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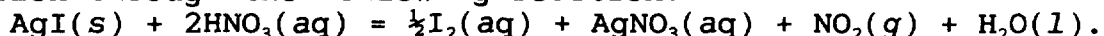
BEHAVIOR OF IODINE IN THE DISSOLUTION OF SPENT NUCLEAR FUELS

by

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Abstract

The results of laboratory-scale experiments concerning the behavior of iodine in the dissolution of spent nuclear fuels, which were carried out at the Japan Atomic Energy Research Institute, are summarized. Based on previous and new experimental results, the difference in quantity of residual iodine in the fuel solution between laboratory-scale experiments and reprocessing plants is discussed. Iodine in spent fuels is converted to the following four states: (1) oxidation into I_2 by nitric acid, (2) oxidation into I_2 by nitrous acid generated in the dissolution, (3) formation of a colloid of insoluble iodides such as AgI and PdI_2 , and (4) deposition on insoluble residue. Nitrous acid controls the amount of colloid formed. As a result, up to 10% of iodine in spent fuels is retained in the fuel solution, up to 3% is deposited on insoluble residue, and the balance volatilizes to the off-gas. Contrary to earlier belief, when the dissolution is carried out in 3 to 4 M HNO_3 at $100^\circ C$, the main iodine species in a fuel solution is a colloid, not iodate. Immediately after its formation, the colloid is unstable and decomposes partially in the hot nitric acid solution through the following reaction:



For high concentrations of gaseous iodine, $I_2(g)$, and NO_2 , this reaction is reversed towards formation of the colloid (AgI). Since these concentrations are high near the liquid surface of a plant-scale dissolver, there is a possibility that the colloid is formed there through this reversal. Simulations performed in laboratory-scale experiments demonstrated this reversal. This phenomenon can be one reason the quantity of residual iodine in spent fuels is higher in reprocessing plants than in laboratory-scale experiments.

I. Introduction

Long-lived ($T_{1/2} = 1.57 \times 10^7$ y) and hazardous, radioiodine, ^{129}I , generated in the dissolution of spent nuclear fuels should be strictly controlled in reprocessing facilities. For gaseous iodine, various kinds of silver-impregnated adsorbents have been developed to very efficiently remove it from the off-gas. Therefore, it is desirable for environmental safety that all possible iodine be expelled from fuel solutions to the dissolver off-gas (DOG) where it will be fixed on an adsorbent such as silver-impregnated silica gel (AgS). The remaining iodine, that not expelled to the DOG, migrates into the Purex process which allows its escape to the environment. Therefore, understanding the chemical species and amounts of iodine in fuel solutions as well as developing a way of expelling it therefrom are important. Extensive work has been performed by many researchers.⁽¹⁾⁻⁽³⁾

Before our research, the main iodine species in fuel solutions was postulated to be iodate (IO_3^-) from the chemical reaction of iodine in

hot nitric acid solution or uranium-nitric acid solution or both. Sparging with NO_x has been recommended for iodate removal from these solutions. More than 99% of input iodine was expelled to the DOG in both laboratory- and plant-scale experiments.^{(1),(2),(4)} According to the reports from an actual reprocessing plant, however, considerable amounts of iodine (up to 5%) remained in spent-fuel solutions and migrated to the Purex process.^{(5),(6)} Although the causes were not clarified, this finding suggests the presence of other iodine species in spent-fuel solutions and/or the presence of some factors that influence the behavior of iodine between laboratory-scale experiments and actual reprocessing plants.

Japan has been constructing a commercial reprocessing plant having a throughput of 800 t/d. Since the release of ¹²⁹I into the environment is strictly regulated, we began to restudy the iodine species in spent-fuel solutions and the methods of expelling this iodine to the DOG. In beginning this study, we labeled other fission products (FPs) in spent-fuel solutions. The interactions of iodine with other FPs were examined for the first time with simulated spent-fuel solutions. These interactions had not been questioned by earlier researchers. It was found that colloids of such insoluble iodides as silver iodide (AgI) and palladium iodide (PdI₂) played an important role in the behavior of iodine in the dissolution stage.

This paper first summarizes the results of our laboratory-scale experiments. The difference in behavior of iodine in the dissolution stage between laboratory-scale experiments and the dissolution process that occurs in reprocessing plants is then discussed.

