PNNL-27765, Rev 0
RPT-DFTP-012, Rev 0

Pacific Northwest
NATIONAL LABORATORY

Off-Gas Condensate and Cast Stone Analysis Results

September 2018

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Executive Summary

A sample of melter off-gas condensate produced during a vitrification demonstration test of the direct-feed low-activity waste (DFLAW) Radioactive Waste Test Platform using waste retrieved from Hanford storage tank AP-105 was analyzed for major cations, anions, total cyanide, Resource Conservation and Recovery Act (RCRA) metals, selected radionuclides, and selected organic compounds. The melter secondary liquid off-gas condensate was concentrated through evaporation and then immobilized in a non-glass waste form using the Cast Stone waste form formulation. After the solid waste forms cured for 28 days, U.S. Environmental Protection Agency (EPA) Method 1311 (EPA 1992) Toxicity Characteristic Leach Procedure (TCLP) tests were conducted on two samples. The TCLP leachates were analyzed for RCRA metals, fluoride, and total cyanide. These chemical analyses were conducted to collect data on the waste form performance and to determine if the waste form would meet the disposal requirements of the Waste Control Specialists LLC (WCS) Federal Waste Disposal Facility (FWF) in Texas (WCS 2015) and the Integrated Disposal Facility at Hanford.

The radionuclide results in the off-gas condensate were used to estimate concentrations in the Cast Stone waste forms; these estimates were then compared to Class C limits (30 TAC 336.362 Appendix E). Inductively coupled plasma-mass spectrometry (ICP-MS) was used to measure most of the radionuclides. All measured radionuclides were determined to be below their respective Class C limits. A mass at 232 was identified by ICP-MS, but this mass component could potentially be Th-232 or U-232 or a combination of both. Th-232 is the dominant isotope of Th (99.98 percent), whereas U-232 is not natural and is only formed through transmutation of Th-232. Production of ^{233}U (through the neutron irradiation of ^{232}Th) invariably produces small amounts of ^{232}U due to parasitic (n,2n) reactions on uranium-233 itself, or on protactinium-233, or on thorium-232; however, because U-233 was determined to be below its EQL, it can reasonably assumed that all the mass at 232 is Th-232. A similar issue occurs at mass 238, which could be U-238 or Pu-238; however, in this case Pu-238 can be ruled out as a contributor to the isotope measured at mass 238 for the following reasons. Pu-238 has a half-life of 87.7 years and its daughter product (U-234) has a half-life of 2.5×10^5 years and a measured concentration of < 0.002 µg/L. If significant concentrations of Pu-238 were present in this waste, then the amount of measurable U-234 would have increased over the decades of storage in the Hanford tanks. Because this was not observed, it is concluded that the isotope measured at mass 238 is all U-238.

The radionuclide concentrations in the Cast Stone were determined from the measured concentrations in the off-gas condensate, the ratio of condensate/evaporate (10.68gm/gm), the amount of evaporate added to the Cast Stone formulation (0.370 gm evaporate/gm Cast Stone), and the density of Cast Stone (1.703 g/mL). These concentrations were compared to applicable Class C limits and determined to be below the Class C limits either by direct analysis of the off-gas condensate or process knowledge (in the case of U-232 and Pu-238).

A total of 68 organic compounds were targeted for analysis in the off-gas condensate. Of these compounds, only nine were measured above their respective minimum reportable concentration. These compounds were acenaphthene, acetone, n-butyl alcohol, p,p'-DDT, methyl ethyl ketone, nitrobenzene, o-nitrophenol, pyridine, and toluene. Of the detectable compounds, only acenaphthene, acetone, o-nitrophenol, and pyridine were above wastewater standards (40 CFR 268.48 - Universal Treatment Standards). None of the organic compounds exceeded the non-wastewater standards (40 CFR 268.48 - Universal Treatment Standards).

Analysis of the TCLP leachates from the Cast Stone waste forms indicated that none of the analytes exceeded the Universal Treatment Standard and, in general, all were well below the standards.

Acknowledgments

The authors thank Amy Rovira for carefully reviewing the calculation packages, Carolyne Burns, and Bill Dey for carefully reviewing the technical report. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the DOE under Contract DE-AC05-76RL01830.

Acronyms and Abbreviations

ASTM	ASTM: (formerly American Society for Testing and Materials)
BFS	blast furnace slag
Ci	curie
DFLAW	direct-feed low-activity waste
EMF	Effluent Management Facility
EPA	US Environmental Protection Agency
FA	fly ash
FWF	Federal Waste Disposal Facility
FY18	Fiscal Year 2018 (October 1, 2017 through September 30, 2018)
g	gram
HLW	high-level waste
IC	ion chromatography
ICP-OES	Inductively coupled plasma–optical emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
ILAW	Immobilized Low-Activity Waste
L	liter
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
m^3	cubic meter
mg	milligram
ng	nanogram
nCi	nanocurie
OPC	ordinary Portland cement
pg	picogram
ppq	part per quadrillion (pg per liter)
ppt	part per trillion (ng per liter)
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
SwRI	Southwest Research Institute
TAC	Texas Administrative Code
TCLP	toxicity characteristic leaching procedure
WAC	waste acceptance criteria
WCP	Waste Control Specialists LLC
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant

