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		Design Authority									
		Design Agent									
2	1	Cog. Eng. D. A. Reynolds	D A Reynolds	10/22/01							
2	1	Cog. Mgr. M.A. Knight	Mallenky	10/22/01							
		QA									
		Safety									
		Env.									

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L. R. Webb 10/23/01 Signature of EDT Originator / Date	N/A Authorized Representative for Receiving Organization / Date	M.A. Knight 10/22/01 Design Authority/ Cognizant Manager / Date	Ctrl No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments

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Hydrogen Generation From Caustic-Aluminun Reaction

D. A. Reynolds
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Richland, WA 99352
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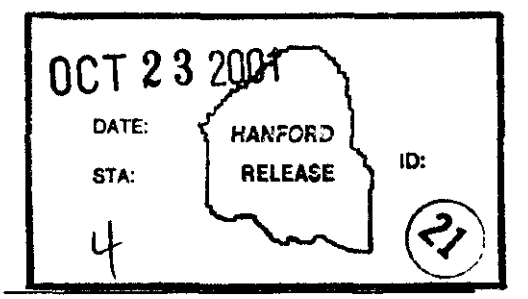

10-23-01

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Analytical Calculations Checklist

Subject: Hydrogen Generation from Caustic-Aluminum Reaction

Originator: D. A. Reynolds D A Reynolds Date: 10/23/01

Checker: M. A. Knight M A Knight Date: 10/23/01

Documents/Engineering Change Notices Reviewed: None

Affected Document(s) (Optional) _____

Yes	No	N/A	
[X]	[ ]	[ ]	Were the design inputs correctly selected?
[X]	[ ]	[ ]	Are assumptions necessary to perform the design activity adequately described and reasonable?
[X]	[ ]	[ ]	Where necessary, are the assumptions identified for subsequent re-verifications when the detailed design activities area completed?
[X]	[ ]	[ ]	Was an appropriate design method used?
[X]	[ ]	[ ]	Is the design output reasonable compared to design inputs?
[X]	[ ]	[ ]	Are the necessary design input and verification requirements for interfacing organizations specified in the design documents or in supporting procedures or instructions?

Checklist Completed By: M A Knight Date: 10/23/01

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Appendix B B-1

1.0 Objective/Purpose:

A "crawler" is to enter the AY farm annulus to clean the metal surface for corrosion measurements. The "crawler" weighs about 190 pounds of which 150 pounds are aluminum. (These values are supplied by the vender of the "crawler".) There is a potential that cleaning the surface of the metal may cause a leak to occur in the primary tank wall and the waste may contact the aluminum. The hydroxide in the waste may react with the aluminum and form hydrogen gas. The purpose of this analysis is to estimate the rate of hydrogen gas generation and the time to reach the lower flammable limit (LFL) in the annulus.

Surface area of the aluminum piece is estimated to be 2 sq.ft. (This value was given by the vender.)

$$SA := 2 \cdot ft^2$$

2.0 Open Items:

The vender supplied information on the surface area of the "crawler" and the mass of aluminum should be considered open items. The surface area directly affects the calculations and a better number could change the results of this analysis.

3.0 Methods of Analysis:

The amount of aluminum that can react with hydroxide is estimated based on information from the PUREX Tech. Manual (Ref. 1). It is assumed that no suppression of hydrogen gas generation occurs due to nitrate ions. It is assumed that the reaction will behave like the aluminum is a massive mass -- not a powder or a foil. Therefore, the reaction will behave similar to decladding the aluminum clad reactor fuel rods with hydroxide as was done in PUREX plant.

4.0 Input Data:

$$MolW_{OH} := 40.01 \cdot \frac{gm}{mole} \qquad MW_{Al} := 26.98 \cdot \frac{gm}{mol}$$

Molecular weights of sodium hydroxide and aluminum.

$$STP := 22.4 \cdot \frac{liter}{mol}$$

Volume of an ideal gas at standard conditions.

