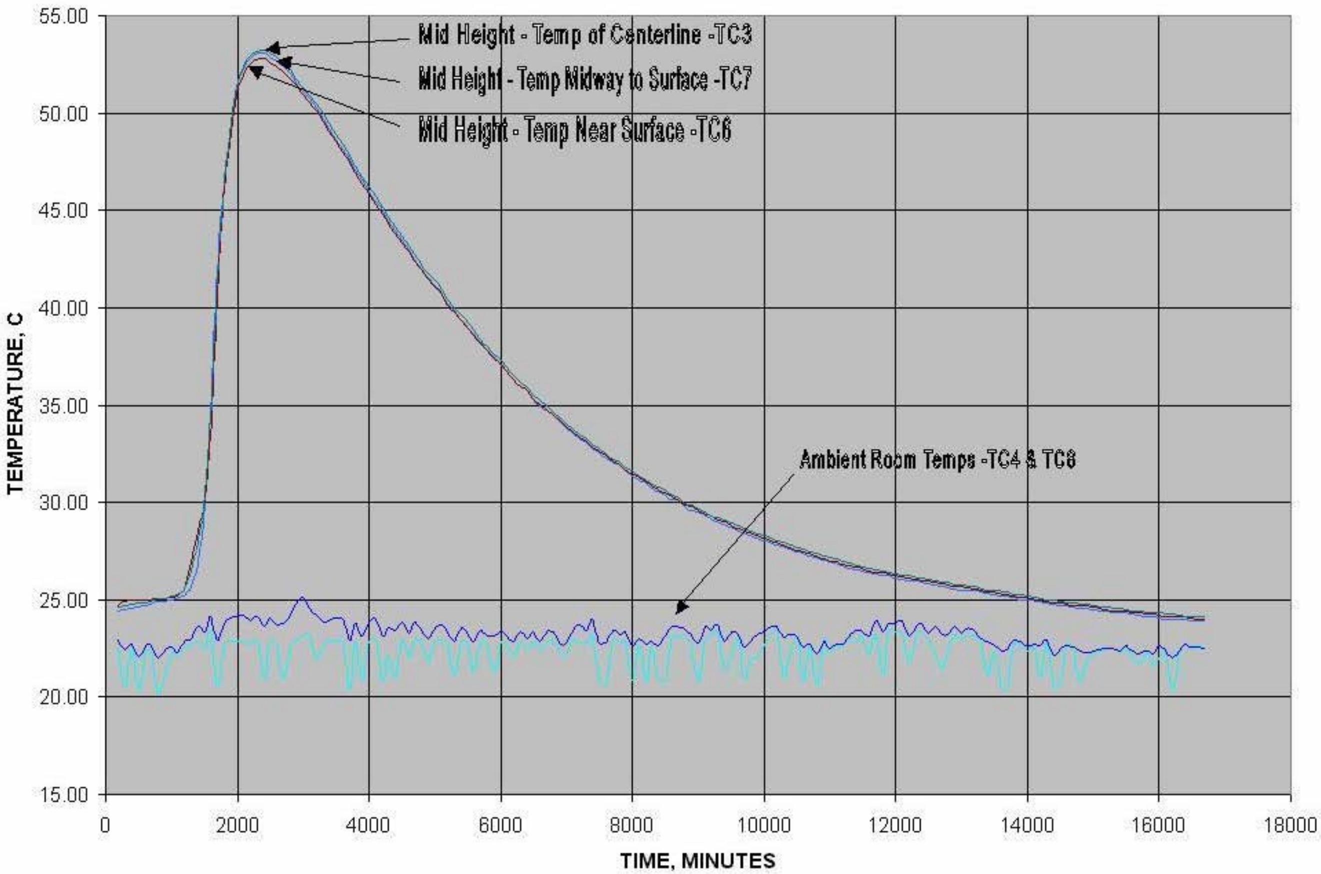
Grout Pour Cool Down (5 gal)



Waste Form Validation Testing with a Selected Nominal Formulation Using Simulant-Based Samples

- Curing at elevated temperatures of 60 to 85 ºC as opposed to room temperature reduces compressive strength. Samples cured at elevated temperatures still have exceptionally high compressive strength, three to four times the required level.

