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SUPPRESSION OF RADIOIODINE RELEASES
FROM A RADIOCHEMICAL SEPARATIONS PLANT

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S. R. Smith

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

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In the Savannah River Plant Purex process, mercury has been tested to suppress the release of radioiodine by complexing the iodine. Suppressing the release of radioiodine would be desirable in the event that short-cooled fuel were inadvertently charged to the dissolver in the plant. When irradiated uranium reactor fuels are processed, radioiodine is normally evolved during dissolution with HNO_3 , clarification, subsequent solvent extraction, and waste evaporation. Normally (without mercury), about 50% of the radioiodine is evolved from the dissolver solution and efficiently sorbed in a silver nitrate bed, but the small amount evolved from the remainder of the process is released to the atmosphere through tall stacks. This release is suppressed by adding mercuric nitrate to the dissolver solution, according to recent tests at the Savannah River Plant. With 0.04M Hg^{2+} in the dissolver solution and a gelatin clarifier, the radioiodine release was reduced 55-fold. A material balance indicated that the Hg-I complex remained in the organic solvent where it was slowly removed by solvent scrubbers

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and subsequently transferred to a seepage basin. In another test, $5 \times 10^{-4} \text{M Hg}^{2+}$ in the dissolver and a MnO_2 clarifier reduced ^{131}I releases a total of 22-fold. In tests without Hg^{2+} , MnO_2 clarification reduced ^{131}I releases 2.5-fold over the normal gelatin clarification. $4 \times 10^{-4} \text{M Hg}^+$ was not more effective than $5 \times 10^{-4} \text{M Hg}^{2+}$ in suppressing ^{131}I evolution.

INTRODUCTION

When nuclear fuels are processed by a radiochemical separations plant, radioiodine is normally evolved. After the accidental dissolving of short-cooled fuel in 1961 at Savannah River Plant (SRP) when an abnormal amount of ^{131}I was released to the atmosphere, a study was undertaken to find a suppresser in the event that short-cooled fuel was again inadvertently charged to a plant dissolver⁽¹⁾. In addition, it is sometimes necessary to process special materials soon after reactor discharge; in these cases ^{131}I suppression is desirable.

Although mercury has been proposed as a suppresser for ^{131}I releases and is used in some processes^(2,4,5,6,7), its effect has never been reported during actual Purex operations. A series of tests were conducted to determine the suppression effect of various mercury concentrations on ^{131}I evolution during routine Purex operations. Since very little ^{131}I is present normally in the process, sufficient short-cooled fuel was added to the process to trace the ^{131}I . All process effluents were carefully monitored.

Figure 1 shows the route of ^{131}I through the Purex process. In the normal dissolution of uranium without Hg^{2+} , about 50% of the iodine in the irradiated uranium is evolved and sorbed efficiently by AgNO_3 in the dissolver off-gas system. The resulting solution of uranyl nitrate is then transferred to the raw metal solution hold

tank and clarified prior to solvent extraction. Normally, a small amount of 1% gelatin solution is added during clarification to coagulate silicious material before centrifugation. However for special material, MnO_2 is used instead of the gelatin because it removes a larger fraction of radioactive material. MnO_2 is generated by first adding manganous nitrate and then slowly adding potassium permanganate. Most of the remaining iodine is released during this clarification step; more ^{131}I is released by gelatin precipitation than by the manganese dioxide precipitation. Plutonium, uranium, and fission products are then separated by solvent extraction with tributyl phosphate dissolved in refined kerosene. The iodine still in the process remains with the kerosene solvent until it is removed by caustic scrubbers, which clean the solvent. During concentration of the caustic waste, part of the ^{131}I is volatilized and eventually transferred to a seepage basin. The remaining ^{131}I is transferred to waste-storage tanks. Mercury greatly reduces the ^{131}I evolution during dissolution and clarification. The Hg-I complex stays in the kerosene solvent for several weeks and is slowly removed by caustic scrubbers.

EXPERIMENTAL

Control Tests

^{131}I behavior in the normal Purex process was determined by dissolving short-cooled fuel containing 27 Ci ^{131}I along with the normal dissolver charge. Table 1 summarizes the overall behavior of ^{131}I . 52% of the total ^{131}I was evolved to the silver nitrate reactor during dissolution. 72% of the total atmospheric release was in the first five days during gelatin clarification. Table 2 summarizes the material balance for this test.