Density of Aluminum

$$\rho_{Al} := 168 \cdot \frac{lb}{ft^3}$$

The volume of the annulus is given in Anatatmula (Ref 3.)

$$AnnulusVol := 22980 \cdot ft^3$$

Natural atmospheric breathing rate is assumed to be 0.45% per day.

$$BrRate := 0.0045 \cdot day^{-1}$$

$LFL := 4\%$ Volume percent hydrogen

Concentrations of AY waste is from Best Basis Inventory Caustic Limits Report as of 10/20/01. (See attachment)

$ConOH_{AY101} := 3.15$ $ConOH_{AY102} := 1.09$ Concentration of Hydroxide in mol/liter

$ConNO3_{AY101} := 8.21 \cdot 10^{-2} \cdot \frac{mol}{liter}$ $ConNO3_{AY102} := 6.61 \cdot 10^{-3} \cdot \frac{mol}{liter}$ Concentration of Nitrate in mol/liter

5.0 Results:

Below are the calculational results.

5.1 Reaction Rate

PUREX Tech. Manual (Ref. 1) on page 303 gives the following data: "The rate of penetration, which is a measure of the reaction rate, increases with NaOH concentration from about 1.5 mm/hr at 5% NaOH to 5 mm/hr at 10% NaOH and to 13 mm/hr at 15% NaOH at the boiling temperature."

$Pntr := \begin{pmatrix} 1.5 \\ 5 \\ 13 \end{pmatrix}$ in mm/hr Penetration rate

The Caustic Soda Handbook from Occidental Chemical Corp. was used to convert from percent to grams per liter.

$OHCon := \begin{pmatrix} 52.811 \\ 111.210 \\ 175.170 \end{pmatrix}$ in gm/liter Corresponds to 5%, 10% and 15% NaOH.

$OHM := \frac{OHCon}{40.01}$ in mole/liter Converts to Molar units

The following does a regression of the form $Y=Ae^{(BX)}$ on the data. This can be transformed into a linear form as ln(Y) = ln(A) +B*X. In this form, ln(A) is the intercept and B is the slope.

$A := \exp(\text{intercept}(OHM, \ln(Pntr)))$ $B := \text{slope}(OHM, \ln(Pntr))$ MathCad functions to get the intercept and slope.

$A = 0.629$ $B = 0.704$

$PenRate(X) := A \cdot \frac{mm}{hr} \cdot e^{B \cdot X}$ *Penetration Rate as a function of X. Concentration of hydroxide is X.*

Tank 241-AY-101 has the highest hydroxide concentration of the two tanks and will be used for worst case.

$PenRate(ConOH_{AY101}) = 5.783 \frac{mm}{hr}$ Penetration rate at the concentration of AY-101 hydroxide.

However, the penetration rate is for boiling temperatures. The PUREX Tech Manual states: "The penetration rate approximately triples between 60 and 100 C." Because 60 C is a bounding temperature for the tanks as *they currently sit, the penetration rate from the equation above will be divided b 3.*

$Pentrate := \frac{PenRate(ConOH_{AY101})}{3}$ *Penetration rate corrected for temperature.*

5.2 Amount of Aluminum Reacting

$VolAl := Pentrate \cdot SA$ *Volume of aluminum reacting is the surface area times the penetration rate.*

$VolAl = 3.582 \times 10^{-4} \frac{m^3}{hr}$

$MolAl := \frac{VolAl \cdot \rho_{Al}}{MW_{Al}}$ Moles of aluminum that react.

5.3 Time to Reach LFL

Aluminum reacts with sodium hydroxide by the following equation

$$2 \cdot Al + 2 \cdot NaOH + 2H2O = 2 \cdot NaAlO_2 + 3 \cdot H_2$$

Three moles of hydrogen gas are formed from 2 moles of aluminum reacted.

$MolH2 := MolAl \cdot \frac{3}{2}$

$VolH2 := MolH2 \cdot STP$

$VolH2 = 0.707 \frac{ft^3}{min}$

It should be pointed out that nitrate ion suppresses the formation of hydrogen gas. This was used in decladding to minimize the amount of hydrogen produced. One estimate is that between 40 and 70% of the aluminum reacted in ways that did not produce hydrogen gas. However, AY-101 has low nitrate concentration so no credit will be taken for it.

