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EFFLUENT TESTING FOR THE OAK RIDGE
MIXED WASTE INCINERATOR:
EMISSIONS TEST FOR AUGUST 27, 1990

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EXECUTIVE SUMMARY

On August 27, 1990, a special emissions test was performed at the K-1435 Toxic Substance Control Act Mixed Waste Incinerator. A sampling and analysis plan was implemented to characterize the incinerator waste streams during a 6 hour burn of actual mixed waste. The results of this characterization are summarized in the present report. Significant among the findings is the observation that less than 3% of the uranium fed to the incinerator kiln was discharged as stack emission. This value is consistent with the estimate of 4% or less derived from long-term mass balance of previous operating experience and with the value assumed in the original Environmental Impact Statement.¹ Approximately 1.4% of the total uranium fed to the incinerator kiln appeared in the aqueous scrubber blowdown; about 85% of the total uranium in the aqueous waste was insoluble (i.e., removable by filtration). The majority of the uranium fed to the incinerator kiln appeared in the ash material, apparently associated with phosphorous as a sparingly-soluble species. Many other metals of potential regulatory concern also appeared to concentrate in the ash as sparingly-soluble species, with minimal partition to the aqueous waste. The aqueous waste was discharged to the Central Neutralization Facility where it was effectively treated by coprecipitation with iron. The treated, filtered aqueous effluent met Environmental Protection Agency interim primary drinking water standards for regulated metals.

WASTE FEED DESCRIPTIONS

The waste fed to the primary combustion chamber (PCC) or rotary kiln was a mixture of denatured alcohol and waste oil materials from the Y-12 Plant at Oak Ridge, Tennessee, and the Feed Materials Production Center at Fernald, Ohio. These materials were blended in feed tank T305, and thief samples were taken for waste characterization. The waste oil from the Fernald facility contained significant quantities of 1,1,1-trichloroethene, whereas the Y-12 waste contained appreciable quantities (i.e., >1%) of tetrachloroethane, fluorine, and phosphorus. The results of this analysis are summarized in Table 1 as predicted values (i.e., preburn data). In addition, the waste feed was sampled during the test burn (50 mL subsamples were taken at 30 min intervals during the 6 h burn and were composited). Results on the analyses for this material are summarized as feed analysis in Table 1. In general, agreement is satisfactory between the in-tank preburn analysis and the analysis on the in-test feed material.

The aqueous waste fed to the PCC was derived from a lead nitrate solution remaining from a previous Resource Conservation and Recovery Act (RCRA) air test for lead and beryllium air emissions. The analytical data for this feed material are summarized in Table 2. Again, "predicted value" refers to analysis of the material in feed tank T-307B approximately five months prior to the burn test, whereas "feed analysis" refers to composited sample taken from the feed line during the actual test. In this instance, preburn and in-burn analyses are in only fair agreement, especially for species that may be expected to form sparingly soluble compounds (e.g., Al, Fe, Pb, Mn, Ni, P, and Zn). The increase in the concentration of Fe, Cr, Mn, and Ni in the waste between the preburn and the in-burn analyses may be the result of corrosion of the steel storage tank and the stainless steel agitator and recirculation piping during the prolonged storage period. [The mass ratio of Cr/Ni for the in-burn aqueous waste (1.8) is consistent with that of 304L stainless steel.]

INCINERATOR OPERATING CONDITIONS

The waste streams identified above were fed to the K-1435 incinerator from 10:50 to 17:00 on August 27, 1990. Incinerator operating parameters are summarized in Table 3. The incinerator was operated at Toxic Substance Control Act (TSCA) conditions (i.e., at an elevated temperature relative to that normally used to destroy RCRA waste).

AIR EMISSIONS SAMPLING

During the August 27 test, 60.1 dry standard cubic feet (dscf) of incinerator off-gas was pulled through an isokinetic gas sampling train. A total of 364 μg of uranium was collected, all of this as particulate material on the inner walls of the probe or on the filter. Thus, the concentration of uranium was 6.06 $\mu\text{g/dscf}$. The flow rate of off-gas from the incinerator was 467,000 dscf/h. Therefore, the discharge rate for uranium during this test was 2.83 g/h. From the feed analysis (Tables 1 and 2) and the feed rate data (Table 3), the average uranium fed to the incinerator during this interval was 96.6 g/h. Thus, the uranium stack emission was

Table 1. Waste characterization analysis

Analysis	Units	Primary Feed (8/27/90)	
		Predicted Value ^a	Feed Analysis (900905-113) ^b
Al	μg/g	28	22
Ba	μg/g	5.8	5.4
Be	μg/g	0.27	0.31
Cd	μg/g	0.30	<0.3
Cl	μg/g	17,500	22,000
Cr	μg/g	257.5	440
Cu	μg/g	13	33
Fe	μg/g	1580	1800
Hg	μg/g	0.5	<0.5
Mn	μg/g	49	91
Na	μg/g	75	42
Ni	μg/g	430	640
P	μg/g	6950	5100
Pb	μg/g	17	23
U (polar)	μg/g	813	918
Zn	μg/g	50.8	61
Alpha act.	pCi/g	548 (±13)	280 (±5)
Beta act.	pCi/g	918 (±17)	560 (±6.5)
Np-237	pCi/g	-0.225 (±0.88)	0.12 (±0.18)
Pa-234m	pCi/g	418 (±11)	560 (±30)
Tc-99	pCi/g	180 (±140)	270 (±110)
Th-234	pCi/g	268 (±1.8)	360 (±5.2)
U alpha	pCi/g	635 (±20)	380 (±8)
U-235	wt. % (isotopic)	0.42	0.41 (±0.02)
U-235	pCi/g		2.58 (±0.28)

^a Average value for thief samples taken from blend tank prior to burn (AnaLIS IDs: 900814-246-249).

