Los Alamos
NATIONAL LABORATORY

Environment, Safety And Health Division
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Date: September 26, 1995
In Reply Refer To: ESH-DO:95-473
Mail Stop: K491
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TA-55

Larry Kirkman
Acting Area Manager
U. S. Department of Energy
Los Alamos Area Office
528 36th Street, MS A316
Los Alamos, New Mexico 87544

Dear Mr. Kirkman:

SUBJECT: LANL POSITION ON CHROMIUM WASTE IN TA-55 EVAPORATOR BOTTOMS

Enclosed is the letter and supporting documentation to demonstrate that the chromium waste in the evaporator bottoms generated from the nitrate-based aqueous process at TA-55 should meet the exclusion for chromium waste for trivalent chromium 20 NMAC 4.1, Subpart II, 261.4(b)(i). Also enclosed is the draft submittal letter to the New Mexico Environment Department (NMED).

Please review, sign and forward the closure plan and certification report to NMED.

Sincerely,

Dennis J. Erickson, Director
Environment, Safety And Health Division

Bruce Matthews, Director
Nuclear Materials Technology Division

DJE:ds

Enclosures: a/s

Cy: J. Plum, DOE/LAAO, MS A136
J. Rochelle, LCGL, MS A187
J. Balkey, NMT-7, MS E501
K. Gruetzmacher, NMT-7, MS E501
J. Ellvinger, ESH-19, MS K490
H. Noskin, ESH-19, MS K490
ESH-DO File, MS K491
ESH-19 Circ. File
CIC-10, MS A150

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PURPOSE

The purpose of this document is to demonstrate that an exclusion applies for chromium, as specified in New Mexico Administrative Code, Title 20, Chapter 4, Part 1 (20 NMAC 4.1), Subpart II, 261.4(b)(6)(i) (hereafter, "chromium exclusion"). The United States Department of Energy (U. S. DOE) and the University of California, as co-operators of Los Alamos National Laboratory (LANL), are responsible for the nitrate-based aqueous process at Technical Area (TA) 55 (Nuclear Materials Technology Division, NMT) and seeks to demonstrate that the evaporator bottoms waste generated from this process fulfills all of the chromium exclusion criteria . Each of these criteria are presented in the discussion below.

BASIS OF REQUEST

Pursuant to 20 NMAC 4.1, Subpart II, 261.4(b)(6)(i), a solid waste is not a hazardous waste if it meets the following criteria:

- It is a waste which fails the test for the Toxicity Characteristic (TC) because chromium is present, or is a listed hazardous waste due to the presence of chromium, which does not fail the test for TC for any other constituent or is not listed due to the presence of any other constituent, and does not fail the test for any other characteristic;
- "The chromium in the waste is exclusively (or nearly exclusively) trivalent chromium; and"
- "The waste is generated from an industrial process which uses trivalent chromium exclusively (or nearly exclusively) and the process does not generate hexavalent chromium ; and"
- "The waste is typically and frequently managed in non-oxidizing environments."

PROCESS DISCUSSION

NMT Division's general function is to safely and efficiently perform special nuclear material research, technology development, and demonstration in support of national defense, energy, and environmental management. One of NMT Division's functions at TA-55 is the production of pure plutonium through various aqueous and pyrochemical processes.

A nitrate-based aqueous process is used to produce a relatively pure plutonium oxide which is used as a feedstock for pyrochemical metal production processes. The nitrate-based aqueous process consists of a series of operations that includes pretreatment, plutonium dissolution (leaching) with nitric acid, anion exchange, plutonium/oxalate precipitation, filtrate evaporation, and cementation of the evaporator bottoms. The influent streams to this process consist of impure plutonium oxides, residues from pyrochemical processes, and non-combustible items contaminated in the plutonium production process.

The waste generated as a result of this process consists of stabilized, cemented evaporator bottoms. Prior to cementation, the evaporator bottoms are collected until a target volume of approximately 13 gallons is accumulated. The evaporator bottoms are always sampled for heavy metals. The bottoms are then adjusted to a pH of 4 and mixed with water and approximately 340 pounds of gypsum cement. When Toxicity Characteristic Leaching Procedure (TCLP) analysis is done, samples are pulled during the cementation process and after the evaporator bottoms and cement are homogeneously mixed. The samples are allowed to dry in the form of 9 mm cubes and the resulting cubes are then sent to the Chemistry-Metallurgical Research building for analysis. These samples are tumbled in an acetic solution according to the TCLP methodology. This solution is then analyzed for all Resource Conservation and Recovery Act (RCRA) and 20 NMAC 4.1, Subpart II, 261.24 heavy metals that may be in the cement. Through this analysis, NMT Division has established that the evaporator bottoms waste generated from the nitrate-based aqueous process does not contain any TC constituents, other than chromium, in concentrations equal to or greater than the maximum concentrations specified in 20 NMAC 4.1, Subpart II, 261.24. The waste exceeds TC limits for chromium due to the leaching of stainless steel in the process lines.