Natural atmospheric breathing rate is assumed to be 0.45% per day.

$$BrRate := 0.0045 \cdot day^{-1}$$

$$VentRate := AnnulusVol \cdot BrRate$$

$$VentRate = 0.072 \frac{ft^3}{min}$$

This is about 1/10th of the hydrogen generation rate. Therefore, the vent rate will be not be taken into account the time to reach the lower flammable limit (LFL). This is conservative as it will make the time shorter than actual.

Assuming that there is no breathing.

$$Time_to_reach_LFL := \frac{AnnulusVol \cdot LFL}{VolH2}$$

$$\boxed{Time_to_reach_LFL = 21.684\,hr}$$ <----------

6.0 Conclusions:

The major uncertainty is the surface area that may be reacted. The analysis is based on an estimate given by Nuclear Safety and Licensing. However, the surface area used is bounding value. There are other uncertainties in this analysis but in all cases, the values chosen are conservative and so the result of 22 hours to reach the LFL can be considered a bounding case. The actual time to reach the LFL will certainly be longer.

7.0 Recommendations:

None.

8.0 References:

1. PUREX Technical Manual, HW-13000, General Electric Company, March 25, 1955

2. Caustic Soda Handbook NaOH, Occidental Chemical Corporation, Dallas, TX

3. Anantatmula, R, Dalpiaz, E, Fedenburg, E., Ogden, D., Thurgood, M., "Double-Shell Tank Annulus Ventilation Engineering Study", RPP-7695, CH2M Hill Hanford Group, Feb 28, 2001

CHAPTER III. FEED PREPARATION

Following a suitable "cooling" period, the irradiated fuel elements (described in Chapter II) are dissolved in nitric acid, and the dissolver solution is prepared as feed for entry into the solvent-extraction columns. The steps in the preparation of the feed which are discussed in the present chapter are removal of the aluminum slug jackets, dissolution of the slugs, off-gas treatment, head-end decontamination, centrifugation, and chemical adjustment of the feed solution. These are discussed from both chemical and process viewpoints. The dissolvers and other equipment are described in Chapter XIII. A Process Flow Diagram, Figure III-2 and Figure III-3 gives an outline of the equipment used in feed preparation and a material balance over these steps. Previous technical manuals (11, 14) described similar, but not identical, feed preparation operations. Physical properties of UNH-HNO_3 solutions are discussed in Chapter IV, Section B.

A. JACKET REMOVAL

1. Introduction

The first step in preparing the radioactive slugs for the separation of uranium, plutonium, and fission products in the solvent-extraction columns is the removal from each slug of its aluminum jacket and the aluminum-silicon bonding layer which joins the jacket to the uranium core. As for previous Hanford separation processes, the slug jackets are removed by dissolution in a sodium hydroxide-sodium nitrate solution. Although the jackets can also be dissolved in nitric acid with mercury as a catalyst, the Purex Plant has been designed for removal of the aluminum cans by the caustic jacket removal process.

2. Caustic Jacket Removal

2.1 General

The aluminum slug jackets are removed by dissolution at the boiling temperature in a solution consisting of about 10% sodium hydroxide (3.3 M) and 20% sodium nitrate (3.0 M) under essentially the same conditions as have been used successfully in the Bismuth Phosphate and Redox Plants. The reaction of aluminum with caustic is given by the equation:

$$2\ Al + 2\ NaOH + 2\ H_2O \longrightarrow 2\ NaAlO_2 + 3\ H_2$$

In the presence of nitrate ion the evolution of hydrogen is suppressed and dissolution proceeds according to a combination of the equations:

$$8\ Al + 5\ NaOH + 3\ NaNO_3 + 2\ H_2O \longrightarrow 8\ NaAlO_2 + 3\ NH_3$$

$$2\ Al + 2\ NaOH + 3\ NaNO_3 \longrightarrow 2\ NaAlO_2 + 3\ NaNO_2 + H_2O$$

$$2\ Al + NaOH + NaNO_2 + H_2O \longrightarrow 2\ NaAlO_2 + NH_3$$

[redacted]

The relative amounts of hydrogen, ammonia, and nitrite ion produced are determined by the sodium nitrate excess as discussed below.

