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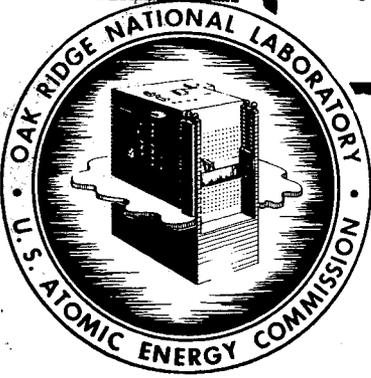
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CAUSTIC DISSOLUTION: PRELIMINARY STUDIES

R. G. Wymer  
D. M. Helton  
A. H. Kibbey  
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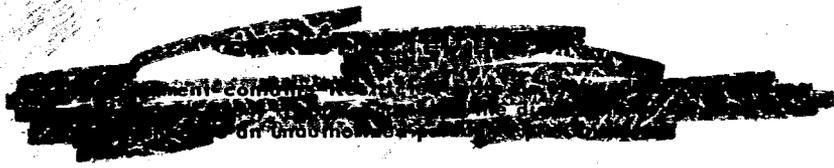
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CAUSTIC DISSOLUTION: PRELIMINARY STUDIES

- R. G. Wymer
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- A. H. Kibbey
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## 1.0 ABSTRACT

Continuous caustic dissolution of uranium-aluminum slugs, which would result in considerably lower waste volumes in uranium processing, was shown to be feasible. The slugs were treated with twice the stoichiometric amount of sodium hydroxide required for the dissolution, and solid uranium oxide particles, more than 50% of which were less than  $0.1 \mu$  in diameter, suspended in caustic-aluminate solution were formed. The uranium product was separated by centrifugation at 980 G's for 1 hr with a uranium loss of 0.05%. The bulk of the fission products accompanied the uranium in the separation step, with cesium and iodine the principal contaminants of the caustic-aluminate solution. The separated solid product was readily dissolved in boiling 6 M nitric acid to form a satisfactory feed for a solvent extraction process.

The continuous dissolution rate of Savannah River slugs in a 5.5-in.-diam. column with a 28-in.-high slug bed and a 6 M sodium hydroxide flow rate of 1 liter/min was calculated to be about 6 kg of uranium per 24 hr, and was experimentally verified.

## 2.0 INTRODUCTION

The high aluminum content ( $> 90\%$ ) of all currently produced uranium-aluminum alloy reactor slugs makes possible the dissolution of these slugs in caustic solutions. It has been recognized for some time that certain advantages are to be gained by caustic dissolution of uranium-aluminum alloy as opposed to mercury-nitric acid dissolution.<sup>(1)</sup> Chief among these are the savings in waste storage costs and the reduced equipment and process control requirements resulting from the much smaller volumes which may be

---

(1) See, for example, "Project Hope, A Chemical Reprocessing Plant for a Nuclear Power Economy", ORNL-1638 (January 21, 1954).

used to process a given amount of uranium.<sup>(2)</sup> The reason for not turning to caustic dissolution earlier is primarily the fact that too little work had been done to adequately define all the problems involved, some of which were thought to be rather serious.

Some development work has been done on caustic dissolving at Hanford Atomic Products Operation,<sup>(3)</sup> and more recently the Idaho Chemical Processing Plant has begun a study of the process.<sup>(4)</sup> It should be emphasized, however, that at these sites a mixed sodium hydroxide—sodium nitrate dissolver solution was used, whereas in the work described in this report sodium hydroxide alone was used. Sodium nitrate reacts with the hydrogen formed in the caustic dissolution and so reduces the hazard from this gas in the dissolver. The formation of hydrogen gas in the closed dissolver system was not considered a problem of great magnitude in the present study since comparable problems have been solved industrially in numerous instances, and enough economies, mainly in waste storage, could be achieved through omitting the sodium nitrate that it was deemed advisable to do so.

The most serious problem encountered in caustic dissolution is the separation of the two phases that result; the desired uranium product is contained in the minor, solid phase. Even though the

- (2) A flowsheet for processing a feed containing 60 g of uranium per liter has been proposed by J. R. Flanary of the Chemical Technology Division, ORNL.
- (3) See "Caustic Disintegration of U-Al Alloy to Produce Low Aluminum Feed for Solvent Extraction", by R. E. Burns, H. S. Gile, and C. H. Holm, HW-31245 (April 1, 1954).
- (4) See "Idaho Chemical Processing Plant Monthly Progress Report", by F. P. Vance (September 16, 1954).

processes of solid-liquid separation are highly developed, the separation necessary in the case of caustic dissolution is extraordinary since less than 0.1% of the uranium can be lost to the liquid phase, and most of the solid particles have diameters less than 1  $\mu$ . Other factors which have been given little or no attention in the past and were included in this study are dissolution rates, uranium losses resulting from unavoidable contaminants in the caustic dissolver solution, e.g., sodium carbonate and hydrogen peroxide, stability of the caustic-aluminate solution, and fission product distribution between the liquid and solid phases.

### 3.0 DISSOLUTION STUDIES

#### 3.1 Nature of the Caustic-Aluminum Reaction

When uranium-aluminum alloy slugs are dissolved in sodium hydroxide, the primary reaction is

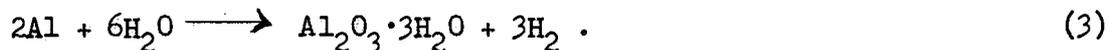


with the formation of solid uranium oxides a chemically inconsequential simultaneous reaction. The sodium aluminate is metastable, and in practice a 1.5- to 2-fold mole excess of sodium hydroxide is used. Under these conditions the sodium aluminate remains in solution for at least 100 hr, which is long enough to permit separation of the insoluble uranium compound from the aluminum solution. In the absence of excess caustic, especially at high temperatures, the sodium aluminate is converted to insoluble aluminum oxide on standing:



The presence of aluminum oxide trihydrate, as gibbsite or bayerite, in the precipitate formed when the sodium aluminate solutions were aged was shown by X-ray analysis. Sodium aluminate and other aluminum compounds were not detected.