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1.0 Introduction

The current plan for the disposal of Hanford tank wastes is through the Hanford Tank Waste Treatment and Immobilization Plant (WTP) where both high-level waste (HLW) and low-activity waste (LAW) will be processed and made into glass. The Low-Activity Waste Pretreatment System (LAWPS) has been initiated to provide for the initial production of immobilized low-activity waste (ILAW) by feeding LAW directly from the tank farms to the WTP LAW Vitrification Facility for immobilization. Prior to the transfer of feed to the WTP LAW Vitrification Facility, tank supernatant waste will be pretreated in the LAWPS to meet the WTP LAW waste acceptance criteria. The key process operations for treating the waste include solids filtration and cesium removal. Once the feed is pretreated, the waste will be sent to the WTP LAW facility for vitrification. The vitrification process generates secondary wastes, including condensate from the melter off-gas system. The baseline approach is to recycle off-gas condensate back into the process to be incorporated into the melter feed after evaporation (Effluent Management Facility (EMF) evaporator bottoms). However, an alternative to recycling the off-gas condensate is being considered. The alternative considered here is to treat and then solidify and immobilize the EMF bottoms waste stream in a waste form that meets a waste disposal acceptance criteria.

Pacific Northwest National Laboratory (PNNL) has been contracted by Washington River Protection Solutions (WRPS) to support the development and deployment of a direct-feed low-activity waste (DFLAW) Radioactive Waste Test Platform. This test platform will include all unit operations within the DFLAW flowsheet to allow for the evaluation of alternative flowsheets and identification of process performance data to support flowsheet models using real waste samples. This support includes the engineering, procurement, set-up, and shakedown of the baseline set of processes for the test platform; initial operations with real waste samples; and analytical work to support unit operations and meet disposal requirements.

To demonstrate that disposal requirements can be met, a representative secondary waste from the melter off-gas system was prepared for stabilization as a solid waste using the Cast Stone formulation (Cantrell et al. 2016). Required chemical analyses were conducted to collect data on waste form performance to evaluate an opportunity to alter the recycling and develop a waste form that meets any disposal site waste acceptance criteria (WAC). Before solid stabilization, samples of the liquid waste were collected for analysis of radionuclides, Resource Conservation and Recovery Act (RCRA) metals, fluoride, total cyanide, and organic compounds. After the solid waste forms were produced and cured, U.S. Environmental Protection Agency (EPA) Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) tests were conducted on selected samples (EPA 1992). TCLP leachates were analyzed for RCRA metals, fluoride, and total cyanide.

2.0 Methods

Methods used to analyze the off-gas condensate, evaporate the condensate, and complete the grouting of the evaporated condensate are described below and in project research records.

2.1 Off-Gas Condensate Analysis

The off-gas condensate was analyzed for inorganic constituents including major cations, anions, Resource Conservation and Recovery Act (RCRA) metals, radionuclides, organic compounds, and total cyanide. Because a small amount of reddish precipitate was observed in the off-gas condensate sample, an acidic digestion was conducted prior to analysis for major cations, RCRA metals, and radionuclides. Acidic digestion consisted of adding 0.8 mL of 16 M HNO_3, 0.2 mL 8 M HCl, and 0.1 mL of 8 M HF to 20 mL of sample, which resulted in a dilution factor of 1.055x.

2.1.1 Inorganic Constituents

Inductively coupled plasma–optical emission spectroscopy (ICP-OES), ICP-mass spectrometry (ICP-MS), and ion chromatography (IC) were used to analyze various inorganic constituents.

2.1.2 Radionuclide Analysis

Most of the radionuclides were analyzed using a PerkinElmer ELAN DRC-II Quadrupole ICP-MS, coupled with an ESI PC3 spray chamber. Tritium and C-14 are not within the analytical capability of our ICP-MS instrumentation; therefore, subsamples for tritium and C-14 were collected and sent to the Southwest Research Institute (SwRI) for analysis. Co-60, Sr-90, and Cs-137 could not be quantified by ICP-MS due to various isobaric interferences. As a result, Co-60 and Cs-137 were quantified by gamma spectroscopy and Sr-90 was determined by separating strontium (Sr) from the sample by dissolving the sample in 8M nitric acid (HNO_3) and then passing the solution through a column of Eichrom SrSpec resin. In this method, Sr is loaded onto the resin, but most other metals and anions pass through. Further, strontium is eluted from the resin with water and the eluate is counted for beta emission to quantify Sr-90.

Conventional ICP-MS trace-element analysis involves the use of both National Institute of Standards and Technology (NIST)-traceable external standards (for calibration of signal intensity to concentrations) and internal standards (for tracing drift from the time of calibration as well as possible fractionation effects). Further, adhering to CAWSRP (Daudt 2018) to comply with Hanford Analytical Services Quality Assurance Requirements Document (HASQARD), Volumes 1 and 4, necessitates a specific order of analyses that includes calibration blanks, checks, standard spikes and multiple dilutions. Due to the nature of the sample, some aspects of this usual methodology could not be applied completely. Most elements present in the sample can be expected to have poorly known, non-natural isotopic compositions. This has the following three implications:

1. It removes the possibility of carrying out conventional corrections for isobaric interferences. Other elements that may be present at the same atomic mass will add additional signal to the desired analyte, but are usually mathematically removed by analyzing for another isotope of the interfering element, assuming natural isotopic composition, and subtracting the portion of the signal contributed by it. Because this analysis is for specific isotopes of elements with non-natural isotopic abundances, the concentrations obtained in this portion of the analysis have not been interference-corrected and are theoretical maximums of the elements in question.