Waste Form Validation Testing with a Selected Nominal Formulation Using Simulant-Based Samples

- It may not be possible to measure the unsaturated hydraulic conductivity of cast stone due to its impermeable nature.

Waste Form Validation Testing with a Selected Nominal Formulation Using Simulant-Based Samples

- The adiabatic temperature rise during curing of cast stone with the nominal formulation and prepared from simulant is approximately 30 °C.

Waste Form Validation Testing with a Selected Nominal Formulation Using Simulant-Based Samples

- Providing the effective average temperature of the low-activity waste (LAW) and DRF being blended to produce cast stone is maintained at or below 40 ºC, the maximum temperature achieved during curing is 70 ºC or less.

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Waste Form Performance Testing with Radioactive (LAW-based) Samples

- For thallium, the method detection limit (MDL) for the analysis was greater than the UTS standard. Volatile organic analyses and SVOA are not present at levels of interest.

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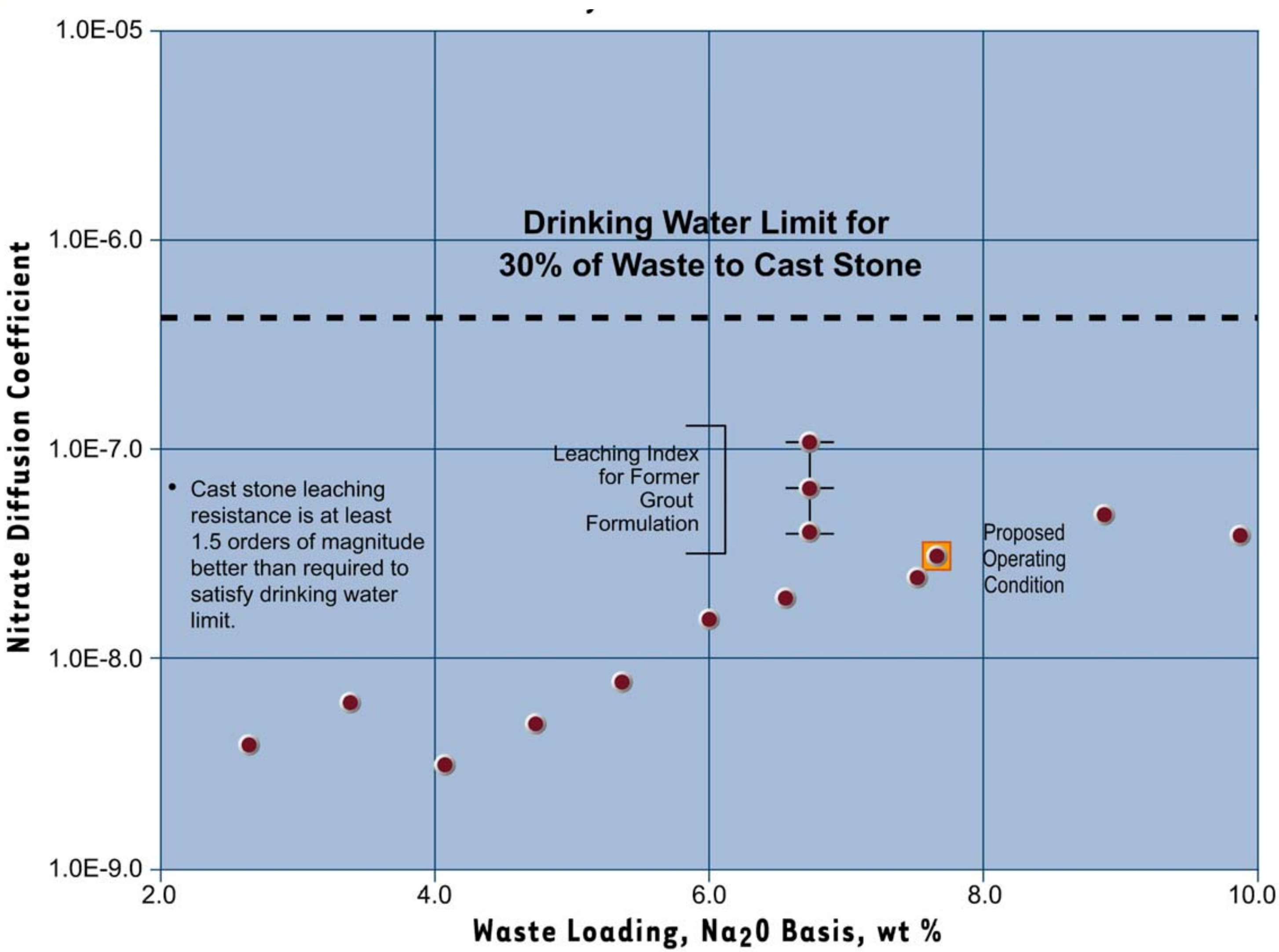
Technetium Getter Testing