A small amount of sodium iodide was added to the Purex dissolver (final concentration $2 \times 10^{-3}M$ NaI) during the second

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test to increase the stable iodine in the process off-gas systems to determine if this would prolong the retention of ^{131}I in this system. Also, the process was spiked with 21.6 Ci of fission product ^{131}I in the dissolver. 44% of the total ^{131}I was evolved to the silver nitrate reactor during dissolution. 69% of the total atmospheric release was in the first five days during gelatin clarification. The results of this test are summarized in Tables 1 and 2. Only 73% of the ^{131}I was accounted for during the test, probably because the process was shut down after two weeks and some of the ^{131}I may not have been completely processed. The sodium iodide did not affect iodine behavior in the process; therefore, the results of these two tests were averaged. The two control tests indicated that about 50% of the iodine is evolved during dissolution and collected by the silver nitrate reactor. Approximately 70% of the total atmospheric release is evolved during gelatin clarification. The average decontamination factor (input divided by atmospheric release) for the ^{131}I remaining in the process after dissolving was 4. The decontamination factor (DF) after dissolution was used for comparison because mercury would normally be added to the process after dissolution. If the material being dissolved is known to contain a large amount of ^{131}I , the overall DF can be doubled by releasing half the iodine to the silver nitrate reactor during dissolution and suppressing the remaining 50% with mercury. If the high ^{131}I content is not known, its presence will not be noted until after dissolution is complete.

Suppression Test with Hg^{2+}

To determine the suppression effect of Hg^{2+} on ^{131}I evolution, sufficient mercuric nitrate was added to the dissolver to obtain a Hg^{2+} concentration of $4 \times 10^{-2}\text{M}$. The normal charge was spiked with short-cooled fuel to obtain 27.7 Ci ^{131}I . Very little ^{131}I was

released during dissolution and gelatin clarification. The Hg-I complex remained in the solvent. After 21 days 70% of the total ^{131}I was in the solvent. This iodine was slowly removed during solvent wash with a carbonate-sodium hydroxide scrub solution. The scrub solution was transferred to the low-activity waste batch evaporators where most of the mercuric iodide remained in the bottom and was sent to waste-storage tanks. A small amount of the iodine volatilized during evaporation and went to the seepage basin via the acid recovery unit. The long retention in the solvent and the subsequent transfer of most of the ^{131}I to the waste-storage tanks reduced ^{131}I releases 55-fold. 63% of the total release occurred at least two weeks after the material was dissolved. (See Tables 1 and 2 for a summary of the results.)

Effect of MnO_2 Precipitation

A change in plant operating conditions required a MnO_2 precipitation during clarification. The effect of the MnO_2 was determined during 14 dissolvings summarized in Table 1. The MnO_2 precipitation reduced ^{131}I releases 2.5-fold over gelatin precipitation. This reduction was apparently due to the sorption of iodine by the MnO_2 ^(3,7).

Suppression Test with Hg^{2+} and MnO_2

To determine the suppression effect of small amounts of mercuric nitrate on ^{131}I , 13 routine dissolver solutions were adjusted to $5 \times 10^{-4}\text{M}$ in Hg^{2+} . Very little ^{131}I was evolved during dissolution or clarification. A MnO_2 precipitation was used for clarification. During these tests, ^{131}I releases were reduced 25-fold over the normal Purex process using a gelatin clarifier. Whether the Hg^{2+} effect is completely independent of the MnO_2 precipitation is not known.

Suppression Test with Hg⁺

The suppression effect of Hg⁺ on ¹³¹I evolution was determined by adding sufficient mercurous nitrate to the raw metal solution hold tank to obtain a Hg⁺ concentration of 4×10^{-4} M. The normal charge was spiked with short-cooled fuel containing 38.8 Ci ¹³¹I. 42% of the ¹³¹I was released to the AgNO₃ reactor during dissolution. The mercurous nitrate was added immediately after transferring the uranyl nitrate solution to the hold tank. The uranyl nitrate solution was then clarified with gelatin. One Ci ¹³¹I was released during the transfer to the hold tank; this reduced the DF after dissolving to 13. The DF for this test was 33 when only the releases after addition of the mercurous nitrate were considered. This indicates that mercurous nitrate was not more effective than mercuric nitrate in suppressing ¹³¹I evolution. The mercurous nitrate apparently was converted to mercuric nitrate before it reacted with the iodine.

