Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 15 April 2003

To cite this Article Mineo, Hideaki , Gotoh, Minoru , Iizuka, Masaru , Fujisaki, Susumu , Hagiya, Hiromichi and Uchiyama, Gunzo(2003) 'Applicability of a Model Predicting Iodine-129 Profile in a Silver Nitrate Silica-Gel Column for Dissolver Off-Gas Treatment of Fuel Reprocessing', Separation Science and Technology, 38: 9, 1981 — 2001
To link to this Article: DOI: 10.1081/SS-120020130
URL: http://dx.doi.org/10.1081/SS-120020130

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 9, pp. 1981–2001, 2003

Applicability of a Model Predicting Iodine-129 Profile in a Silver Nitrate Silica-Gel Column for Dissolver Off-Gas Treatment of Fuel Reprocessing

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ABSTRACT

The applicability of a mathematical model predicting iodine-129 profile in a silver nitrate silica-gel (hereinafter referred to as Ag-S) column for radioactive iodine treatment was examined using actual off-gas from a dissolution step of a spent nuclear fuel reprocessing test rig, where PWR spent fuels with burnups up to 44,000 $MWdt^{-1}$ were dissolved. The iodine-129 profile predicted by the model showed good agreement with the iodine profile obtained in the experiment. It was suggested that the model would be useful to predict iodine profiles in an Ag-S column operated at 423 K for the off-gas treatment of actual spent fuel dissolution. Also, the values of the parameters used in the prediction, i.e., the effective diffusion coefficient and

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DOI: 10.1081/SS-120020130 0149-6395 (Print); 1520-5754 (Online)

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the Langmuir coefficient, were supposed to be applicable within the volumetric NO_2 concentration range lower than 1%.

INTRODUCTION

^{129}I is major radioactive iodine (radioiodine) contained in spent nuclear fuels and has a very long half-life, 1.57×10^7 years. The iodine released in a dissolution step of reprocessing can easily diffuse over the extraction and partitioning processes of reprocessing and, finally, to the environment. Management of the iodine is, therefore, indispensable to ensure the safety of a reprocessing plant. The release of radioiodine can be controlled in dissolution step of spent fuel before the extraction process by expelling as much as possible from the dissolver solution to the dissolver off-gas (DOG) and then removing the iodine from the DOG using caustic scrubbers and/or adsorbent.

Because an adsorbent system has advantages over the caustic scrubbing system,[1,2] several types of adsorbents for iodine have been developed. Among them, silica gel impregnated with silver nitrate (hereinafter referred to as Ag-S) was developed in Germany.[3] The adsorbent has been employed for about two decades in the treatment system for the DOG in Karlsruhe reprocessing plant (WAK).[4]

Although many studies were carried out to evaluate the performance of the adsorbent,[2–6] a theoretical model to predict axial iodine profile in a packed bed of Ag-S particles was scarcely developed. Recently, a simple mathematical model was proposed by the authors,[7] which could well predict the iodine profiles in Ag-S columns obtained at around 423 K in previous works under different experimental conditions. Furthermore, the effect of silver contents on the iodine profiles was reasonably predicted.

It was expected that the proposed model would give important information for the design of adsorption columns containing Ag-S. Validation of the model was, however, made using iodine profiles obtained only in tracer experiments previously reported. It is, therefore, necessary to examine the applicability of the model using data obtained under actual spent fuel dissolution conditions, where factors affecting the iodine adsorption behavior may present.

In the present study, dissolution tests, including radioiodine removal by Ag-S adsorbent, were conducted using PWR spent fuel burned up to 44,000 $MWdt^{-1}$. The predicted iodine profile by the proposed model was compared with the radioiodine profile in Ag-S adsorbent columns obtained in the dissolution test. The applicability of the model is examined.

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ADSORPTION MODEL

Adsorption Mechanism

The capturing of radioiodine from dissolver off-gas (DOG) is carried out by introducing the off-gas into a column of Ag-S particles. In the model, iodine contained in DOG is assumed to be I_2. Ag-S particles are silica-gel sphere particles impregnated with $AgNO_3$.