^b Composited samples taken from feed line during burn campaign.

Table 2. Aqueous feed characterization

Analysis	Units	Aqueous Feed (8/27/90)	
		Predicted Value ^a	Feed Analysis (900905-114) ^b
Al	mg/L	0.21	21
Ba	mg/L	0.11	0.54
Be	mg/L	<0.003	<0.03
Cd	mg/L	<0.03	<0.29
Cl	mg/L	2.7	1370
Cr	mg/L	0.15	43
Cu	mg/L	0.26	8.7
Fe	mg/L	170	1100
Hg	μg/g		<0.5
Mn	mg/L	0.40	22
Na	mg/L	440	440
Ni	mg/L	0.69	25
P	mg/L	4.5	120
Pb	mg/L	426	160
Zn	mg/L	1.6	58
Alpha act.	pCi/g	NR ^c	6.8 (±0.8)
Beta act.	pCi/g	NR	14 (±1.1)
Np-237	pCi/g	NR	0.03 (±0.11)
Tc-99	pCi/g	NR	-9.5 (±7.8)
U alpha	pCi/g	NR	0.37 (±0.75)
U (polar)	μg/g	NR	1.5
U-235	wt. % (isotopic)	NR	0.92
U-235	pCi/g	NR	0.35 (±0.75)

^a Average value for thief samples taken from blend tank prior to burn (AnaLIS IDs: 900411-079; 900330-133).

^b Composited samples taken from feed line during burn campaign.

^c NR indicates value not recorded.

Table 3. Radionuclides emissions test process conditions

Parameter	N	Mean	Min	Max	St Dev
Kiln temperature, °F	26	1,847	1,835	1,861	6.0
SCC temperature, °F	26	2,176	2,151	2,211	22.0
PCC liquid waste feed rate, lb/hr	26	232.0	210.0	262.0	15.0
SCC liquid waste feed rate, lb/hr	0	0.0	0.0	0.0	0.0
Aqueous waste feed rate, lb/hr	26	126.0	104.0	148.0	9.0
Sludge waste feed rate, lb/hr	0	0.0	0.0	0.0	0.0
Solid waste feed rate, lb/hr	--	0.0	--	--	--
Kiln natural gas rate, mscfh	26	10,927	10,020	12,100	465
SCC natural gas rate, mscfh	26	12,520	8,910	14,640	1,250
Kiln face pressure, in wc	26	-0.2	-0.5	-0.1	0.1
Quench temperature, °F	26	182.0	177.0	184.0	3.0
Quench recycle flow, gpm	26	124.2	122.9	125.9	0.9
Venturi pressure differential, in wc	26	8.8	7.52	9.11	0.47
Venturi recycle flow, gpm	26	157.0	155.0	158.0	1.0
Packed bed recycle flow, gpm	26	194.0	194.0	195.0	0.0
Packed bed pH	26	7.0	6.7	7.3	0.2
IWS #1 recycle flow, gpm	26	530.0	509.0	816.0	59.0
IWS #2 recycle flow, gpm	26	534.0	512.0	542.0	6.0
IWS #1 voltage, kv	26	22.1	0.0	26.1	4.9
IWS #2 voltage, kv	26	22.8	0.0	27.0	4.9
Total APC system blowdown, gpm	26	16.3	8.8	21.7	4.0
Combustion gas velocity, ft/sec	26	23.1	21.2	24.1	0.7
Stack gas CO concentration, ppmv ^a	26	1.2	0.0	3.0	0.9
Stack gas O ₂ concentration, % vol ^a	26	10.9	10.0	11.8	0.5
Stack gas CO ₂ concentration, % vol ^a	26	6.3	0.0	7.3	1.3

^a(Gas analyses are on a dry volume basis.)

about 2.9% of the total amount fed. This value is consistent with an estimate of 4% or less derived from long-term mass balance of previous operating experience and with the value of 3.6% assumed in the original Environmental Impact Statement.¹

The radioactivity collected in the off-gas sampling system was analyzed to estimate the emission rates for radionuclides; this data is summarized below. During this test, the only statistically significant radioactivity in the air emission was alpha radiation from uranium and beta radiation from its short-lived daughter products (e.g., Th-234):

Radionuclide emissions

Contaminant	Stack emission rate ($\mu\text{Ci/hr}$)
Alpha activity	9.17 ± 1.54
Beta activity	14.2 ± 22.7
Tc-99	27.4 ± 20.8
Cs-137	2.11 ± 2.80
Th-234	7.36 ± 4.35
Pa-234	75.7 ± 175

The actual air emission rates for other metals were not determined for the August 27, 1990, test. The aqueous feed (Table 2) was a lead nitrate solution left over from a lead and beryllium air emissions test performed June 19-21, 1990. This earlier testing was performed under RCRA conditions—PCC at 1600°F and secondary combustion chamber (SCC) at 1900°F, compared to PCC at 1850°F and SCC at 2175°F for the present test (see Table 3). The partitioning of the total Be fed to the incinerator was determined to be $(0.70 \pm 0.11)\%$ to air emissions and $(6.2 \pm 6.3)\%$ to the aqueous blowdown, whereas the corresponding partition of the total lead fed to the incinerator was $(0.94 \pm 0.05)\%$ to air emissions and $(12.5 \pm 0.9)\%$ to the aqueous blowdown. Based on mass balance considerations, it may be inferred that the preponderance (>80 to 90%) of beryllium and lead were concentrated to the ash waste or residual slag.