II. Main Iodine Species in Spent-Fuel Solutions

2.1 Preliminary Study with a Simulated Spent-Fuel Solution

To obtain preliminary information about iodine species in spent-fuel solutions, experiments were performed using a uranyl nitrate-nitric acid solution and a simulated spent-fuel solution that contained uranium and simulated FPs equivalent in composition to a solution of spent fuel with a burnup of 40 GWd/t. Varying amounts of potassium iodide labeled with ¹³¹I were added to these solutions (30 to 50 ml) at 100°C and the iodine species produced were analyzed using the carbon tetrachloride extraction method. This analysis determined the quantities of dissolved iodine (I₂(aq)), I⁻, IO₃⁻, and organic iodine using an analytical scheme and considered the remaining species in the aqueous phase as non-ionic submicroparticles.⁽⁷⁾ The following results were obtained concerning the main iodine species in the solutions.^{(8),(9)}

(1) The main iodine species in the simulated spent-fuel solution was submicroparticles, while iodate was the main species in uranium-nitric acid solution.

(2) The quantity of iodine in the submicroparticles increased with increasing concentrations of Ag⁺ and Pd²⁺. When heated in 3 to 4 M HNO₃, the submicroparticles released molecular iodine (I₂).

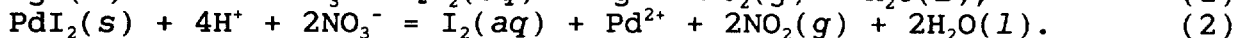
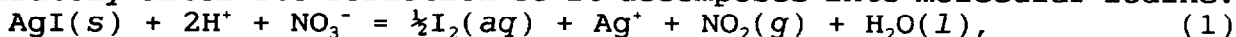
(3) When the simulated spent-fuel solution containing the submicroparticles was subjected to ultracentrifugation of 65,000 rpm, a decrease of ¹³¹I radioactivity was observed in the upper portion of the solution.

(4) A thermochemical calculation indicated that iodate cannot be the main iodine species because it is reduced to I₂ by NO_x produced in dissolution of fuels.⁽⁹⁾

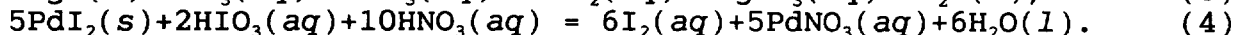
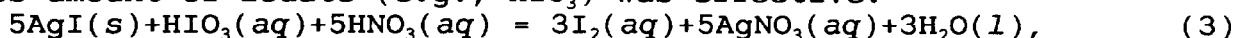
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From these results, it was concluded that the submicroparticles, the main iodine species, were colloids of AgI and PdI₂. The measured solubilities of these iodides also supports this conclusion.⁽¹⁰⁾

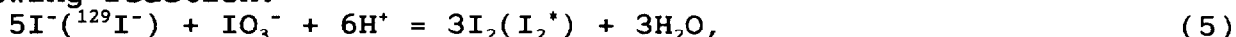
The colloidal iodine is unstable in hot nitric acid solution immediately after its formation so it decomposes into molecular iodine:



Concurrently with this process, however, the remaining colloidal iodine ages and changes to stable species. For decomposition of the stabilized colloidal iodine, it was found that the addition of an excess amount of iodate (e.g., HIO₃) was effective:



These reactions are illustrated in Fig. 1 and essentially refer to the following reaction:



where the asterisk denotes radioactive iodine, ¹²⁹I. Based on these results, the following two-step process for expulsion of the iodine remaining in spent-fuel solutions was proposed.^{(10),(11)}

Step One - Heat the fuel solution without supplying NO_x to decompose the colloidal iodine. When aging of colloidal iodine has proceeded after dissolution, an excess amount of iodate should be added.

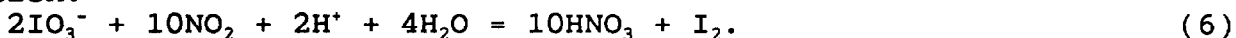
Step Two - Sparge (bubble) NO_x through the solution while heating to reduce the iodate(¹²⁹IO₃⁻) to form volatile I₂. This process is necessary because there is a possibility of formation of the iodate during Step One.

The same process was proposed by Boukis and Henrich for decomposition of non-volatile organic iodides that originated from organic impurities in nitric acid.⁽¹²⁾

In our experiments, however, the amounts of organic impurities were negligibly small.

2.2 Demonstration of the Main Iodine Species Using Actual Spent-Fuel Solutions

Expulsion of iodine from solutions of spent PWR-fuel with burnups of 21 to 39 GWD/t was performed to identify the main iodine species in actual spent-fuel solutions. Two procedures were used and their efficiencies were compared.^{(8),(9)} One procedure was conventional NO_x sparging to reduce iodate to volatile iodine (I₂) through the following reaction:



The other procedure was as described above, viz., the addition of iodate to decompose colloidal iodine through Reactions (3) and (4). This process was also applied to the solution subjected to the NO_x sparging to determine the amount of iodine remaining after NO_x sparging.

