washington river protection solutions

Assessment of Pertechnetate Getters, Reductants, and Stabilization

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Previous Work on Cement-Stabilized Waste Forms

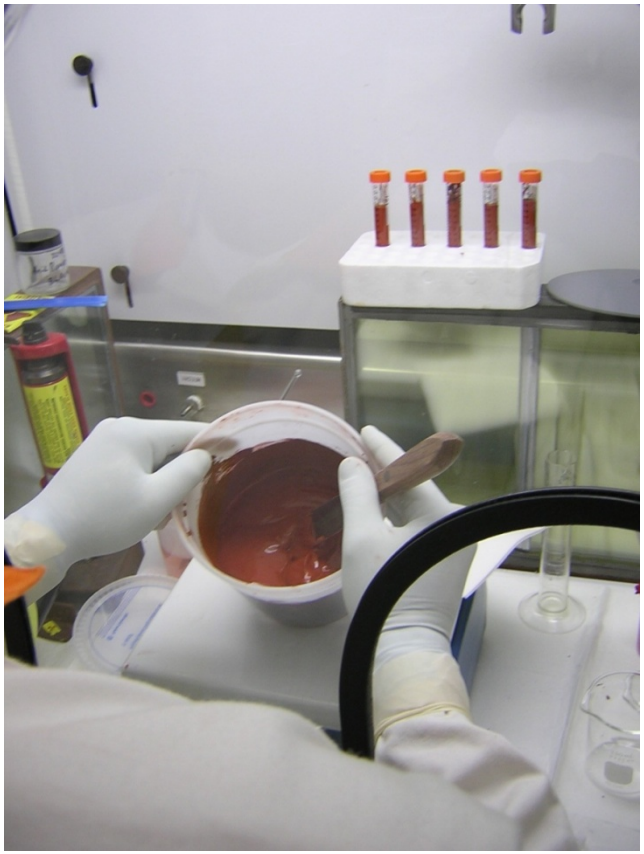
Stabilization of 5 molar sodium salt solutions:

G. A. Cooke, K. M. Bishop, and L. L. Lockrem, September 2003, Contributing Authors to "Containerized Cast Stone Facility, Task 1 – Process Testing and Development Final Test Report," Fluor Federal Services (entered into IDMS as

RPP-RPT-26742, 07-13-2005, "Hanford Containerized Cast Stone Facility Task 1 – Process Testing and Development Final Test Report," text through

Appendix E, and Appendix F through Appendix J, CH2M HILL Hanford Group, Inc. (CH2M HILL)

Encapsulation of K-Basin Sludge for WIPP:



CH2M-0304553, E. S. Aromi and R. E. Raymond to R. J. Schepens, 11-26-2003, “Test Reports for treating Bulk Vitrification and Cast Stone Technologies for Treatment and Disposal of K-Basin Sludge, “ CH2M HILL

Sequestration of Iodine and Mercury with Silvered Zeolite:

RPP-RPT-26725, L. L. Lockrem, 07-14-2005, “Cast Stone Technology for Treatment and Disposal of Iodine-Rich Caustic Waste Demonstration Final Report,” CH2M HILL

Solidification of Basin 42 Ammonium Sulfate Brine for ETF:

RPP-RPT-31740,
G. A. Cooke,
L. L. Lockrem,
M. D. Guthrie,
K. J. Lueck, and
M. Avila, 11-10-2006,
“Development and Testing of a Cement Based Solid Waste Form Using Synthetic UP-1 Groundwater,”
CH2M HILL.