AQUEOUS BLOWDOWN

The aqueous effluent from the incinerator results from use of wet scrubbers to remove contaminants (especially acid gases) from the combustion gases produced in the thermal destruction of hazardous and toxic wastes (see Fig. 1). The scrubber fluid is recirculated,

Fig. 1. TSCA incinerator.

concentrating soluble constituents and entrained particulates. A portion of the scrubber fluid (blowdown) is removed, and fresh scrubber fluid (makeup) is added. The discharged air pollution control (APC) system blowdown (about 16.25 ± 4.0 gal/min during the reported testing; see Table 3) is collected in one of two purge sumps—T-602A or T-602B, each with a nominal capacity of 30,000 gal. The surge tank is sampled for polychlorinated biphenyls (PCBs). If the analysis indicates less than 1 part per billion (ppb) of PCBs, the effluent is transferred directly to the F-240B neutralization tank at the Central Neutralization Facility (CNF). If the criterion for PCBs is exceeded, the effluent is recirculated through packed-bed activated carbon columns to sorb the PCBs before the effluent is transferred to the CNF.

The TSCA Incinerator has partially implemented the changes recommended by Dr. Roger Anderson to optimize performance of the wet scrubber system and to minimize the environmental effect of the incinerator blowdown.² These changes included an alteration in blowdown valving to improve control of scrubber fluid flow and solution pH at the ionizing wet scrubber (IWS) and packed bed scrubber. Spent scrubber fluid is recirculated to the quench chamber prior to blowdown.

Analysis of the combined quench water blowdown composite sample collected during the emissions test is given in Table 4. An aliquot of the slurried sample was filtered through a $0.45\text{-}\mu\text{m}$ membrane to determine the fraction of total constituents that are soluble in the blowdown effluent; this information is also summarized in Table 4. In general, many species of potential regulatory concern are present in the quench blowdown at relatively low concentrations and are predominantly in the form of insoluble particulates, presumably from entrained ash from the kiln. An exception is Tc-99, which is essentially soluble in the quench blowdown.

A partition coefficient can be defined operationally as the fraction of total constituent fed to the incinerator that appears in a given effluent stream. Estimates for the partition of selected constituents into the quench water blowdown during the emissions test are given in Table 5. Most metals of potential regulatory concern do not partition well into the aqueous effluent, especially in the form of soluble constituents.

The IWS blowdown line was independently sampled, and the data are summarized in Table 6. Data are similar to those from the total quench blowdown (Table 5). In general, however, most constituents demonstrate a lower total concentration (but a higher soluble fraction) for the IWS blowdown than for the total quench blowdown.

TREATMENT OF THE TSCA AQUEOUS EFFLUENT AT THE CNF

Table 7 reports the analytical results for TSCA aqueous effluent as it was transferred to the CNF and treated. TSCA sump (T602A) samples in Table 7 are grab samples (see Fig. 2), representing the first 9,000 gal of blowdown on August 27, 1990. [Note: It is difficult to obtain a truly representative sample from a large tank, especially when the sample contains suspended solid material.] The contents of this sump were transferred to CNF tank 240B. As-received samples in the table are grab samples from the bottom of the CNF tank before treatment chemicals were added.

Table 4. Quench water blowdown characterization

Analysis	Units	Quench Water Blowdown (8/27/90)		
		Raw (900905-108)	Filtered ^a (900905-109)	Fraction Soluble (Filtered/Raw)
Al	mg/L	2.6	0.14	0.054
Ba	mg/L	0.55	0.011	0.020
Be	mg/L	0.021	<0.0003	<0.014
Ca	mg/L	210	52	0.25
Cd	mg/L	0.0089	<0.003	<0.34
Cl	mg/L	2590	1850	0.71
Co	mg/L	0.014	<0.005	<0.35
Cr	mg/L	0.33	<0.01	<0.03
Cu	mg/L	1.0	0.052	0.05
Fe	mg/L	51	0.35	0.007
Hg	mg/L	<0.002	<0.002	
Mn	mg/L	0.65	0.013	0.02
Na	mg/L	1400	1300	0.93
Ni	mg/L	0.29	0.024	0.08
P	mg/L	220	46	0.21
Pb	mg/L	1.6	<0.05	<0.03
Zn	mg/L	3.1	0.089	0.03
U (fluor)	mg/L	0.366	0.054	0.15
Alpha act.	pCi/L	1.05E4 ($\pm 6.4E2$)	3.55E2 ($\pm 1.6E2$)	0.034 (± 0.015)
Beta act.	pCi/L	3.25E4 ($\pm 1.2E3$)	5.29E3 ($\pm 5.6E2$)	0.16 (± 0.02)
Tc-99	pCi/L	5.52E3 ($\pm 2.3E3$)	5.98E3 ($\pm 2.3E3$)	1.08 (± 0.61)
U alpha	pCi/L	1.08E4 ($\pm 2.3E2$)	2.28E0 ($\pm 1.4E1$)	0.0002 (± 0.0013)

^aFiltered through 0.45 μ m Nalge membrane.