In the presence of stoichiometric amounts of sodium hydroxide the net reaction for caustic dissolution of aluminum would be the sum of Eqs. 1 and 2:



Although this might indicate that the sodium hydroxide is only a catalyst, and that only catalytic amounts would be required for the overall reaction, such is not the case. The formation of sodium aluminate, for which a stoichiometric amount of sodium hydroxide is needed, is a necessary intermediate step in the dissolution, and the mechanism leading to the precipitation of  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  is very slow compared to that of dissolution and may actually approach zero velocity under some conditions. Also, an appreciable concentration of caustic is needed to attack the  $\text{Al}_2\text{O}_3$  which coats all aluminum and aluminum alloy that has been exposed to the atmosphere, and to remove a very adherent black oxide coating which forms on the surface of uranium-aluminum alloy when insufficient caustic is used.

### 3.2 Kinetics of Dissolution

Batch Studies. Data obtained in batch studies on caustic dissolution of uranium-aluminum alloy slugs were characteristic of heterogeneous, first-order reactions. From the known slug areas and dissolver solution volumes, the specific reaction rate constant for the reaction  $2\text{Al} + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$  was calculated as  $\sim 2.6 \times 10^{-4}$  liter/min/cm<sup>2</sup> for all batch dissolutions. This value is equivalent to an aluminum dissolution rate of 36 mg/min/cm<sup>2</sup> in 6 M sodium hydroxide, which is slightly greater than the optimum rate reported for the acid system<sup>(5)</sup> for zero aluminum concentration. Unlike the acid system, in which the dissolution rate is

(5) See "Nitric Acid Dissolution of Uranium Aluminum Alloy", by R. E. Burns and C. H. Holm, HW-18414 (August 12, 1952).

optimum at 4.5 M nitric acid and decreases with increasing aluminum nitrate concentration, the caustic system has a dissolution rate that is directly proportional to the caustic concentration over at least as great a range as 3 to 7.65 M sodium hydroxide.

The kinetic equation for batch caustic dissolution, if slug surface area and dissolver solution volume are assumed constant, is

$$\ln (c_0/c) = kst/v, \quad (4)$$

where  $c_0$  and  $c$  are the caustic molar concentrations initially and at time  $t$ , respectively;  $s$  is the available slug surface area, in square centimeters; and  $v$  is the dissolver solution volume, in liters. If either  $s$  or  $v$  is not constant ( $s$  is obviously not constant when a batch dissolution is carried to completion), this variable must be introduced into the differential rate expression as the appropriate function of the caustic concentration. An equation of the form

$$\ln [(Ac + B)/c] = kBt + \text{constant of integration}, \quad (5)$$

where  $A$  and  $B$  are constants that depend on the area/volume ratios and slug shape, is obtained when the dependence of  $s$  upon  $c$  and  $c_0$  is introduced into the instantaneous rate equation and the integration performed.

The velocity of the dissolution reaction was followed continuously by measuring the instantaneous pressure of the hydrogen gas generated in the dissolution as it issued from orifices of various sizes. When the instantaneous pressures of the evolved gas, as measured with a manometric flowmeter, were plotted against time on semilogarithmic paper, straight lines were obtained whose slopes varied directly as the ratio of the slug area to the dissolver solution volume. Most of the dissolutions from which the specific rate constant was determined were made with cast 7.5% uranium—92.5% aluminum alloy slugs. However,

values of the rate constant determined with extruded alloy slugs containing 5.37% uranium were not significantly different.

The type of apparatus in which the batch studies were made is shown in Fig. 3-1. The dissolver pot, which is enclosed in a heating mantle in the figure, was made of stainless steel.

Column Studies. From the data obtained in dissolution studies made in a 1-in.-diam. continuous trickle type glass column dissolver, the specific reaction rate constant was calculated as approximately  $9 \times 10^{-5}$  liter/min/cm<sup>2</sup>, which is only one-third the value found for the batch studies. The difference is most probably attributable to a "wetting factor" of the column. Based on the assumptions that the caustic feed rate to the column and the distribution of slug area per inch of column height are constant, both of which assumptions are justifiable, and that there is no channeling of caustic as it passes through the column, the equation describing the dissolution can be shown to be

$$\ln (C_0/C) = Xk'S/V, \quad (6)$$

where  $k'$  is the adjusted specific reaction rate constant;  $X$  is the slug bed height in inches;  $S$  is the slug area per unit height of bed in square centimeters per inch;  $V$  is the flow rate in liters per minute; and  $C_0$  and  $C$  are the caustic molar concentrations in the feed and product, respectively.

After the value of the rate constant had been determined, Eq. 6 was used to predict the caustic concentration of the product for different feed conditions; the predicted values agree with those obtained in experimental runs (see Table 3-1). In similar experiments in a 2-in.-i.d. column the value of  $S$  was increased 4-fold because the 2-in.-i.d. column has 4 times as much slug surface area per unit height of column as the 1-in.-i.d. column, and similar agreement between calculated and experimental