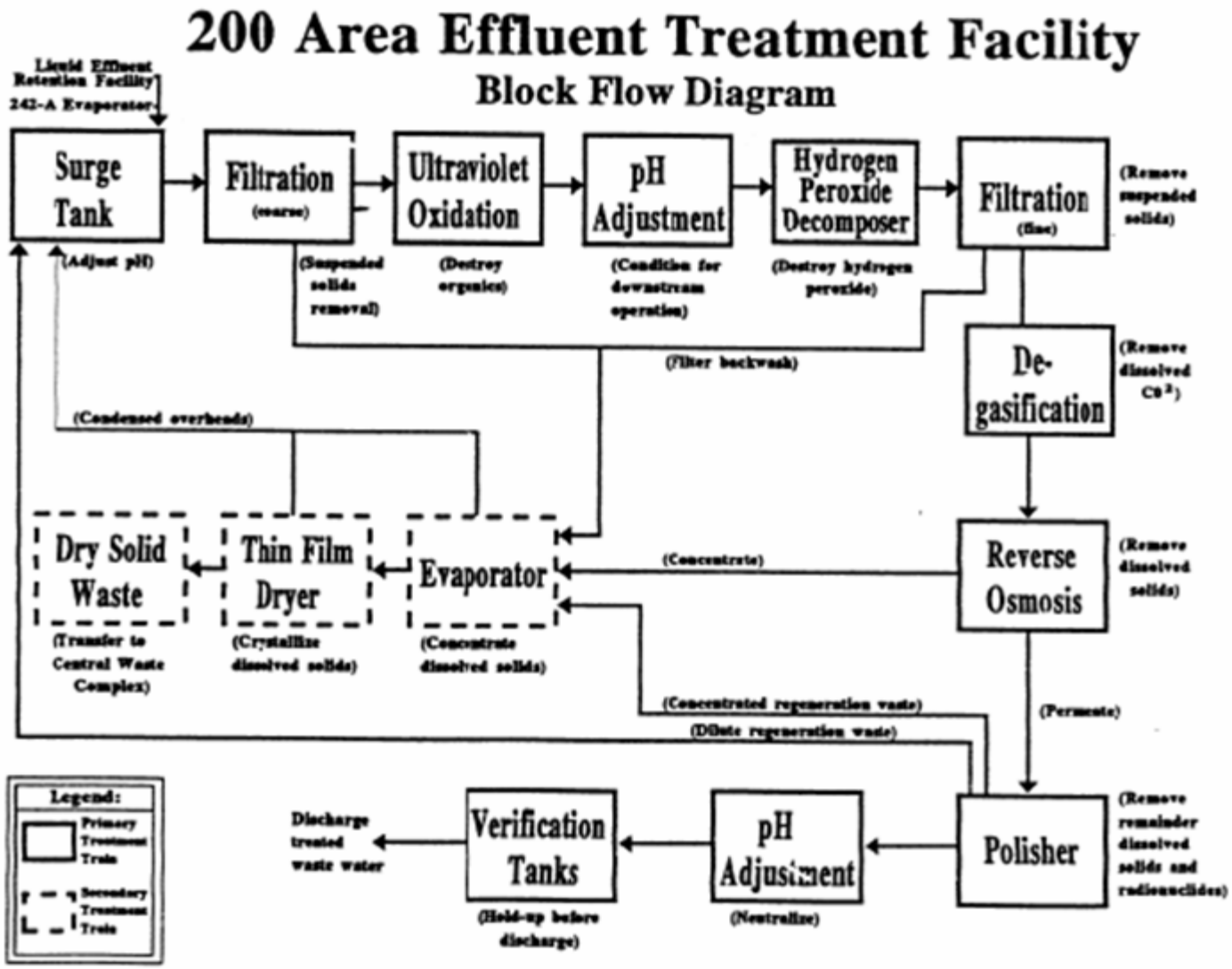
This Study

- The Effluent Treatment Facility (ETF), is a state-of-the art industrial wastewater treatment facility and receives waste streams from landfill leacheate, 242-A Evaporator condensate, contaminated groundwater, and will receive the Waste Treatment Plant offgas scrubber waste stream. All of these waste streams will contain TcO_4^-
- The unit processes employed by the ETF flowsheet will direct the TcO_4^- to the secondary waste stream. The secondary waste stream is subjected to the evaporator, then the thin film dryer
- The thin film dryer does not provide stabilization of TcO_4^-
- Therefore, the test matrix was a simulant of Liquid Effluent Retention Facility (LERF) (Basin 43) waste stream from the evaporator to the thin film dryer and contained approximately 28.9% solids

The Hanford 200 East Area Effluent Treatment Facility (ETF)

- The ETF includes (2025-E) miscellaneous support buildings structures, Areas Facilities (200 TEDF) LERF
- Process condensate from 242-A Evaporator, operated by WRPS, and other wastewater are treated at the RCRA-permitted ETF facility, which has design capacity to process 150 gallons per minute
- Treated effluent is disposed of at State-Approved Land Disposal Site (SALDS) under a WAC 173-216 Discharge Permit