Table 5. Partition of constituents into quench water blowdown

Analysis	Quench Water (8/27/90) Composition (mg/L)		Partition Coefficient	
	Predicted ^a	Actual (Total)	As Total Constituent	As Soluble Constituent
Al	13.7	2.6	0.20	0.01
As	<0.10	<0.10		
Ba	2.3	0.55	0.24	0.005
Be	0.11	0.021	0.19	<0.0026
Cd	0.19	0.045	0.047	<0.016
Cl	9320	2590	0.28	0.20
Cr	190.0 ^b	0.33	0.0017	<0.00005
Cu	15.4	1.0	0.065	0.0034
Fe	981	51	0.052	0.0004
Hg	<0.2	<0.002		
Mn	42	0.65	0.015	0.0003
Na	115	1400		
Ni	268.0 ^b	0.29	0.001	0.00009
Pb	45.0 ^b	1.6	0.036	<0.001
U	377	0.366	0.001	0.0001
Zn	38.0 ^b	3.1	0.082	0.002

^aPredicted on basis of 100% partition of constituent from feed materials to aqueous waste stream (using in-burn feed composition).

^bPredicted value exceeds CNF acceptance criterion.

Table 6. IWS blowdown characterization

Analysis	Units	IWS Blowdown (8/27/90)		Fraction Soluble (Filtered/Raw)
		Raw (900905-110)	Filtered ^a (900905-111)	
Al	mg/L	0.95	<0.20	<0.21
Ba	mg/L	0.089	<0.01	<0.11
Be	mg/L	0.013	<0.003	<0.23
Ca	mg/L	32	14	0.44
Cd	mg/L	<0.030	<0.030	
Ce	mg/L	208	207	0.995
Cl	mg/L	0.20	0.13	0.65
Co	mg/L	<0.050	<0.050	
Cu	mg/L	0.83	0.11	0.13
Fe	mg/L	25	0.60	0.024
Hg	mg/L	<0.002	<0.002	
Mn	mg/L	0.41	0.034	0.08
Na	mg/L	530	520	0.98
Ni	mg/L	0.24	0.10	0.41
P	mg/L	350	300	0.86
Pb	mg/L	1.5	0.054	0.036
U (fluor)	mg/L	2.21	0.573	0.26
Zn	mg/L	2.1	0.36	0.17
Alpha act.	pCi/L	7.63E3 ($\pm 5.5E2$)	7.58E2 ($\pm 2.1E2$)	0.099 (± 0.028)
Beta act.	pCi/L	1.34E4 ($\pm 7.9E2$)	5.38E3 ($\pm 5.7E2$)	0.40 (± 0.05)
Tc-99	pCi/L	4.09E3 ($\pm 2.2E3$)	4.13E3 ($\pm 2.2E3$)	1.01 (± 0.76)
U alpha	pCi/L	6.40E3 ($\pm 1.7E2$)	3.69E2 ($\pm 3.9E1$)	0.058 (± 0.006)

^aFiltered through 0.45 μ m Nalge membrane.

Table 7. TSCA aqueous effluent characterization

Analysis	Units	TSCA Sump T602A ^a	CNF Tank 240B			Drinking Water Standard
			As Received ^b	As Treated ^c	Treated & Filtered ^d	
Al	mg/L	0.021	0.32	0.75	0.041	--
Ba	mg/L	0.014	0.062	0.070	0.008	1.0 ^e
Be	mg/L	<0.0003	0.0012	0.0012	<0.0003	--
Ca	mg/L	44	73	150	94	--
Cd	mg/L	<0.003	0.0030	<0.003	<0.003	0.01 ^e
Cl	mg/L	469	463	565	558	250 ^f
Co	mg/L	<0.05	0.005	0.0072	<0.005	--
Cr	mg/L	0.056	0.042	0.042	<0.010	0.05 ^{e,f}
Cu	mg/L	0.013	0.062	0.24	0.023	1.0 ^g
Fe	mg/L	0.14	7.2	21	<0.004	0.3 ^g
Hg	mg/L	<0.0004	<0.0004	<0.0004	<0.0004	0.002 ^e
Mn	mg/L	0.0033	0.074	0.14	0.0033	0.05 ^g
Na	mg/L	290	300	290	290	--
Ni	mg/L	<0.010	0.030	0.034	<0.010	--
P	mg/L	18	28	29	2.6	--
Pb	mg/L	<0.050	0.11	0.26	<0.050	0.05 ^e
U (fluor)	mg/L	0.039	2.05	3.05	0.047	--
Zn	mg/L	0.0033	0.25	0.34	0.0056	5.0 ^g
Alpha act.	pCi/g	0.048 (±0.087)	1.00 (±0.17)	1.70 (±0.22)	-0.007 (±0.079)	--
Beta act.	pCi/g	1.50 (±0.26)	3.40 (±0.33)	4.90 (±0.37)	0.130 (±0.26)	--
Np-237	pCi/g	0.00 (±0.034)	0.011 (±0.055)	0.010 (±0.020)	0.00 (±0.030)	--
Tc-99	pCi/g	--	--	--	--	--
Th-234	pCi/g	1.20 ± 0.3	7.10 ± 0.79	2.80 ± 0.82	--	--
U alpha	pCi/g	-0.01 (±0.06)	1.10 (±0.23)	1.40 (±0.27)	0.00 (±0.068)	--

^aGrab sample from TSCA sump T602A at 16:30 on August 27, 1990, representing the first 9,000 gal of blowdown (900905-102).

^bGrab sample from the bottom of CNF tank 240B before treatment (900905-104).

^cUnfiltered sample slurry after treatment [nominal Fe(III) dosage, 15 mg/L] and polymer addition at CNF tank 240B (900905-105).

^dTreated sample after filtration through 0.45 μ m membrane (900905-106).

^eEPA interim primary drinking water standard (maximum level).

^fDrinking water standard limit for hexavalent chromium [Cr(VI)].

^gEPA proposed secondary drinking water standard (maximum level).