2. The calibration curves obtained by running external standards must be handled by using a specific mass of an isotope rather than the isotopic mass distribution of an element. Because most radioisotopes being analyzed are not present in nature, the elements were instead analyzed for a natural isotope in the standard with the assumption of equal instrument sensitivity between different isotopes of the same element (in all practicality, there is no known reason to assume otherwise).
3. The fact that the standards and the samples involve the analysis of different isotopes means that the usual standard spikes conducted as part of CAWSRP are not possible.

Given these constraints, the choice was made to divide the analyses into three major blocks by mass: Ni to Tc, Ru to Eu, and Ra to Cm. A mixed standard comprised of the elements in the block were run at five dilutions, followed by blank checks and calibration checks. The sample was then run at both a 10x dilution and a 1000x dilution, both to serve as a check and to better validate the results by demonstrating that concentrations would scale as expected. This process was repeated for the other two element blocks.

Low sensitivity at lower masses, typical of ICP-MS, combined with polyatomic argon interferences hindered the analysis of some of the analytes in the low mass block. Most susceptible were Ni and Se, demonstrated by their failure to pass their final calibration check, probably due to drifts in the formation of interferences. Some sources of interferences were addressed in the data. Any interference derived solely from the ICP-MS itself and not the sample could be addressed to a degree either in the non-zero intercept of the calibration curve for the standards (though the assumption that the formation of the interference was constant throughout the run may not be true, as mentioned previously), or by the described method of assuming a natural isotopic composition of the interference. Using the second approach, interference corrections were conducted for I-129 and Cs-134 by measuring Xe-131. Because the Xe present is natural Xe contamination in the argon plasma gas, it can be assumed to have a natural isotopic composition. This assumption can then be used to calculate and later subtract the counts on mass 129 and mass 134 contributed by Xe instead of the sample isotope.

For the high mass block, in the cases of Ra, Ac, Cm, a lack of certified standards limits the quantification to an estimation, with the assumption they have the same sensitivity as uranium. Note this is not necessarily true (e.g., plutonium has a higher sensitivity than uranium), but the estimates are likely to be within an order of magnitude of the true value. Due to a lack of well-established, formalized procedures, specific quantification limits were not established for this set of analyses; however, a good idea of whether the concentrations reported were real or merely noise amplified by the calibration curve and dilution corrections can be garnered by first referring to the two dilution runs. If the more concentrated sample dilution scales accordingly (even if it is limited to just being in the same order of magnitude), then it is likely that the concentration is real. If not, then further verification can be obtained by referring to the baselines and rinse blanks measured during the runs. If the raw counts per second of the sample fall within the standard deviation of the baseline or rinse blanks, then it is unlikely that the analyte is present at measurable quantities.

Linear calibration curves were obtained from the five standards run in the form of $Y = mX + b$, where Y is the concentration, m is the slope of the curve, X is the counts per second, and b is the y-intercept of the curve. Conventional elemental analysis typically fits the counts per second of the data directly as the X value and solves for Y using the full equation; m is representative of the response rate of the instrument's counts per second for a specific concentration, and b is representative of the background signal present (this signal can be due to electronic backgrounds or background contamination of the isotope or isobaric interferences). Because this portion of the analysis is calibrated for certain isotopes using a different isotope for the same element, the b value of the calibration curve was left out because it cannot be assumed that the standard isotope and the sample isotope have the same background level; only the response rate m are shared between the two. This does leave the potential for the sample isotope to

have a systematic error of a background value that is unaccounted for; however, the isotope can be qualitatively checked by monitoring the blanks between the samples to inspect for any significant background.

2.1.3 Organic Analyses

Sample aliquots for organic analysis were collected and sent to SwRI for analysis. SwRI used EPA methods 8015B (nonhalogenated organic compounds), 8081B (organochlorine pesticides), 8082A (polychlorinated biphenyls), 8260C (volatile organic compounds), and 8270D (semi-volatile organic compounds) (EPA 1996, 2006, 2007a, 2007b, 2014).

2.1.4 Cyanide Analyses

Total cyanide was measured by SwRI using EPA method 9012B (EPA 2004).

2.2 Off-Gas Condensate Evaporation

A total of 11.821 L of off-gas condensate was received from the Radiochemical Processing Laboratory. From this, 4.845 L was removed for analytical samples sent offsite. The remaining sample (6.976 L) had an initial density of 1.01 g/mL and a pH of less than 1.0. The off-gas condensate was concentrated by evaporative heating on a hot-plate (between 70ºC and 90ºC) while being stirred to reach the density goal. The final density of the evaporated condensate was 1.106 g/mL. The final weight of the sample after the evaporation process was 514.02 g. An 11.06 gm sample of evaporate was removed, resulting in a net 502.96 g (454.8 mL) of evaporated condensate. The pH of the evaporated condensate was adjusted to 12.00 by adding 37.5 mL of 2.62 M NaOH and 84.5 mL of 10.00 M NaOH. The pH adjusted evaporate weighed 653.11 gm and had a density of 1.108 g/mL. The final ratio of condensate to evaporate was 10.68 g/g.

