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DPST-72-328

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MULTIPURPOSE DISSOLVER FOR MPPF

FY-73, 74 Equipment Budget

The attached Technical Data Summary, by W. J. Jenkins, provides the design basis for a small dissolver in module 17.3, F-canyon, adjacent to the Multi-Purpose Processing Facility. Process filters, important but separately replaceable equipment pieces have not yet been specified. As soon as the current development work on filtration is complete, an addendum will be issued giving filter requirements.

[redacted]

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DPST-72-328

Technical Data Summary

MULTIPURPOSE DISSOLVER FOR MPPF

W. J. Jenkins
April, 1972

Table of Contents

Technical Data Summary

MULTIPURPOSE DISSOLVER FOR MPPF

Introduction

This technical data summary describes the recommended design, based on existing technology, of a small multipurpose dissolver to provide small quantities of feed as needed by the new Multipurpose Processing Facility (MPPF). The aluminum is removed from the targets by caustic dissolution, decanting, filtration, and washing before dissolving the remaining actinide-lanthanide crude fraction in nitric acid. This crude fraction is suitable, after evaporation and acid adjustment, for separation of the actinides by rapid ion exchange in MPPF.[1]

Background

A small multipurpose dissolver is required to provide the small quantities of feed needed by MPPF to meet 252-Cf market demands with a minimum out-of-reactor decay time. The extensive equipment flushing required to prevent cross-contamination with other campaigns makes processing of small batches through mainline equipment impractical. Campaigning of large batches through mainline equipment and storage until needed, as originally intended,[2] would give excessive decay.

Process Design Criteria

The design basis is 49 pounds of aluminum per batch with a submerged surface area of 61.6 square feet; four Mark 18A outer target housings are shown in the attached flowsheet but smaller batches containing less aluminum with less surface area can also be dissolved if required. Each of these housings is 4.22 inches outside diameter and contains about 11 pounds of aluminum when cut to 6 ft $10\frac{1}{4}$ inches length after discharge from the reactor. Four of these housings can be bundled for dissolving with about 5 pounds of aluminum bundle material.

Since multipurpose service is expected from this dissolver in the future, the design must include the capability of dissolving the widest possible range of feeds as shown on the next page:

- one or more slugs per batch
- one to four tubes per batch
- tubes up to 168 inches maximum length
- slurries of solids

Sufficient air purge is required to dilute the off-gas concentrations below the lower explosive limits. Pressurization of the dissolver must be prevented to maintain containment. A pressure of minus 0.30 inches water column relative to the canyon is available on the vessel vent system of the 221-F Hot Canyon. A maximum pressure drop of 0.15 inches of water is available for flow of off-gas and air purge from the dissolver through the reflux condenser column and vessel vent piping if the dissolver pot is maintained at minus 0.15 inches water column relative to the canyon during dissolution.

The reflux condenser column must be capable of removing the heat of reaction and cooling the noncondensable off-gases below the ambient temperature (about 30°C) of the vessel vent system.

No equipment for removal of iodine from the dissolver off-gas is included in this flowsheet since there is a total of less than 0.55 curie[3] of ^{131}I in all these targets after 120 days cooling and 98%[4] of that will remain in the caustic waste solution. A facility for removal of iodine from the 221-F canyon process vessel vent system can be considered on a separate project at a future date if more effective containment of ^{131}I must be achieved.

Location

The multipurpose dissolver will be located in 221-F Hot Canyon section 17.3 adjacent to the 17.3 Raw Feed Evaporator; this available space was reserved for this dissolver. This location is convenient for transfer of the feed solution into the 17.3 Raw Feed Evaporator and also for disposal of filtrate waste into 17.2 Waste Tank.

Nuclear Safety

There is no nuclear safety hazard in processing the Mark 18A outer target housings,[5] because the total quantities of fissionable isotopes are small; the entire Cf-I campaign contains only 24 grams of fissionable ^{245}Cm (the greatest potential criticality hazard) mixed with approximately 2 kg of nonfissionable curium isotopes; no fissionable plutonium isotopes are expected. The maximum safe mass for ^{245}Cm in this mixture is 42 grams. The nuclear safety of future feeds, however, would have to be considered individually before processing.

Process Safety

The process described in the Technical Data Summary is well within previous SRP processing experience. Sodium nitrate solution is used to suppress hydrogen evolution during the aluminum dissolution. Ammonia is evolved instead during this dissolution and must be diluted below the lower explosive limit with air purge.