The results showed that, while 27.4 to 45.7% of the initial iodine quantity in the solutions remained after NO_x sparging, the iodine was completely removed by the process of adding iodate. This clearly indicates that the main iodine species in actual spent-fuel solutions is colloidal iodine, not iodate.

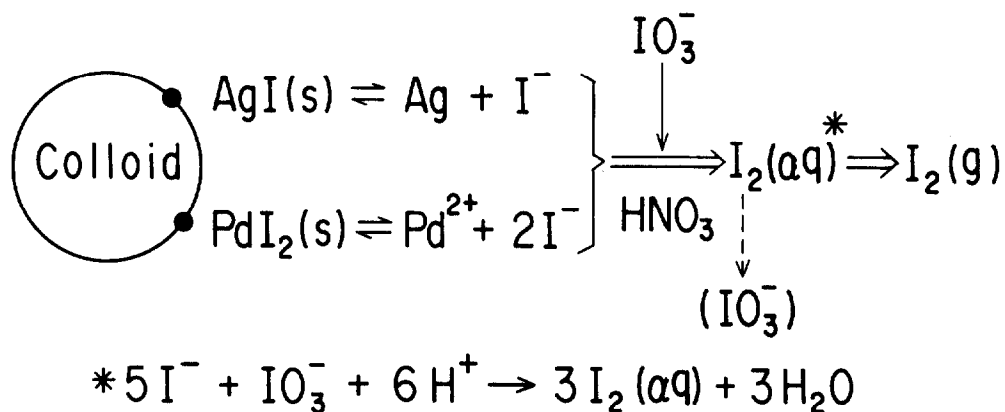


Figure 1 Mechanism for decomposition of colloids of AgI and PdI₂ by addition of iodate

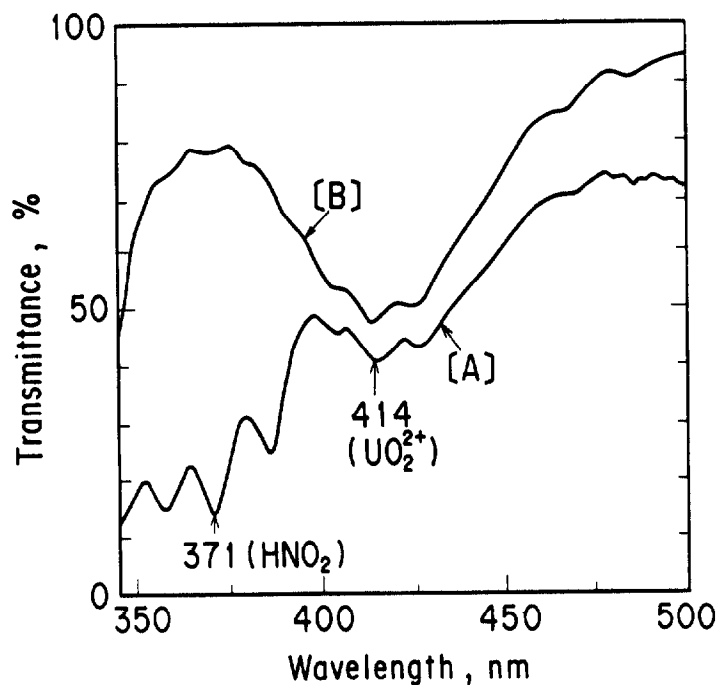


Figure 2 Influence of the dissolution rate of UO₂ on the concentration of HNO₂ produced during UO₂ dissolution in 3.5 M HNO₃ at 100°C

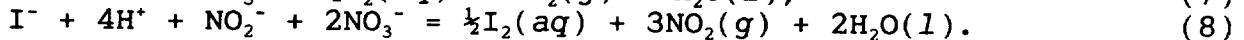
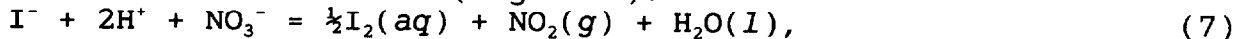
Production of HNO₂ was observed spectrophotometrically. Dissolution rate was [A] about 2 min for 0.909 g UO₂ powder and [B] 2.5 h for a 0.9321 g UO₂ pellet.

