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NON-PRODUCTION FUELS REPROCESSING,
CENTRIFUGATION STUDIES ON VARIOUS DISSOLVER EFFLUENT SOLUTIONS

By

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CENTRIFUGATION STUDIES ON VARIOUS DISSOLVER EFFLUENT SOLUTIONSINTRODUCTION

The proposed flowsheets for reprocessing of non-production fuels include centrifugal separation of particulate matter from various dissolver effluent solutions. Thus, UO_2 particles will be recovered from Zirflex and Sulfex cladding waste solution, and core-dissolver solutions will be centrifuged for removal of zirconium oxide, metallic slimes, siliceous matter, and uranium-bearing solids. The settling characteristics of these particles in typical process solutions have been determined to provide basic information which would assist centrifuge manufacturers in designing a suitable centrifuge for the separations job.

SUMMARYUranium Oxide

Particles of uranium dioxide (UO_2) settle rapidly in either Zirflex or Sulfex cladding waste solutions. The uranium dioxide particles exposed during cladding removal operations are, generally, large and heavy. More than 99 wt. % of the UO_2 consists of large pieces and particles larger than 5 microns. Less than 0.1 wt. % is smaller than 1 micron. Particles as small as 1 micron are settled rapidly in the centrifuge (1 minute hold up at 1500 G). Laboratory centrifugation (2 minutes at 1000 G) removed all particulate uranium from Zirflex and Sulfex solutions either hot or cold (i.e., no further particulate settling occurred on prolonged standing). Prolonged exposure to either Zirflex or Sulfex solution does not affect the settling characteristics of UO_2 particles. However, Sulfex solution dissolves UO_2 if an oxidizing agent (air or nitrate ion) is present, and the solubility loss in Zirflex solution increases with time of exposure, reaching approximately 1 g U/l after 12 hours.

UO_2 packs to form a wet cake containing about 4 g UO_2 /ml. The cake is not sticky or cohesive and is easily removed from the centrifuge wall. However, the heavy particles are difficult to hold in suspension during fluid transfer of the slurry unless the flow is turbulent (Reynolds number greater than 3000).

Uranous Fluoride

Uranous fluoride, UF_3 , is formed in small amounts by digestion of UO_2 in Zirflex solution and is precipitated either as discreet crystals or by occlusion on other particles when the solution is cooled. Laboratory centrifugation for 2 minutes at 1000 G removed all particulate UF_3 from Zirflex solution.

Zirconium Oxide

Zirconium oxide particles suspended in Zirflex solution are mostly in the two to five micron range. Removal of these solids by a centrifuge requires up to three minutes residence time at 1500 G. Zirconium dioxide is crystalline and forms a granular cake containing 2.5 g ZrO_2 /ml. Even for heavily oxidized zirconium, the cake volume is expected to be less than 0.1% of the solution volume.

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Siliceous Matter

Although trace amounts of silicon exist as impurities in some of the fuels and claddings currently scheduled for Hanford processing, pilot plant studies to date have not encountered significant amounts of troublesome silicon in either the cladding or core solutions resulting from Sulfex, Zirflex and core dissolving studies. On the basis of these studies, it is anticipated that the silicon content of the various solutions will be kept at a "tolerable" level approximating that currently encountered in the separations plants.

Elemental crystalline silicon will be partially removed in the centrifuge but colloidal siliceous materials will not be removed by conventional centrifugation techniques but will continue to pass through the processing equipment to slowly build up as interface "cruds" and packing deposits.

Some fuel fabricators (e.g., PRTR) contemplate the use of appreciable concentrations of siliceous materials as corrosion inhibitors in reactor fuels. If decisions are made to fabricate and process such fuels, detailed studies will be required to determine methods for handling such fuels within the NPF complex.

Uranium Molybdate

Uranium molybdate precipitate, which may be formed by faulty operation during dissolving of U-Mo alloy fuel, is voluminous and gelatinous. The precipitate centrifuges completely in two minutes at 1000 G, but the cake may occupy 15% of the original solution volume and weigh 2.4 lb per gallon of original solution.