CONCLUSIONS

Material balances indicated that during normal Purex operations, dissolution releases about 50% of the total ¹³¹I inventory to the AgNO₃ reactor. Approximately 70% of the total atmospheric release takes place in the first five days during clarification. A MnO₂ clarifier will reduce ¹³¹I releases 2.5-fold. Mercuric nitrate added to the dissolver solution suppresses the release of ¹³¹I by forming a Hg-I complex which is retained in the solvent for a long time. With 0.04M Hg²⁺ added to the dissolver, ¹³¹I atmospheric releases were reduced 55-fold over normal releases. The degree of suppression is a function of the Hg²⁺ concentration. Approximately 60% of the total ¹³¹I release to the environs occurred at least two weeks after dissolution when Hg²⁺ was present in the

process. Normally 70% of the total release would be during clarification. Hg^+ was not more effective than Hg^{2+} in suppressing ^{131}I evolution, apparently because of the rapid conversion of Hg^+ to Hg^{2+} .

REFERENCES

1. W. L. Marter, "Radioiodine Release Incident at the Savannah River Plant," Health Physics, 9, 1105 (1963).
2. C. H. Holm, "Retention of Iodine in Process Solutions by Mercuric Salts," HW 21103 (Del), Hanford Works (1951).
3. C. J. Towhill, "The Removal of Radionuclides from Water and Waste-Water by Manganese Dioxide," PhD Thesis 1964, Rensselaer Polytechnic Institute.
4. G. K. Cederberg and D. K. MacQueen, "Containment of Iodine-131 Released by the RaLa Process," IDO 14566, Phillips Petroleum Co. (1961).
5. R. W. Stromatt, "Removal of Radio-Iodine from Purex Off-Gas with Nitric Acid and with Nitric-Acid-Mercuric Nitrate Solutions," HW 55735, Hanford Works (1958).
6. E. M. Shank, "Eurochemic Assistance: Comments by ICPP on Questions from Eurochemic," ORNL-CF-60-6-30, Oak Ridge National Laboratory (1960).
7. R. C. Feber. Progress in Nuclear Energy Series III Process Chemistry, Vol. 2, Edited by F. R. Bruce, J. M. Fletcher, and H. H. Hyman, p. 255, Pergamon Press, New York (1958).

TABLE 1

¹³¹I Behavior in Purex Process

	1st Control Test with Gelatin	2nd Control Test with Gelatin	0.04M Hg ²⁺ Test with Gelatin	Control Test with MnO ₂	5x10 ⁻⁴ M Hg ²⁺ Test with MnO ₂	4x10 ⁻⁴ M Hg ⁺ Test with Gelatin
No. of Dissolvings	1	1	1	14	13	1
Total ¹³¹ I Added, Ci	26.9	21.6	27.7	20.6	9.9	38.8
¹³¹ I After Dissolving, Ci	12.8	12.1	27.7	10.7(b)	(a)	22.4(e)
% ¹³¹ I to AgNO ₃	52	44	<1	48(b)	<1	42
¹³¹ I Released to Atmosphere, Ci	2.7	3.65	0.126	1.08	0.1	1.7
DF Before Dissolving(c)	10.1	5.9	220	19	99	(e)
DF After Dissolving(d)	4.8	3.3	220	10	99	13
Average Control DF	4.0					
Suppression(f)			55	2.5	25	3

(a) Not determined

(b) Estimated based on previous tests

(c) DF = ¹³¹I in dissolver/¹³¹I released to atmosphere

(d) DF = ¹³¹I in process after dissolving/¹³¹I released to atmosphere

(e) Mercurous nitrate added after dissolving

(f) Suppression = $\frac{\text{Test DF after dissolving}}{\text{Control DF after dissolving}}$

TABLE 2

Material Balances (a)

	<u>1st Control</u> <u>Test with</u> <u>Gelatin</u>	<u>2nd Control</u> <u>Test with</u> <u>Gelatin</u>	<u>0.04M Hg²⁺</u> <u>Test with</u> <u>Gelatin</u>
¹³¹ I after dissolving, Ci	12.8	12.1	27.7
Time after dissolving ^(d)	29 days	29 days	21 days
¹³¹ I in dissolver, Ci	-	-	0.6
solvent, Ci	1.5	trace	19.3
solvent washer, Ci	-	0.5	1.8
seepage basin, Ci	5.7	1.9	0.5
out stack, Ci	4.7	6.4	0.5
% Accounted for	94	73 ^(b)	82 ^(c)

- (a) All numbers corrected for decay to day of dissolving.
 (b) Purex process was shut down two weeks after this test.
 (c) ¹³¹I also detected in a second solvent washer, in low-activity waste system, and in acid recovery, but the ¹³¹I content could not be accurately calculated.
 (d) Number of days after dissolving that material balance was determined.

FIG. 1 PUREX PROCESS