The ammonia evolution rate is controlled by limiting the caustic addition rate into the dissolver during dissolution. Hydrogen evolved from radiolysis of process solutions can be diluted to <2% in the vapor space by purging with air at a rate of at least 15 cc/min per watt of radiation energy absorbed by the solution.[8] The lower explosive limit is 4% hydrogen.

Process Description

The recommended flowsheet, shown in Figures 1 and 2, consists of a two-step dissolution which removes the aluminum first by caustic dissolution, decanting, filtration, and washing before dissolving the remaining actinide-lanthanide crude fraction in nitric acid. The aluminum is dissolved in a solution of caustic and sodium nitrate at the boiling point. The sodium nitrate is used to suppress the evolution of hydrogen by altering the reaction so that ammonia is produced. The reactions involved during this step are shown by the next four equations:[7]

$$2\ Al + 2\ NaOH + 2\ H_2O \longrightarrow 2\ NaAlO_2 + 3\ H_2 \tag{1}$$

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

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

$$2\ Al + NaOH + NaNO_2 + H_2O \longrightarrow 2\ NaAlO_2 + NH_3 \tag{4}$$

The following equation, derived empirically from laboratory scale studies under simulated plant conditions, best represents the total reaction:[8]

$$Al + 0.70\ NaOH + 0.58\ NaNO_3 + 0.11\ H_2O \longrightarrow NaAlO_2 + 0.28\ NaNO_2 + 0.30\ NH_3 + 0.009\ H_2$$

Aluminum is attacked rapidly by sodium hydroxide concentrations at the boiling temperature as shown in Figure 3.[9]

The actinide-lanthanide fraction, however, is highly insoluble in sodium hydroxide solutions; the actinide-lanthanide losses to the aluminum removal are limited, therefore, by the ability to retain these solids while removing the aluminum solution.

A minimum of 2.5M free NaOH is used in the final aluminum solution to stabilize the solution and prevent precipitation of aluminum oxide trihydrate by the hydrolysis of sodium aluminate. This amount of caustic is about a 240% excess over that required for complete dissolution of the aluminum, but it is necessary to prevent any precipitation of the aluminum if the complete removal of the aluminum from the actinide-lanthanide solids is to be obtained. The stability of $NaAlO_2$-NaOH solutions is shown in Figure 4.[10]

The sodium nitrate solution does not materially aid in the aluminum dissolution reaction, but it suppresses the formation of potentially hazardous hydrogen. The degree of this suppression is highly dependent upon the concentration of sodium nitrate as shown in Figure 5.[11] Ammonia is formed instead of hydrogen in this reaction and must be diluted below the lower explosive limit of 14%[12,13] with air purge. About 14½ times more air purge would be required to dilute hydrogen below the lower explosive limit of 4% if the sodium nitrate was not used.

Since the off-gas capacity is limited by a maximum pressure drop of 0.15 inches of water column, the addition rate of 23% sodium hydroxide must be limited to 2.80 lbs/min based on aluminum dissolution rate of 0.6 lb/hr-ft^2;[14] 15 scfm of air purge is required for dilution at this addition rate. The caustic addition must be located where caustic will not contact bare aluminum metal that is not submerged below the sodium nitrate solution.

The solids are allowed to settle, then most of the aluminum solution is decanted and then filtered into an existing 17.2 Waste Tank. The solids are washed several times with sodium hydroxide to remove all the residual aluminum solution, then with water to remove most of the sodium hydroxide. A wash distributor or spray is required to remove solids from coil surfaces and pot walls with the minimum possible volume of wash solution. These washes are also decanted then filtered into 17.2 Waste Tank. The decanting is accomplished by transfer of the supernate out of the dissolver pot at sufficient height above the bottom to allow a 0.5 ft^3 heel of settled solids to remain in the dissolver pot. The remaining actinide-lanthanide solids are then dissolved in nitric acid and filtered from a bottom outlet of the dissolver into the existing 17.3 Raw Feed Evaporator followed by dilute nitric rinses to assure complete removal of the actinide-lanthanide solution from the dissolver, filters, and piping. The filtration of this solution may be extremely difficult because of silica solids pluggage of the filters; design of the filters will not be specified until demonstration tests of prototype filters are completed. Evaporation, acid adjustment, and storage in 17.3 until transfer to MPPF are covered in existing Technical Standards.[15] The chemical processes associated with MPPF are the subject of a separate Technical Data Summary.[16] The dissolver and filters are then flushed with hot caustic followed by water to remove silica and unplug the filters. The volume of flush required is minimized by recycling flush back and forth between the dissolver and filters.

All chemical or water additions to the dissolver and filters must be prefiltered to remove all trash and prevent frequent replacement of the dissolver filters because of unnecessary pluggage.