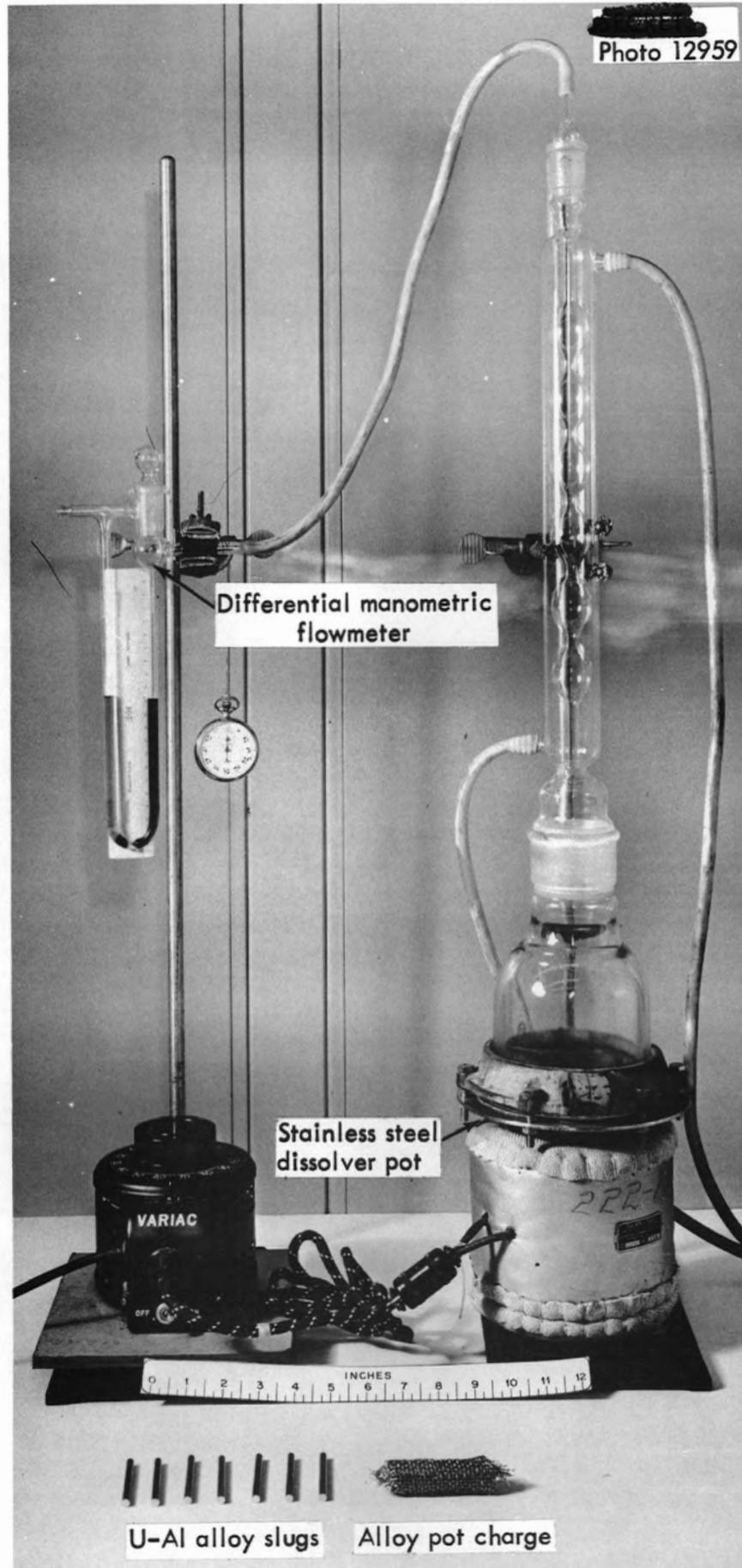


Fig. 3.1. Laboratory Batch Dissolver Used in Rate Studies.

Table 3-1

Calculated and Experimental Caustic Concentrations of Product from a 1-in.i.d. Glass Column Continuous Dissolver

Height of Slug Bed (in.)	Feed Flow Rate (liters/min)	NaOH Concentration (M)			% Error
		Feed	Product		
			Calc'd	Exp'tl	
7	0.050	4.1	2.2	2.0	+10
	0.150	4.1	3.3	3.0	+10
	0.068	6.0	3.8	3.7	+ 2.7
	0.093	6.0	4.3	4.4	- 2.3
	0.099	6.0	4.4	4.2	+ 4.8
	0.067	8.0	5.0	4.7	+ 6.4
	0.088	8.0	5.6	5.7	- 1.8
	0.100	9.7	7.1	7.7	- 7.8
14	0.100	4.1	2.2	1.9	+16
	0.160	4.1	2.8	2.7	+ 3.7
	0.060	9.7	3.4	4.2	-19
	0.100	9.7	5.2	6.0	-13

results was obtained. For these experiments miniature extruded slugs, one-fifth the size of Savannah River slugs, made of 5.37% uranium—94.63% aluminum alloy were used. Substitution of stainless steel pipe for the glass in the reaction zone had no effect on the dissolution.

The glass column used in the continuous dissolution studies is shown in Fig. 3-2, where the 1-in.-i.d. dissolver section is shown in place.

Rate of Dissolution of Uranium-Aluminum Alloy in Caustic. In a continuous trickle type glass 5.5-in.-i.d. dissolver with a 28-in.-high slug bed, using 5.37% uranium—94.63% aluminum alloy type Savannah River slugs (12 in. long and 1 in. in diameter) and 6 M sodium hydroxide at a flow rate of 1 liter/min, 6.14 kg of uranium, as the dioxide, would be produced in one 24-hr period of operation. This rate is determined as follows:

Substitution of the data in Table 3-1 in Eq. 6 gives an average value of 0.0045 for the term  $k'S$  for a 1-in.-i.d. column. For a 5.5-in.-i.d. column using full-size slugs, the value of  $S$  is increased 5.5-fold, and  $k'S = 5.5 \times 0.0045 = 0.0247$ . The slug bed height necessary to give this value of  $k'S$  with 6 M sodium hydroxide flowing at a rate of 1 liter/min is

$$x = \frac{1 \times \ln 6.13}{0.0247} = 28 \text{ in.}$$

Since 1 liter of 3 M sodium aluminate product is formed per minute, it follows that  $3 \times 60 \times 24 = 4320$  moles of sodium aluminate is formed in a 24-hr period. The slugs are assumed to be 5% uranium by weight; therefore for each mole of sodium aluminate produced,  $(5/95) \times 27 = 1.42$  g of uranium (as the oxide) is formed, or, in a 24-hr period,  $1.42 \times 4320/1000 = 6.14$  kg of uranium. The product under these conditions would be 3 M in sodium hydroxide and 3 M in sodium aluminate, with the uranium oxide present as a slurried oxide solid. It is important to note that the slurried oxide product does not become trapped in the slug bed or on the retainer plate, but passes readily through the dissolver column and into the receiving vessel. (6)

- (6) The quantitative correctness of the above calculation has been confirmed by work done by D. L. Foster et al., of the Chemical Technology Division, ORNL, using a 5.5-in.-i.d. dissolver column.