Sodium hydroxide dissolves practically all of the aluminum-silicon alloy in the bonding layer. However, there is an appreciably residue of solid material, known to be siliceous, and believed to consist in part of uranium silicides and carbides. The greater part of this solid material is removed from the dissolver with the coating waste solution. The coating waste solution normally contains less than 0.1% by weight of these suspended solids.

The pH of the coating waste solution is about 12 to 13.

2.2 Effect of sodium hydroxide concentration

Aluminum is attacked rapidly by sodium hydroxide over a concentration range of 5 to 50% NaOH. The rate of penetration, which is a measure of the reaction rate, increases with NaOH concentration from about 1.5 mm./hr. at 5% NaOH to 5 mm./hr. at 10% NaOH and to 13 mm./hr. at 15% NaOH at the boiling temperature.(59) With initial NaOH concentrations above 10% the rate of reaction is too great to be easily controlled in the plant dissolvers. The penetration rate approximately triples between 60° and 100°C.(7) Uranium losses are very slight in solutions up to 30% NaOH but become appreciable in 50% NaOH.(9)

The maximum caustic concentration which can be used is limited by the reaction rate and by the necessity of having sufficient volume of solution to cover the slugs. At a caustic concentration of 8% (with 16% $NaNO_3$ and a 1.25 NaOH/Al mole ratio) precipitation of alumina was observed after the solution had stood for several days.(9) At the normal coating-removal conditions of 10% sodium hydroxide (1.65 NaOH/Al mole ratio) and 20% sodium nitrate, a concentration of about 5% NaOH is present in the waste solution after reaction and no precipitation of Al_2O_3 occurs even after long storage periods.

2.3 Effect of sodium nitrate concentration

The presence of sodium nitrate serves to suppress the evolution of hydrogen which might otherwise constitute an explosion hazard. The relative amounts of hydrogen, ammonia, and nitrite ion produced in the presence of various concentrations of sodium nitrate are indicated in Figure III-1. Under Purex coating-removal conditions the initial $NaNO_3$/Al mole ratio is 1.5. The curves of Figure III-1 apply for an initial NaOH concentration of 15 wt. per cent, and should be taken only as qualitatively correct at other NaOH concentrations.

2.4 Slug rinsing

Following the removal of the coating-waste solution, the slugs are given two rinses to flush the dissolver of residual alkalinity and to remove additional suspended solids. While the first is water, the second may be either 5% nitric acid (to dissolve the bonding layer) or water.