Fig. 2. Liquid waste management system for the TSCA incinerator.

The treatment protocol employed at the CNF consisted of coprecipitation with ferric iron. A similar treatment has been demonstrated to be cost-effective for the removal of trace elements (especially heavy metals) from power plant discharges.³ Specific treatment protocol at the CNF consisted of (1) lowering the pH to a value between 4.5 and 5.5 by addition of HCl; (2) treatment with commercial ferrifloc reagent $[\text{Fe}_2(\text{SO}_4)_3]$ to a dosage of 0.4 lb/1,000 gal [to give a Fe(III) concentration of about 14 mg/L]; (3) mixing via air sparge; (4) addition of lime slurry to readjust pH to a value between 7.5 and 8.5; (5) addition of Betz 1138 polymer (to enhance flocculation of coprecipitated metals) at a dosage of about 10 mg/L; and (6) solids removal by use of a sludge thickener and pressure filtration.

The samples labeled "As Treated" in Table 8 represent the treated TSCA effluent before sample filtration. A comparison of the Fe analysis for the "As Received" and the "As Treated" samples in Table 7 indicates that 13.8 mg/L Fe was added, in excellent agreement with the prescribed amount of 14 mg/L. The samples in Table 7 labeled "Treated and Filtered" represent the treated, filtered TSCA effluent. Comparison with drinking water standards indicates that the criteria for metals have been met through use of the CNF treatment.

Table 8 summarizes the treatment of the TSCA aqueous effluent at CNF in terms of removal efficiency (after solids removal); for most species of potential regulatory concern, the removal efficiency was in excess of 80 to 90%.

EXAMINATION OF ASH AND RELATED MATERIAL

The ash content for the feed materials used in the August 27, 1990, test was relatively low; estimates are 0.93 wt % ash for the primary feed material and 0.13 wt % ash for the aqueous waste. Therefore, total ash production during the 6 h test burn would only have been about 14 lb (6,330 g). Due to the manner in which the ash was collected in the wet ash handling system, ash from the August 27, 1990, test was contaminated with ash from previous campaigns, notably with ash from the June 19-21, 1990, air emissions tests. In these tests soil was added as an inert solid feed, thus generating a considerable volume of ash material. For reference purposes, bulk analysis for ash collected on June 21, 1990, is given in Table 9, together with some results from the Toxicity Characteristic Leaching Procedure (TCLP) extraction test used by the Environmental Protection Agency (EPA) to define leachate toxicity. The bulk analysis for this particular ash material was dominated by the constituents from the soil feed (e.g., high concentrations of iron and aluminum). The ash of June 21, 1990, was not hazardous according to the TCLP criteria.

When the TSCA Incinerator kiln temperature was raised from RCRA conditions to the higher TSCA conditions, some melting of slag in the kiln occurred, with a resultant deslagging of material to the ash handling system. Wet ash collected on August 27, 1990, thus contained ash from that day's burn, probably contaminated with ash from the June 1990 testing and with slag accumulated from previous burns. Ash material submitted for analysis was processed by physical removal of large slag chunks, filtration to remove the majority of the associated ash water, drying, and sieving through an 80-mesh screen. Analysis results for

Table 8. Treatment of the TSCA aqueous effluent at the CNF

Emissions Test (8/27/90)	
Analysis	CNF Treatment: Removal Efficiency (%) ^a
Ba	89
Be	>75
Cr	>76
Cu	90
Mn	98
Ni	>70
P	91
Pb	>80
U	98
Zn	98
Alpha activity	~100
Beta activity	97

^aComputed as $100\% \times \{1 - [\text{Treated and Filtered Sample}] / [\text{As-Treated Sample}]\}$; see Table 7.

Table 9. Analysis of ash from air emissions test (June 21, 1990)

Analysis	Raw Ash (900629-255) ($\mu\text{g/g}$)	TCLP Extract	
		From Raw Ash (900629-256) (mg/L)	Regulatory Limit (mg/L)
As	3.1	0.048	5.0
Ba	10	0.051	100
Cd	0.40	<0.003	1.0
Cr	2.3	<0.010	5.0
Pb	21	0.16	5.0
Hg	<1.0	<0.0002	0.2
Se	<0.5	<0.005	1.0
Ag	<0.77	<0.006	5.0
Al	1300	0.053	
Be	0.051	<0.0003	
Fe	3300	0.053	
Ni	3.8	0.047	
P	640	NR ^a	
U	181	0.155	
Zn	8.2	0.078	

^aNR = Not Recorded

the processed ash sample are summarized in Table 10, along with an analysis of the filtered ash water. [Note: The value for uranium alpha activity reported for raw ash sample 900905-107 is inconsistent with the U concentration and the total alpha activity, and is presumed to be incorrect.] This bulk analysis is of limited value for mass balance computations, but the data do suggest that many metals of potential regulatory concern accumulate in the ash handling system and that in general these metals are only sparingly soluble, as indicated by the ash water analysis.

Particulate material filtered from the scrubber blowdown (see Tables 5 and 7) is believed to originate from entrained ash and may give the best index to ash generated during the August 27, 1990, test. Microcharacterization of bulk ash, slag, and material collected from filtration of scrubber blowdown is described in detail in the Appendix prepared by Dr. D. P. Hoffmann. Significant findings include the facts that (1) Cr in the ash material appears to originate from steel corrosion (see also the discussion of aqueous feed sample, above); and (2) uranium-containing particles collected on the blowdown filter medium had particle sizes in the range of 0.5 to 3.0 microns and were associated with phosphorus, with the species uranyl oxonium phosphate hydrate⁴ being identified by X-ray diffraction analysis.