2.3 Cast Stone Monolith Preparation

Because of the limited sample volume, only one grout formulation was made. The formulation used was the Cast Stone formulation (i.e., 8 percent ordinary Portland cement [OPC], 45 percent class C fly ash [FA], and 47 percent blast furnace slag [BFS]). The grout was made by adding 470.6 g of the pH adjusted evaporate to 64.0 g OPC, 360.0 g FA, and 376.0 g BFS.

The cementitious waste form specimens were prepared by adding the dry blend materials into a plastic bag and manipulating the bag by hand until the dry mixture appeared to be homogenous. The dry blend mix was then added slowly to an appropriate aliquot of the melter off-gas condensate evaporate waste sample just prior to making the grout specimens, and the waste-dry blend slurry then stirred until the paste appeared homogeneous (i.e., approximately 15 minutes in a lab-scale mixer). For consistency with previous work, mixing was done using the same equipment and laboratory procedures previously used to prepare secondary liquid waste Cast Stone samples (Saslow et al. 2017a, 2017b). The thoroughly mixed paste was transferred to plastic molds (right circular cylinders approximately 2 in. in diameter and 4 in. long). After being filled with wet slurry, the entire mold was vibrated, as needed, until no bubbles were observed at the surface of the wet paste. A perforated cap was placed on the mold and the molds transferred to a humidity chamber at room temperature and ≥80 percent relative humidity where the grout cured for 28 days. The waste form specimens were cured per ASTM C192/C192M, *Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory.*

The waste form specimens were visually monitored for the presence of free liquids after the curing began until no free liquids were visually observed during the curing period. No free liquids were observed after 7 days.

2.4 Cast Stone Monolith TCLP Testing

After curing for 28 days, select waste form specimens were sent to SwRI for analysis by Toxicity Characteristic Leaching Procedure (TCLP), EPA Method 1311 testing (EPA 1992). TCLP tests are used to demonstrate if a waste form meets the RCRA land disposal restrictions for hazardous wastes. The melter off-gas condensate evaporate could potentially contain RCRA metals including As, Cr, Hg, and Se and potentially high concentrations of Zn. In addition, some of the dry materials may include these same or other hazardous materials.

3.0 Results

3.1 Off-Gas Condensate Analysis

3.1.1 Inorganic Constituents

Table 1 through Table 3 present the results of the inorganic analysis results of ICP-OES, ICP-MS, IC, and total cyanide for the off-gas condensate.

Table 1. ICP-OES Results for Melter Off-Gas Condensate

Analyte	Result (µg/L)	EQL
Aluminum (Al)	36,500	165
Antimony (Sb)	ND	298
Arsenic (As)	ND	415
Barium (Ba)	67.4	32.8
Beryllium (Be)	ND	15.4
Bismuth (Bi)	ND	470
Boron (B)	194,000	2,520
Cadmium (Cd)	ND	42.3
Calcium (Ca)	14,200	336
Chromium (Cr)	11,500	23.2
Cobalt (Co)	ND	40.9
Copper (Cu)	126	78.5
Gadolinium (Gd)	ND	500
Iron (Fe)	30,000	100
Lead (Pb)	ND	138
Lithium (Li)	375	240
Magnesium (Mg)	812	27
Manganese (Mn)	178	23.9
Molybdenum (Mo)	989	98.8
Nickel (Ni)	323	140
Phosphorous (P)	2,500	408
Potassium (K)	71,200	1610
Rhenium (Re)	326	99.4
Silicon (Si)	41,400	5,480
Sodium (Na)	1,050,000	4,470
Strontium (Sr)	ND	62.8
Sulfur (S)	39,700	477
Titanium (Ti)	2,130	23.7
Vanadium (V)	ND	85.3
Zinc (Zn)	51,700	61.6
Zirconium (Zr)	2,390	19.1

EQL = estimated quantitation limit
ND = not detected above the EQL

Table 2. ICP-MS Results for Melter Off-Gas Condensate

Analyte	Result (µg/L)	EQL
Antimony (Sb)	ND	5.4
Arsenic (As)	288	42
Barium (Ba)	79.6	3.1
Cadmium (Cd)	28	7
Copper (Cu)	84	8.7
Cesium (Cs)	26,200	128
Chromium (Cr)	13,400	346
Lead (Pb)	65.4	2.4
Molybdenum (Mo)	1,150	5.3
Mercury (Hg)	21.5	3.3
Rhenium (Re)	312	3.0
Ruthenium (Ru)	998	4.7
Selenium (Se)	1,190	136
Silver (Ag)	13.7	3.8
Thorium (Th)	ND	4.8
Uranium (U)	21.7	7.1