The heating and cooling coils should be located in the lower section of the pot as close to the bottom as possible so that the volume of liquid required to cover the coils is as small as possible.

Equipment Description and Specification

DISSOLVER POT

General

The dissolver must be designed for maximum flexibility if widely varying batch sizes are to be processed efficiently. Large volumes are required to dissolve the aluminum relative to the small quantities of solids which have to be washed, dissolved, and removed. As shown in Figure 6, a pot is required having a small diameter lower section, a large diameter upper section, a steeply sloped reduction section in between, and a steeply sloped bottom.

Total Liquid Capacity

300 gallons minimum volume at 100% fill

Length/Diameter

- Lower section L/D of 3 minimum
- Upper section L/D of ½ maximum

Slope

- Reduction slope between upper and lower sections of 45° for efficient washing and removal of solids from pot.
- Bottom slope of 45° for efficient washing and removal of solids from pot.

Transfer Outlets

- One outlet located at sufficient height above the bottom to leave 0.5 cu ft of solids heel in the pot during removal of supernatant after decanting.
- One outlet located at low point of bottom for complete removal.

Transfer Inlets

- One for recirculation from filters during flushing.
- Two (minimum) for chemical additions; caustic addition must be located such as to prevent direct contact of caustic to bare aluminum metal surfaces which are not submerged in sodium nitrate solution.
- One for slurry additions.
- One for wash distributor or spray for washing solids from coil surfaces and pot walls.

Agitation

Single dip-tube sparge (not ring) with open end located within $\frac{1}{2}$ inch of the bottom at the low point of bottom. Air sparge rate of 15 scfm maximum flow designed for: slurrying solids off the bottom, washing of solids, removing solids, and mixing of pot contents.

Air Purge

- 15 scfm air flow to the vapor space during dissolution of aluminum to dilute ammonia in the off-gases below 14% lower explosive limit.
- 0.2 scfm minimum air flow to the vapor space (376 watts x 15 cc/min-watt) for dilution of radiolytically generated hydrogen to <2%.

Cooling

500,000 Btu/hr which must be located below 74 gallons liquid level; based on removing the heat of reaction for control of the aluminum dissolution reaction.

Heating

500,000 Btu/hr which must be located below 50 gallons liquid level for heat up of pot contents to boiling.

Charging Hatch

- 12-inch inside diameter capable of receiving a bundle of 4 tubes (4.22 inches OD by 168 inches maximum length) including sufficient clearance for bundle bail.

- Slug funnel and pivot point capable of receiving slugs from bucket.
- Hatch cover with seal having less than 2 scfm air inleakage at 1-inch water column negative test pressure inside dissolver pot.

Material of Construction

304L SS

REFLUX CONDENSER COLUMN

General

The reflux condenser column is welded directly to the top of the dissolver pot around the charging hatch column which also transports vapor to the top of the condenser. The condenser is downdraft and must cool the noncondensable off-gases and air purge as well as condense the vapors generated by the heat of reaction during aluminum dissolution.

Heat Removal

- 500,000 Btu/hr (minimum) from the heat of reaction.
- Cool noncondensable off-gases and air purge to less than ambient temperature (~30°C) of process vessel vent system.

Pressure Drop

The total pressure drop of the condenser column plus all the vessel vent piping must be less than 0.15 inches water column.

Material of Construction

304L SS

FILTERS

Design to be specified later after prototype tests are completed.

STEAM JETS

Design to be specified later after prototype tests are completed.

CHEMICAL ADDITIONS

General

All chemical additions must be prefiltered to prevent premature pluggage of the process filters. Seal pots are required in all chemical addition lines to prevent backup from process equipment into clean areas. The addition rate of 23% NaOH (Flowsheet Line #3) must be limited to 2.80 lbs/min during aluminum dissolution to limit the reaction rate.

Flowsheet Line No.	Concentration	Chemical
2	23%	$NaNO_3$
3	23%	NaOH
7	10%	NaOH
8	-	Water
9	64%	HNO_3
10	1.6%	HNO_3
12	1.6%	HNO_3
13	23%	NaOH
15	-	Water

Caustic Addition Tank

A new tank is required for makeup and addition of the following streams to the dissolver: Flowsheet lines #3, 7, 8, 13, and 15.

- Liquid capacity 200 gallons at 100% fill
- 50% NaOH addition line
- Process water addition line
- Agitator
- Liquid level 0 to 100% fill
- Specific gravity 1.0 to 1.5

Sodium Nitrate Addition Tank

A new tank is required for makeup and addition of 23% sodium nitrate solution for flowsheet line #2.