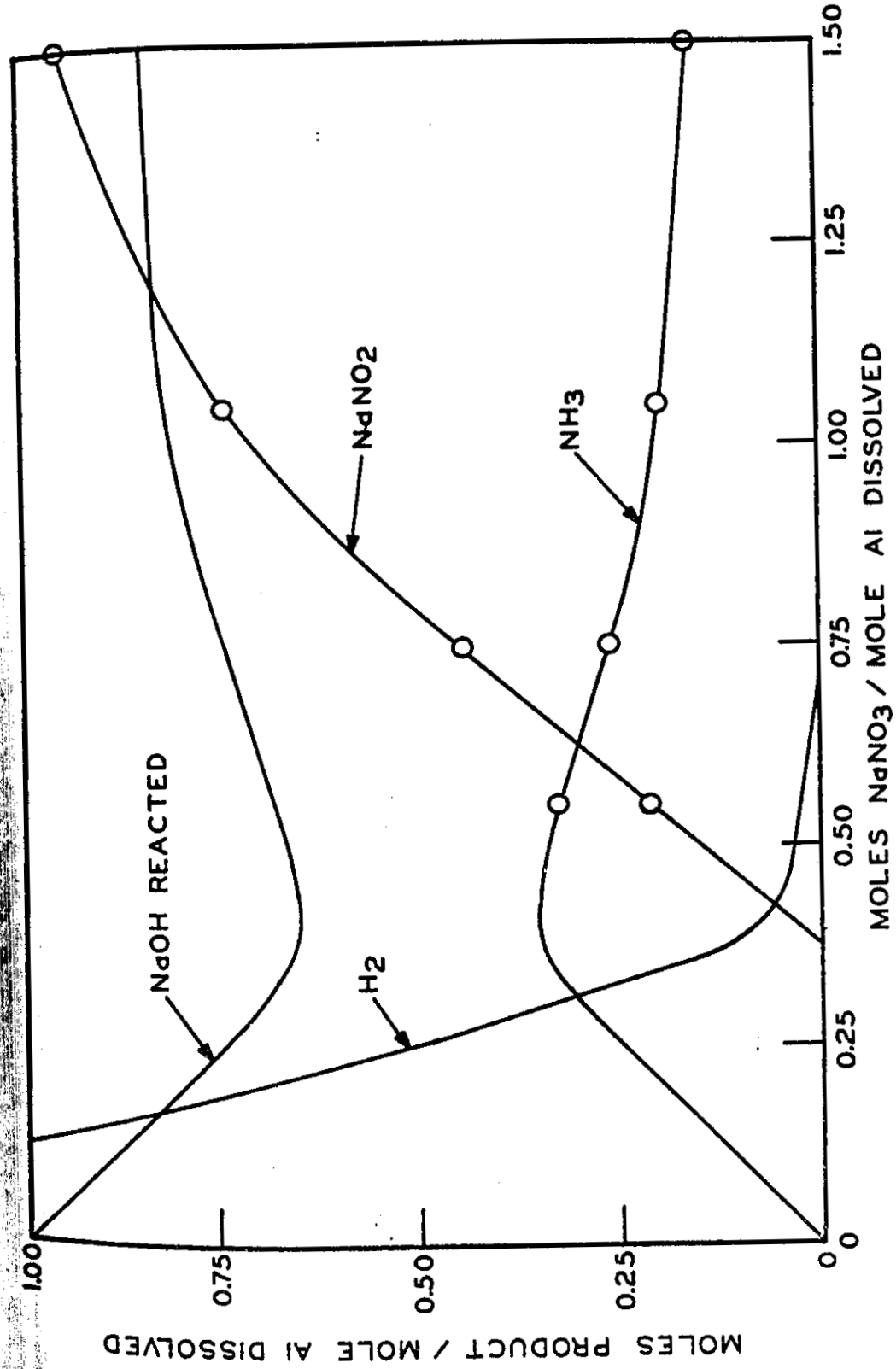

FIGURE III-1

SODIUM HYDROXIDE JACKET REMOVAL

EFFECT OF SODIUM NITRATE

INITIAL NaOH CONCENTRATION = 15 % — SOURCE OF DATA - ORNL 1208

Technical Data

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Table 1 Density and Caustic Soda Content of Rayon/Membrane Grade Caustic Soda Solutions at 60°F