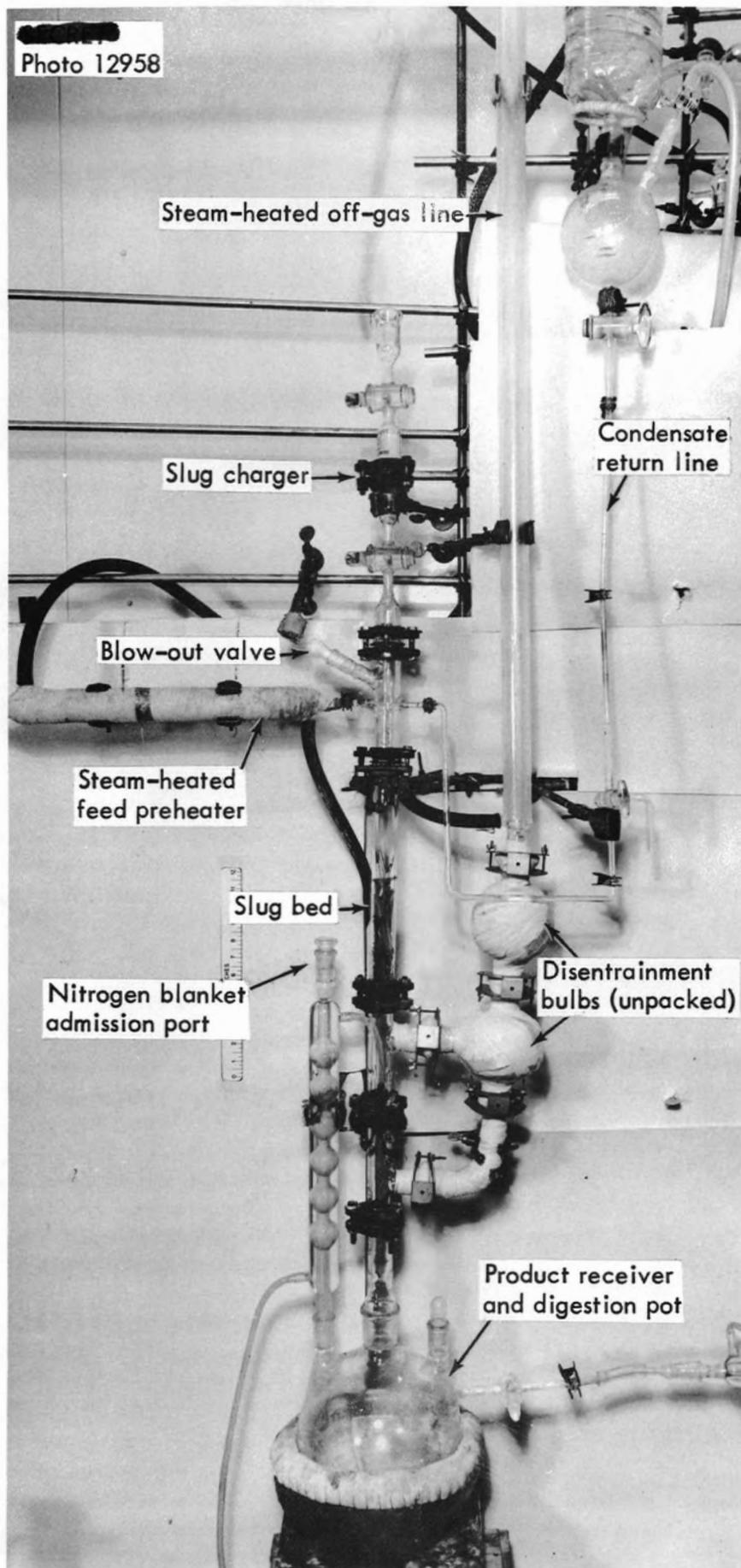


Fig. 3.2. Laboratory Trickle-Type Continuous Dissolver.

If the flow rate and bed height are both tripled, an estimated 20.4 kg of uranium would be processed in the same 24-hr period.

### 3.3 Heat Generation in Column Dissolutions

In the continuous dissolution, considerable heat, estimated from heats of formation to be 100 kcal per mole of sodium aluminate formed, was generated. It seems reasonable to assume that with larger dissolver columns heat dissipation will be a problem. Vaporization of the water as the caustic solution moves down the column will supply a mechanism for the removal of much of this heat, the water being condensed externally and returned to the top of the column where it would join the caustic feed. If very concentrated caustic feed, e.g., 10 M sodium hydroxide, were employed, it is doubtful that vaporization of water would be adequate, or even desirable, for heat removal, since local high concentrations of caustic, and hence viscous solutions, would be created. Actually, in batch experiments with 9.5 M sodium hydroxide the caustic was too viscous to give satisfactory dissolution, and subsequent solids separation was extremely troublesome. Therefore more dilute caustic feed, say, 6 or 7 M sodium hydroxide, should probably be used. The rate of heat generation will be lower for a given flow rate, and the amount of water available to remove the heat will be greater. At the same time, dissolution rates, as shown previously, would be quite satisfactory.

### 3.4 Effect of Carbonate and Peroxide

Several batch dissolutions of uranium-aluminum alloy wafers were made with caustic to which sodium carbonate had been added in order to ascertain the effect of carbonate ion on uranium losses to the liquid phase upon separation of uranium-bearing solids, and to see if the alkalinity introduced as carbonate affected the rate of dissolution. Concentrations up to 1.25 M  $\text{Na}_2\text{CO}_3$  caused no noticeable uranium loss,

and dissolution rates were those which would be expected from the caustic alone, as though no sodium carbonate had been present.

In a series of batch experiments on the effect of hydrogen peroxide, which might be formed from the water by the radioactivity from the fission products, up to 8% of the total uranium was lost under extreme conditions. The compound  $V_2O_5$  was able to remove the hydrogen peroxide by an oxidation-reduction reaction when it was present in 10-fold excess over the hydrogen peroxide added. Sodium iodide was effective in catalytic amounts, provided that the solutions were kept at the boiling point (see Table 3-2).