Cake Removal

In all cases the cake can be removed from the centrifuge wall by the action of a stream of water of reasonable force and velocity. In the 12 in. bowl used for the tests, the experimental nozzle delivered a single stream passing 2 gal/min at 80 psi with a velocity of approximately 90 ft/sec. The resulting slurries contain up to 5% solids and can be transferred by jet in the usual manner, but the approach to the jet dip leg must be well-sloped to assure that heavy particles will be flushed to the dip leg.

Separations Efficiency

The ultimate efficiency of solids removal will depend not only on the settling characteristics of the particles, but to a large degree will be affected by the design and operation of the centrifugal machinery procured for the facility. The foregoing estimates of ease of separation are based on the assumption that the centrifuge obtained for this work will have centrifugation properties at least equivalent to those of machines presently in use at Hanford (40 to 48 inch diameter, solid-bowl machines, operating at 1500 G).

Nuclear Safety

Present specifications for NPF reprocessing equipment call for the centrifuge and allied vessels to be geometrically safe when full of heterogeneous material containing 5% enriched uranium. This restriction will affect the design of the centrifuge by dictating either a small diameter (about 7.8 inches) or a filled-in center section leaving only an annulus for liquid hold up.

METHODS AND MATERIALSCorrelation of Data

In this investigation the settling characteristics of process solids were determined in water and in "cold" process solutions. Settling was accomplished at 1G in suitable containers on the laboratory bench, and in some cases at 500 G or 1000 G in a clinical (test tube) centrifuge. A few combinations were run in a Bird, 12-inch, solid-bowl centrifuge at 1500 G. Results were correlated by use of Stokes' law. The correlation was excellent for all cases of quiet settling, and Stokes' law was then used for extrapolation to process conditions. It is noted that the performance of a continuous centrifuge is never as good as that predicted by theoretical extrapolations from data on settling in a quiet pool. Actual performance becomes worse with decreasing particle size. In general, for separations of the class being considered here a given separation requires 1-1/2 to 2 times as long in a continuous centrifuge as would be predicted by Stokes' law.

Preparation of Solutions

Process solutions used were those obtained during pilot plant dissolution studies under flow sheet conditions except that no irradiated materials were used. The properties of these solutions are listed below:

<u>Solution</u>	<u>Composition</u>	<u>Specific Gravity</u>	<u>Viscosity at 20 C</u>
Water	H ₂ O	1.0	1.0 cps
Zirflex	0.6M ZrF ₄ 0.6M F ⁻	1.03	1.4
Sulfex	1M Fe, Cr, Ni (Combined) 2.7M H ₂ SO ₄	1.42	25
UNE	2M UNE 1M HNO ₃	1.7	30

Solids

The UO₂ powder used was Mallinckrodt's PWR grade, as received. Greater than 99 wt. % of the powder was larger than 5 microns. Less than 0.1 wt. % was finer than 1 micron. It is believed that UO₂ powder in the as received condition (clean and dry) is more typical of the particles that might be released from an irradiated fuel element than would be powder treated with binder or lubricant in preparation for loading into a fuel element, but still unirradiated.

Some UF₄ powder was obtained for settling studies. About 2 wt. % of the powder was smaller than 5 micron, less than 0.1% was of 1 micron size.

The Zirconium dioxide powder used in the centrifugation tests was obtained during actual Zirflex dissolution of oxidized Zircalloy-2. The Zircalloy had been oxidized by roasting in a furnace at 425 C for one week. This treatment produced 0.15 g ZrO₂ per gallon of Zirflex solution. Approximately 5 wt % of the zirconium dioxide was in the two to five micron range. There were no particles smaller than 1 micron in the samples obtained.

Uranium molybdate (or a similar uranium-molybdenum complex) in ferric nitrate-nitric acid-UNH solution was obtained from Chemical Engineering Development personnel who were studying the dissolution of U-Mo alloy. It is typical of the slurries which might be obtained during the dissolution of U-Mo alloys if acidity were not properly controlled. The composition of the supernate was:

U	250	g/l
H ⁺	0.8	
Mo	5.5	
Fe ⁺⁺⁺	45	

The solid was yellow and gelatinous, it settled (at 1000 G) to 15% of the original solution volume. The precipitate contained 30 wt % U.