WT% NaOH	% Na2O	SPECIFIC GRAVITY	DEGREES BAUMÉ [AM STD]	NaOH G/L	NaOH LB/GAL	SOLUTION LB/GAL	TOTAL WT NaOH LB/CU FT	TOTAL WT SOLUTION LB/CU FT
1.0	0.775	1.0120	1.706	10.118	0.084	8.437	0.631	63.113
2.0	1.550	1.0230	3.259	20.457	0.171	8.529	1.277	63.804
3.0	2.325	1.0342	4.782	31.019	0.259	8.622	1.935	64.497
4.0	3.100	1.0453	6.274	41.803	0.349	8.715	2.608	65.191
5.0	3.874	1.0564	7.736	52.811	0.440	8.807	3.295	65.885
6.0	4.649	1.0676	9.170	64.042	0.534	8.900	3.995	66.581
7.0	5.424	1.0787	10.580	75.496	0.630	8.993	4.710	67.277
8.0	6.199	1.0899	11.960	87.174	0.727	9.087	5.438	67.973
9.0	6.974	1.1010	13.310	99.076	0.826	9.180	6.181	68.670
10.0	7.748	1.1122	14.630	111.210	0.927	9.273	6.937	69.367
11.0	8.523	1.1234	15.930	123.550	1.031	9.366	7.707	70.063
12.0	9.298	1.1345	17.200	136.130	1.136	9.459	8.492	70.759
13.0	10.080	1.1457	18.440	148.920	1.242	9.552	9.290	71.455
14.0	10.850	1.1569	19.660	161.930	1.351	9.645	10.110	72.150
15.0	11.630	1.1680	20.850	175.170	1.461	9.738	10.930	72.845
16.0	12.400	1.1791	22.030	188.630	1.573	9.830	11.770	73.539
17.0	13.180	1.1902	23.170	202.300	1.687	9.923	12.620	74.231
18.0	13.950	1.2013	24.300	216.200	1.803	10.020	13.490	74.922
19.0	14.730	1.2124	25.400	230.310	1.921	10.110	14.370	75.612
20.0	15.500	1.2234	26.480	244.640	2.040	10.200	15.260	76.300
21.0	16.280	1.2344	27.530	259.180	2.162	10.300	16.170	76.987
22.0	17.050	1.2454	28.570	273.940	2.285	10.390	17.090	77.672
23.0	17.830	1.2563	29.590	288.910	2.409	10.480	18.030	78.355
24.0	18.600	1.2672	30.580	304.090	2.536	10.570	18.970	79.035
25.0	19.370	1.2781	31.550	319.470	2.664	10.660	19.930	79.713
26.0	20.150	1.2889	32.510	335.070	2.794	10.750	20.910	80.389
27.0	20.920	1.2997	33.440	350.870	2.926	10.840	21.890	81.062
28.0	21.700	1.3105	34.350	366.870	3.060	10.930	22.890	81.731
29.0	22.470	1.3212	35.250	383.070	3.195	11.020	23.900	82.398
30.0	23.250	1.3317	36.120	399.450	3.331	11.110	24.920	83.057
31.0	24.020	1.3424	36.980	416.070	3.470	11.200	25.960	83.722
32.0	24.800	1.3529	37.830	432.860	3.610	11.280	27.010	84.379
33.0	25.570	1.3634	38.650	449.850	3.751	11.370	28.070	85.033
34.0	26.350	1.3738	39.450	467.010	3.895	11.460	29.140	85.681
35.0	27.120	1.3842	40.240	484.370	4.039	11.540	30.220	86.327
36.0	27.900	1.3944	41.020	501.910	4.186	11.630	31.310	86.968
37.0	28.670	1.4046	41.770	519.630	4.333	11.720	32.420	87.605
38.0	29.450	1.4148	42.510	537.520	4.482	11.800	33.530	88.237
39.0	30.220	1.4248	43.230	555.590	4.633	11.880	34.660	88.864
40.0	31.000	1.4348	43.940	573.830	4.785	11.970	35.800	89.487
41.0	31.770	1.4447	44.640	592.240	4.939	12.050	36.950	90.105
42.0	32.550	1.4545	45.310	610.810	5.094	12.130	38.110	90.717
43.0	33.320	1.4643	45.980	629.530	5.250	12.210	39.270	91.324
44.0	34.100	1.4739	46.630	648.420	5.407	12.290	40.450	91.926
45.0	34.870	1.4835	47.260	667.450	5.566	12.370	41.640	92.522
46.0	35.650	1.4930	47.880	686.640	5.726	12.450	42.840	93.113
47.0	36.420	1.5023	48.480	705.970	5.887	12.530	44.040	93.697
48.0	37.200	1.5116	49.080	725.440	6.049	12.610	45.260	94.275
49.0	37.970	1.5208	49.650	745.040	6.213	12.680	46.480	94.847
50.0	**38.740**	**1.5298**	**50.220**	**764.780**	**6.377**	**12.760**	**47.710**	**95.412**
51.0	39.520	1.5388	50.770	784.640	6.543	12.830	48.950	95.971
52.0	40.290	1.5476	51.310	804.630	6.710	12.910	50.200	96.523

PROCESS

General

The operations of coating removal and metal dissolving are carried out consecutively in the dissolvers. These are vertical tanks equipped to receive charges of the active slugs and conduct operations at the boiling point under slightly less than atmospheric pressure. There are three dissolvers in each Canyon Building; located in Sections 3-L, 3-R, and 4-L, and designated as 3-5L, 3-5R, and 4-5L respectively.

The metal is charged into the dissolvers in batches of 3 long tons (8 buckets of 105 slugs each). In order to increase the rate of solution by use of a large amount of reacting surface, a metal heel of approximately 1 long ton is carried in the dissolver. Thus the dissolver contains approximately 4 long tons of metal just after charging and approximately 1 ton after three 1-ton batches of metal have been dissolved.