ANALYTICAL SUPPORTING DOCUMENTATION

A quantitative analysis, including TCLP results, on samples taken from three drums containing evaporator bottoms is included as Attachment 1. This information confirms that this waste exceeds TC limits for chromium only.

Results of a stainless steel corrosion study indicate that extreme conditions are necessary to oxidize trivalent chromium to hexavalent chromium. These conditions include high nitric acid concentration and high temperature for an extended period of time. Only one of the unit operations currently in use within the nitrate-based aqueous process at TA-55 satisfies these conditions (i.e., the leaching process). The results of a semi-quantitative test on solutions generated during the leaching process are presented in Attachment 2. In summary, less than 20% of the total chromium present was in the hexavalent oxidation state while more than 80% was in the trivalent oxidation state. However, subsequent processing of this solution involves the adjustment of the plutonium oxidation state that simultaneously adjusts the chromium oxidation state to trivalent. In addition, since there is no subsequent step in the overall process where the extreme conditions exist that would reoxidize the chromium to the hexavalent state, chromium can only exist in the trivalent state for the remainder of the operations.

There are three major factors that will establish a reducing atmosphere within the remainder of the process and thus hinder the formation and/or stabilization of hexavalent chromium:

1. The standard electrochemical potential required for the oxidation of trivalent chromium to hexavalent chromium is +1.33 volts (v). The positive voltage value represents the energy required for this reaction to occur. Conversely, the standard electrochemical potential required for the oxidation of metallic chromium to trivalent chromium is -0.774 v. Except under extreme conditions (i.e., those present in the leaching

process), the chromium in the process will be trivalent. Any hexavalent chromium, if present, will act as an oxidizing agent, oxidizing metallic chromium to trivalent chromium, and as a result, reducing itself to trivalent chromium.

2. The influent to the ion exchange unit is chemically treated to adjust the plutonium in the process to the +4 oxidation state. Trivalent chromium is the thermodynamically stable species in this solution.

3. Oxalic acid is used in fairly high concentrations to precipitate and collect the plutonium near the end of the process. If there is any hexavalent chromium still present as the solution proceeds to the oxalate precipitation unit, it will be reduced back to trivalent chromium by the excess oxalic acid in this unit.

Attachment 3 contains a report on a study conducted to determine chromium speciation in the nitrate-based aqueous process. The findings of this study further confirm that the chromium present in the waste stream will largely be, if not entirely, in its trivalent form.

CONCLUSION

NMT Division has established through knowledge of the process feed stream and through sampling of the waste stream that, except for chromium, the limits for any TC constituent are not exceeded. The chromium content of the influent stream is dependent on the volume of plutonium contaminated stainless steel items entering the process as well as the degree of exposure to stainless steel lines. Through pH adjustments and an understanding of the process environment, NMT Division has established that the waste at the end of the process is not ignitable, corrosive, reactive, or a listed hazardous waste.

Our conclusion, after review of the processes involved and analytical data available, is that the waste stream described does meet the exclusion criteria of: (1) only failing the TC for chromium, (2) the chromium in the waste is exclusively (or nearly exclusively) trivalent, (3) the waste is generated from an industrial process which uses trivalent chromium exclusively (or nearly exclusively) and the process does not generate hexavalent chromium, and (4) the waste is typically managed in non-oxidizing environments.

REQUEST

Based on the demonstration contained in this letter and its attachments, LANL hereby requests confirmation of the applicability of the chromium exclusion to the nitrate-based aqueous process at TA-55.

ATTACHMENT 1

Quantitative Chemical Analysis and Toxicity Characteristic Leaching Procedure Results of Evaporator Bottoms