EQL = estimated quantitation limit
ND = not detected above the EQL

Table 3. IC and Total Cyanide Results for Off-Gas Condensate

Analyte	Result (mg/L)	EQL
Bromide (Br^-)	ND	50
Chloride (Cl^-)	937	25
Fluoride (F^-)	22.7	10
Nitrate (NO_3^-)	17,100	500
Nitrite (NO_2^-)	ND	50
Phosphate (PO_4^{3-})	ND	75
Sulfate (SO_4^{2-})	85.7	75
Total Cyanide	8.01	0.125

EQL = estimated quantitation limit
ND = not detected above the EQL

3.1.2 Radionuclide Analysis Results

Table 4 presents the results of the radionuclide analyses. Several radioisotopes listed in Table 4 could not be quantified with certainty by ICP-MS due to isobaric interferences (i.e., Co-60, Sr-90, Y-90, Zr-93, Nb-93m, Cs-137, Ba-137m, Th-232, U-232, U-238, and Pu-238). As a result, Co-60 and Cs-137 were determined by gamma spectroscopy and Sr-90 was determined by wet-chemical separation followed by beta particle emission counting. Both tritium and C-14 were quantified by beta spectroscopy.

The mass shown as Y-90 (1,157 µg/L) in Table 4 was determined to have a large interference that was consistent with Zr-90. The total Zr concentration measured by ICP-OES (Table 1) was 2,390 µg/L. Using

the natural abundance of Zr-90 (51.45 percent), suggests a Zr-90 concentration of 1,230 µg/L. This value is similar to the value determined by ICP-MS for Y-90 and illustrates why both Y-90 and Sr-90 could not actually be quantified by ICP-MS. The mass at 93 could not be differentiated between Zr-93 or Nb-93m, so for the purposes of this analysis all the mass at 93 was assumed to be both Zr-93 and Nb-93m in Table 4. This provides a maximum concentration estimate for these two isotopes. Different concentrations were determined for each of these isotopes because different elements have different sensitivities in mass spectrometry.

Table 4. Radionuclide Analysis Results for Off-Gas Condensate and Their Specific Activities (all values in this table are for information only with the exception of H-3, C-14, Co-60, Sr-90, Tc-99 and Cs-137)

Radionuclide	Half-life (years)	Specific Activity (Ci/g)	Result (µg/L)	EQL (µg/L)	Result (µCi/L)	EQL (µCi/L)
H-3	12.33	9.66×10^{3}	-	-	0.297	2.06×10^{-3}
C-14	5.73×10^{3}	4.46	-	-	0.000	1.12×10^{-3}
59-Ni	7.50×10^{4}	8.09×10^{-2}	8.30	0.07	0.671	-
60-Co	5.271	1.13×10^{3}	NA	-	1.57×10^{-3}	-
63-Ni	96.0	59.2	47.6	2.2	2,820	-
79-Se	6.50×10^{4}	0.0698	1,481	69	103	-
90-Sr	29.1	137	NA	-	1.56	-
90-Y*	7.31×10^{-3}	5.45×10^{5}	1157	6.6	-	-
93-Zr	1.53×10^{6}	2.52×10^{-3}	4.87	0.011	0.0123	-
93m-Nb	13.6	2.83×10^{2}	6.00	0.014	1,700	-
99-Tc	2.13×10^{5}	1.70×10^{-2}	2,570	3.3	43.7	-
106-Ru	1.009	3.35×10^{3}	15.53	0.02	52,000	-
113m-Cd	13.6	2.33×10^{2}	2.51	0.01	585	-
125-Sb	2.77	1.03×10^{3}	0.008	0.004	8.24	-
126-Sn	1.00×10^{5}	2.84×10^{-2}	0.018	0.006	5.12×10^{-4}	-
129-I	1.57×10^{7}	$1.77x\ 10^{-4}$	461	41	0.0816	-
134-Cs	2.062	1.30×10^{3}	1.88	0.04	2,440	-
137-Cs	30.0	87.2	NA	-	0.368	-
137-Ba	Stable	Stable	9.15	0.061	-	-
151-Sm	90	26.4	0.076	0.002	2.00	-
152-Eu	13.33	1.77×10^{2}	0.143	0.002	25.3	-
154-Eu	8.8	2.64×10^{2}	0.141	0.004	37.2	-
155-Eu	4.96	4.66×10^{2}	0.190	0.004	88.5	-
226-Ra	1600	0.991	0.001	0.004	9.91×10^{-4}	-
227-Ac	21.8	72.5	0.001	0.003	0.0725	-
228-Ra	5.75	273	0.001	0.004	0.273	-
229-Th	7340	0.213	0.001	0.003	2.13×10^{-4}	-
231-Pa	3.28×10^{4}	4.74×10^{-2}	0.001	0.003	4.74×10^{-5}	-
232-Th	1.41×10^{10}	1.10×10^{-7}	2.27	0.3	2.49×10^{-7}	-
232-U	72	21.4	2.22	0.01	47.5	-
233-U	1.59×10^{5}	9.70×10^{-3}	0.002	0.003	1.94×10^{-5}	-
234-U	2.45×10^{5}	6.26×10^{-3}	0.002	0.002	1.25×10^{-5}	-
235-U	7.04×10^{8}	2.17×10^{-6}	0.121	0.002	2.63×10^{-7}	-