A silica precipitate was prepared by acidifying one-half pound of 40°Be sodium silicate in five gallons of water with 500 ml of 10M HCl. The resulting gel was centrifuged in the 12-inch Bird machine during cake removal studies with sticky, cohesive cakes.

Experimental Methods

To determine the settling rate of a given solid, a dilute slurry (not over 2% solids) was dispersed in the chosen liquid and poured into a settling vessel. After a predetermined length of time, a small sample was withdrawn at a given depth (usually 5 or 10 cm) by means of a thin pipette. The size of the largest particles in the sample was determined by examination under a microscope with a graduated reticle (good for measurements down to 1 micron). The largest particles in the sample were assumed to have fallen the whole distance from the surface to the sample level. The diameter of a particle settling this distance could also be determined by Stokes' law and compared to the observed particle size.

Settling rates of particles in a test-tube centrifuge at 500 or 1000 G were found in a similar manner by determining the size of the largest particles that were not completely settled in a given time. This method lacked precision because of the unknown effects of starting and stopping.

Performance of certain slurries in a 12 inch, solid-bowl centrifuge was determined by operating the centrifuge at 1500 G and adjusting the slurry feed rate to give a clear overflow solution. At the end of the run, the cake was examined for ease of removal. In most cases the cake was slurried by the turbulent action of the bowl liquid when the centrifuge was braked to a stop. If the cake resisted this action, it was slurried by the action of a stream of water from a nozzle made by partially flattening the end of a length of 3/8-inch stainless steel tubing. When full water-line pressure was applied to this wash nozzle, the water flow was two gallons per minute.

Stokes' Law

Stokes' law as used here for correlation and extrapolation of data is expressed as

$$v = \frac{gD^2 (\rho_s - \rho_l)}{18 \mu}$$

where V = settling rate, cm/sec
 g = acceleration of gravity, cm/sec²
 D = particle diameter, cm
 ρ_s = density of solid particle, g/cm³
 ρ_L = density of liquid, g/cm³
 μ = viscosity of liquid, g/(sec)(cm) or poise.

According to this relation, the unhindered settling velocity of a particle in a still liquid is proportional to the gravitational field, to the net sinking force as expressed by the difference in densities, to the square of the particle size, and inversely proportional to the viscosity of the liquid. This relation assumes quiet settling of a single particle in an infinite expanse of homogeneous liquid. The law is upset in the case of very small particles (less than 0.1 micron) by Brownian movement and in the case of very large particles by eddy formation around the particle. Over the size range of concern in this study, the law holds as long as the slurries are reasonably dilute and gross liquid turbulence is avoided.

DISCUSSION OF RESULTS

Separations

Comparative settling rates for the various solids in the process solutions are tabulated below:

PARTICLE SETTLING RATES, Inch/min

<u>Solids</u>	<u>Process Solutions</u>			
	<u>Water</u>	<u>Zirflex</u>	<u>Sulfex</u>	<u>2M UNH</u>
<u>Particle Size</u> <u>and G</u>	<u>SpG = 1.0</u> <u>Vis = 1.0</u>	<u>SpG = 1.03</u> <u>Vis = 1.4</u>	<u>SpG = 1.42</u> <u>Vis = 2.5</u>	<u>SpG = 1.7</u> <u>Vis = 30</u>
UO ₂ , SpG = 10				
5-micron, 1G	0.28	0.19	0.004 0.004	(1)
2-micron, 1G	0.05	0.03	0.008	
2-micron, 1000G	50	30	28	
UF ₄ , SpG = 7				
5-micron, 1G	0.18	0.12	(1)	(1)
2-micron, 1G	0.03	0.02		
2-micron, 1000G	33	20		
ZrO ₂ , SpG = 5.5				
5-micron, 1G	0.14	0.10	(1)	0.003
2-micron, 1G	0.022	0.016		0.0005
2-micron, 1000G	22	16		0.5
Silica, SpG = 2.2				
5-micron, 1000G				0.01

(1) These particles not present in this solution

The rates listed for 1000 G have been calculated by Stokes' law. Although plant centrifuges operate at more than 1000 G (1500 and up), due to the limitations of a continuous machine, the rate calculated for quiet settling at 1000 G is considered more indicative of actual performance and may even be optimistic. The very high settling rates, 16 inches/min and higher, would not actually be realized even in quiet settling, because of eddy formation and turbulent drag at such high velocities. However, the actual settling rate is high enough that separation is assured in any reasonable equipment.