DRUM NUMBER: LA00000055307 **pH=4.23**

ITEM ID	VOL. (L)		Silver (Ag)	Arsenic (As)	Barium (Ba)	Cadmium (Cd)	Chromium (Cr)	Mercury (Hg)	Lead (Pb)	Selenium (Se)
10OX26AF1[a]	8.5	PPM	< 1.00	< 5.00	34.00	4.10	2900.00	< 5.00	85.00	< 8.00
		Sub.Tot. (g)	0.01	0.04	0.29	0.03	24.65	0.04	0.72	0.07
10EVDIST27BF1[a]	11.7	PPM	< 1.00	< 5.00	80.00	21.00	7000.00	< 5.00	360.00	< 8.00
		Sub.Tot. (g)	0.01	0.06	0.94	0.25	81.90	0.06	4.21	0.09
11EVDIST1BF1[a]	24.0	PPM	< 10.00	< 50.00	70.00	< 10.00	5700.00	< 50.00	300.00	< 80.00
		Sub.Tot. (g)	0.24	1.20	1.68	0.24	136.80	1.20	7.20	1.92
FT1111693[b]	44.2	Total (g)	0.26	1.30	2.91	0.52	243.35	1.30	12.13	2.08
DRUM[c]	43.6	Amount to Drum (g)	0.26	1.28	2.87	0.51	240.05	1.28	11.97	2.05

ITEM ID	VOL. (L)		Ag	As	Ba	Cd	Cr	Hg	Pb	Se
11EVDIST8AF1[a]	14.3	PPM	< 1.00	< 5.00	48.00	9.00	4200.00	< 25.00	110.00	< 8.00
		Sub.Tot. (g)	0.01	0.07	0.69	0.13	60.06	0.36	1.57	0.11
	0.0	PPM								
		Sub.Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.0	PPM								
		Sub.Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FT[b]	14.3	Total (g)	0.01	0.07	0.69	0.13	60.06	0.36	1.57	0.11
DRUM[c]	7.2	Amount to Drum (g)	0.01	0.04	0.35	0.06	30.24	0.18	0.79	0.06

LA00000055307[d]	51.4	Total (g)	0.26	1.32	3.21	0.58	270.29	1.46	12.76	2.11

TCLP SAMPLES			Ag	As	Ba	Cd	Cr	Hg	Pb	Se
55307B2	TCLP	PPM	<1	<2	<5	<0.5	7.00	<0.2	<1	<1
55307B1	TCLP	PPM	<1	<2	<5	<0.5	8.00	<0.2	<1	<1

L = liters
PPM = parts per million
g = grams
TCLP = Toxicity Characteristic Leaching Procedure
[a] evaporator bottoms
[b] feed tank for evaporator bottoms
[c] amount transferred from feed tank to drum
[d] drum

DRUM NUMBER: LA00000055308 pH=4.33

ITEM ID	VOL. (L)		Silver (Ag)	Arsenic (As)	Barium (Ba)	Cadmium (Cd)	Chromium (Cr)	Mercury (Hg)	Lead (Pb)	Selenium (Se)
11EVDIST8AF1[a]	14.3	PPM	< 1.00	< 5.00	48.00	9.00	4200.00	< 25.00	110.00	< 8.00
		Sub. Tot. (g)	0.01	0.07	0.69	0.13	60.06	0.36	1.57	0.11
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FT113093[b]	14.3	Total (g)	0.01	0.07	0.69	0.13	60.06	0.36	1.57	0.11
DRUM[c]	6.6	Amount to Drum (g)	0.01	0.03	0.32	0.06	27.72	0.17	0.73	0.05

ITEM ID	VOL. (L)		Ag	As	Ba	Cd	Cr	Hg	Pb	Se
11EVDIST17BF1[a]	17.1	PPM	< 1.00	< 5.00	51.00	4.60	4000.00	< 5.00	140.00	< 8.00
		Sub. Tot. (g)	0.02	0.09	0.87	0.08	68.40	0.09	2.39	0.14
11LR16AF1[a]	14.7	PPM	< 1.00	< 5.00	70.00	6.50	520.00	< 5.00	200.00	< 8.00
		Sub. Tot. (g)	0.01	0.07	1.03	0.10	7.64	0.07	2.94	0.12
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FT2121493[b]	31.8	Total (g)	0.03	0.16	1.90	0.17	76.04	0.16	5.33	0.25
DRUM[c]	31.1	Amount to Drum (g)	0.03	0.16	1.86	0.17	74.37	0.16	5.22	0.25

ITEM ID	VOL. (L)		Ag	As	Ba	Cd	Cr	Hg	Pb	Se
5EVDIST25BF1[a]	20.0	PPM	< 1.00	< 5.00	81.00	23.00	5300.00	< 5.00	350.00	< 8.00
		Sub. Tot. (g)	0.02	0.10	1.62	0.46	106.00	0.10	7.00	0.16
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FT2121593[b]	20.0	Total (g)	0.02	0.10	1.62	0.46	106.00	0.10	7.00	0.16
DRUM[c]	14.8	Amount to Drum (g)	0.01	0.07	1.20	0.34	78.44	0.07	5.18	0.12