- Liquid capacity 100 gallons at 100% fill
- 40% $NaNO_3$ addition line
- Process water addition line
- Agitator
- Liquid level 0 to 100% fill
- Specific gravity 1.0 to 1.3

Nitric Acid Addition Tanks

Two existing MPPF chemical addition tanks, #5-1-2 and #5-1-3, are used for addition of 64% HNO_3 and 1.6% HNO_3 on flowsheet lines #9, 10, and 12.

Chemical Additions Funnel

Chemical additions funnel of 5 gallon capacity for backwash addition to filters.

Prefilter Efficiency

Removal of 100% of the solids which will not pass through the process filters.

INSTRUMENTATION

Pressure

- Static

Pot pressure + 1" W. C. to 0 to -1" W. C.
Filter pressure +30" Hg to 0 to -30" Hg

- Differential

Pot to Column	0 to 1" W. C. negative or positive
Filters	0 to 30" Hg negative or positive

Temperatures

Pot	0 to 125°C
Filters	0 to 100°C
Off-Gas	0 to 100°C

Liquid Level

Pot 0 to 100% fill

Specific Gravity

Pot 1.0 to 1.5

Foam Level

1 ft below top of pot

Sampler

Pot

REFERENCES

1. DP-71-1-10, SRL Monthly Report, page 8 (Secret).

2. DPSTD-221F-Pu-Al-Cf, Technical Data Summary, 221-F Processing of Pu-Al Housing from Californium-I Irradiations, by W. C. Perkins, W. E. Prout, and M. C. Thompson, June, 1971.

3. Calculated by CINDER Code, assuming 15 months irradiation in the High Flux charges of the Cf-I campaign, followed by about 4 months cooling, further irradiation in ED charges for about 4 months, and 4 months cooling.

4. Trip Report ORNL-TRU, H. P. Holcomb-W. J. Jenkins to E. L. Albenesius-A. S. Jennings, February 24, 1971, page 4.

5. DPSTD-221F-Pu-Al-Cf, page 12.

6. DPSTS-MPPF-1.03, limit 5, pages 2 and 3.

7. DP-500, Processing of Irradiated Natural Uranium at Savannah River, by T. J. Cohen, C. W. Cline, and A. E. Wible, August, 1960, page VII-1 (Secret).

8. DP-500, page VII-1.

9. ORNL-1208, Recovery of Nitrogen Oxides and Rare Gas Fission Products from Nitric Acid Dissolution of Irradiated Uranium, by A. T. Gresky, 1952, page 21 (Secret).

10. ETR-133, Dissolution in the Recirculation Dissolver of Aluminum by Sodium Hydroxide, by J. Van Caenegham and Y. Marchant, June, 1962, page 13.

11. DP-500, page VII-4.

12. Recueil des Lravaux Chimiques des Pays-Bas 45: 224-231 (1926), Explosion Regions, VII: The Explosive Regions of Hydrogen-Ammonia-Air and Hydrogen-Ammonia-Oxygen Mixtures, by W. P. Jorissen and B. L. Ongkiehong.

13. Rec. Trav. Chim, 49, 876-83 (1930), Reaction Regions XX: The Influence of Various Circumstances on the Extension of Explosive Regions, by W. P. Jorissen, J. Boog, and J. Van Heiningen.

14. DPST-58-25-39, Caustic Dissolution of Aluminum Alloys Containing Magnesium, by T. A. Halpin and D. E. Neighbors, January 23, 1959, page 4 (Secret).