Table 10. Processed ash characterization

Analysis	Units	TSCA Ash (8/27/90)		Drinking Water Standards
		Raw Ash Sample (900905-107)	Filtered Ash Water (900905-112)	
Al	μg/g	27000	0.22	
Ba	μg/g	71	0.042	1.0 ^a
Be	μg/g	27	<0.0003	
Cd	μg/g	6.9	<0.003	0.01 ^a
Cl	μg/g	14	13	250 ^b
Cr	μg/g	100	<0.01	0.05 ^{a,c}
Co	μg/g	7.6	<0.005	
Cu	μg/g	130	<0.004	1.0 ^b
Fe	μg/g	83000	0.031	0.3 ^b
Hg	μg/g		<0.002	0.002 ^a
Mn	μg/g	480	0.0043	0.05 ^b
Na	μg/g	1200	8.1	
Ni	μg/g	790	<0.01	
P	μg/g	10000	0.76	
Pb	μg/g	160	<0.05	0.05 ^a
U (fluor)	μg/g	1192	0.328	
Zn	μg/g	260	0.042	5.0 ^a
Alpha act.	pCi/g	1.30E2 (±7.5)	7.78E-1 (±2.1E-1)	
Beta act.	pCi/g	2.58E2 (±10)	1.14E0 (±4.0E-1)	
Np-237	pCi/g		1.04E-3 (±3.6E-3)	
Tc-99	pCi/g		-1.49E0 (±2.0E0)	
U alpha	pCi/g	-4.79 (±2.9)	2.39E-1 (±3.3E-2)	
U-235	wt. % (isotopic)	0.60		

^aEPA interim primary drinking water standard (maximum level).^bEPA proposed secondary drinking water standard (maximum level).^cDrinking water standard limit for hexavalent chromium [Cr(VI)].

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APPENDIX

**CHARACTERIZATION OF TSCA ASH
RADIONUCLIDE EMISSIONS TEST**

**CHARACTERIZATION OF TSCA ASH
RADIONUCLIDE EMISSIONS TEST**

August 27, 1990

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I would like to acknowledge the assistance of the following people in the collection of the data and the production of this report.

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Ruben Melton

BACKGROUND

The Surface Analysis Group received samples of ash and filtered suspended solids from the August 27, 1990, radionuclide emission test for characterization. The ash sample had been collected from the wet ash handling system. It was subdivided (by J. L. Shoemaker) into three categories: (1) material larger than 4 mesh, (2) material between 4 and 80 mesh, and (3) material smaller than 80 mesh. The filtered samples were of suspended solids from the quench blowdown and the ionizing wet scrubber aqueous solutions.

Dr. Bostick informed us that the ash was from an incineration of radioactively contaminated liquids, and that slag from inside of the rotary kiln had become loose and was collected with the ash. So the sample should have contained ash representative of the test burn plus, possibly, slag material formed from many burn scenarios and residual ash from the previous burn.

The purpose of our investigation was to characterize the ash, slag, and filter material in order to complement the analytical chemistry data being collected. The main objectives of this investigation were to:

- determine which crystalline phases, if any, were present in the ash, slag, and filter material;
- identify elemental distributions for the various ash, slag, and filter samples; and
- search for and determine the particle size and common elemental associations for elements of interest (e.g., Cr, Ni, Zn, Tc, Pb, Hg, Th, U).

In order to accomplish these tasks, a multi-technique approach was used. X-ray diffraction (XRD) was used to identify crystalline phases. Use of Scanning Electron Microscopy (SEM), utilizing both Secondary Electron Imaging (SEI) and Backscattered Electron Imaging (BEI) in conjunction with Energy Dispersive X-ray Analysis (EDS), allowed analysis of morphology, particle size, and elemental distributions.

RESULTS

GENERAL

The ash material received was identified by the code of 221-115-80(P). Figure A.1 reproduces a photograph of the large ash material. The majority of the larger pieces were identified as slag material because of their glassy and multi-layered appearance. The largest slag piece was approximately 6 cm on each side. Figure A.2 duplicates a photograph of the medium-sized ash particles. Inspection of these particles revealed a mixture of slag-like and ash-like materials. When examined by optical microscopy, the smaller than 80 mesh material was similar in appearance to the medium-sized ash material, but seemed to have a higher ash content.

A-2

Figure A.1
Photograph of Large Slag Material

Figure A.2
Photograph of Medium Size Slag Material

The two filtered, suspended solids were identified as follows:

- #221-1151 for the quench blowdown (QBD) and
- #221-1152 for the ionizing wet scrubber (IWS).

The QBD filter material was a gray, pasty material that showed extensive mud-flat cracking when dried. The IWS filter material was sandy-brown in color and appeared to be much finer in texture than the QBD material.

SLAG CHARACTERIZATION

Through inspection of the slag material, several representative forms could be identified. The four most prevalent types (labeled on Fig. A.1) were chosen for characterization. The samples were polished cross-sectionally to allow examination by EDS to check the homogeneity. XRD was used where applicable to identify any crystalline phases present.

Figure A.3 shows a polished cross section of slag (#1) with five regions (a through e) labeled on the figure. The elemental distributions for these regions are listed in the figure caption. With the exception of a trace of phosphorous in regions C and D, the elemental character of the material is fairly uniform. The relative distribution of the elements was found to vary from region to region. XRD determined the black material on the outer surface of the slag to be amorphous in nature, as might be expected given its glassy appearance. The white material encapsulated by the black glassy material was identified by XRD as being Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$, JCPDS #15-776). The comment section of the JCPDS card file indicated that mullite is formed from a stoichiometric amount of Al_2O_3 and SiO_2 being repeatedly ground and heated. This action is consistent with the nature of the ISCA rotary kiln for slag material, and the results agree with those of the EDS analysis.

