

RECORDS ADMINISTRATION



R0060639

ACC# 135007
DP-MS-78-42

SRL
RECORD COPY

CLARIFICATION OF LIGHT WATER REACTOR DISSOLVER SOLUTIONS

by

M. J. Plodinec*

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina

A paper proposed for publication in
Nuclear Technology

* Send proofs to M. J. Plodinec, Phone
803-649-6211, extension 2313.

Number of pages, 11; number of tables, 4; number of figures, 3.

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900, email: orders@ntis.fedworld.gov online ordering: <http://www.ntis.gov/ordering.htm>

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865) 576-8401, fax: (865) 576-5728, email: reports@adonis.osti.gov

CLARIFICATION OF LIGHT WATER REACTOR DISSOLVER SOLUTIONS*

by

M. J. Plodinec

E. I. du Pont de Nemours and Co. :
Savannah River Laboratory
Aiken, South Carolina 29801

ABSTRACT

When high-burnup light water reactor (LWR) fuels are reprocessed, undissolved fission products remain suspended in the dissolver solution and can cause problems in solvent extraction. Several methods for clarifying LWR dissolver solutions have been evaluated. Chemical treatment as well as centrifugation will be necessary to clarify the feed for solvent extraction. Addition of an organic flocculant is the most promising method. The best flocculant tested, *Primaflow C-3* (trademark of Rohm and Haas Company of Philadelphia, Pennsylvania), clarified dissolver solutions noticeably even at flocculant concentrations of only 0.2 ppm. Unlike observed behavior of some other flocculants, no redispersion or flotation of solids was observed, even at the highest concentration tested (8300 ppm).

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Department of Energy.

The standard Purex MnO_2 treatment clarified test solutions adequately, but significantly added to the solids in the aqueous wastes. No fission product decontamination was obtained and there was evidence of dissolution of the fission product, PuO_2 , during MnO_2 precipitation.

INTRODUCTION

When high-burnup light water reactor (LWR) fuels are processed, undissolved fission products remain in the dissolved fuel as a fine suspension. These can cause problems in solvent extraction (1,2), by increasing the solvent radiolysis and decreasing the efficiency of fission product decontamination. However, this clarification should not increase the amount of solid waste generated.

As reported previously (3), laboratory dissolution of test pieces of irradiated UO_2 fuel rods from H. B. Robinson-2 produced a black, opaque solution. The solution could not be clarified by filtration through a fine-pore glass frit that can remove particles as small as 5 μm . Even after centrifugation, the solution was gray. Analysis of the extremely radioactive, undissolved black residue by spark-source mass spectrometry showed that the major components were fission products of masses 95 to 110 (Table I). The ^{106}Ru concentration was too low to be detected by spark-source mass spectrometry, but leaching of the black residue with 8M HNO_3 showed that ^{106}Ru contributed significantly to the high radioactivity of the residue.

During solvent extraction of the gray solution, black solids collected at several stages at the aqueous/organic interface. These solids could plug mixer-settlers or other equipment. Because of their high ^{106}Ru content, these solids also increase the radiolytic decomposition of the solvent and thereby decrease the efficiency of decontamination. Thus, the elimination of these solids is most desirable.

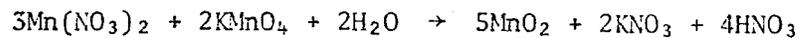
Several methods for clarifying LWR dissolver solutions were evaluated. Preliminary data indicate that a chemical treatment and centrifugation will be necessary to provide clarified feed for solvent extraction. Addition of a polymeric flocculant is the most promising method. An MnO_2 treatment, while effectively clarifying the solution, adds to the solid waste and may increase the amount of fission product ruthenium in the solvent extraction feed.

MnO_2 AND GELATIN TREATMENTS

The usual method of clarifying the Purex dissolver solution at Savannah River Plant (SRP) is precipitation of MnO_2 . The clarification is often done in the presence of gelatin (4). A similar treatment clarified LWR dissolver solution, but increased the amount of solid waste and increased the amount of ^{106}Ru in the solution. When the amount of MnO_2 precipitated was 10% of the total waste excluding MnO_2 , no decontamination was observed. At higher levels (40 wt % of the waste), some decontamination of the solution was observed. However, the maximum DF achieved for

Zr-Nb was less than 2. Gelatin had no significant effect on clarification or decontamination, and probably leads to black gelatinous solids in the organic feed stages during solvent extraction.