LA00000055308[d]	52.5	Total (g)	0.05	0.26	3.37	0.57	180.53	0.39	11.12	0.42

TCLP SAMPLES			Ag	As	Ba	Cd	Cr	Hg	Pb	Se
55308B1	TCLP	PPM	<1	<2	<5	<0.5	6.00	<0.2	<1	<1

L = liters
PPM = parts per million
g = grams
TCLP = Toxicity Characteristic Leaching Procedure
[a] evaporator bottoms
[b] feed tank for evaporator bottoms
[c] amount transferred from feed tank to drum
[d] drum

DRUM NUMBER: LA00000055309 pH=4.03

ITEM ID	VOL. (L)		Silver (Ag)	Arsenic (As)	Barium (Ba)	Cadmium (Cd)	Chromium (Cr)	Mercury (Hg)	Lead (Pb)	Selenium (Se)
5EVDIST25BF1[a]	20.0	PPM	< 1.00	< 5.00	81.00	23.00	5300.00	< 5.00	350.00	< 8.00
		Sub. Tot. (g)	0.02	0.10	1.62	0.46	106.00	0.10	7.00	0.16
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.0	PPM								
		Sub. Tot. (g)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FT2121593[b]	20.0	Total (g)	0.02	0.10	1.62	0.46	106.00	0.10	7.00	0.16
DRUM[c]	5.4	Amount to Drum (g)	0.01	0.03	0.44	0.12	28.62	0.03	1.89	0.04

ITEM ID	VOL. (L)		Ag	As	Ba	Cd	Cr	Hg	Pb	Se
12OX17AF1[a]	20.0	PPM	2.80	< 5.00	36.00	1.90	2100.00	< 5.00	60.00	< 8.00
		Sub. Tot. (g)	0.06	0.10	0.72	0.04	42.00	0.10	1.20	0.16
12OX13AF1[a]	15.9	PPM	< 1.00	< 5.00	35.00	3.20	2800.00	< 5.00	75.00	< 8.00
		Sub. Tot. (g)	0.02	0.08	0.56	0.05	44.52	0.08	1.19	0.13
12EVDIST6AF1[a]	12.7	PPM	< 1.00	< 5.00	37.00	3.80	5000.00	< 5.00	76.00	< 8.00
		Sub. Tot. (g)	0.01	0.06	0.47	0.05	63.50	0.06	0.97	0.10
FT1011194[b]	48.6	Total (g)	0.08	0.24	1.75	0.14	150.02	0.24	3.36	0.39
DRUM[c]	48.7	Amount to Drum (g)	0.08	0.24	1.75	0.14	150.33	0.24	3.36	0.39

LA00000055309[d]	54.1	Total (g)	0.1	0.3	2.2	0.3	178.9	0.3	5.3	0.4

TCLP SAMPLES			Ag	As	Ba	Cd	Cr	Hg	Pb	Se
55309B1	TCLP	PPM	<1	<2	<5	<0.5	4.00	<0.2	<1	<1

L = liters
PPM = parts per million
g = grams
TCLP = Toxicity Characteristic Leaching Procedure
[a] evaporator bottoms
[b] feed tank for evaporator bottoms
[c] amount transferred from feed tank to drum
[d] drum

ATTACHMENT 2

Chromium Reduction Tests

Los Alamos
NATIONAL LABORATORY
memorandum

Nuclear Materials Technology
Actinide Process Chemistry
NMT-2

To/MS: Kathleen Gruetzmacher, NMT-7, MS E501
From/MS: Vance Hatler, NMT-2, MS E511
Phone/fax: 5-4015/5-1780
Symbol: NMT-2:FY95-408
Date: July 12, 1995

SUBJECT: Results of Chromium Reduction Tests.

In January of 1993 Ron Blankenship and myself performed a set of quick and quantitative tests to predict the oxidation state of chromium in a 8M nitric acid feed solution. We used a test kit obtained from Steve Yarbro, which was called a chormate kit. This kit consisted of indicator paper and low molar nitric acid. The tests were performed by diluting the feed solution with the low molar nitric acid and dipping the indicator paper into the solution. A reaction occurred yielding a color which could be matched to a chart, which correlated the percentage of chromium $^{+}3$ and chromium $^{+}6$. Although the tests were quantitative and open to interpretation, the results indicated that greater than 80 percent of the chromium was in the $^{+}3$ state. We were performing these test during the RCRA stand down in order to expedite approvals to resume aqueous processing operations. If there are any questions regarding this please call me at 5-4015.

cy: Keith Fife, NMT-2, MS E511

ATTACHMENT 3

Report entitled "Chromium in Aqueous Nitrate Process Streams: Corrosion of 316 Stainless Steel and Chromium Speciation"