- Of the nine candidate technetium getters tested, Cosmic Black[1] bone char produced the best results, with a technetium leachate concentration at 62 % of the technetium leached from a sample with no getter added.

[1]Cosmic Black is a trade name of Ebonex Corporation, Melvindale, Michigan.

Cast Stone Waste Form Performance
Nitrate Diffusion-ANSI/ANS 16.1 Leach Test
Primary Cast Stone Formulation



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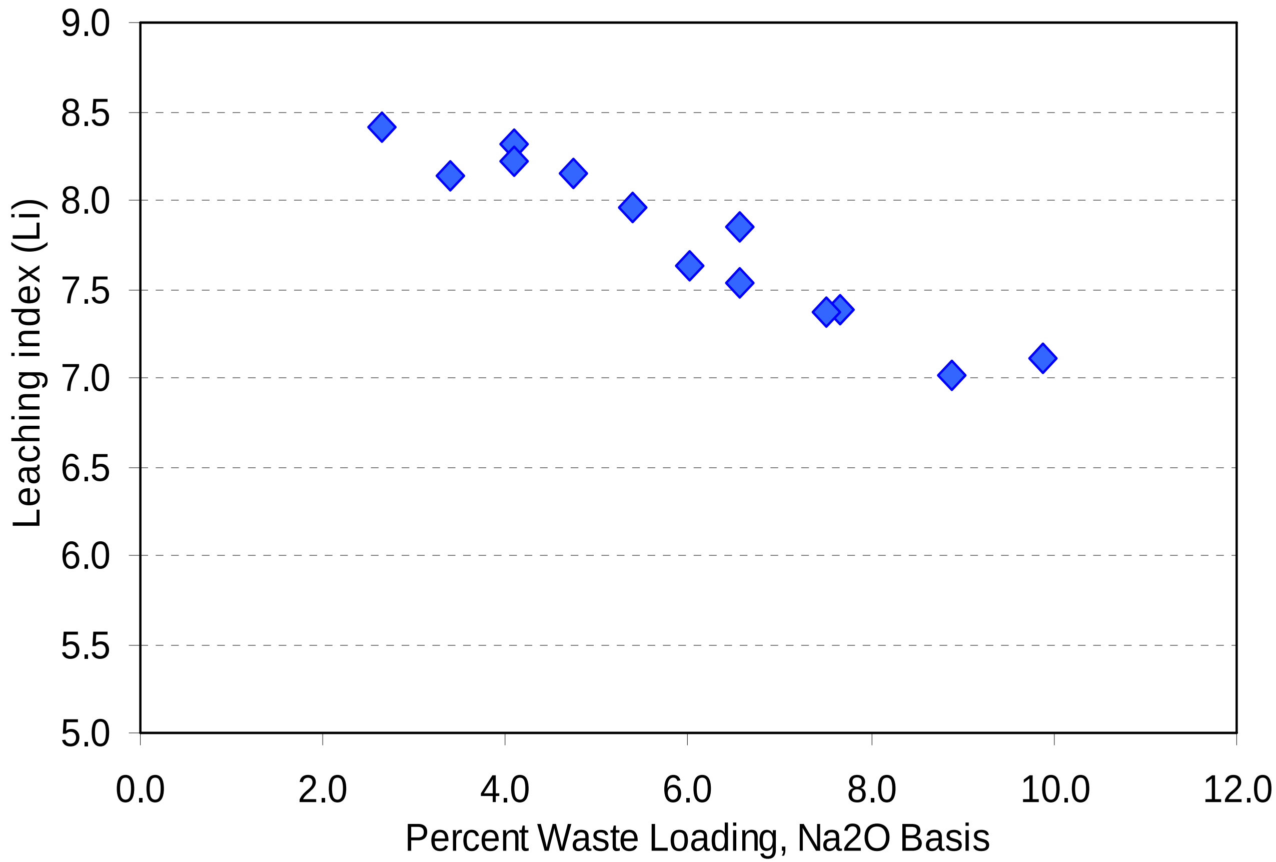
ANSI NO_2 Leaching Index vs. Waste Loading 90-Day Results for DRF2