At SRP, MnO_2 is usually precipitated *in situ* by adding $KMnO_4$ to an excess of $Mn(NO_3)_2$. This produces MnO_2 according to



This is often done in the presence of gelatin to remove Si (as SiO_2) produced from irradiation of the Al cladding. Since LWR fuels are clad in Zircaloy, gelatin is unnecessary. However, since gelatin has some ion exchange capacity, it also was tested for clarification and decontamination of the LWR dissolver solution.

Screening tests on 10 mL of centrifuged dissolver solution containing 300 g/L U, 2.5 g/L Pu, 2.8M HNO_3 , and 7 g/L fission products showed that gelatin alone neither clarified nor decontaminated the dissolver solution. When 0.10M MnO_2 (equal to 40 wt % of the waste solids without MnO_2) was generated in the solution, no reduction in the levels of ^{134}Cs , ^{137}Cs , ^{144}Ce , or ^{154}Eu was observed. The amount of ^{106}Ru was increased 25%. Reliable data were not available on Zr or Nb. However, the solution was clarified significantly. The results were the same with or without gelatin.

Based on the screening tests, a full charge (~400 mL) of dissolver solution was clarified by precipitating 0.01M MnO₂ in 0.1 wt % of gelatin. The solution was clarified, but during solvent extraction a small amount of black gelatinous solid collected in the feed stages. This is typical of the interaction between polyvalent cations and gelatin (5).

Subsequent charges of dissolver solution were clarified with MnO₂ without gelatin. This eliminated the black gelatinous solid. Again, the amount of ¹⁰⁶Ru increased slightly (20%). However, the amount of ⁹⁵Zr decreased slightly (DF=1.7).

The experiment was repeated, but only 0.025M MnO₂ was added. This corresponds to 10% of the waste excluding MnO₂ and is a more acceptable amount. Again, treatment with MnO₂ increased ¹⁰⁶Ru in solution by 20%. No Zr decontamination was observed.

The results show that MnO₂ precipitation adequately clarifies the dissolver solution (Table II). Also, the precipitation could be done even a few weeks after the dissolution of the fuel rods and still clarify the dissolver solution. However, this clarification:

- (1) Added solid MnO₂ to the waste and thus increased storage and handling problems
- (2) Added 20-25% more Ru to the solution and this increased the burden on solvent extraction

- (3) Did not reduce Zr in the solution, except when added in large quantities.

HEAD-END TREATMENT WITH ORGANIC FLOCCULANTS

Probably the most widely used method for clarifying aqueous systems is coagulation of solids with an organic flocculant. Forty flocculants were screened according to their ability to clarify simulated dissolver solution. Seventeen were tested further with H. B. Robinson-2 dissolver solution. All but four of these seventeen flocculants clarified the dissolver solution better than MnO₂ precipitation. Two of the flocculants, *Primaflow C-3** and *Percol E-24***, clarified the dissolver solution quickly without centrifugation.

Advantages and Disadvantages of Organic Flocculants

Organic flocculants are advantageous because:

- They do not add to the volume of the final waste. Used at high dilution (1 g flocculant/10⁵ g solution), they will be destroyed by radiation and acidity in the waste solution or by high temperatures during the glass-making process.
- They are relatively inert chemically and should not dissolve any of the solids suspended in the dissolver solution.

* Trademark of Rohm and Haas.

** Trademark of Allied Colloids.

However, they may have disadvantages:

- Destruction of flocculants by radiation and HNO_3 might be so rapid that they are destroyed before flocculating the solids. This would limit the time between flocculation and separation of solids from the dissolver solution.
- The high ionic strength of dissolver solutions might interfere with ionically charged flocculants. Anionic flocculants could be neutralized by the high acid concentrations; cationic flocculants could have difficulty competing with highly charged cations for negative particles. Nonionic flocculants, which are usually amphoteric, could be susceptible to both effects.

Preliminary Tests

Forty organic flocculants were screened with simulated dissolver solution (300 g UO_2/L , 2.5M HNO_3 , 0.01M $\text{ZrO}(\text{NO}_3)_2$, plus about 2 g insoluble ZrO_2/L in suspension). Each flocculant was tested by mixing 1 mL of solution containing 1 g flocculant/L with 4 mL of water and 30 mL of this suspension. All mixtures were centrifuged, and the solids were washed, dried, and weighed. Flocculants which did not precipitate the equivalent of 2 g solids/L suspension were not tested further.