The aluminum jackets are removed from the slugs by reaction with sodium hydroxide in the presence of sodium nitrate solution. The sodium nitrate prevents the evolution of hydrogen which might reach an explosive concentration in the dissolver. Part of the silicon bonding alloys is dissolved, and part forms scale or sludge which is flushed out with the coating removal solution or with the water and acid washes which follow the coating removal step.

The metal is dissolved in batches of 2200 lbs. each by adding 5000-5400 lbs. of 60-62% nitric acid and digesting until a specific gravity of 1.80-1.82 at the boiling temperature is reached. Each batch of metal solution is diluted in the dissolver to approximately 55% UNH to prevent crystallization, cooled, and jetted to Section 4R where previously accumulated wash water dilutes it to approximately 40% UNH. Sulfuric acid is then added to give a concentration of 0.338 lb. H_2SO_4/lb. metal. After agitation the solution is ready for transfer to the extraction section.

During metal dissolving the off-gases, which include air, oxides of nitrogen, and small quantities of radioactive elements, are removed from the vessel via a stainless steel line and vent jet to the 291 Building stack for dilution and disposal to the atmosphere.

Under unfavorable weather conditions, e.g., no wind, down draft, or fog, the 291 Building facilities do not dilute the radioactive gases to a safe level and the dissolvers can not be operated. However, two dissolvers can produce metal solution faster than it can be processed. This excess capacity permits a 4-day stock of metal solution to be accumulated; the third dissolver is held as a spare.

Chemistry of Coating Removal

Each metal slug of 7.85 lbs. average weight is enclosed in an aluminum jacket when received in the 200 North Area. The jacket wall thickness is

0.035 inches and the heavier and pieces are approximately 0.375 inches thick, one being integral with the aluminum tube and the other welded on after the slug is placed in the jacket. The aluminum and uranium surfaces are bonded together with molten aluminum-silicon, which produces aluminum - silicon - uranium alloys on the surface of the slug. The total coating material on a finished jacketed slug weighs 115-120 grams (0.265 lb.) of which 80-90 grams are aluminum.

Two methods have been developed for removing aluminum jackets: the mercury catalyzed 10% nitric acid procedure, and the 10% sodium hydroxide - 20% sodium nitrate procedure. The HNO_3 - Hg procedure was used extensively in the pilot plant where there was no problem of silicon bonding material. It has not been used at Hanford because control of the reaction with multiple batch charges is questionable and a caustic treatment is necessary to remove the bonding alloys.

Two versions of the 10% NaOH - 20% $NaNO_3$ procedure have been used: with the metal charge in the vessel, (1) all the caustic is added to the cold $NaNO_3$ solution, the temperature allowed to rise, and the heat of reaction removed with coil cooling water, or (2) the caustic is added slowly to the boiling $NaNO_3$ solution, and the heat of reaction removed by the column condenser water. The latter method is now being used; the chemistry of the two variations is essentially the same.

In the absence of sodium nitrate the theoretical mol ratio of caustic to aluminum is 1 (Equation 1 below), but in the presence $NaNO_3$ it may be either 5/8 to 1 (Equation 2 below) if ammonia is formed or 1 (Equation 3 below) if sodium nitrite is formed. [redacted]

1) $2\ Al + 2\ NaOH + 2H_2O \longrightarrow 2Na\ AlO_2 + 3\ H_2$

2) $8\ Al + 5\ NaOH + 3NaNO_3 + 2H_2O \longrightarrow 8NaAlO_2 + 3\ NH_3$

3) $2\ Al + 2NaOH + 3NaNO_3 \longrightarrow 2NaAlO_2 + 3NaNO_2 + H_2O$

Laboratory experiments have shown that a NaOH/Al mol ratio of 1.25 provides an adequate excess for solution of the aluminum. However, this ratio is not great enough to insure that Al_2O_3 will not precipitate if the solution is allowed to stand for a day. Experimental results have shown that a NaOH/Al mol ratio of 1.65 prevents precipitation even if the solution is held for long periods of time. In the plant this ratio is approximated by the use of 1070 lbs. of 50% NaOH to dissolve about 220 lbs. of coating material from a 3-ton metal charge.