III. Distribution of Iodine in Spent-Fuel Dissolution

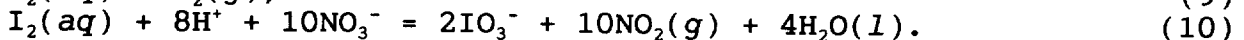
In the dissolution of spent fuels in laboratory-scale experiments, radioiodine in spent fuels (assumed as CsI) was distributed among the off-gas, fuel solution, and insoluble residue as follows.⁽¹¹⁾

3.1 Volatilization into DOG

The majority of the iodine (90% or more) was expelled to the off-gas through its oxidation by HNO_3 and by the nitrous acid (HNO_2) produced in the dissolution (Figure 2):



The dissolved iodine, $\text{I}_2(\text{aq})$, then volatilizes and is expelled to the off-gas, leaving a small fraction as iodate in solution:

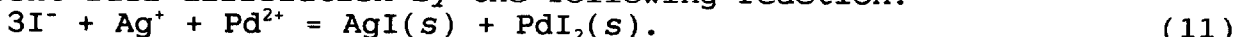


Since the iodate is reduced to I_2 by the NO_x and HNO_2 produced in fuel dissolution, only small quantities of iodate can be produced in fuel dissolution occurring in 3 to 4 M HNO_3 .

Of the iodine volatilized to the off-gas, 7% or less consisted of organic iodides, which were probably produced through the reactions of I^- or I_2 or both with organic impurities in the fuel solutions.⁽⁹⁾

3.2 Retention of Iodine Species in Spent-Fuel Solutions

Besides I_2 and a small amount of IO_3^- , colloidal iodine is produced in spent-fuel dissolution by the following reaction:



Since this reaction competes with Reaction (8), the amount of colloids produced decreased for high dissolution rates, even with high burnup fuels.⁽¹¹⁾ This occurs because high dissolution rates result in high concentrations of NO_x and HNO_2 . On the other hand, when the concentrations of NO_x and HNO_2 are too high, secondary formation of colloidal iodine may result. In high concentrations, NO_x and HNO_2 react with the iodine produced in Reactions (7) and (8) reversing Reaction (1) and forming AgI . Details are discussed below.

In experiments with simulated spent-fuel solutions, the iodine species in the solutions consisted of 60% colloidal iodine, 20% I_2 , and 20% iodate.

3.3 Deposition onto Insoluble Residue or to a Precipitate or both

Part of the iodine in spent fuels is transferred to insoluble residue or to a precipitate or both via. formation of colloidal iodine. Of the iodine in spent PWR-fuels, 3% or less was deposited onto insoluble residue.⁽¹⁰⁾

In dissolution of simulated spent-fuel pellets, an increase in UO_2^{2+} concentration in the solution beyond 170 g U/l resulted in the precipitation of large quantities of metal molybdates on which iodine was deposited.⁽¹³⁾ The causes have not yet been clarified.

The behavior of iodine in the present laboratory-scale dissolution at JAERI (the Japan Atomic Energy Research Institute) with the results earlier researchers have reported is summarized in Fig. 3. The differences noted are partially attributed to differences in the concentration of nitric acid used.

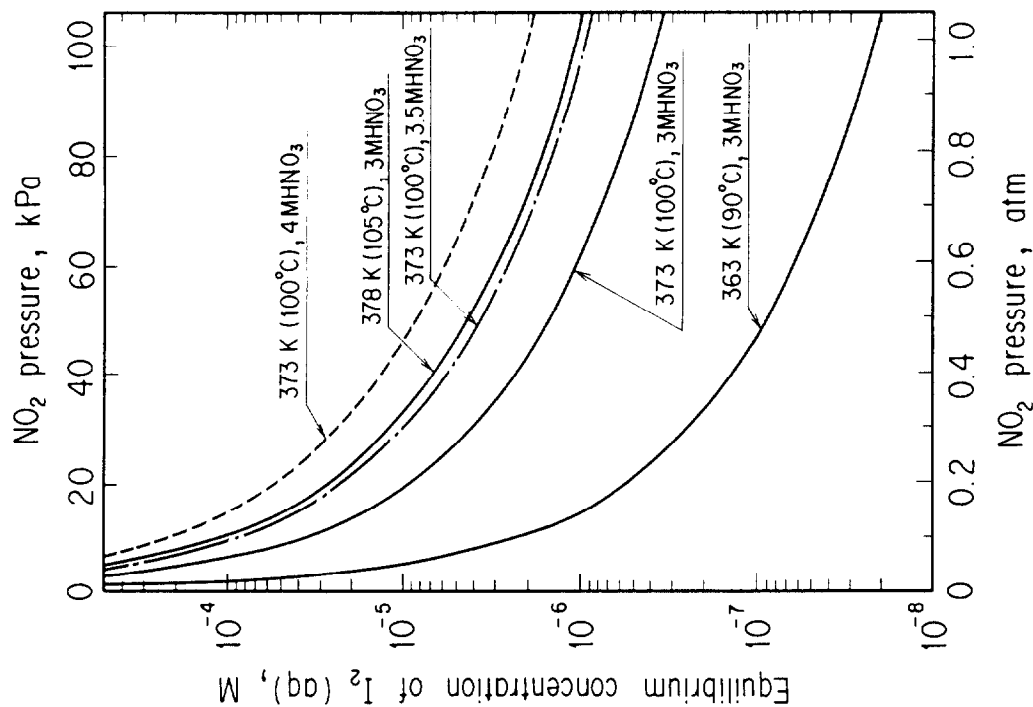
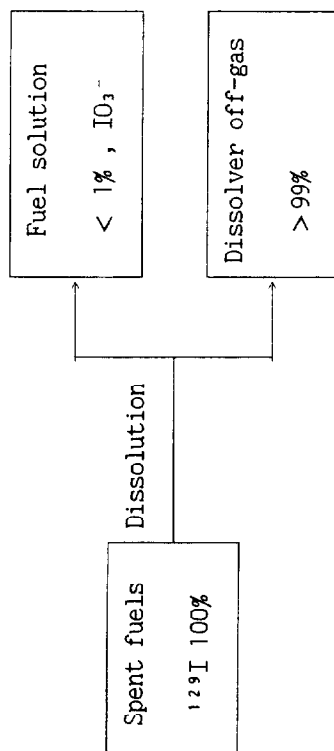