The separation of 2-micron ZrO_2 from UNH is a borderline case. The separation could be accomplished easily in a well-designed centrifuge, but would be incomplete in a machine that allowed liquid turbulence. This conclusion was demonstrated in a 12-inch, solid-bowl centrifuge operating at 1500 G. The Zirflex effluent always contained a trace (less than 0.01%) of ZrO_2 fines even if the hold-up time were 5 minutes or more.

It would seem from the calculated settling rate that the separation of fine silica from UNH solution would be practically impossible. However, silica is not expected to be present in amounts great enough to cause particular concern.

Cake Removal

The granular solids, UO_2 and ZrO_2 , did not form adherent cakes at 1500 G in the 12-inch centrifuge. The cake slurried cleanly in the residual bowl liquid (after skimming) upon stopping the machine.

To obtain a cohesive cake for removal study, a special suspension of precipitated silica hydrogel was prepared by treating a dilute solution of sodium silicate with acid. The centrifuge cake of this silica preparation stuck tightly to the bowl wall. It was removed from the wall and successfully slurried by the action of a heavy spray of water delivering 2 gallons/minute under an applied pressure of 80 psi. The spray nozzle for this use was made by flattening the end of a 3/8" tube and delivered a single stream.

Slurries containing more than 5 wt % solids can be slurried in the centrifuge, but are difficult to remove by jet. For transfer by pipeline, a slurry containing no more than 5% solids is recommended.

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July 17, 1959

R. J. Sloat, Supervisor
Process Equipment Development
Chemical Research and Development

NPF CLARIFICATION STUDIES

In the course of your proposed studies on clarification of NPF solutions, it would be deeply appreciated if answers to the following questions could be supplied.

1. What are the settling rates (1G) of UF_4 particles and undissolved oxides of zirconium resulting from the Zirflex process for (a) oxidized and (b) unoxidized fuel?
2. How do these vary as a function of density, viscosity and temperature of solution?
3. What are the answers to the above questions at 800 Gs? At 1600 Gs?
4. What are the settling rates (1G) of UO_2 particles in typical Zirflex and Sulfex waste solutions, for UO_2 particle sizes of 5, 10, 30, 100 microns?
5. What are the answers to questions 2 and 3 above, when applied to question 4?
6. On the basis of the answers to the questions above, can relationships be established which will tie the degree of clarification to liquid hold-up time in the centrifuge and the G value?
7. Will clarification of feed solution for the solvent extraction battery be required to assure nuclear safety in the solution storage tanks? If so, what are the characteristics of the particulate matter to be removed?

/s/ M. K. Harmon

M. K. Harmon, Manager
Redox Technology
Research and Engineering Operation

MKH:mk

cc: RG Barnes
RE Burns
VR Cooper
WA Graf-RA Kennedy
MK Harmon
OF Hill
AM Platt
WH Reas
RL Stevenson
RE Tomlinson

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APPENDIX B

September 24, 1959

R. J. Sloat, Supervisor
Process Equipment Development
Chemical Research and Development
HANFORD LABORATORIES OPERATION
326 BUILDING 300 AREA

NON-PRODUCTION FUEL CLARIFICATION STUDIES

M. K. Harmon to R. J. Sloat, 9-17-59
Question 7

With our present processing complex (Sulfex and Zirflex) and scheduled fuels we will have dissolver solutions of three different types to store. These will be, (1) solution from dissolution of uranium dioxide following a Sulfex decladding, (2) solution from dissolution of U-Mo alloy following caustic-nitrate decladding and (3) solution from dissolution of UO_2 following Zirflex decladding.

Type (1). This solution should be essentially the same as current dissolver solutions. The only source of constituents other than those now present is from incomplete removal of decladding solution prior to core dissolution. Small amounts of the decladding solution can be present in uranyl nitrate -- low nitric acid (0-1 M) solution without precipitation of stainless steel components. Of course, if large amounts of decladding solution are left during core dissolution, the result is essentially a Darex type dissolver solution and data on the stability toward precipitation obtained for Darex solutions would apply. We have no data on the amount of plutonium or uranium which solids precipitated from such solutions would carry.