Table 4. (contd)

Radionuclide	Half-life (years)	Specific Activity (Ci/g)	Result (µg/L)	EQL (µg/L)	Result (µCi/L)	EQL (µCi/L)
236-U	2.34×10^{7}	6.48×10^{-5}	0.006	0.003	3.89×10^{-7}	-
237-Np	2.14×10^{6}	7.06×10^{-4}	0.026	0.002	1.84×10^{-5}	-
238-Pu	87.7	17.2	16.7	0.003	287	-
238-U	4.47×10^{9}	3.37×10^{-7}	16.2	0.03	5.46×10^{-6}	-
239-Pu	2.41×10^{4}	6.23×10^{-2}	0.006	0.002	3.74×10^{-4}	-
240-Pu	6537	0.228	0.002	0.001	4.56×10^{-4}	-
241-Am	432	3.44	0.002	0.002	6.88×10^{-3}	-
241-Pu	14.4	103	0.002	0.002	0.206	-
242-Cm	0.446	3.32×10^{3}	0.001	0.004	3.32	-
242-Pu	3.76×10^{5}	3.94×10^{-3}	0.001	0.004	3.94×10^{-6}	-
243-Am	7380	0.200	0.001	0.004	2.00×10^{-4}	-
243-Cm	28.5	51.7	0.001	0.004	0.0517	-
244-Cm	18.11	81.1	0.001	0.003	0.0811	-

EQL = estimated quantitation limit
NA = not analyzed
* The value for Y-90 was determined to be Zr-90

Similarly, Cs-137 and Ba-137m could not be quantified by ICP-MS due to a large interference from stable Ba-137. The total barium concentration determined by ICP-OES was 67.4 µg/L. Using the natural abundance for Ba-137 of 11.23 percent and the total barium concentration measured by ICP-OES, suggests a concentration of 7.6 µg/L for Ba-137. This is similar to that determined by ICP-MS (9.1 µg/L). Although Cs-137 is expected in the off-gas condensate, measurable Ba-137m is highly unlikely due to its short half-life (2.6 minutes) and the many decades that AP-105 waste has been stored since its production. As a result of these factors, Cs-137 was determined by gamma spectroscopy.

A mass at 232 was identified by ICP-MS, but this mass component could potentially be Th-232 or U-232 or a combination of both. Th-232 is the dominant isotope of Th (99.98 percent), whereas U-232 is not natural and is only formed through transmutation of Th-232. Production of ^{233}U (through the neutron irradiation of ^{232}Th) invariably produces small amounts of ^{232}U due to parasitic (n,2n) reactions on uranium-233 itself, or on protactinium-233, or on thorium-232; however, because U-233 was determined to be below its EQL, it can reasonably assumed that all the mass at 232 is Th-232.

Likewise, an isotope at mass 238 was identified by ICP-MS that could be U-238 and/or Pu-238; however, Pu-238 can be ruled out as a contributor to mass 238 for the following reasons. Pu-238 has a half-life of 87.7 years and its daughter product (U-234) has a half-life of 2.5×10^{5} years and a measured concentration of < 0.002 µg/L. If significant concentrations of Pu-238 were present in this waste, measurable U-234 would have increased during the many decades of storage in the Hanford tanks and this was not the case.

The radionuclide concentrations in the Cast Stone were determined from the measured concentrations in the off-gas condensate, the ratio of condensate/evaporate (10.68gm/gm), the amount of evaporate added to the Cast Stone formulation (0.370 gm evaporate/gm Cast Stone), and the density of Cast Stone (1.703 g/mL). These concentrations were compared to applicable Class C limits (30 TAC 336.362 Appendix E) in Table 5. All radionuclides concentrations in the Cast Stone were determined to be below

the Class C limits either by direct analysis of the off-gas condensate or process knowledge (in the case of U-232 and Pu-238).

Table 5. Radionuclides in Cast Stone Compared to Class C Limits (30 TAC 336.362 Appendix E)