Hanford Facility Dangerous Waste Permit Application, DOE/RL-93-03, Rev. 0



Assessment of Pertechnetate Getters, Reductants, and Stabilization

Major ETF Waste Streams:

- Process Condensate from 242-A Evaporator (Basin 42)
- RPP-31803-VA
- UP-1 Groundwater (Basin 43) This Study
- Spent Nuclear Fuels, 105-F, H, K, and N Basin Waters
- ERDF Leachate (Basin 44)
- Waste Treatment Plant Condensate/Scrubber Water (Planned)

Current ETF Disposal Path:

- Treated water is discharged to drain field north of 200 West Area (SALDS)
- Solids are placed in 55-gallon drums for disposal at ERDF landfill

Assessment of Pertechnetate Getters, Reductants, and Stabilization

Current Research Objective:

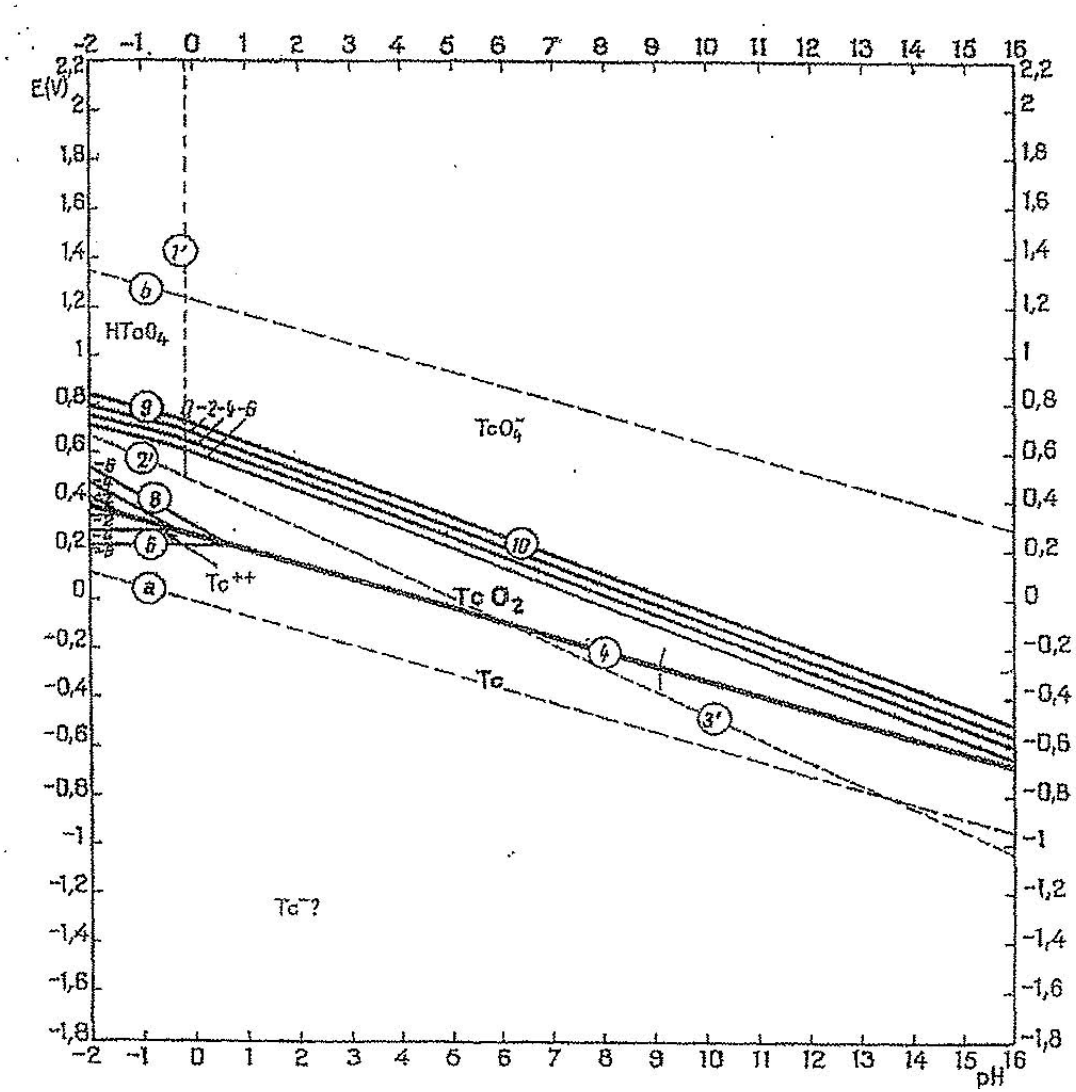
- To sequester pertechnetate as pertechnetate by the use of getters, and/or
- To reduce pertechnetate to technetium dioxide, and
- Determine Leach characteristics of technetium in a cementitious matrix