15. DPSTS-221-8.10, Evaporating Dilute Americium-Curium Solutions, June, 1971 (Secret).

16. DPSTD-221F-Cf, Technical Data Summary, 221-F Californium Separations Facility (to be issued).

Figure 1

MULTIPURPOSE DISSOLVER FLOWSHEET

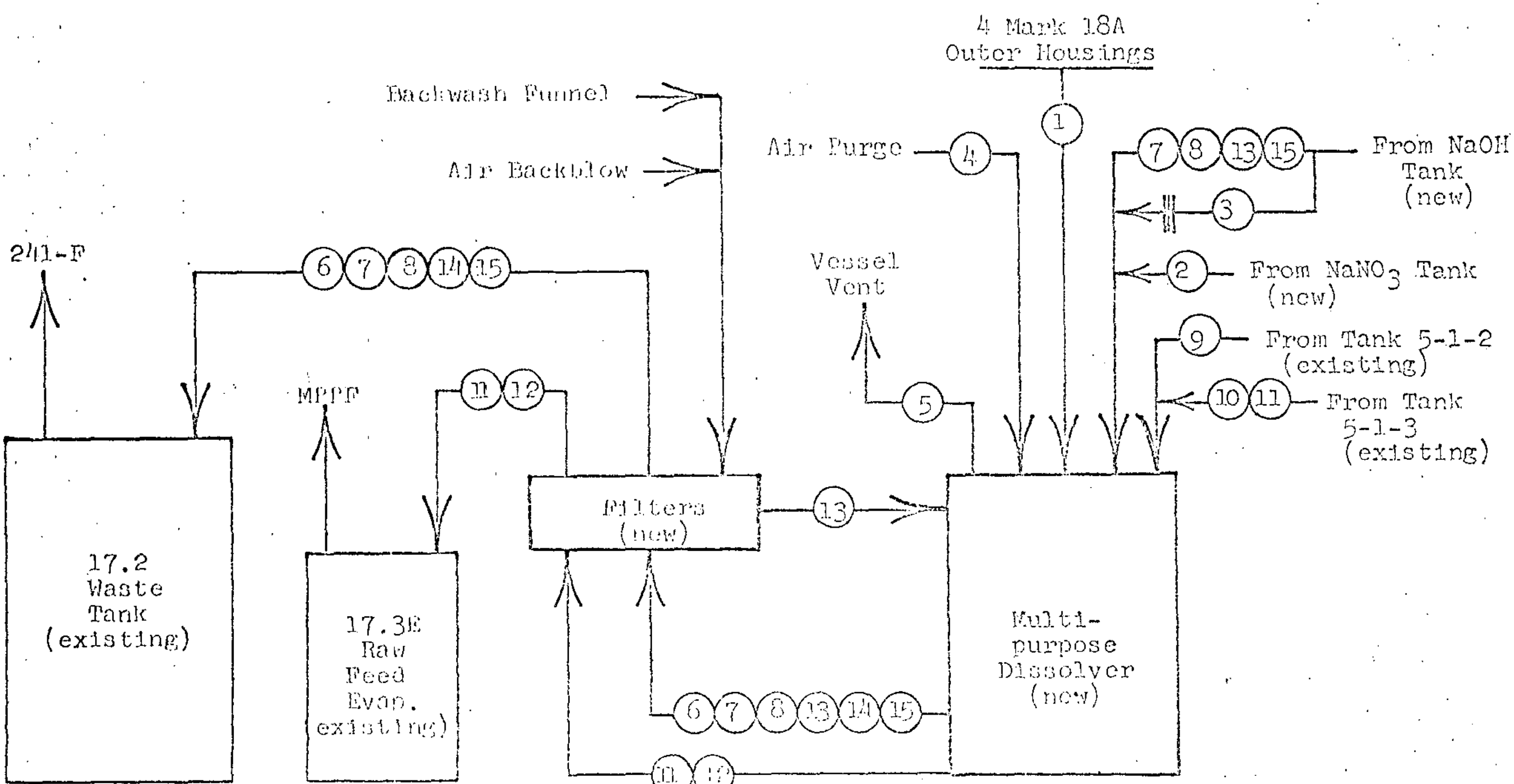


Figure 2

MULTIPURPOSE DISSOLVER FLOWSHEET

Line No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Process Material	4 Mark 18A Outer Housings	23% $NaNO_3$	23% NaOH	Air Purge	Aluminum Dissolution Off-Gas	Caustic-Aluminum Waste	10% NaOH Washes*	Water Rinses*	64% HNO_3 Dissolution	1.6% HNO_3 Dilution	Actinide-Lanthanide Solution	1.6% HNO_3 Dissolver Rinses*	23% NaOH Si Flush	Si Flush Solution	Water Rinses*
Total Cm, gm	132	-	-	-	-	-	-	-	-	-	132	-	-	-	-
^{244}Cm, gm	88	-	-	-	-	-	-	-	-	-	88	-	-	-	-
^{243}Am, gm	3.2	-	-	-	-	-	-	-	-	-	3.2	-	-	-	-
Total Pu, gm	8.8	-	-	-	-	-	-	-	-	-	8.8	-	-	-	-
Total Cf, mg	128	-	-	-	-	-	-	-	-	-	128	-	-	-	-
^{252}Cf, mg	100	-	-	-	-	-	-	-	-	-	100	-	-	-	-
Total Lanthanides, gm	112	-	-	-	-	-	-	-	-	-	112	-	-	-	-
Decay Heat, watts	376	-	-	-	-	-	-	-	-	-	376	-	-	-	-
^{131}I, curies	<0.033	-	-	-	<0.002	<0.031	-	-	-	-	-	-	-	-	-
Aluminum, lbs	49**	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Silicon, lb	~0.4	-	-	-	-	-	-	-	-	-	-	-	-	~0.4	-
$NaNO_3$, lb	-	165	-	-	-	75	-	-	-	-	-	-	-	-	-
NaOH, lb	-	-	172	-	-	121	139	-	-	-	-	-	360	360	-
$NaNO_2$, lb	-	-	-	-	-	35	-	-	-	-	-	-	-	-	-
$NaAlO_2$, lb	-	-	-	-	-	149	-	-	-	-	-	-	-	-	-
NH_3, lb	-	-	-	-	9.3	-	-	-	-	-	-	-	-	-	-
H_2, lb	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-
Air Purge, scfm	-	-	-	15	15	-	-	-	-	-	-	-	-	-	-
HNO_3, lb	-	-	-	-	-	-	-	-	474	12	486	20	-	-	-
H_2O, lb	-	552	576	-	2	1122	1248	1251	266	710	976	1239	1206	1206	1251
Total, lb	50	717	748	-	-	1502	1387	1251	740	722	1463	1259	1566	1566	1251
Solids, %	100	23	23	-	-	25	10	0	-	-	<1	-	23	23	-
Sp. gr.	-	1.167	1.252	-	-	1.24	1.109	1.000	1.387	1.007	1.201	1.007	1.252	1.252	1.000
Gallons	-	74	72	-	-	146	150*	150*	64	86	146	150*	150	150	150*

NOTES: *150-gallon washes and rinses are divided into three successive 50-gallon washes or rinses.
**Includes 5 lbs of aluminum bundle