Tables III and IV show that 23 flocculants passed the screening test. Of these, 17 were subsequently tested with actual H. B. Robinson-2 dissolver solution in the Savannah River Laboratory (SRL) High Level Caves as follows. Each was added to

a portion of the dissolver solution at a concentration of 3 g flocculant/10⁴ g dissolver solution. Settling rates of suspended solids in the dissolver solutions were recorded for 18 to 24 hours, the samples were then centrifuged, and the clarified dissolver solutions were sampled for radiometric analyses. Based on these results, three of the flocculants were tested further.

Settling Tests

The three organic flocculants (*Primaflow C-3 (C-3)*, *Primaflow A-10** (A-10), and *Percol E-24 (E-24)*) were added to dissolved H. B. Robinson-2 fuel (350 g U/L in 3.1M HNO₃) in concentrations of 0.19, 1.9, 19, 190, 560, 1700, and 8300 ppm. For all but the highest concentration, 25 mL of dissolver solution was added to 5 mL of the appropriate flocculant concentration. For 8300-ppm samples, 25 mL of 1 wt % flocculant solution was added to 5 mL of dissolver solution.

Within one hour, solids in all the 8300-ppm samples had started to settle. After 1.5 hours, solids in all samples containing 190 ppm or more had started to settle. After two hours, solids in all samples were settling. In general, samples containing *C-3* settled faster than the others.

At 8300 ppm, *C-3* was clearly superior to the other two (Figure 1). *E-24* caused flotation of much of the solids, which could make separation difficult. The sample containing *A-10*

* Trademark of Rohm and Haas.

separated into three regions: the top of the sample was clarified, some solids settled to the bottom, while some were apparently redispersed in the middle.

At 1700 ppm (Figure 2), both *C-3* and *A-10* clarified the solution acceptably. However, *E-24* again caused many of the solids to float. There was no apparent difference among the flocculants at less than 1700 ppm, except that at a given concentration *C-3* settled solids faster.

Stability in Dissolver Solution

Two samples containing 190 ppm *C-3* were used to evaluate flocculant stability in dissolver solutions. One sample was heated for 6 hours in a water bath at 80 to 90°C, the other was not disturbed. After two weeks, solids in both samples gave no indication of flocculant degradation. After three weeks, a slight amount of redispersion above the solid was apparent in both samples.

Analysis of Solids

Solids flocculated by *C-3* and *E-24* were combined, washed five times with 0.5M HNO₃, and then dissolved in hot HCl. Analysis of this solution by spark-source mass spectrometry showed that the solids contained about 18% of the total ruthenium and only 0.02% of the plutonium originally present in the dissolver solution. There was too little uranium to be quantitatively determined (<0.001 wt %).

Solvent Extraction

Solutions containing up to 200 ppm *Primaflow C-3* have successfully undergone solvent extraction without interference from the flocculant. There has been no emulsification and no evidence of dispersion of the flocculant in the TBP layer. In fact, attempts to measure the concentration of flocculant in TBP solutions have been unsuccessful due to the extremely minute flocculant concentration.

CONCLUSIONS

On the basis of the work reported here, we conclude that chemical treatment of LWR dissolver solutions will be necessary to provide clarified feed for solvent extraction. While MnO_2 and organic flocculants both provide adequate clarification, an MnO_2 treatment adds to the solid waste. Thus, clarification by organic flocculants, in particular *Primaflow C-3*, seems to be a much better way to clarify these solutions.

REFERENCES

1. K. L. Huppert, K. P. Schulze, and H. Wiese. "The Reprocessing of Irradiated Nuclear Fuels on a Semi-Industrial Scale." *Kerntechnik* 18, 262 (1976).
2. K. L. Huppert, W. Issel, and W. Knoch. *Solvent Extraction*. p. 2063, Society of Chemical Industry, London (1974).
3. D. R. Johnson, submitted to *Nuclear Technology* for publication.
4. H. D. Harmon. *Decontamination of Dissolved U-Al Fuel by Simultaneous Treatment with Gelatin and MnO₂*. USERDA Report DP-1376, E. I du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1975).
5. C. E. K. Mees and T. H. James. *The Theory of the Photographic Process*. 3rd ed., p. 54-64, the MacMillan Co., New York (1966).