Assessment of Pertechnetate Getters, Reductants, and Stabilization

- Apatite Getters
  - Bone Black (from Ebonex)
  - Fish Bone Fines (Ground PIMS from UFA Ventures)
- Reductants
  - Zero Valent Iron Powder (Reagent Grade ~325 mesh)
  - Iron (III) Phosphate (Reagent Grade)
  - Tin (II) Apatite (Robert Moore Sandia Laboratory)
  - Ferrous Sulfate (1M)
- Ion Exchange Resin
  - Purolite®* A530-E and A532-E

* Purolite is a trademark of The Purolite Company, Bala Cynwyd, Pennsylvania.

Pourbaix Diagram



Basin 43 Simulant Formulation (to make 1 liter)

Reagent	Mass
$NaNO_3$	140.7948
$MgSO_4$	19.6177
$AlCl_3$	0.1337
KCl	2.7886
$Na_2CrO_4\ 4H_2O$	0.2146
$Ca(OH)_2$	5.5384
$Ca(NO_3)$	72.7003
$NaHCO_3$	37.8555
BaCl	0.0235
NaF	1.4126
$CaCl_2$	7.9349
Total	289.0146

Assessment of Pertechnetate Getters, Reductants, and Stabilization

Technetium

- Analytical Standards
  - AEA Technology, QSA TCZ44, 1.32 µCi /mL
  - AEA Technology, QSA TCZ64, 13.34 µCi /mL

- Spiking Material Ammonium Pertechnetate, NH_4TcO_4

  Obtained from Oak Ridge National Laboratory, dissolved in water to produce spiking solution at 117 µCi /mL

Assessment of Pertechnetate Getters, Reductants, and Stabilization - Experimental Design

Getters (0.25 gm in 25 mL Basin 43 simulant; 0.293 mg ^{99}Tc)		**Sn(II)Apatite[1] (0.0115, 0.1153, 1.1457 g each in in 25 mL Basin 43 simulant; 0.293 mg ^{99}Tc)**	**Resin1* (0.0197, 0.1972, 1.9676 g A530-E; 0.0156, 0.1556, 1.5540 g A532-E each in 25 mL Basin 43 simulant; 0.293 mg ^{99}Tc)**
Challenged at pH 5-6 with 0.29 mg ^{99}Tc		Challenged at pH 5-6	Challenged at pH 5-6
Rotomixed for ~12 hours; aliquot withdrawn for analysis		Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis
Adjust pH to 12	Adjust to pH 12, adjust ORP to -400 mV challenge	Adjusted to pH 12, no ORP adjustment	Adjusted to pH 12, no ORP adjustment
Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis

* Based on dry weight.

Percent Reduction at pH 5-6

Reagent	% Reduction of Technetium
Bone Black	20
Fishbone	19
Iron Powder	25
Iron (III) Phosphate	16
Sn(II) Apatite	29
A530-E	96
A532-E	97.2