Removal of iodine is done by the reaction between I_2 and $AgNO_3$. The reaction mechanism is not simple. Patil et al investigated the reaction between I_2 and $AgNO_3$ intensively and proposed a sequence of reactions, (1), (2), and (3), where INO_3 was considered as an intermediate.[8] They reported that under temperatures ranging between 363 and 453 K, I_2 and INO_3 could react with other reactants rapidly. The decomposition reaction of INO_3 occurred at lower probability. Based on their results, at a temperature range between 403 and 423 K, where Ag-S column is usually operated, it can be assumed that the reaction sequence (1) and (2) dominantly and rapidly occur in Ag-S particles,[7]

$$AgNO_3 + I_2 \rightarrow AgI + INO_3 \tag{1}$$

$$2INO_3 + AgNO_3 \rightarrow AgIO_3 + 3NO_2 + \frac{1}{2}I_2 \tag{2}$$

$$INO_3 \rightleftarrows NO_2 + \frac{1}{2}O_2 + \frac{1}{2}I_2 \tag{3}$$

Considering that Ag-S particles are porous, the iodine in DOG can be adsorbed by an Ag-S particle according to the major steps shown as follows:

1. Mass transfer from bulk flow to the inside of Ag-S particle through boundary film surrounding the particle,
2. Diffusion inside the particle through the pores,
3. Adsorption of iodine,
4. Reaction of iodine with $AgNO_3$.

Mathematical Model

Gas phase mass balance of iodine in the bulk of the adsorption column is given by:

$$\varepsilon_b \frac{\partial C_G}{\partial t} + u \frac{\partial C_G}{\partial z} + \rho_b \frac{\partial \bar{Q}_P}{\partial t} = 0 \tag{4}$$

Leslie and Dryden investigated the reaction of iodine with silver nitrate plate. They employed a diffusion model, where iodine diffusion through the pores and product layer was taken into account.[9] Schon measured radial concentration profiles of iodine and silver in an Ag-S particle after adsorption operations at a temperature of 333 K.[10] It was shown that the iodine concentration was found to be high at the near surface of the particle and very low around the center. The radial profile of silver concentration did not change very much. This could indicate that the adsorption rate was controlled by an iodine diffusion step inside the Ag-S particle. The study obtained an iodine profile after adsorption at a higher temperature, 393 K, which showed, however, almost uniform concentration, suggesting chemical reaction control. In general, at higher temperatures, the chemical reaction rate would become higher and the rate-limiting step of gas–solid reaction tends to be the diffusion of gaseous species.[11] It is, therefore, necessary to treat the latter result obtained at higher temperature by Schon, carefully. Tang et al measured the axial profiles of a decontamination factor with respect to iodine in a column of adsorbent similar to Ag-S at different temperatures between 373 and 433 K. They showed that there was a very small effect of temperature on the profile.[12] This could imply that the adsorption rate was not controlled by reaction. Those studies suggested the possibility of the diffusion-controlled adsorption of iodine. In the proposed model, therefore, the rate-limiting step of iodine adsorption is assumed to be the iodine diffusion inside the adsorbent particle rather than chemical reaction, although no conclusive evidence was obtained so far. The mass balance of iodine at a radius, r, inside of the Ag-S particle is given by:

$$\rho_s \frac{\partial Q_p}{\partial t} = D_{ea}\left(\frac{\partial^2 C_P}{\partial r^2} + \frac{2}{r}\frac{\partial C_P}{\partial r}\right) \tag{5}$$