Figure 4 Relationship between dissolved iodine, $I_2(aq)$, and NO_2 in the chemical equilibrium, $AgI(s) + 2H^+ + NO_3^- = \frac{1}{2}I_2(aq) + Ag^+ + NO_2(g) + H_2O(l)$. Concentration of Ag^+ was assumed to be $2.37 \times 10^{-4} M$ for a spent-fuel solution with a burnup of 40 Gwd/t.

A) Earlier studies⁽⁴⁾. (12)



B) Present studies at JAERI

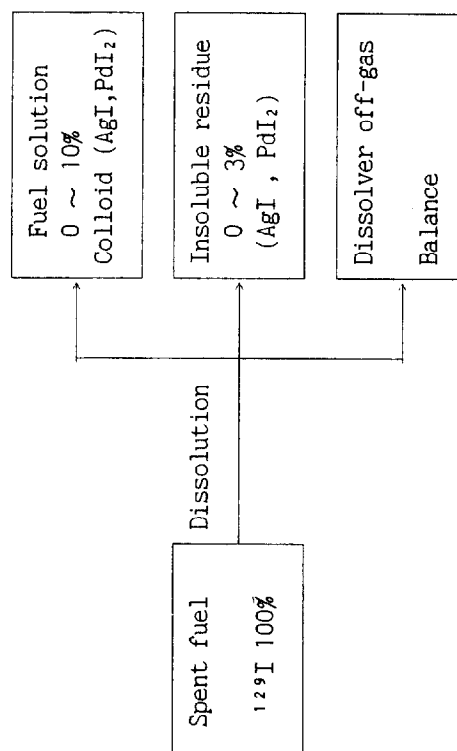


Figure 3 Distribution of iodine (^{129}I) from dissolution of spent fuels in laboratory-scale experiments

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Table 1 Comparison of the amount of iodine in spent-fuel solutions

Scale	Literature	Burnup of fuel, Gwd/t	Wt. of fuel dissolved	¹²⁹ I in the fuel solution, %	Conditions of the dissolution
Laboratory	N.Boukis and E.Henrich (1991) ^(1,2)	45	80 g	0.7	7.5 M HNO ₃ (0.22 g), 97°C, 2h
	A.Leudet et al., (1983) ⁽⁴⁾	32	Half of a fuel pin	< 1	Boiling
Plant	F.J.Herrmann et al., (1993) ⁽⁵⁾		15 ~20t/y (WAK plant)	≤ 5	

Table 2 Calculation for secondary formation of colloid(AgI) at the liquid surface of an assumed plant-scale dissolver

Conditions of the dissolver: Size, 5 × 0.3 × 2 m;
 Liquid surface, 1.5 × 10⁴ cm²; 3.5 M HNO₃ 3 m³(100°C);
 Bottom air supply, 40 Nm³/h;
 Throughput of spent fuels, 5 t/d (burnup 40 GWd/t).

Concentrations at the liquid surface	Chemical equilibrium concerned	Equilibrium concentration of I ₂ (aq)	
I ₂ (g) 88 ppm	I ₂ (g) = I ₂ (aq)	2.3 × 10 ⁻⁵ M ... (a)	Since (a) > (b), AgI will be formed.
NO ₂ 36%	AgI(S) + 2 HNO ₃ (aq) = 1/2 I ₂ (aq) + AgNO ₃ (aq) + NO ₂ (g) + H ₂ O(l)	7.2 × 10 ⁻⁶ M ... (b)	

IV. Iodine Behavior Differences between Laboratory-Scale Experiments and Reprocessing Plants

Table 1 cites an instance where the quantity of iodine remaining in a spent-fuel solution is greater in a reprocessing plant than in several laboratory-scale experiments. While laboratory-scale dissolution of high burnup fuels left only 1% or less of the iodine in spent-fuel, up to 5% of the iodine remained in spent-fuel solutions at the WAK reprocessing plant. Several factors may cause this difference. Through our studies, however, we noted the possibility that colloidal iodine (AgI) is formed secondarily at the liquid surface of a plant-scale dissolver. The reasons are discussed below.