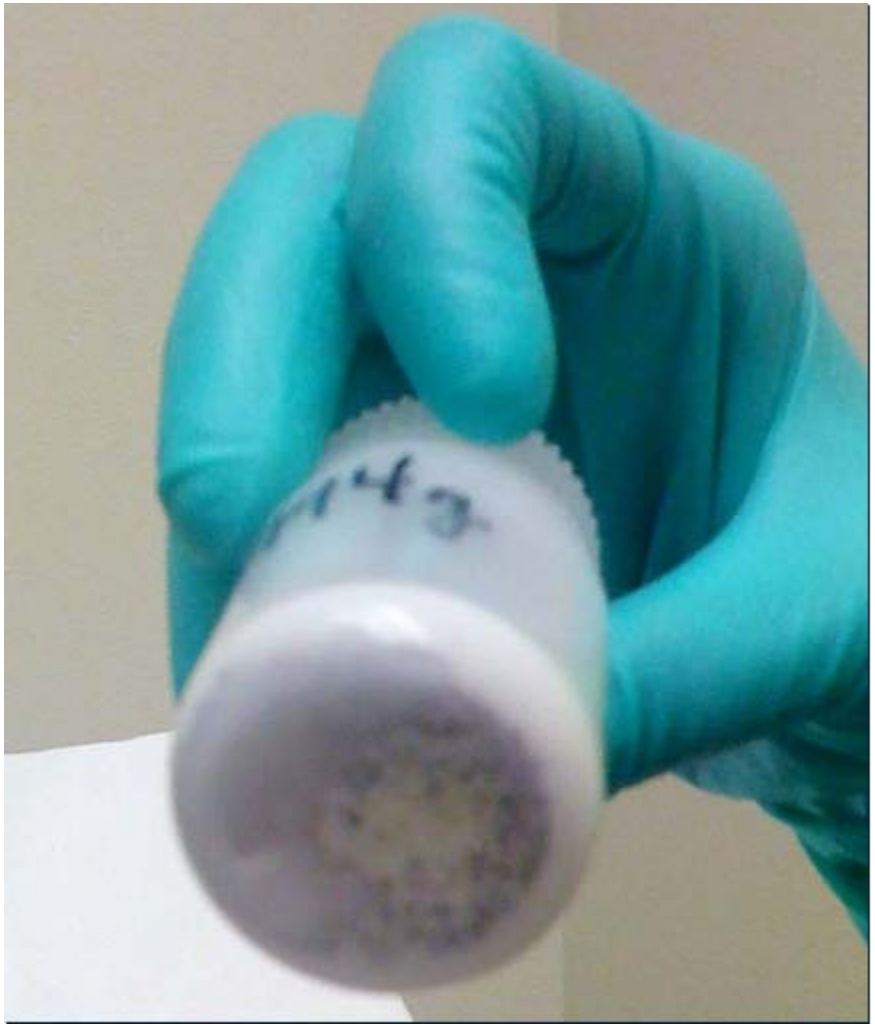
Percent Reduction at pH 12 of Technetium

Bone Black	13
Fishbone	17
Iron Powder	17
Iron (III) Phosphate	36
Sn(II) Apatite	95
A530-E	97.2
A532-E	98.7

Percent Reduction by ORP Adjustment to -400 mV vs SHE, Tc(VII) to Tc(IV)

Bone Black	99
Fishbone	99
Iron Powder	99
Iron (III) Phosphate	96

TcO_2 In Sn(II)Apatite and Brine Simulant



Cement Formulation, Planned vs. Actual

Materials	RPP-PLAN-33338 Rev 1A Amount (g)	Experimental Formulation Amount (g)
Brine: Solids Ratio	1.3:1	1.1:1*
Basin 43 Groundwater Simulant	100	110
Portland Cement	38.5	66.64
Blast Furnace Slag	38.5	33.36

* When added, getter was an additional 10 g making the brine:solidsratio 1:1
When added, technetium concentration in brine was 1.2 ppm

Toxicity Characteristic Leaching Procedure (TCLP)

- TCLP was conducted in accordance with EPA SW-846 method 1311,Toxicity Characteristic Leaching Procedure
- The monoliths to be used for TCLP testing were cured for 28 days, then crushed in their casting vessels to <3/8-inch grain size
- Each monolith yielded ~40 to 50 g of sample which was added to 800 to 1000 g of TCLP extraction fluid 2 (glacial acetic acid at pH of 2.88) and then subjected to continuous rotation at 30 ±2 rpm for 18 ±2 hours
- The leached cementitious portions continued to be subjected to the acetic acid environment for an additional 24 hours prior to the removal of aliquots for inductively coupled plasma-mass spectroscopy preparation and analysis via EPA 3005A and
- EPA 200.8