TABLE I

Composition of Undissolved Solids

<i>Nuclide</i>	<i>Amount, wt %</i>
^{238}U	2
Total Rare Earths	<0.01
$^{113}, ^{114}\text{Cd}$	<0.5
^{109}Ag	2
$^{105}, ^{106}, ^{107}, ^{108}, ^{110}\text{Pd}$	7
^{103}Rh	7
$^{101}, ^{102}, ^{104}\text{Ru}$	42
^{99}Tc	3
$^{95}, ^{97}, ^{98}, ^{100}\text{Mo}$	16
$^{90}, ^{91}, ^{92}, ^{94}, ^{96}\text{Zr}$	1
^{16}O	8

TABLE II

Effects of MnO_2 and Gelatin on the Presence of Solids During Solvent Extraction

<i>Clarification Treatment</i>	<i>Time After Dissolution</i>	<i>Observation</i>
Centrifugation (twice)	Immediately	Large amount of black solids in extraction stages.
MnO_2 -Gelatin Centrifugation	Immediately	Black gelatinous solids in feed stage.
MnO_2 Centrifugation	16 Days	No visible solids.
Same	Immediately	No visible solids.

Anionic and Nonionic Flocculants

<i>Flocculant</i> ^a	<i>Vendor</i>	<i>Test Results</i> ^b		<i>Dosage Limits,</i> <i>ppm</i>
		<i>Simulated</i>	<i>Actual</i>	
1100	Betz	P	P	U
1140 (N)		F		
WT2690 (N)	Calgon	F		
WT2700		P	P	U
WT3000		F		
A-10	Rohm and Haas	P	P	2 - 1700
TFL352	Petrolite	P	P	U
<i>Hercofloc</i> ^c 818.2	Hercules	P	P	U
<i>Hercofloc</i> 847		P	P	U
<i>Hercofloc</i> 853		P	F	
<i>Percol</i> ^d E-24	Allied Colloids	P	P	600
<i>Percol</i> 155		P	P	U
<i>Percol</i> 156		P		
<i>Percol</i> 351 (N)		P	U	U
XF4111	Dow	F		
N200 (N)		F		

a. (N) denotes nonionic; others are anionic.

b. P = passed, F = failed, U = unknown.

c. Trademark of Hercules Co., Wilmington, Delaware.

d. Trademark of Allied Colloids.

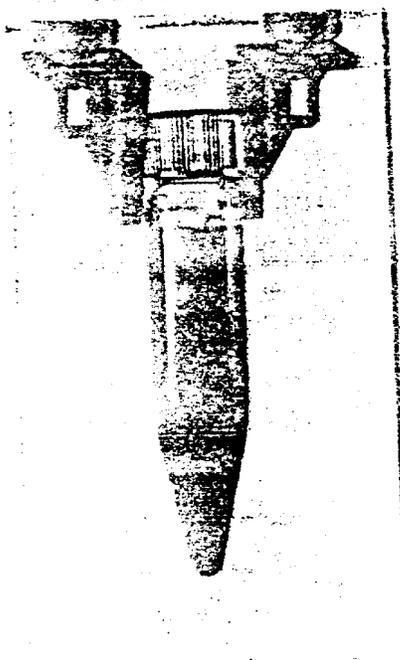
Flocculant	Vendor	Test Results		Dosage Limits, ppm
		Simulated	Actual	
1175	Betz	F		
1180		F		
1185		F		
1190		F		
TL700	National Starch	F	F	U
WT2575	Calgon	P		
WT2640		P		
WT2820		P		
WT2870		P		
Primaflow ^a C-3	Rohm and Haas	P	P	≥0.2
Primaflow C-7		P	P	U
TFL 553	Petrolite	F		
Hercofloc ^b 812.3	Hercules	F		
Hercofloc 844		P	P	U
Parcol ^c 352	Allied Colloids	P	F	
Parcol 455		P	U	U
B6134	Nalco	P	F	
XFS4145L	Dow	P	F	
C-31		P	U	U
C-41		F		
XF-4231		P	U	U
SFS45080		F		
Cat Flocc ^d T	American Cyanamid	F		
Magnifloc ^d 5730		F		

a. Trademark of Rohm and Haas.