4.1 Chemical Equilibrium

As already described, colloidal iodine is partially decomposed in hot nitric acid solution through Reactions (1) and (2). However, Reaction (1) can be reversed near the liquid-gas interface of a plant-scale dissolver. The liquid surface may have high concentrations of $I_2(g)$ and NO_2 because bubbles containing these gasses rise through the liquid after formation. When dissolution of fuel proceeds continuously at a constant rate, the concentrations of $I_2(g)$, $I_2(aq)$, NO_2 , Ag^+ , and HNO_3 remain constant with time at the liquid surface. This condition is regarded as a state of quasi equilibrium among these species; thus, an approximate chemical equilibrium treatment is appropriate for the system. Figure 4 shows the chemical equilibrium relationships of Reaction (1), in which the abscissa denotes NO_2 pressure and the ordinate represents the corresponding concentration of dissolved iodine, $I_2(aq)$. These relationships were derived from the following commonly accepted set of thermochemical equations:⁽¹⁴⁾

$$\ln (K(T_2)/K(T_1)) = \int_{T_1}^{T_2} (\Delta H^\circ_T / RT^2) dT, \quad (a)$$

$$H_T^\circ = H_{T_1}^\circ + \int_{T_1}^T \Delta C_p dT, \quad (b)$$

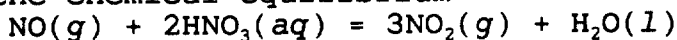
$$C_p = A + B 10^{-3} + C 10^5 T^{-2} + D 10^{-6} T^2, \quad (c)$$

where H_T° is the standard enthalpy of formation at T K, C_p is the heat capacity, and A, B, C, and D are constants specific to each substance. The equilibrium constant $K(T_1) = 298$ K; H_{298}° and C_p were adopted from the literature.⁽¹⁵⁾⁻⁽¹⁷⁾

In a fuel solution, when the concentration of $I_2(aq)$ increases beyond the curve corresponding to its temperature and HNO_3 concentration under a specific value of P_{NO_2} , colloidal AgI is formed through the reversal of Reaction (1). By assuming a simplified continuous dissolver, the concentrations of NO_2 and I_2 near the liquid surface were estimated (see below).

4.2 Concentrations of NO_2 and I_2 in a Plant-Scale Dissolver

The assumed dissolver, similar to a continuous dissolver in a reprocessing plant described in the literature,^{(2),(3)} is $5 \times 0.3 \times 2$ m with a liquid-gas interface of 1.5×10^4 cm². To stir the solution in this dissolver, 40 Nm³/h of air is fed from the bottom. Spent fuels with a burnup of 40 GWd/t are dissolved at a rate of 5 t/d in 3 m³ of 3.5 M HNO_3 at 100°C. The NO_x produced consists of 80% NO_2 and 20% NO for the chemical equilibrium



at 100°C. Fuel solution containing 250 g U/ℓ overflows toward downstream processes. Calculations indicate that gaseous iodine, $I_2(g)$,

and NO_2 volatilize at rates of 4.1×10^{-3} mol I_2/min and 16.6 mol NO_2/min , respectively. The bottom fed air increasingly collects these gasses as it rises through the solution. At the liquid surface, the air consists of 35.8% (0.358 atm) of NO_2 and 88.4 ppm of $\text{I}_2(\text{g})$. The concentration of dissolved iodine, $\text{I}_2(\text{aq})$, corresponding to 88.4 ppm $\text{I}_2(\text{g})$, was calculated to be 2.3×10^{-5} M using the equilibrium constant

$$K(373) = P_{\text{I}_2}/[\text{I}_2(\text{aq})] = 3.798$$

of Reaction (9) where P_{I_2} is in atm. Figure 4 shows that the concentration of $\text{I}_2(\text{aq})$ (in 3.5 M HNO_3) in equilibrium with 0.358 atm NO_2 (36 kPa) is 7.2×10^{-6} M, which is lower than the foregoing value (2.3×10^{-5}) in equilibrium with 88.4 ppm $\text{I}_2(\text{g})$. This excess $\text{I}_2(\text{aq})$ causes the reversal of Reaction (1) and the secondary formation of colloids of AgI at the liquid surface of the plant-scale dissolver (Table 2).