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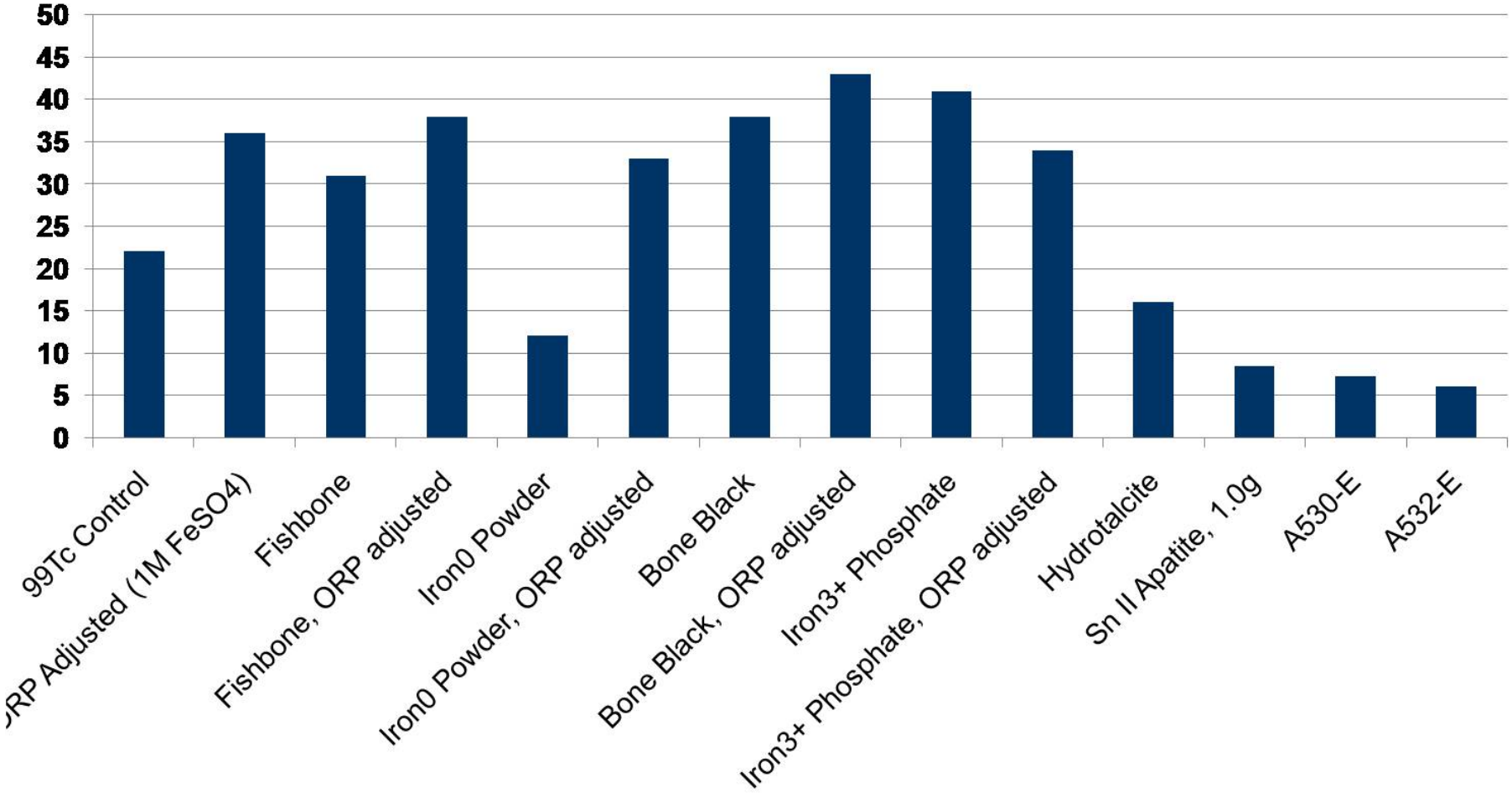
TCLP Results. Percent of available Tc leached