Hydrogen peroxide was added continuously during dissolutions in caustic of various concentrations at a rate 10 times that at which it would be formed by the  $\beta$  radiation from a 20-day-irradiated, 20% burned-up, 30-day-cooled uranium-aluminum alloy fuel element of 5.37% original uranium content. The hydrogen peroxide additions were unrealistically large because it was felt that an effort should be made to obviate the problem in its extreme; losses under actual conditions would thus be less than those determined. It was assumed that three  $H_2O_2$  molecules were formed per 100 ev (i.e., a  $G$  value of 3), and that  $\beta$  energy was 100% effective in forming  $H_2O_2$ . Under these exaggerated conditions, 8% of the total uranium was lost with 3 M caustic. The losses were less when more concentrated caustic was used as dissolvent; for example, dissolution in 6 M sodium hydroxide led to only 2% loss.

The materials which were introduced in the hope that they might either catalyze the peroxide decomposition or remove the hydrogen peroxide by a straight-forward oxidation-reduction reaction when present in excess were those capable of possessing more than one equilibrium valence in alkaline media. Substances tried were  $MnO_2$ ,  $KMnO_4$ ,  $Na_2CrO_4$ ,  $V_2O_5$ ,  $PbO_2$ , and NaI. Uranium losses when 3 M NaOH containing  $5 \times 10^{-2}$  M  $V_2O_5$  was used

Table 3-2

Uranium Losses to Dissolver Solution  $7 \times 10^{-3}$  M in Hydrogen Peroxide  
Dissolvent: 3 M NaOH

Material Added	Concentration (M)	Uranium Loss (% of total)
MnO <sub>2</sub>	$6.0 \times 10^{-2}$	4.7
MnO <sub>2</sub>	$6.0 \times 10^{-3}$	6.0
KMnO <sub>4</sub>	$2.0 \times 10^{-3}$	8.1
Na <sub>2</sub> CrO <sub>4</sub>	$3.0 \times 10^{-2}$	4.7
V <sub>2</sub> O <sub>5</sub>	$5.5 \times 10^{-2}$	0.30
V <sub>2</sub> O <sub>5</sub>	$6.0 \times 10^{-4}$	4.3
PbO <sub>2</sub>	$5.5 \times 10^{-2}$	5.1
NaBr	$6.0 \times 10^{-4}$	7.3
NaI	$6.0 \times 10^{-4}$ (kept at b.p.)	0.03

as the dissolvent were negligible. It was discovered, however, that catalytic concentrations of NaI,  $6 \times 10^{-4}$  M, were equally efficacious in the destruction of  $H_2O_2$  in the 3 M NaOH dissolver solution experiments, provided that the solutions were kept at the boiling point. With it, uranium losses were reduced from 8% to less than 0.1%. (When uranium losses are of the order of 0.1% of the total, poor filtration or insufficient centrifugation is very likely the cause; see Sec 4.0.)

### 3.5 Hydrogen Off-Gas Disposal

Since for every mole of aluminum dissolved 1.5 moles of hydrogen are liberated (Eq. 3), it is obvious that hydrogen off-gas disposal poses a problem. Possibilities being considered for its disposal are dilution with air to below the explosive limit ( $< 5\%$   $H_2$  by volume), and catalytic recombination with oxygen. Dilution would be preferred if practicable because of its simplicity and economy.

## 4.0 LIQUID-SOLID SEPARATION

The most serious problem in caustic dissolution is separation of the solid and liquid phases. This is true whether insoluble uranium-bearing solids are separated from caustic aluminate wastes, as is now being studied, or insoluble aluminum solids are separated from dissolved uranium product. In laboratory experiments the uranium-bearing solid was sometimes separated with losses as low as 0.01%, although losses of about 0.04% are more nearly representative of many runs. To facilitate the phase-separating process, aluminum concentrations should be kept low and temperatures high so that viscosities are not excessive. Solutions containing 3 M sodium hydroxide and 3 M sodium aluminate are easily handled, and represent a convenient compromise between dissolving rate and physical and chemical properties.

#### 4.1 Physical Data on Liquids and Solids

Viscosities of Dissolver Solutions. The viscosities of solutions of various sodium hydroxide and sodium aluminate concentrations were measured at 28 and 87°C and plotted (see Fig. 4-1). A temperature coordinate on which centigrade temperatures could be plotted directly was chosen so that the calculation of reciprocal absolute temperatures, usually required for plotting such data, was unnecessary. It is noteworthy that the caustic-aluminate solutions are highly viscous at room temperature (28°C), but become less viscous rapidly as the boiling point is approached, until, finally, over a very wide solution concentration range, a low viscosity is approached. Such behavior is typical of lyophilic sols, and lends support to the idea that the caustic-aluminate solutions are not entirely true solutions under most conditions of caustic concentration likely to be encountered in a caustic dissolution, but are partly sols, containing only a relatively small concentration of ionized aluminum-containing particles. The rapid approach to a low viscosity as the boiling points of the various solutions are approached also explains, in a large measure, why the caustic dissolutions appear to be first order reactions over such a large range of caustic and aluminum concentrations. The reason is that heterogeneous reactions are, primarily, diffusion-controlled. Since diffusion is governed by viscosity it follows that maintaining the viscosity nearly constant fixes the diffusion coefficient and permits other effects, in this case that of the caustic concentration, to be felt directly.