Type (2). The HNO_3 - $Fe(NO_3)_3$ procedure is assumed for dissolution of U-Mo alloy cores. If the dissolution conditions are correct, the resulting dissolver solutions contain no visible solids. Centrifugation for 5-10 minutes in a clinical centrifuge brings down no more than a trace of solids. During the first few weeks of storage at room temperature a small amount (< 0.05 w/o of uranium charged) of solids will settle out. It is not known definitely whether these are present as colloids at the end of dissolution or are formed during storage. Solids deposition essentially ceases after a few weeks storage at room temperature.

The solids which deposit during storage are heavy and crystalline. On an air dried basis they are about 40 percent by weight uranium and 20-30 percent molybdenum. They tend to form a self-adherent cake and would be somewhat difficult to suspend by agitation. Once suspended, they settle rapidly and would be easily centrifuged. Molybdenum and uranium are readily solubilized from these solids by sodium carbonate. Iron, if present, remains as hydrated oxides. We do not have, but are obtaining, data on the carrying of plutonium by these solids. Addition of dichromate (0.2 M) to these solutions appears to retard solids formation.

If mistakes in dissolution procedures are made, formation of large volumes of solids is possible. If no iron is added, voluminous solids containing up to 10 percent of the uranium may be formed depending on the terminal acidity. These are gelatinous solids, easily centrifuged and soluble in sodium carbonate. Centrifuged volume may

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September 24, 1959

be as much as 10 percent of the solution volume (1 M UNH-U3 w% Mo alloy). Experiments with cold U-Mo dissolved in HNO_3 spiked with Pu(IV) indicate greater than 50 percent of the plutonium present will be carried on such solids. The solids may be solubilized by adding the appropriate amount of ferric nitrate and digesting the resulting slurry. If an inadequate amount of ferric nitrate is added during dissolution, solids similar to those just described will be formed but in lesser amount depending on the deficiency of ferric ion.

If dissolution is carried to a terminal acidity which is too low, uranyl molybdate will form first. Hydrated ferric oxides will form on even further reduction in acidity. We are currently studying means of solubilizing the uranyl molybdate which might form under these conditions with minimum departure from the dissolver solution composition desired. The hydrated ferric oxides may be redissolved by returning the acidity to flowsheet terminal conditions and digesting. We do not have data on the carrying of plutonium by these solids; it is expected that the amount carried will vary with the acidity.

Elevated temperature increases solids deposition in stored solutions. If solutions of marginal acidity for room temperature storage are permitted to increase in temperature, solids will form. These continue to form for a long time (Deposition of solids in samples held at 50 C has, in cases, continued for as much as six weeks). They are of the dense crystalline variety (apparently uranyl molybdate) mentioned previously. The degree of plutonium coprecipitation is not yet known. Experiments to determine the plutonium carrying are in progress. Uranium and molybdenum are readily solubilized from the solids by sodium carbonate.

Type (3). The Zirflex flowsheet proposed by A. M. Platt and C. R. Cooley, HW-60597, includes clarification of the dissolver solution to remove fines of undissolved Zr-2 and ZrO_2 . Assuming proper functioning of the dissolution procedures, no criticality problems should be involved in this centrifugation. Laboratory studies are in progress to determine the stability (towards solid formation) of the resulting dissolver solution during acidity adjustment for preparation of a Redox feed.

In summary, if the dissolution processes are done correctly, clarification of the dissolver solutions prior to storage will not be required, except for removal of extraneous solid matter such as undissolved cladding or cladding oxide. Centrifugation for this purpose should not involve criticality problems. If the dissolver solution becomes too low in acid during dissolution of U-Mo alloys, solids bearing fissionable materials will be formed. The amount of these solids formed will depend on the time the low-acid solution is held at elevated temperature. It is possible that the quantity formed could be enough to be significant from a criticality standpoint. Current studies indicate dissolution of the solids in the dissolver will be different.

/s/ R. E. Burns

R. E. Burns, Supervisor
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RE Burns:pc

cc: LC Amos OF Hill
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