Radionuclide	Class C Limit	Cast Stone Concentration
3-H	(a)	2.0×10^{-3} Ci/m^3
14-C	8 Ci/m^3	0.00 Ci/m^3
59-Ni	(a)	4.48×10^{-3} Ci/m^3
60-Co	(a)	1.05×10^{-5} Ci/m^3
63-Ni	700 Ci/m^3	18.8 Ci/m^3
79-Se	(a)	0.688 Ci/m^3
90-Sr	7000 Ci/m^3	0.0104 Ci/m^3
93-Zr	(a)	8.18×10^{-5} Ci/m^3
93m-Nb	(a)	11.3 Ci/m^3
99-Tc	3 Ci/m^3	0.291 Ci/m^3
106-Ru	(a)	347 Ci/m^3
113m-Cd	(a)	3.90 Ci/m^3
125-Sb	(a)	0.0552 Ci/m^3
126-Sn	(a)	3.41×10^{-6} Ci/m^3
129-I	0.08 Ci/m^3	5.44×10^{-4} Ci/m^3
134-Cs	(a)	16.3 Ci/m^3
137-Cs	4600 Ci/m^3	2.45×10^{-3} Ci/m^3
151-Sm	(a)	0.0133 Ci/m^3
152-Eu	(a)	0.169 Ci/m^3
154-Eu	(a)	0.249 Ci/m^3
155-Eu	(a)	0.590 Ci/m^3
226-Ra	100 nCi/g	0.0178 nCi/g
227-Ac	100 nCi/g	1.31 nCi/g
228-Ra	(a)	4.92 nCi/g nCi/g
229-Th	100 nCi/g	3.84×10^{-3} nCi/g
231-Pa	100 nCi/g	8.53×10^{-4} nCi/g
232-Th	100 nCi/g	4.49×10^{-6} nCi/g
232-U	100 nCi/g	857 nCi/g
233-U	100 nCi/g	3.49×10^{-4} nCi/g
234-U	100 nCi/g	2.26×10^{-4} nCi/g
235-U	100 nCi/g	4.72×10^{-6} nCi/g
236-U	100 nCi/g	7.01×10^{-6} nCi/g
237-Np	100 nCi/g	3.31×10^{-4} nCi/g
238-Pu	100 nCi/g	5.16×10^{3} nCi/g
238-U	100 nCi/g	9.82×10^{-5} nCi/g
239-Pu	100 nCi/g	6.73×10^{-3} nCi/g
240-Pu	100 nCi/g	8.22×10^{-3} nCi/g
241-Am	100 nCi/g	0.124 nCi/g
241-Pu	3,500 nCi/g	3.72 nCi/g
242-Cm	20,000 nCi/g	59.8 nCi/g
242-Pu	100 nCi/g	7.09×10^{-5} nCi/g
243-Am	100 nCi/g	3.60×10^{-3} nCi/g
243-Cm	100 nCi/g	0.932 nCi/g
244-Cm	100 nCi/g	1.46 nCi/g

(a) No Class C limits established

3.1.3 Organic Analysis Results

Results of the organic compound analyses of the off-gas condensate are presented in Table 6. Of the 68 compounds analyzed only 9 were measured above their respective minimum detection limits. These results are highlighted in bold font for ease of identification. These compounds were acenaphthene, acetone, n-butyl alcohol, p,p'-DDT, methyl ethyl ketone, nitrobenzene, o-nitrophenol, pyridine, and toluene. Of the detectable compounds, only acenaphthene, acetone, o-nitrophenol, and pyridine were above their wastewater standards (40 CFR 268.48 - Universal Treatment Standards). None of the organic compounds exceeded the non-wastewater standards (40 CFR 268.48 - Universal Treatment Standards).

Table 6. Organic Compound Results in Melter Off-Gas Condensate along with their Universal Treatment Standards for Wastewater and Non-Wastewater

Organic Constituent (common name)	CAS Number	Wastewater Standard (mg/L)	Non-Wastewater Standard (mg/kg)	Result (mg/L)
Acenaphthene	83-32-9	0.059	3.4	**0.064**
Acetone	67-64-1	0.28	160	**1.30 E**
Acetophenone	98-86-2	0.010	9.7	0.0049 U
alpha-BHC	319-84-6	0.00014	0.066	0.000125 U
beta-BHC	319-85-7	0.00014	0.066	0.000125 U
gamma-BHC	58-89-9	0.0017	0.066	0.000125 U
Benzene	71-43-2	0.14	10	0.0010 U
Benzo(a)anthracene	56-55-3	0.059	3.4	0.0049 U
Benzo(k)fluoranthene	207-08-9	0.11	6.8	0.0049 U
Benzo(g,h,i)perylene	191-24-2	0.0055	1.8	0.0049 U
n-Butyl alcohol	71-36-3	5.6	2.6	**2.6 E**
Butyl benzyl phthalate	85-68-7	0.017	28	0.0049 U
Carbon disulfide	75-15-0	3.8	4.8 (mg/L TCLP)	0.0010 U
Carbon tetrachloride	56-23-5	0.057	6.0	0.0010 U
Chlorobenzene	108-90-7	0.057	6.0	0.0010 U
bis(2-Chloroethyl)ether	111-44-4	0.033	6.0	0.0049 U
Chloroform	67-66-3	0.046	6.0	0.0010 U
p-Chloro-m-cresol	59-50-7	0.018	14	0.0049 U
2-Chlorophenol	95-57-8	0.044	5.7	0.0049 U
Chrysene	218-01-9	0.059	3.4	0.0049 U
o-Cresol	95-48-7	0.11	5.6	0.0049 U
m-Cresol & p-Cresol	65794-96-9	0.77	5.6	0.0049 U
Cyclohexanone	108-94-1	0.36	0.75 (mg/L TCLP)	0.0050 U
o,p′-DDD	53-19-0	0.023	0.087	0.000250 U
p,p′-DDD	72-54-8	0.023	0.087	0.000250 U
o,p′-DDT	789-02-6	0.0039	0.087	0.000250 U
p,p′-DDT	50-29-3	0.0039	0.087	**0.00151**
o-Dichlorobenzene	95-50-1	0.088	6.0	0.0049 U
1,2-Dichloroethane	107-06-2	0.21	6.0	0.0010 U
1,1-Dichloroethylene	75-35-4	0.025	6.0	0.0010 U
Dieldrin	60-57-1	0.017	0.13	0.000250 U
2,4-Dimethyl phenol	105-67-9	0.036	14	0.0049 U
Dimethyl phthalate	131-11-3	0.047	28	0.0049 U
Di-n-butyl phthalate	84-74-2	0.057	28	0.0049 U
2,4-Dinitrotoluene	121-14-2	0.32	140	0.0049 U
Di-n-octyl phthalate	117-84-0	0.017	28	0.0049 U