Figure A.4 shows a polished cross section of a second slag (#2) sample with five regions (a through e) labeled on the figure. The elemental distributions for these regions are listed in the figure caption. With the exception of region B, all regions appear similar in elemental composition. XRD determined the crystalline phase Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$, JCPDS #20-20) was present.

Figure A.5 shows a polished cross section of a third slag (#3) sample with four regions (a through d) labeled on the figure. Elemental distributions are listed in the figure caption for the four regions. Note the calcium-rich nature of regions B, C, and D compared to the aluminum- and silicon-rich nature of region A. No XRD was collected on this sample.

Figure A.6 shows a polished cross section of a fourth slag (#4) sample with four regions (a through d) labeled on the figure. The results of the EDS analysis for the four regions are listed in the figure caption. All regions showed different distributions. No XRD was collected on this sample.

Figure A3

Polished slag cross-section (#1, Figure A1). The elemental distributions of the labeled region are listed below in order of decreasing peak intensity.

a: Al, Si, Ti, Fe, Ca, K
b: Si, Al, Ti, Ca, Fe, K
c: Ca, Fe, Si, Ti, Al, K
d: Si, Ti, Ca, Al, Fe, K
e: Si, Ca, Al, Ti, Fe, K, P

Figure A.4

Polished slag cross-section (#2, Figure A.1). The elemental distributions of the labeled region are listed below in order of decreasing peak intensity.

- a: Fe, Si, Al, Ca, Ti, K, Mn
- b: Si, Al, Ti, Fe, Ca
- c: Ca, Si, Al, Fe, Ti, K, Cu
- d: Ca, Fe, Si, P, K, Al, Ti, Zn, Mn
- e: Fe, Ca, Si, Al, Ti, K, P, Cu, Zn

Figure A.5
Polished slag cross-section (#3, Figure A.1). The elemental distributions of the labeled region are listed below in order of decreasing peak intensity.

a: Si, Al, Ti, K, Fe, Ca
b: Ca, Fe, Ti, Si, Al, K
c: Ca, Fe, Ti, Si, Al, K
d: Ca, Fe, Ti, Si, P, Al, K

Figure A.6
Polished slag cross-section (#4, Figure A.1). The elemental distributions of the labeled region are listed below in order of decreasing peak intensity.

a: Si, Al, Ca, Ti, Fe, K
b: Ca, Si, Al, Fe
c: Al, Ti, Si, Fe
d: Si, Al, Ti, Fe, K

ASH CHARACTERIZATION

The powder ash material provided to the Surface Analysis Group was ground even finer in an agate mortar and pressed into a pellet (powder pack). The EDS spectrum shown in Fig. A.7 was collected at 20x magnification in order to best represent the bulk sample. Through the use of a standardless semi-quantitative analysis routine the weight percents of select elements could be obtained. Table A.1 lists the weight percents determined by EDS for the ash sample.

Table A.1. Relative weight percents determined by ICP and EDS analysis

Element	ICP	EDS Analysis		
		Ash	QBD	IWS
Mg	1.4	1.2	9.0	0.9
Al	16.7	19.1	0.8	0.3
Si	0.4	36.6	2.9	6.3
P	6.2	2.9	36.1	33.2
Cl	0.01	3.3	2.3	0.0
K	0.5	1.1	0.0	4.9
Ca	22.2	8.9	31.0	15.5
Ti	0.4	0.6	0.0	0.0
Cr	0.06	0.1	0.0	0.0
Fe	51.7	26.3	12.7	26.5
Cu	0.1	0.0	0.0	1.1
Zn	0.2	0.0	1.5	2.5
U	0.7	0.0	3.8	8.9

Also included in Table A.1 are the weight percents obtained by ICP analysis. The ICP results are based on the results for sample 221-115-80P. The weight percent was calculated by setting the summation of the weight determined by ICP for the elements listed to 100%. (*Note:* The detection limit for EDS is approximately 0.1 wt %.) XRD analysis of the sample identified the following phases:

<u>Phase</u>	<u>I/I_{MAX}</u>
SiO ₂	100
Al ₂ O ₃	12
Fe ₂ O ₃	10
CaAl ₂ Si ₂ O ₈	9 ,

where the I/I_{MAX} is determined from the most intense diffraction line with the most intense diffraction line for the sample.

Figure A.7
 EDS spectrum representative of "bulk" ash sample

The smaller-than-80-mesh-ash sample was searched for heavy elements using BEI. Since the contrast of BEI is proportional to the average atomic number (the darker image having the lower atomic number), the sample could be scanned for bright images, and their elemental composition could be identified by EDS. Using this single particle search method, the samples were analyzed for U, Pb, Cr, and any other metal that would be classified as a hazardous material.

Figure A.8.1 shows a BEI micrograph of a chromium-containing material. Figure A.8.2 shows the EDS spectrum representative of the same material. The relative amounts of Cr, Fe, and Ni are representative of steel. For all particle searching on this TSCA sample to date, no free Cr or Ni has been found. All Cr or Ni was associated with Fe and appeared to be an oxidized steel material. During the search individual particles containing Th, Ba, and W were found, but these have been isolated findings.