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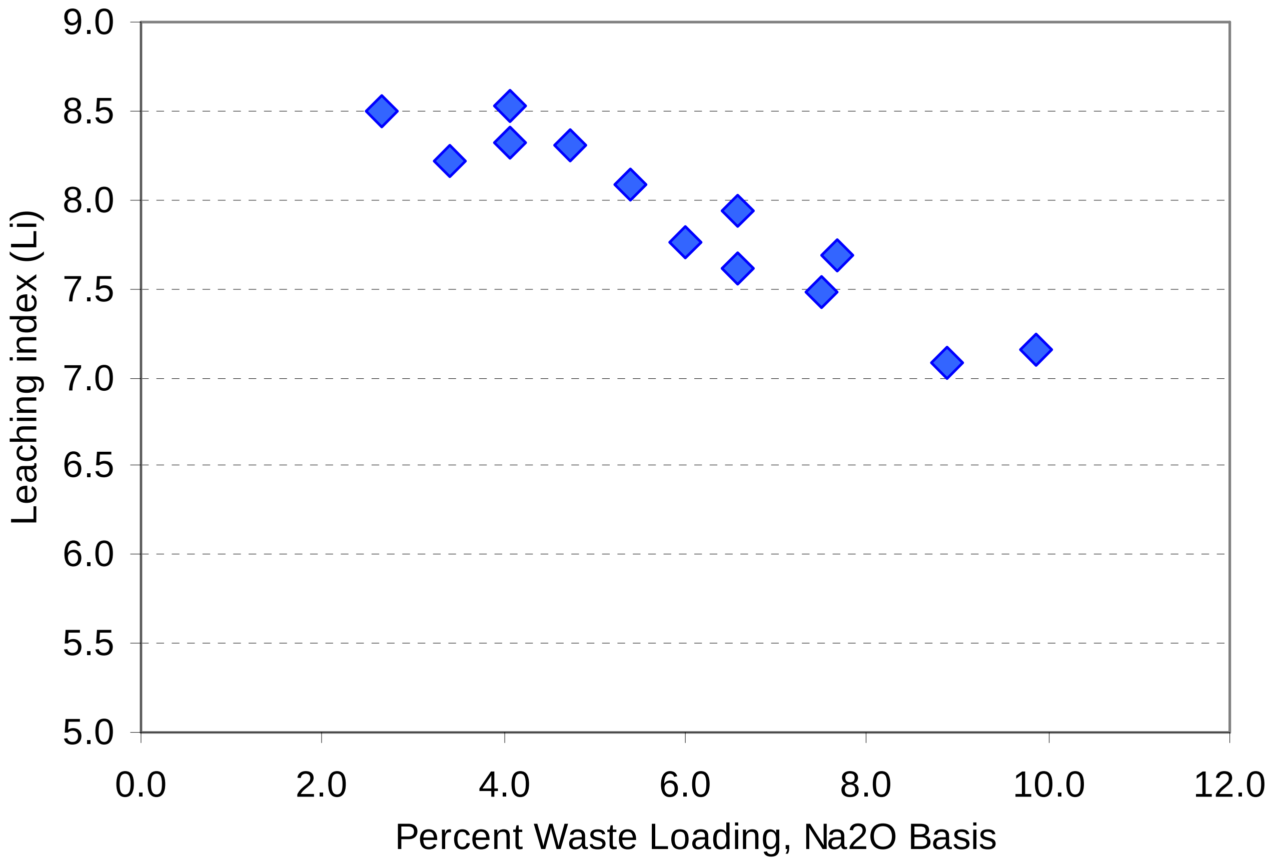
ANSI NO_3 Leaching Index vs. Waste Loading 90-Day Results for DRF2