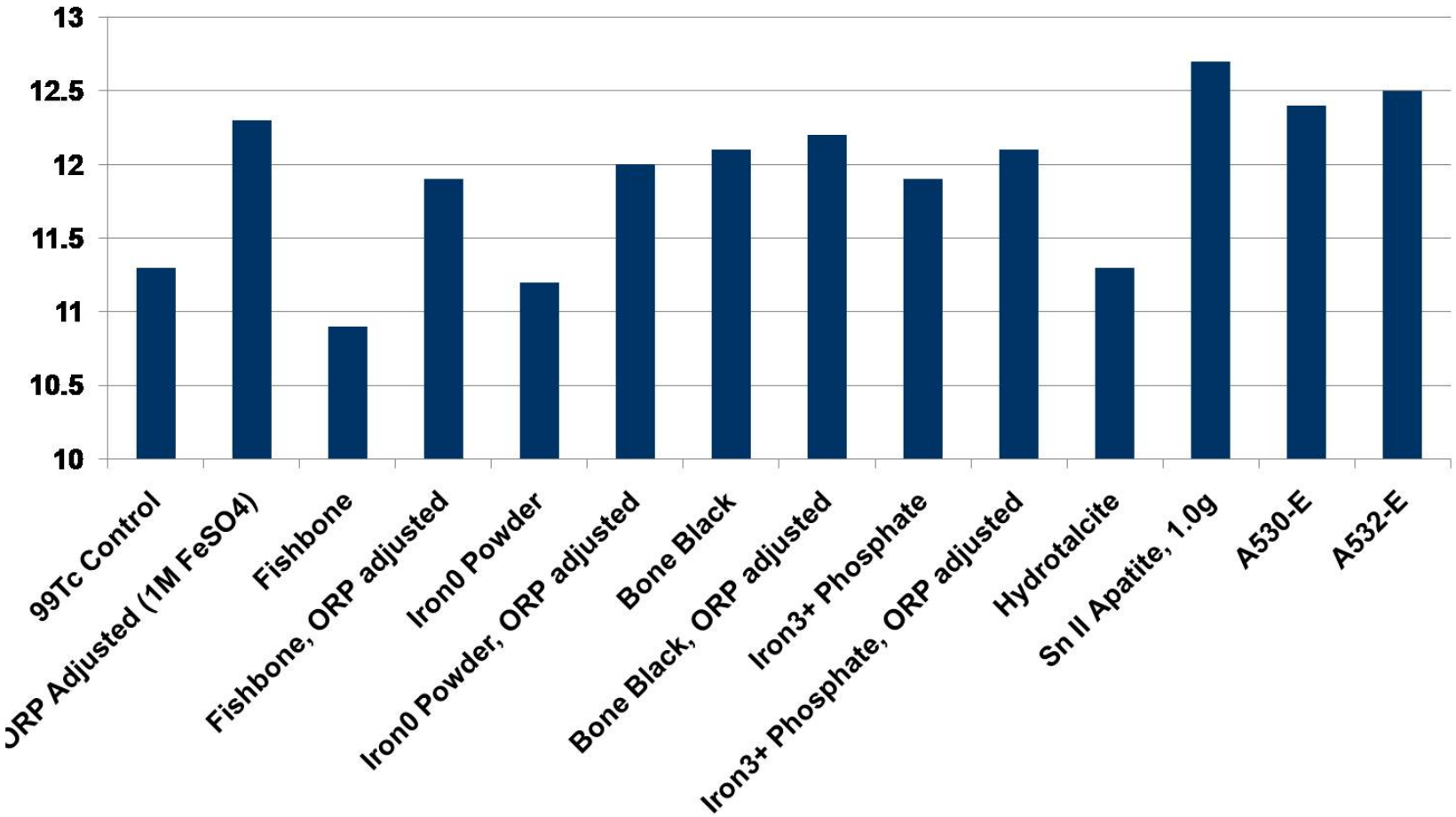


ANSI/ANS 16.1-2003 Leach Procedure

- Reference: American National Standard method ANSI/ANS-16.1-2003, “Measurement of the Leachability of Solidified Low-Level Radioactive Waste by a Short-Term Test Procedure.”
- Cylinder of cement (cured for 28 days) is submerged in distilled water [ratio volume leach water (mL) to cylinder surface area (cm^2) = 10:1]
- Water changed and analyzed after 2, 7, 24, 48, 72, 96, and 120 hours.

ANSI 16.1 Leach Test Results

(L.I. = ANSI Leach Index, the negative exponent of the diffusion coefficient)



Conclusions

- Encapsulation in cement monolith provides good retention of Tc by itself (ANSI Leach Index >11)
- $CaPO_4$ getters do not work at high salt and pH
- ORP adjust does work at high salt and pH
- Resin and Sn(II)apatite do work at high salt and pH
- Leach indices greater than 12 is readily achievable

Future Work

- Understand the fundamentals of the Tc (VII) reduction and association with Sn(II)Apatite.
- Explore selectivity coefficients and distribution coefficients in matrices of concern.
- Formulate cement and study leaching for additional waste brine compositions
- Extend ANSI Leach Index studies to longer time periods
- Examine initial and leached cement monoliths using scanning electron microscopy to determine failure modes.