Figure 3

CAUSTIC DISSOLUTION OF ALUMINUM

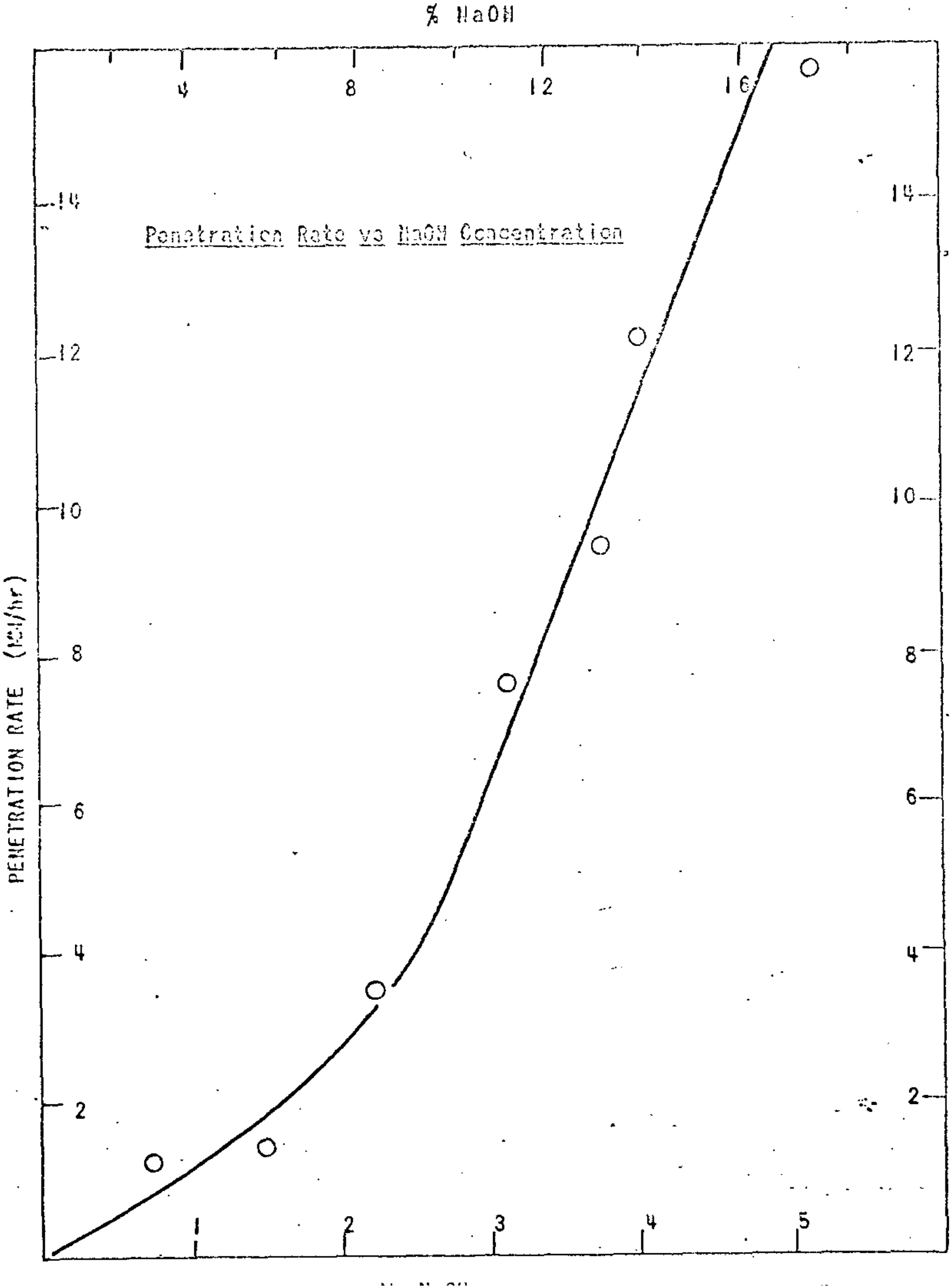


Figure 4

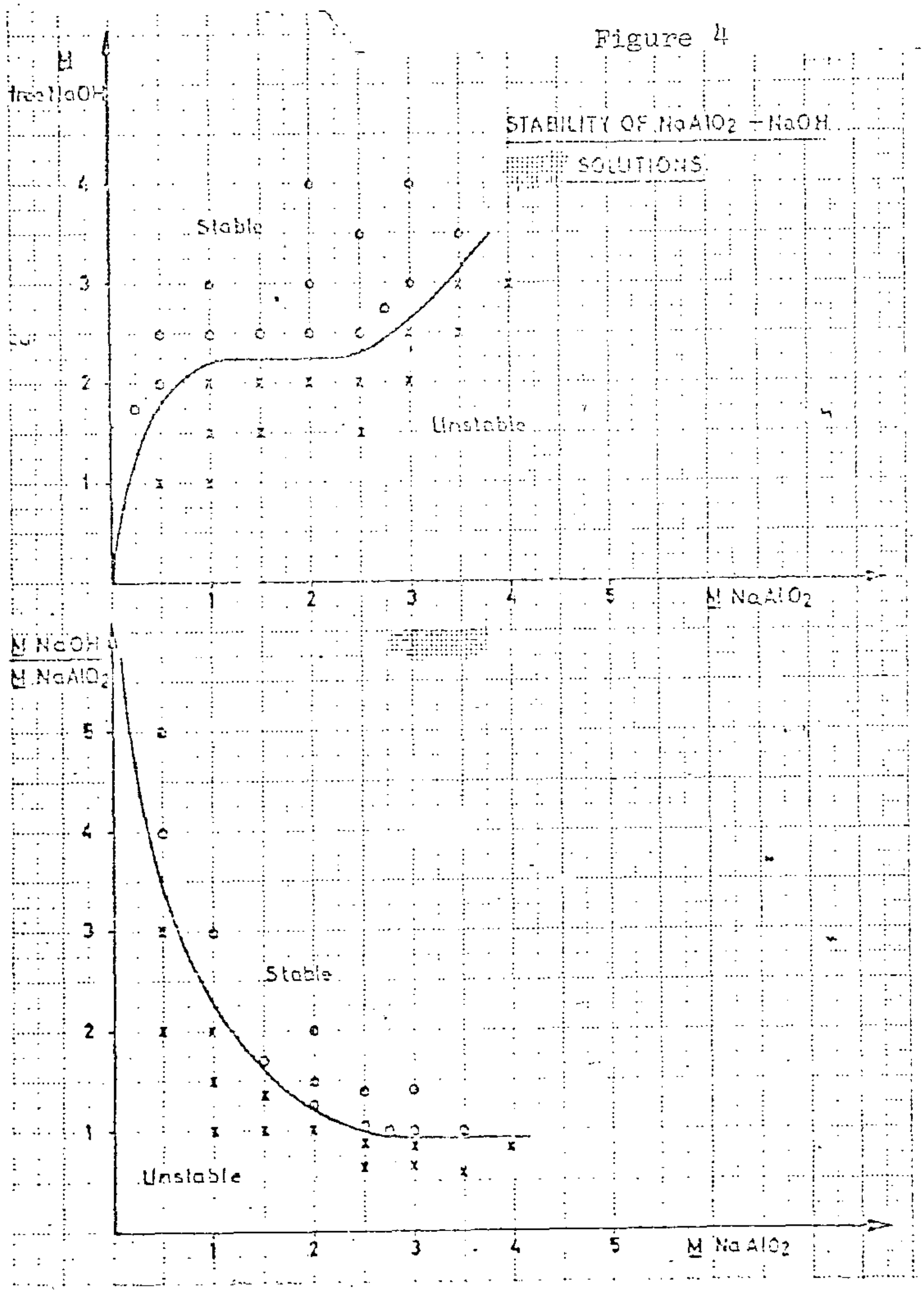
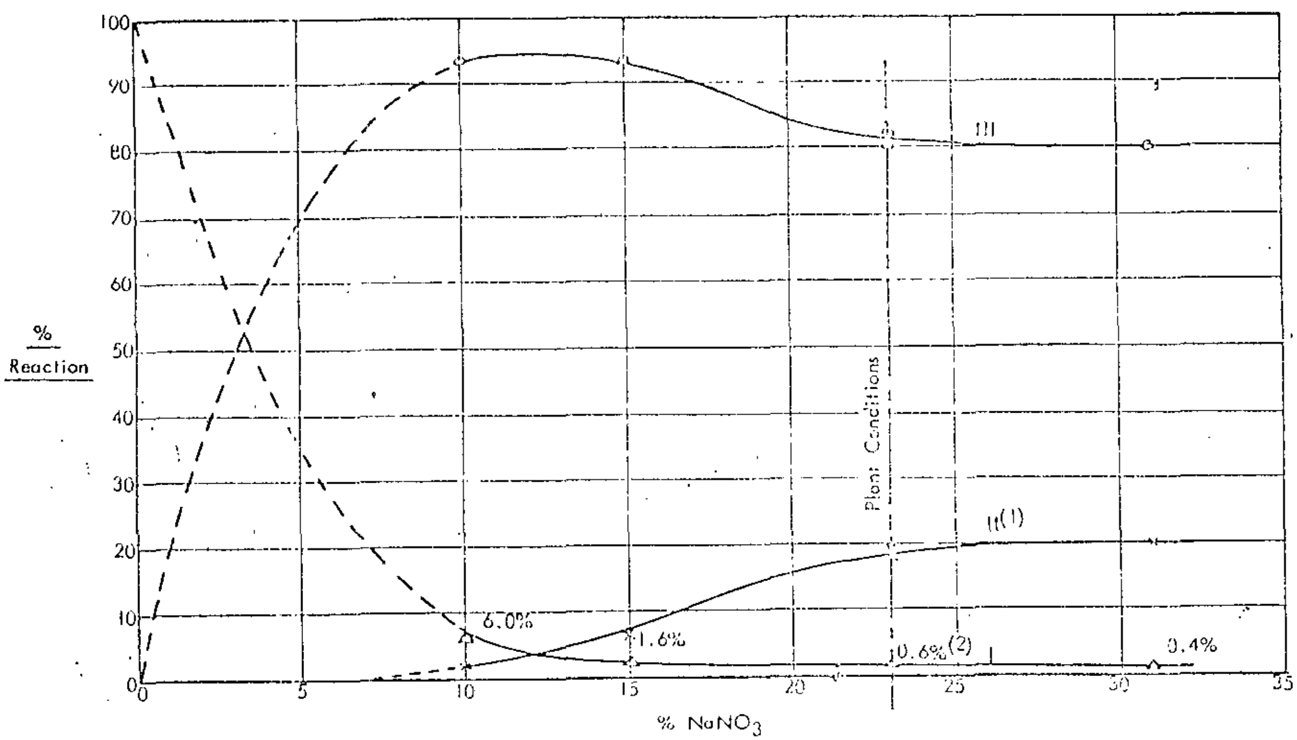

STABILITY OF $NaAlO_2$ – NaOH SOLUTIONS
M free NaOH
Stable
Unstable
M $NaAlO_2$
M NaOH / M $NaAlO_2$
Stable
Unstable
M $NaAlO_2$

Figure 5

EFFECT OF $NaNO_3$ ON CAUSTIC DISSOLUTION OF ALUMINUM



(1) Not analyzed, obtained by difference.

(2) 0.6% by Reaction I is equivalent to 7 c.c. H_2/gm Al dissolved.

Reactions:

I - $Al + NaOH + H_2O \longrightarrow NaAlO_2 + 1.5H_2$

II - $Al + NaOH + 1.5\ NaNO_3 \longrightarrow NaAlO_2 + 1.5\ NaNO_2 + 0.5\ H_2O$

III - $Al + 0.625\ NaOH + 0.375\ NaNO_3 + 0.25\ H_2O \longrightarrow NaAlO_2 + 0.375\ NH_3$

Figure 6

MULTIPURPOSE DISSOLVER