Cast Stone TCLP Test Results Chromium Leaching vs. Waste Loading Primary Formulation

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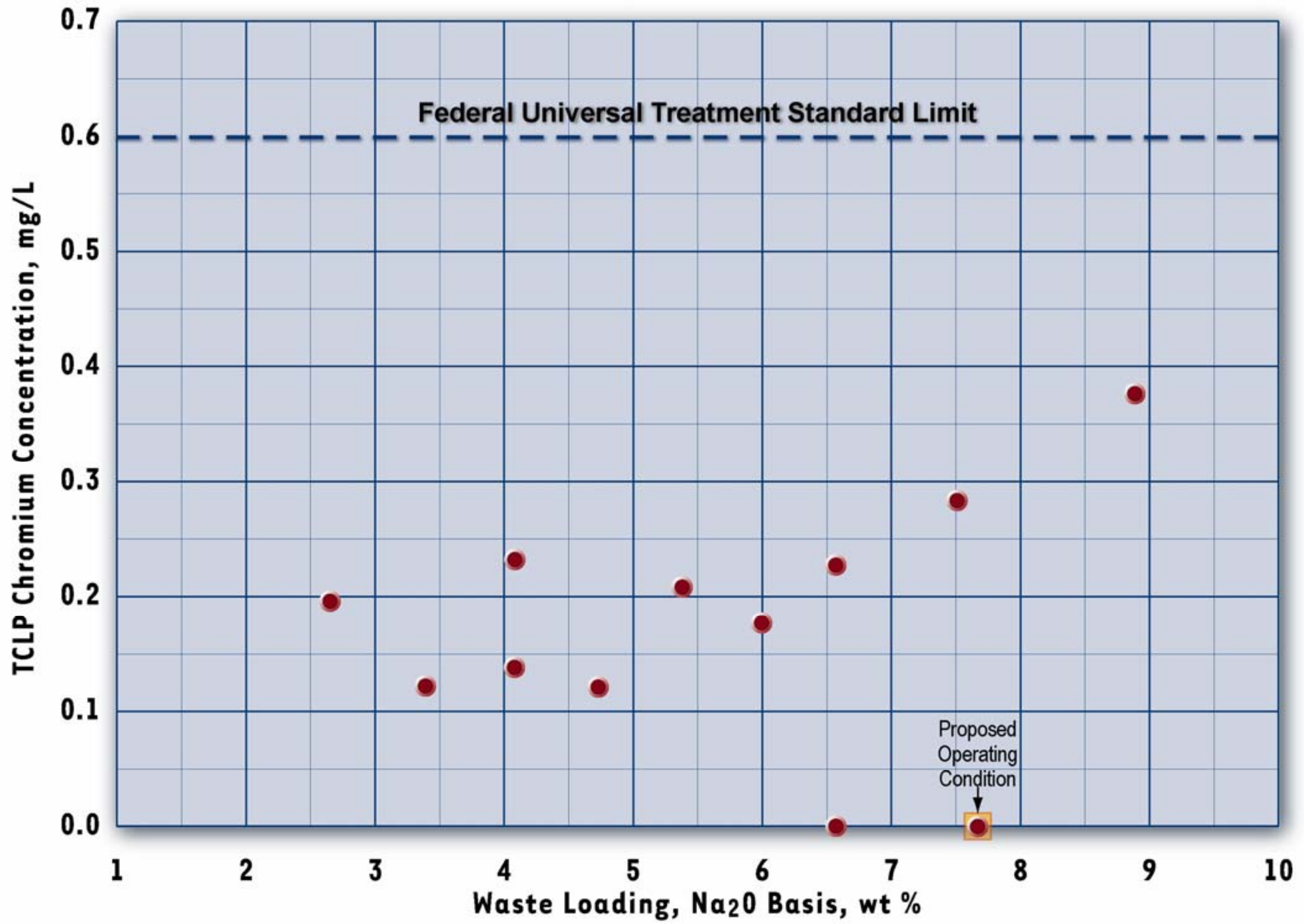