Densities of Dissolver Solutions. Densities of various possible dissolver solutions were measured at 28 and 87°C and plotted on plain coordinate paper (see Fig. 4-2). The density decreased as the temperature increased. A linear plot between only two points was chosen for the density

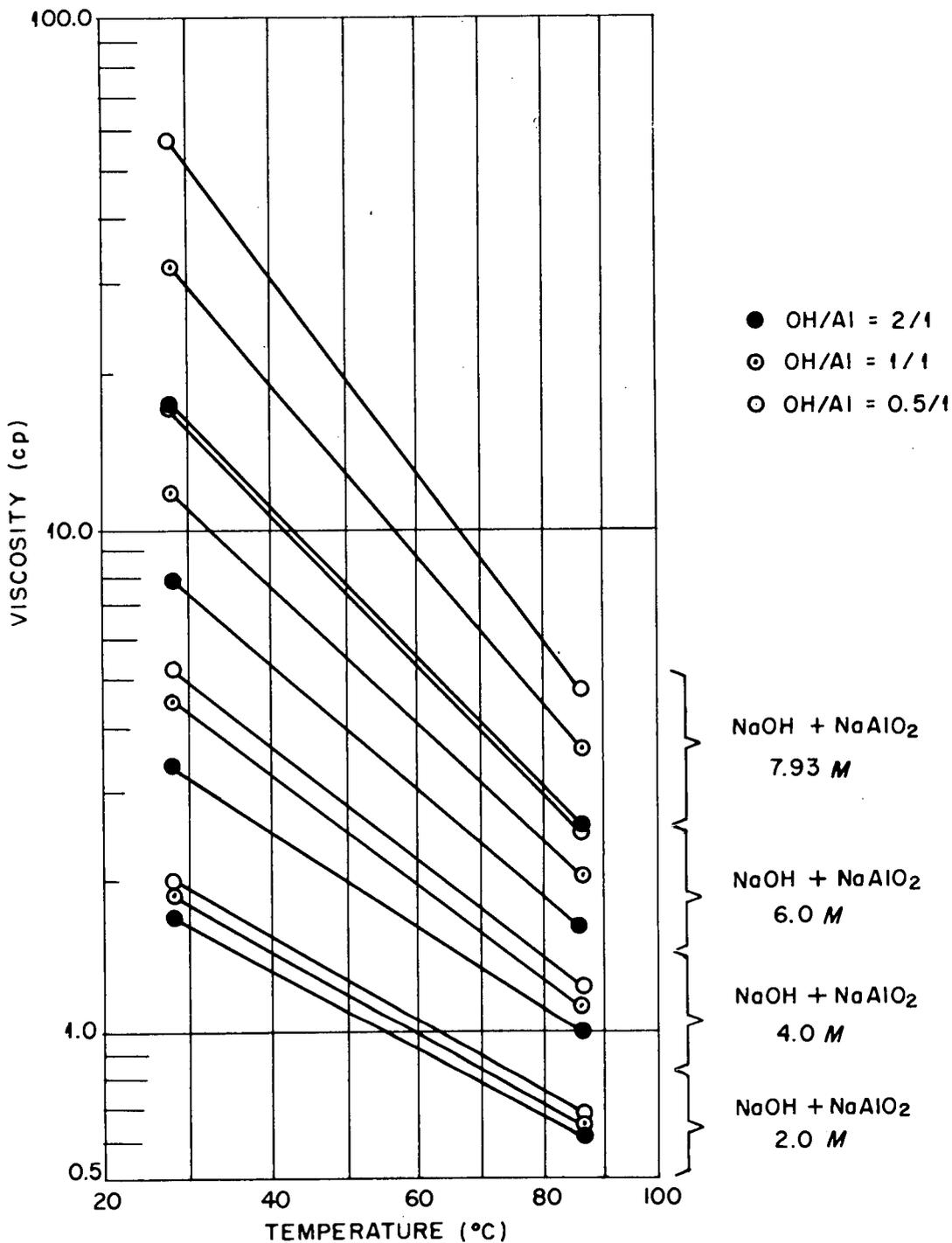
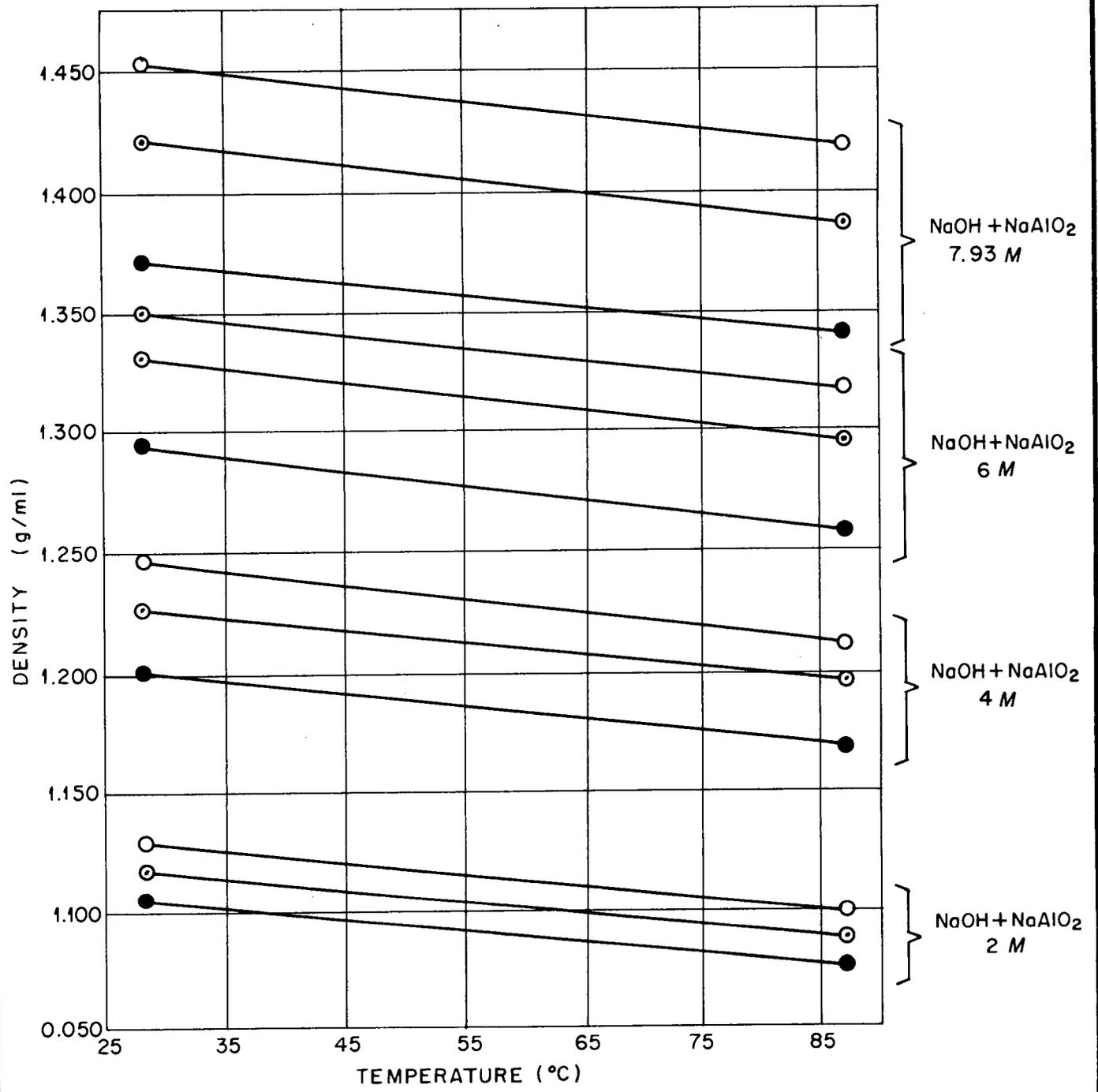