4.3 Experiments to Reverse Reaction (1)

To verify the progression of the reversal of Reaction (1) under conditions similar to those at the liquid surface of the assumed dissolver, laboratory-scale experiments were performed using the apparatus shown in Fig. 5. A 30 ml volume of 3.5 M HNO_3 solution containing 7.5 g U/30 ml (250 g U/l) and 0.8 mg $\text{Ag}^+/30$ ml was heated to 100°C and bubbled with nitrogen flow (22 ml/min) containing 88 ppm $\text{I}_2(\text{g})$ labeled with ^{131}I and 36% NO_2 for 1 h (Run 1). After its radioactivity was measured, 20 ml of the solution was transferred to a centrifuge tube (solution depth, 4 cm) and subjected to centrifugation of 4,500 rpm for 5 min. The top 10 ml was then examined by gamma spectrometry. Table 3 lists the results. The radioactivity of the solution decreased to 8% of the initial value and a whitish yellow sediment was observed on the bottom of the centrifuge tube. This confirmed that supplying 88 ppm $\text{I}_2(\text{g})$ and 36% NO_2 produced a colloid of AgI at 100°C ; that is, Reaction (1) was reversed. In Run 2, also listed in Table 3, a higher concentration of $\text{I}_2(\text{g})$ (263 ppm) and 38% NO_2 was fed to 30 ml of 3.5 M HNO_3 solution containing 12 mg $\text{Pd}^{2+}/30$ ml, 7.5 g U/30 ml, and 0.8 mg $\text{Ag}^+/30$ ml for 1 h. In this case, precipitate was observed on the bottom of the dissolver flask before centrifugation. The same sedimentation as in Run 1 was produced by the centrifugation.

The foregoing assumed dissolver is a simplified one. In actual (plant-scale) dissolvers, however, concentrations of I_2 and NO_2 would be higher near the liquid-gas interface because these gasses rise through the liquid after their formation. Due to the difference in fluid depth of spent-fuel solutions, the concentrations of these gasses at the liquid surface would be higher in a plant-scale dissolver than in a laboratory-scale dissolver. The experiments suggest that when their concentrations increase beyond the equilibrium conditions shown in Fig. 4, colloidal iodine is formed. This phenomenon can be one reason for the residual iodine quantity in spent-fuel solutions being greater in reprocessing plants than in laboratory-scale experiments.

V. Conclusions

(1) In the laboratory-scale dissolution of spent-fuels with burnups of 21 to 39 GWd/t, up to 10% of the ^{129}I in the spent fuel remains in fuel solutions, up to 3% deposits on insoluble residue, and the balance volatilizes and is expelled to the DOG.

(2) Of the iodine in the DOG, 7% or less is organic.

(3) The main iodine species in fuel solution are the colloids of

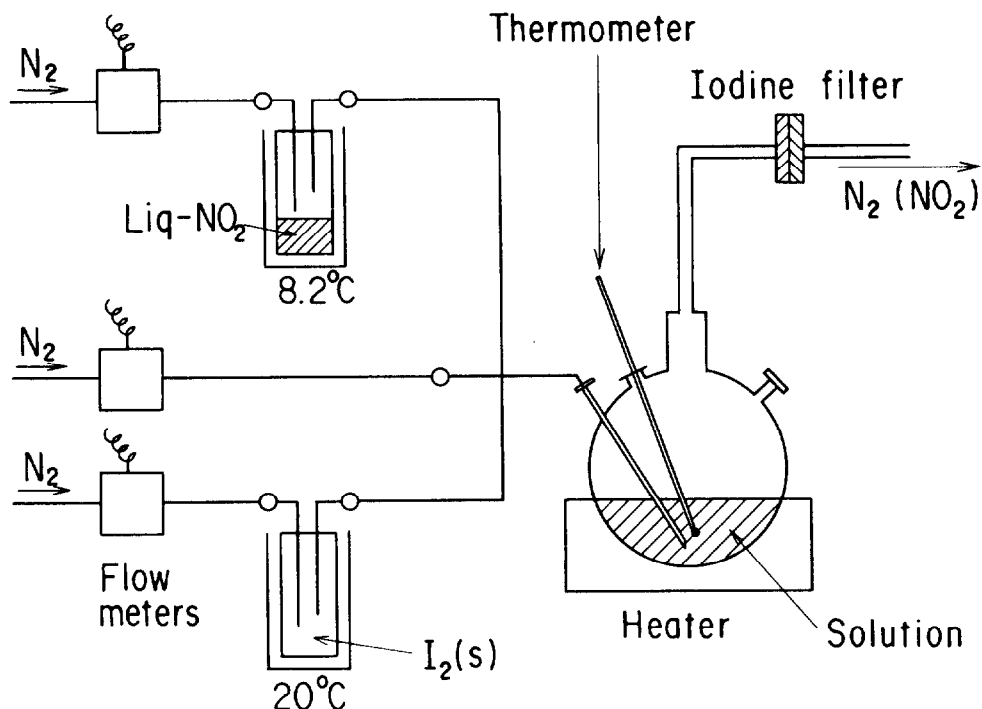


Figure 5 Experimental apparatus used for demonstrating the reversal of Reaction (1)