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Comparison of Simulant and Actual LAW Composition

Analyte	LAW Simulant (M)	Actual LAW (M)	Difference (%)
Al	0.058	0.208	-72
B	N/A	0.0021	N/A
C_2O_4	0.0097	0.0105	-7.4
CO_3 (TIC)	0.484	0.533	-9.1
Ca	N/A	0.0014	N/A
Cl	0.0430	0.0415	3.6
Cr	0.0097	0.0186	-48
F	0.030	0.018	63
K	0.0118	0.0090	30
Na	4.75	5.10	6.9
NO_2	0.414	0.414	0
NO_3	2.34	2.44	-4.4
Free OH	0.52	0.51	2.2
PO_4	0.0461	0.0515	-11
Si	N/A	0.0039	N/A
SO_4	0.0891	0.0932	-4.5
Other Soluble TOC (e.g., acetate)	0.36	N/A	N/A
TOC	0.285	0.233	22.6

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Leaching Observations

- Similar Values Measured
  - Part 2 and 3 Testing
    - Nitrate ANSI/ANS 16.1
      - Decreased as waste loadings increased
    - Nitrite
      - Decreased as waste loadings increased
  - With Simulant and with LAW
- Crystal formation during evaporation to increase waste loading does not appear to influence nitrate leaching

Waste Form Performance Testing with Radioactive (LAW-based) Samples

- A formulation condition with a waste loading of 18.8 wt% (TDS basis), or 7.60 wt % (Na_2O basis), provides satisfactory waste form testing results, can be obtained by use of evaporation to reduce the LAW volume by slightly less than 50%, and is acceptable as the nominal (design basis) formulation.

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Waste Form Performance Testing with Radioactive (LAW-based) Samples

- ANSI/ANS 16.1 leaching indices for nitrate, nitrite, and technetium increase as waste loadings decrease.