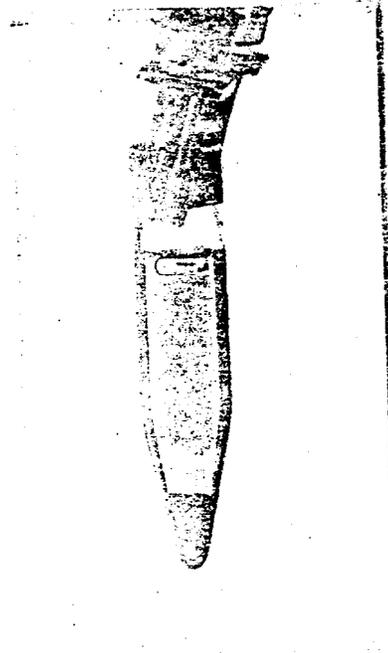
b. Trademark of Hercules Co., Wilmington, Delaware.

c. Trademark of Allied Colloids.

d. Trademark of American Cyanamid Co.



A-10

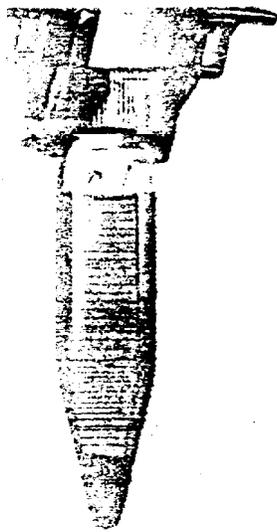


C-3

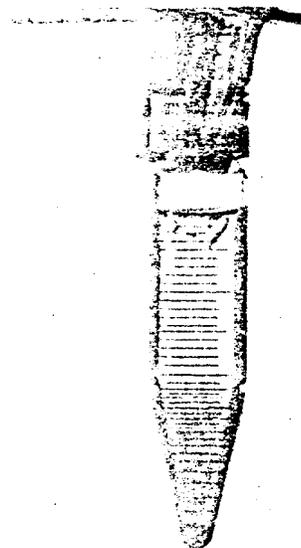


E-24

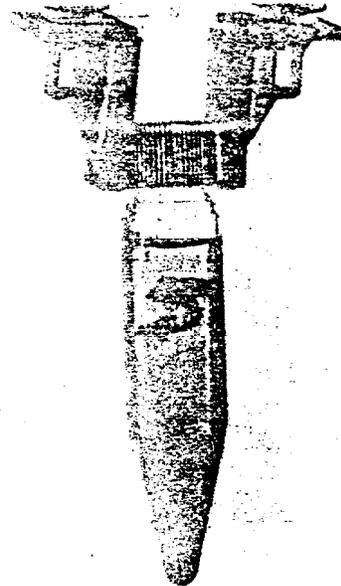
FIGURE 1. LWR Dissolver Solutions Containing 8300 PPM Organic Flocculant.



A-10

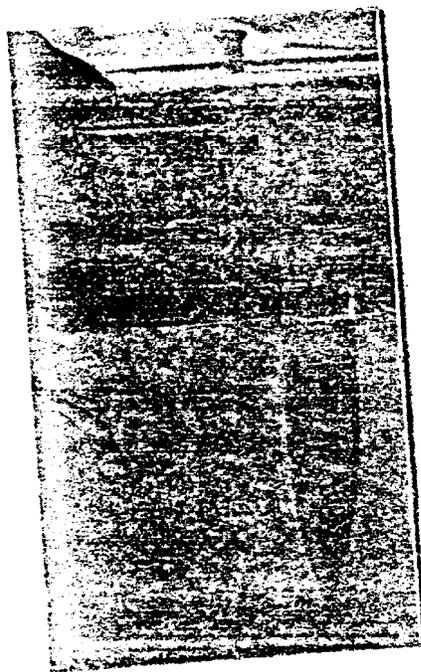


C-3

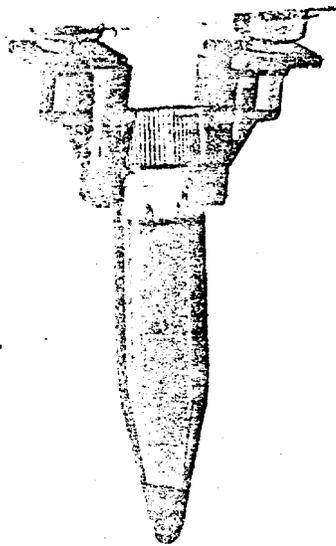


F-24

FIGURE 2. LWR Dissolver Solution Containing 1700 PPM Organic Flocculant.



BEFORE CLARIFICATION



AFTER CLARIFICATION

FIGURE 3. Unclarified and Clarified Dissolver Solutions. Solution on Right Contains 0.2 PPM Organic Flocculant.