Table 3 Evidence of the formation of colloid by the reaction of $I_2(g)$ with NO_2 in simulated spent-fuel solutions at $100^\circ C$

[Run 1] 30 ml-3.5 M HNO_3 solution containing 7.5 g-U/30 ml and 0.8 mg- Ag^+ /30 ml

[Run 2] 30 ml-3.5 M HNO_3 solution containing 7.5 g-U/30 ml, 0.8 mg- Ag^+ /30 ml and 12 mg- Pd^{2+} /30 ml.

Time period of the supply of $I_2(g)$ and NO_2 , 1h

Centrifugation, 4,500 rpm for 5 mm.

Run No.	I_2 supplied	NO_2 supplied	N_2 flow rate	Iodine remaining in the solutions		
				① Before centrifugation	② After centrifugation	Ratio of the decrease, ②/①
1	88 ppm (1.8 mg)	36 % (12 ml/min)	22 ml/min	417 μg /30 ml ($1.1 \times 10^{-4} M-I$)	32 μg /30 ml ($8.4 \times 10^{-6} M-I$)	0.08
2	263 ppm (3.3 mg)	38 % (13 ml/min)	20 ml/min	216 μg /30 ml* ($5.7 \times 10^{-5} M-I$)	13 μg /30 ml ($3.4 \times 10^{-6} M-I$)	0.06

* Before centrifugation, precipitate was observed on the bottom of the dissolver flask.

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insoluble iodides, such as AgI and PdI₂.

(4) The amount of colloidal iodine tends to decrease with increasing concentrations of nitrous acid (HNO₂) and NO_x produced in the dissolution. So, for spent fuels with high dissolution rates, the amount of colloidal iodine is small, even if the fuel is high burnup fuel.

(5) High concentrations of I₂ and HNO₂ (or NO_x) cause formation of colloidal AgI. This is because the following reaction is reversed by conditions described above:



The reversal of this reaction has been confirmed experimentally.

(6) This reaction can also be reversed at the liquid surface of plant-scale dissolves where the concentrations of NO₂ and I₂ are higher than in laboratory-scale experiments. This phenomenon can be one reason the residual iodine in spent-fuel solutions is higher in a reprocessing plant than in laboratory-scale experiments.

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DISCUSSION

HERRMANN: I have a question about Point B . You have marked 0-10% in the fuel solution, 0-3% in insoluble residue. Is the value of 0% not too low? Does this mean that the rest, 87%, is in the offgas?

SAKURAI: In our laboratory-scale dissolutions, iodine quantities in the fuel solution and in the insoluble residue varied in the range of 0 to 10% and 0 to 3%, respectively, largely depending upon the rate of dissolution of the spent-fuel specimens. The fuel specimen with a burnup of 39GWd/t dissolved quickly, leaving little iodine in the solution and 0.6% in the residue. But the fuel-specimen with a low burnup of 21GWd/t took a long time to dissolve and 9.7% of the iodine remained in the fuel solution, and 2.3% in the residue. As a whole, the iodine quantity volatilized into the off-gas varied between 88 and 100%.

JUBIN: I found this very interesting and I have one additional question. In your laboratory studies, have you had an opportunity to try to identify the iodine in the dissolver solution? Have you identified through your centrifugation at the end a reduction in the iodine concentration? Have you been able to conduct any experiments using spent fuel to see if it does the same? Have you had an opportunity to look for the formation of iodine in the form of the colloid in actual dissolver solution?

SAKURAI: Not directly. However, iodine species in spent-fuel solution showed the same behavior in the expulsion process as the colloid of AgI and PdI₂ did. It is almost impossible to directly identify iodine species in spent-fuel solutions because of the extremely high radioactivity of the solution and the weak radioactivity of ¹²⁹I. We had to identify them through their behavior in separating from the fuel solution. The expulsion of iodine was performed in two different ways for the fuel solution. The insoluble residue had already been separated by centrifugation. From their behavior in the two expulsion processes, the main iodine species in the actual spent-fuel solution was concluded to be the colloidal iodine already mentioned.