Fig. 4-1. Viscosity of NaOH-NaAlO<sub>2</sub> Solutions as a Function of Temperature and NaOH Concentration.



- OH/Al = 0.5:1
- ⊙ OH/Al = 1:1
- OH/Al = 2:1

Fig. 4-2. Density of NaOH-NaAlO<sub>2</sub> Solutions as a Function of Temperature.

graph because, with other systems in which considerable solvation of partially ionized materials has occurred, linear plots of density versus temperature have been obtained.

Density of Solids. The density of the uranium-bearing solids was determined pycnometrically for solids obtained in four different batch dissolvings. The average value was  $5.0 \pm 0.7$  g/cc. The uranium in these solids was anywhere from 0 to 100% U(IV). In the main, the solids are  $UO_2 \cdot xH_2O$ , and an average batch dissolution gives a solid with a uranium content of 70%, about 90% of which is U(IV).

The bulk density of the solids is about 1.1 to 1.2 g/cc, and it changes very little when caustic aluminate solution is substituted for air in the interparticle spaces. Bulk density, as used here, should be understood to mean the number of grams of solids per cubic centimeter occupied by those solids. The volume occupied could be measured, for example, by putting a known weight of solids in a graduated cylinder, shaking to settle them, and reading the volume directly.

Particle Size of Solids. Measurements made on photomicrographs of material from 10 different batch runs indicate that the particle size of the uranium-bearing solids is usually smaller than  $0.05 \mu$ . It must be remembered, however, that if only 1% of the particles are  $1 \mu$  or larger, and if, say, 50% are less than  $0.1 \mu$  then 20 times as much weight of material is above  $1 \mu$  as is below  $0.1 \mu$ . Therefore, the particle size data are not as discouraging as they appear at first sight, but they do indicate that complete uranium recovery would be very difficult, and that the permissible loss of  $U^{235}$  will probably dictate the design of the separation equipment.

The uranium-bearing solids are indicated by X-ray analysis to be amorphous, but they have good properties from the point of view of handling. They are completely nongelatinous and are easily drained dry and washed.

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#### 4.2 Filtration

Despite the small size of the particles, the uranium-bearing solids were filtered with average losses of about 0.05% of the total uranium. Filtration losses were about the same whether the filtration was through fine-pore paper or sintered stainless steel of G or H porosity. In all cases it is necessary to build up a mat of precipitate before high retention is achieved, and this means that recycling of the first portion of filtrate is necessary. Filtration rates measured at 40 to 50°C through a G-porosity sintered stainless steel filter and ~1 mm of filter cake under a pressure differential of 60 to 65 cm Hg are of the order of 0.2 ml/min/cm<sup>2</sup> for solutions 3 M in sodium hydroxide and 3 M in sodium aluminate. They are about 0.1 ml/min/cm<sup>2</sup> for solutions 3 M in sodium hydroxide and 3 M in sodium aluminate at 27°C. Increasing the temperature results in a marked increase in the filtration rates because of the exponential decrease of viscosity with increasing temperature. Conversely, decreasing temperature has an equally marked adverse effect on filtration rates.

#### 4.3 Centrifugation

Uranium losses were as low in centrifuging as in filtering off the solid phase. Centrifugation is the more desirable method of separation, partly because air oxidation of the uranium solids can occur on a dry filter cake, leading to formation of higher oxides, or of sodium diuranate in the presence of residual caustic. The higher oxides, and especially the diuranate, have somewhat poorer handling properties than uranium dioxide, and are more readily solubilized by complex ion formation. The presence of an aqueous layer in centrifugation excludes air and so reduces air oxidation to a negligible amount; it also provides a heat

transfer agent for fission product heat dissipation. Also, from an engineering point of view, centrifugation lends itself more readily to this type of radioactive application.

Uranium solids removal by centrifugation has been studied as a function of centrifugation time (see Table 4-1) in a centrifuge capable of exerting  $\sim 1000$  G's at the periphery. It may be seen that centrifugation times of 20 min or more were adequate to reduce uranium losses to less than 0.1%, while times of more than 30 min were hardly justifiable because of the small additional gains. The centrifugations were performed at temperatures of 35 to 45°C on material from a batch dissolution; the solutions were 3 M sodium hydroxide—3 M sodium aluminate. It should be pointed out that the product particle size from a column dissolving is not necessarily the same as that from a batch experiment. Indeed, settling rates of the uranium solids from column runs are several-fold greater, indicating either larger particle size or better agglomeration, or both, for column-produced material. At temperatures near 100°C the settling rate of the uranium oxide solids from column runs was of the order of several hours for the bulk of the solids, as opposed to several days at room temperature. This rate is, of course, a direct function of viscosity as well as of particle size.