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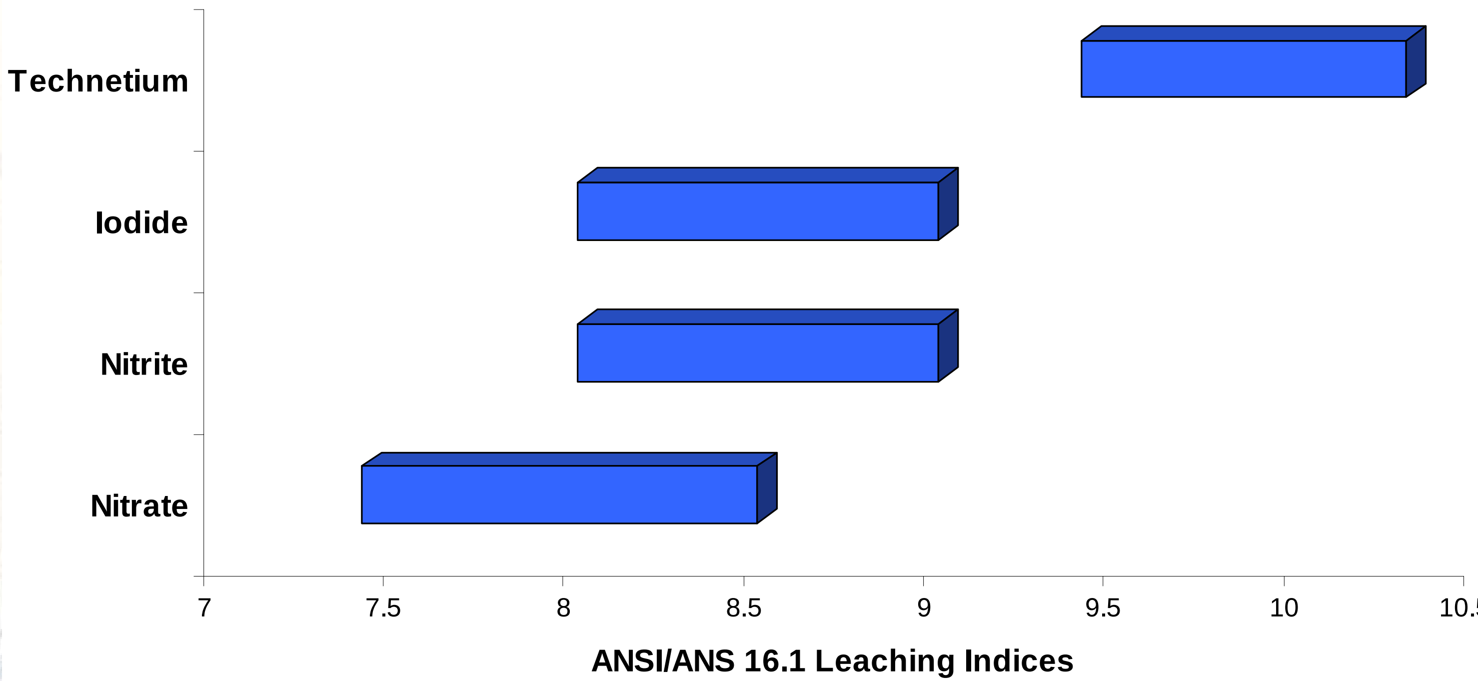
Samples Prepared from DRF2 and LAW and Waste Loadings of 10.2 to 24.2 wt% (TDS basis), or 4.12 to 9.79 wt% (Na_2O basis)



Waste Form Performance Testing with Radioactive (LAW-based) Samples

- For samples prepared from DRF2 and LAW and for waste loadings of 10.2 to 24.2 wt% [total dissolved solids (TDS) basis], or 4.12 to 9.79 wt% (Na_2O basis) ^{129}I concentrations in the leach liquids were below the quantification limit.

Waste Form Performance Testing with Radioactive (LAW-based) Samples

- With the possible exception of thallium, samples prepared from DRF2 and LAW do not exceed the leaching requirements of the Toxicity Characteristics List in the WAC-173-303, “Dangerous Waste Regulations,” and Federal Universal Treatment Standards for all conditions studied.

Waste Form Performance Testing with Radioactive (LAW-based) Samples

- Uranium and cesium leach indices could not be calculated due to uncertainties in the LAW source terms and barium interference with the inductively coupled plasma/mass spectroscopy (ICP/MS) analysis of the leach liquids.

Cast Stone A Viable Waste Form