Table 6. (contd)

Organic Constituent (common name)	CAS Number	Wastewater Standard (mg/L)	Non-Wastewater Standard (mg/kg)	Result (mg/L)
Endrin	72-20-8	0.0028	0.13	0.000250 U
Ethyl acetate	141-78-6	0.34	33	0.0020 U
Ethyl benzene	100-41-4	0.057	10	0.0010 U
Ethyl ether	60-29-7	0.12	160	0.0010 U
Fluoranthene	206-44-0	0.068	3.4	0.0049 U
Heptachlor	76-44-8	0.0012	0.066	0.000125 U
Hexachlorobutadiene	87-68-3	0.055	5.6	0.0049 U
Hexachloroethane	67-72-1	0.055	30	0.0049 U
Indeno(1,2,3-c,d) pyrene	193-39-5	0.0055	3.4	0.0049 U
Isobutyl alcohol	78-83-1	5.6	170	0.010 U
Methanol	67-56-1	5.6	0.75 (mg/L TCLP)	5.00 U
Methylene chloride	75-09-2	0.089	30	0.0010 U
Methyl ethyl ketone	78-93-3	0.28	36	**0.024**
Methyl isobutyl ketone	108-10-1	0.14	33	0.0020 U
Naphthalene	91-20-3	0.059	5.6	0.0049 U
Nitrobenzene	98-95-3	0.068	14	**0.0611**
o-Nitrophenol	88-75-5	0.028	13	**0.0419**
Total PCBs	1336-36-3	0.10	10	0.0500 U
Phenol	108-95-2	0.039	6.2	0.0049 U
Pyrene	129-00-0	0.067	8.2	0.0049 U
Pyridine	110-86-1	0.014	16	**1.360 E**
Tetrachloroethylene	127-18-4	0.056	6.0	0.0010 U
Toluene	108-88-3	0.080	10	**0.0078**
1,1,1-Trichloroethane	71-55-6	0.054	6.0	0.0010 U
1,1,2-Trichloroethane	79-00-5	0.054	6.0	0.0010 U
Trichloroethylene	79-01-6	0.054	6.0	0.0010 U
Trichlorofluoromethane	75-69-4	0.020	30	0.0010 U
2,4,5-Trichlorophenol	95-95-4	0.18	7.4	0.0049 U
2,4,6-Trichlorophenol	88-06-2	0.035	7.4	0.0049 U
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.057	30	0.0010 U
Vinyl chloride	75-01-4	0.27	6.0	0.0010 U

CAS Number is a unique numerical identifier assigned by the Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature
U = indicates compound not detected at the reported concentration
E = concentration exceeded the calibration range

3.2 Cast Stone Monolith TCLP Testing Results

Results of the TCLP testing are shown in Table 7 along with the Universal Treatment Standards (40 CFR 268.48). None of the analytes exceeded their Universal Treatment Standard. All constituents with measureable results were an order of magnitude or less than their standards. All other constituents were below their detection limits.

Table 7. TCLP Results Compared to Universal Treatment Standards for Inorganic Constituents in Nonwastewater (40 CFR 268.48)

Regulated Constituent	Universal Treatment Standard (mg/L TCLP)	Sample Result 18-CEW-TB1-1 (mg/L)	Sample Result 18-CEW-TB1-2 (mg/L)	Average (mg/L)
Antimony (Sb)	1.15	<0.0250	<0.0250	<0.0250
Arsenic (As)	5.0	<0.0250	<0.0250	<0.0250
Barium (Ba)	21	0.536	0.525	0.531
Beryllium (Be)	1.22	<0.00500	<0.00500	<0.00500
Cadmium (Cd)	0.11	<0.00500	<0.00500	<0.00500
Chromium (Cr)	0.60	0.0537	0.0573	0.0555
Cyanides (CN-total)	590	0.402	0.389	0.396
Fluoride (F)	NA	2.09	1.84	1.97
Lead (Pb)	0.75	<0.00750	<0.00750	<0.00750
Mercury (Hg)	0.025	<0.000100	<0.000100	<0.000100
Nickel (Ni)	11	0.245	0.234	0.240
Selenium (Se)	5.7	0.0294 J	0.0313 J	0.0304
Silver (Ag)	0.14	<0.0100	<0.0100	<0.0100
Thallium (Tl)	0.2	<0.0750	<0.0750	<0.0750
Vanadium (V)	1.6	0.0359	0.0371	0.0365
Zinc (Zn)	4.3	0.435	0.484	0.460

J = result is greater than or equal to the limit of detection and less than the limit of quantitation
NA – not applicable

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40 CFR 268.48 - Universal Treatment Standards. https://www.gpo.gov/fdsys/pkg/CFR-2010-title40-vol26/pdf/CFR-2010-title40-vol26-sec268-48.pdf.

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