#### 4.4 Solution Stability

In order for the uranium to be separated from the aluminum by a solid-liquid phase separation, the metastable sodium aluminate must remain in solution until the solid uranium-containing phase has been removed. It was found that, in general, as the caustic concentration in the dissolver solution decreased, the permissible aluminum concentration in the dissolver solution decreased and the permissible aluminum concentration for a stable solution, or sol, decreased more rapidly. Dissolver solutions

Table 4-1

Effect of Centrifugation Time on Uranium Solids Removal  
from 3 M NaOH—3 M NaAlO<sub>2</sub> at 35 to 45°C

Laboratory batch centrifuge operating at 980 G's at the periphery

Centrifugation Time (min)	Uranium Lost to Supernatant (% of total)
1.5	2.9
3.0	1.8
4.5	1.6
6.0	0.65
10	0.13
20	0.083
30	0.069
40	0.065
50	0.055
60	0.055

3 M in sodium hydroxide and 3 M in sodium aluminate were stable indefinitely at room temperature, probably as supersaturated solutions. At a sodium hydroxide concentration of 2 M, a sodium aluminate concentration of only 1 M could be tolerated: filtrates 1.5 M each in sodium hydroxide and sodium aluminate deposited solids after several days' standing. A 6 M sodium hydroxide feed to a dissolver column of proper size, at a rate which would permit using up half the caustic strength, should therefore give a column product stable enough to permit any handling operations, including removal to storage facilities. Equilibrium phase diagrams for the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  system are in the literature.<sup>(7)</sup> From these data it is obvious that none of the above-mentioned solutions is thermodynamically stable.

Precipitation of part of the aluminum before the uranium-containing phase is separated makes quantitative separation much more of a problem because the aluminum solids which separate from caustic-aluminate solutions are difficultly soluble, especially if permitted to age. It is conceivable, of course, that a process in which the uranium is leached from the aluminum solids (gibbsite and bayerite) might be developed. Such a process would have the advantages that stability of the sodium aluminate would be of no consequence and that less caustic would be used since only stoichiometric rather than excess amounts would be required for dissolution. In addition, precipitation of the  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  carries down some of the fission products, notably zirconium and niobium, leaving a less radioactive supernatant and contaminated solid to be stored. No development work has been carried out on such a process.

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(7) See "Equilibrium Diagram of the System  $\text{Al}_2\text{O}_3-\text{Na}_2\text{O}-\text{H}_2\text{O}$ ", F. F. Vol'f and S. I. Kuznetsov, J. Appl. Chem. USSR, 26:265, English translation (p. 298 of Zhur. Priklad. Khim.) (1953)

#### 4.5 Fission Product Distribution

Very great importance is attached to the way the fission products released into a caustic dissolver solution from irradiated uranium-aluminum alloy slugs are distributed between the uranium-bearing solids and the caustic-aluminate supernatant. It is apparent that if the fission products go wholly to one phase or to the other, the problems of chemical processing and of waste disposal are greatly simplified. Such, however, is not the case; the situation is, nonetheless, quite favorable. The bulk of the fission products is precipitated with the uranium solids, leaving cesium, iodine, zirconium, and niobium as the major contaminants of the liquid phase, of which zirconium and niobium are not present to more than several tenths of one percent of their total amounts.

Information based on a dissolution of part of a Hanford "J" slug irradiated to about 14% burnup and cooled ~9 months gives the distributions shown in Table 4-2 for the fission products between solid and liquid phases separated by filtration. The ratio given is the fraction of the radioactivity of the species in the solid phase divided by the fraction of that species in the liquid phase.

Table 4-2

Fission Product Distribution Ratios

Radioactive Species	Ratio; $\frac{\text{fraction in solid phase}}{\text{fraction in liquid phase}}$
Gross $\beta$	28
Gross $\gamma$	6.7
Total rare earth $\beta$	$> 2.6 \times 10^4$
Pu	$1.5 \times 10^3$
Sr $\beta$	$> 6.2 \times 10^5$
Nb $\beta$	$9.3 \times 10^2$
Zr $\beta$	$2.8 \times 10^2$
Ru $\beta$	$2.4 \times 10^3$
Cs $\beta$	$2.2 \times 10^{-3}$
I*	- -

\*Dissolutions of short-term-irradiated alloy have shown that iodine remains with the liquid phase to about the same extent as cesium does.

## 5.0 DISSOLUTION OF URANIUM SOLIDS IN NITRIC ACID

The uranium oxide solids formed in caustic dissolutions of uranium-aluminum alloy must be dissolved in nitric acid to form a feed for the solvent extraction process. The uranium oxides from batch dissolutions were shown to be readily soluble in boiling 6 M as well as 3 M nitric acid at uranium concentrations from 2 to 60 g/liter. This concentration range was chosen because of possible fission product radiation damage to the solvent with uranium concentrations much above 60 g/liter, and because many of the advantages of caustic dissolution over acid dissolution (for example, reduced volumes and nitric acid salting) are sacrificed when concentrations as low as 2 g/liter are used.<sup>(8)</sup>

It has been found that a 5-mole portion of nitric acid is required to dissolve 1 mole of uranium as oxide solids when the solids are about 70% uranium (as they generally are), and when the bulk of this uranium is quadrivalent, as it is in batch dissolutions. In column dissolutions the situation is somewhat altered because of the presence of  $UAl_3$  in variable amounts. When  $UAl_3$  is present a somewhat higher mole ratio of nitric acid to uranium is necessary

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(8) When mercury-catalyzed nitric acid dissolution of uranium-aluminum alloy slugs is used, the feed to the solvent extraction process is nearly saturated with aluminum nitrate ( $\sim 2$  M aluminum nitrate) when it contains approximately 2 g of uranium per liter. This is true because of the high aluminum/uranium ratio in the slugs. Caustic dissolution has as its essential feature the removal of the aluminum from the uranium so that the uranium concentration could be equal to its solubility, but for the fact that the attendant fission product activity would probably then be prohibitively high.