Aluminum is vigorously attacked by sodium hydroxide over a tested concentration range of 5-50%; the reaction rate increases with increased caustic strength. Uranium metal loss by caustic attack is very slight in solutions up to 30% NaOH, but the rate of solution becomes appreciable in 50% NaOH. In the coating removal step, dilute caustic is desirable to limit the rate of reaction and to obtain sufficient solution volume to cover the slugs in the dissolver without using an unreasonably large excess of caustic. Precipitation of

alumina may occur in the coating waste if the caustic concentration is as low as 8% based on final solution weight. At 10% NaOH and a NaOH/Al mol ratio of 1.65 or above, alumina does not precipitate even after a long storage period.

The concentration of sodium nitrate used is less critical than that of the caustic. Concentrations as low as 10% are satisfactory for supression of hydrogen formation, but there is some evidence that solid residues are more completely removed from the dissolver with the coating waste solution if 20% sodium nitrate is used.

Caustic dissolves aluminum-silicon alloy, but the aluminum-silicon-uranium scale may be removed by undercutting and the disintegrating action of the alkali. A large fraction of this suspended material is removed with the coating waste. The dissolver is given a water flush and a 5% nitric acid wash to remove any residual material. The coating solution, water wash, and acid wash are combined in Section 15 for disposal to the waste storage area. The resultant solution is sufficiently alkaline for storage; the specific gravity is 1.5 and the freezing point is below -10°C. Pilot plant data show a maximum product loss of 0.1% in this solution.

Chemistry of Metal Dissolving

Uranium metal is dissolved and oxidized by nitric acid to uranyl nitrate hexahydrate ($UO_2(NO_3)_2 6H_2O$). The rate of this reaction increases with increased temperature and increased nitric acid concentrations. The acid consumed in the reaction can vary between the extremes indicated in the following equations:

$$U + 4\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO + 2H_2O$$

$$U + 8\ HNO_3 \longrightarrow UO_2(NO_3)_2 + 6NO_2 + 4H_2O$$

Actual acid consumption lies between these two extremes and has averaged approximately 5.5 mols acid/mol metal in pilot plant and plant operation. Acid utilization may vary with dissolver column design, gas velocity in the column, (which in turn is affected by the amount of air leakage into the vessel) and condenser water temperature and flow. Essentially no acid is regenerated until the contents of the dissolver reach the boiling point and the flow of reflux (containing water, acid, and dissolved oxides) begins in the column.

The heat of reaction of metal with nitric acid is 1472 to 2713 BTU/lb. With nitric acid of 60% or higher concentration and adequate metal surface, this heat is sufficient to keep the reaction mixture at the boiling point.

The product, contained in the slugs of metal, is oxidized by nitric acid to either the (III) or (IV) state and forms soluble nitrates. There has been no indication in pilot plant or plant operation of the oxidation of any appreciable amount of product to the (VI) state. The wide variety of fission-formed radioactive elements, or by-products, include nitric acid soluble, insoluble, and volatile materials. The nitric acid insoluble materials are present in very small quantities and do not seriously affect the handling of metal solution. The volatile materials of greatest importance are xenon and iodine with a small quantity of argon. These two principal elements appear in the dissolver

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Caustic Limits Report As Of Oct., 2001

Tank Name	Waste Phase	Inventory Effective Date	Mean NO3 Molarity	NO3 Lower 95% Limit	Mean OH Molarity	OH Lower 95% Limit	Mean NO2 Molarity	NO2 Lower 95% Limit
241-AY-101	Supernatant	01-Jul-01	8.21E-02	7.61E-02	3.15E+00	2.98E+00	6.82E-01	6.71E-01
241-AY-101	Sludge (Liquids)	01-Jul-01	1.09E-01	5.46E-02	1.51E+00	1.48E+00	1.42E+00	3.75E-01
241-AY-102	Supernatant	01-Jul-01	6.61E-03	5.10E-03	1.09E+00	1.04E+00	1.29E-01	1.12E-01
241-AY-102	Sludge (Liquids)	01-Jul-01	4.76E-03		4.16E-03	NA	4.98E-03	