The two hazardous metals most commonly found in the TSCA ash have been U and Pb. Figure A.9.1 shows a BEI micrograph of a relatively homogenous U-containing particle, and Fig. A.9.2 shows the associated EDS spectrum. Not all the U found was mixed in the ash matrix in a homogenous manner. Figure A.10.1 shows an SEI micrograph of all-containing particle, and Fig. A.10.2 shows a BEI micrograph of the same particle. These micrographs clearly reveal a high level of interaction of U with the ash matrix for this sample. Figure A.10.3 shows the EDS spectrum for this sample.

Particles of Pb closely associated with the ash matrix were also found. Figure A.11.1 shows a SEI and Fig. A.11.2 shows a BEI micrograph of a Pb-containing piece of ash. Figure A.10.6 shows the EDS spectrum of this material.

The ash material was scanned for U- (ICP analysis ~1192 ppm) and Pb- (ICP analysis ~160 ppm) containing particles. The particle size and EDS spectrum of each particle was collected. Table A.2 lists the particle size information and elemental associations for the number of particles found. The elemental association is the percentage of the particles (U or Pb) whose EDS analysis indicated the presence of the particular element. Note that on average Pb particles are larger than U particles, that P was associated with 81% of the U particles, that no P was associated with the Pb particles, and that *no* Cl was found with either set of particles. Al, Si, and Fe are the most common elements in the ash matrix. This finding is consistent with the results listed in Table A.1.

QUENCH BLOWDOWN FILTER CHARACTERIZATION

The QBD filter was analyzed by XRD. The filtered material was primarily amorphous with a few weak diffraction lines. Not enough information was obtainable from the diffraction pattern to make any phase identification. Figure A.12 shows the EDS spectrum that is representative of the bulk filter sample. The results from the standardless analysis are listed in Table A.1. The most notable change is the presence of U. Figure A.13 shows a BEI micrograph of a representative section of the QBD material. All bright particles shown on this micrograph contain uranium. Figure A.14 shows the EDS spectrum from a single U-rich

Figure A.8.1
BEI micrograph of ash material containing Cr.

Figure A.8.2
EDS spectrum of Cr containing ash material show in Figure A.8.1.

Figure A.9.1
BEI micrograph of ash material containing U.

Figure A.9.2
EDS spectrum of U containing ash material shown in Figure A.9.1.

Figure A.10.1
SEI micrograph of ash material containing U.

Figure A.10.2
BEI micrograph of ash material containing U.

Figure A.10.3

EDS spectrum of U containing material shown in Figures A.10.1 and A.10.2.

Figure A.11.1
SEI micrograph of ash material containing Pb.

Figure A.11.2
BEI micrograph of ash material containing Pb.

Figure A.11.3

EDS spectrum of Pb containing material shown in Figures A.11.1 and A.11.2.

Table A.2. Particle size and elemental association information for ash sample

	Uranium	Lead
Number of particles	28	13
Average size (microns)	8.7	14.5
One Sigma ($\pm \sigma$)	4.7	9.1
High value (microns)	25.0	40.0
Low value (microns)	3.0	3.0
Chemical associations (% of particles)		
Al	96	100
Si	100	100
Cl	0	0
P	81	0
Ca	70	82
Fe	100	100
Cr	4	0
Ni	8	0
Zn	11	0

Figure A.12
EDS spectrum representative of "bulk" QBD filter

Figure A.13
BEI micrograph of QBD filter material

Figure A.14
EDS spectrum of a single U particle on QBD filter.

particle. The EDS spectrum suggests that this particle is a U-P phase. The particle size of the U phase ranged from 0.5 to 3.0 microns, with the average being approximately 2.0 microns.

IONIZING WET SCRUBBER FILTER CHARACTERIZATION

The material from the filter was analyzed by EDS in a bulk analysis mode. Figure A.15 shows the EDS spectrum representative of the IWS material. The results of the standardless analysis are listed in Table A.1. Note the increase in the relative amount of U. Figure A.16 shows a BEI micrograph of a representative section of the IWS material. All bright particles seen on this micrograph contain U. An EDS spectrum of a single U particle is shown in Fig. A.17. The particle size of the U phase ranged from 0.5 to 3.0 microns, with the average being approximately 2.0 microns. This range is consistent with that of the material from the QBD filter. The IWS filter was analyzed by XRD. The diffraction pattern collected was determined to be a U-P phase. All 24 peaks that were collected matched with the phase of uranyl oxonium phosphate hydrate ($\text{H}_3\text{O}(\text{UO}_2)(\text{PO}_4) \cdot 3\text{-xH}_2\text{O}$, JCPDS #37-374). This finding is consistent with that of the EDS analysis for the single particle.

CONCLUSIONS

These results show a great deal of heterogeneity in the slag material. The presence of Al, Si, Ca, and Fe in all samples suggests that these elements may be originating in the rotary kiln (i.e., due to slag or past incineration material), as well as in the feed material.

The ash material proved to be rich in Al, Si, and Fe. Several elemental associations of importance were determined. Cl was found in the ash material, but was never determined to be associated with U, Pb, or Cr. The U particles were found to be associated with P (81% of the U particles), whereas the Pb particles had no association with P. The particle size for the U and Pb particles found indicated that the average size of the Pb particles was slightly larger than that of the U particles.

Both the QBD and IWS filters had highly dispersed (0.5 to 3.0 micron) U particles. The EDS analysis of individual U particles showed that U was associated primarily with P. This finding agrees with that of the XRD analysis of the IWS filter material, which found a uranyl oxonium phosphate hydrate.

Figure A.15
EDS spectrum representative of "bulk" IWS filter.

Figure A.16
BEI micrograph of IWS filter material

Figure A.17
EDS spectrum of single U particle on IWS filter.

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