Tang et al measured the adsorption isotherm of iodine on silver-impregnated silica gels and showed that the adsorption of iodine was a chemical adsorption and it could be described by a Langmuir-type equation.[12] As Patil et al suggested, those reactions proceeded quickly.[8] It can be assumed that the adsorbed iodine per unit volume of adsorbent Q_P and the C_P at a radius, r(m) in the particle will reach at equilibrium quickly. According to the result by Tang et al the relationship between Q_p and C_p can be given as follows:

$$Q_P = q_0 \frac{KC_P}{1 + KC_P} \tag{6}$$

At the boundary film between the bulk and the inside of particle, the following boundary conditions in terms of iodine concentration can be considered:

$$D_{ea}\left.\frac{\partial C_P}{\partial r}\right|_{r=R_a,t>0} = k_f(C_G - C_{P_S}) \tag{7}$$

$$D_{ea}\left.\frac{\partial C_p}{\partial r}\right|_{r=0,t>0} = 0 \tag{8}$$

Equation (7) also gives the adsorption mass flux of iodine from the bulk to the boundary film, which can be given by:

$$k_f(C_G - C_{P_S}) = \frac{1}{av}\rho_b\left(\frac{\partial \bar{Q}}{\partial t}\right) \tag{9}$$

The value of the mass transfer coefficient, k_f, is estimated using Carberry's equation.[13]

The iodine concentration in the bulk at the entrance of the adsorption column would change depending on the spent fuel dissolution mode, i.e., batch operation or continuous operation. The proposed model, however, requires the entrance iodine concentration to be constant, which can be given by Eq. (10). This point is discussed later. Additionally $AgNO_3$ is assumed to uniformly distribute over an adsorbent particle.

$$C_G|_{z=0,t>0} = \text{const.} = C_{G0} \tag{10}$$

The initial condition is:

$$C_G|_{0\le z\le Z,t=0} = 0 \tag{11}$$

The initial conditions of the iodine concentration within the pores of the particle and the weight of adsorbed iodine per unit weight of adsorbent can be given as:

$$C_P|_{0\le r\le R_a,t=0} = 0 \tag{12}$$

$$Q_P|_{0\le r\le R_a,t=0} = 0 \tag{13}$$

Factors Affecting Iodine Adsorption Behavior

The major constituent of DOG is air, NOx, H_2O, and gaseous fission products (I_2, Kr, and Xe).[14] According to Reaction (2), it can be expected that

the NO_2 contained in DOG would affect on the removal efficiency. The efficiency may decrease with the increase of NO_2 concentration in DOG.[3]

When the operating temperature of adsorption is low, H_2O can easily adsorb on Ag-S and plug the pores of the adsorbent, which would result in the decrease of the iodine removal efficiency. It is, therefore, necessary to operate Ag-S adsorption columns at temperatures higher than 373 K to prevent condensation of H_2O_3.[3] It can be expected that the operation temperature ranging between 403 and 423 K is high enough to prevent the condensation.

EXPERIMENTAL

Dissolution Test Rig

Details of experimental reprocessing head-end equipment used in the study have been shown in the research literature.[15] The dissolution process comprised a dissolver, an iodine-stripping tank, a dissolver solution filter, an extraction-feed tank, a condenser, a scrubber, a HEPA filter, iodine adsorbent columns, and a blower. Those were installed in a heavily shielded concrete cell, except for the adsorbent columns and blower. The adsorption columns were accommodated in a glove box above the cell. The blower is used to maintain the dissolution process under negative pressure for all operating condition.

Figure 1 exhibits a schematic diagram of the adsorbent columns. The off-gas from the dissolver or the iodine-stripping tank was introduced into the columns through the condenser, the scrubber, and the HEPA filter in the cell. The first column (column A) contained MS-3A. The next three columns (columns B, C, and D) were filled with Ag-S (silica-gel impregnated with silver nitrate). Columns B and C were used for iodine removal in dissolution tests. Each column was consisted of seven cartridges containing Ag-S to measure the iodine profile. The cartridge is made of stainless steel with an inner diameter of 25 mm and 9 mm thick. Ag-S particles in the cartridge were supported by stainless steel net. Each cartridge contained 3.38 g of the adsorbent. Column D was used for iodine removal during the changing of adsorbent in columns B and C. The operating temperature of column A was 333 K. The temperature of other three columns, B, C, and D, were maintained at 423 K to prevent the condensation of H_2O. In addition, a Kr monitor and an NO_2 monitor were installed. The pipe workings between the dissolver and Ag-S columns were heated up and thermally insulated to avoid iodine adherence to the inner surface of the off-gas line.

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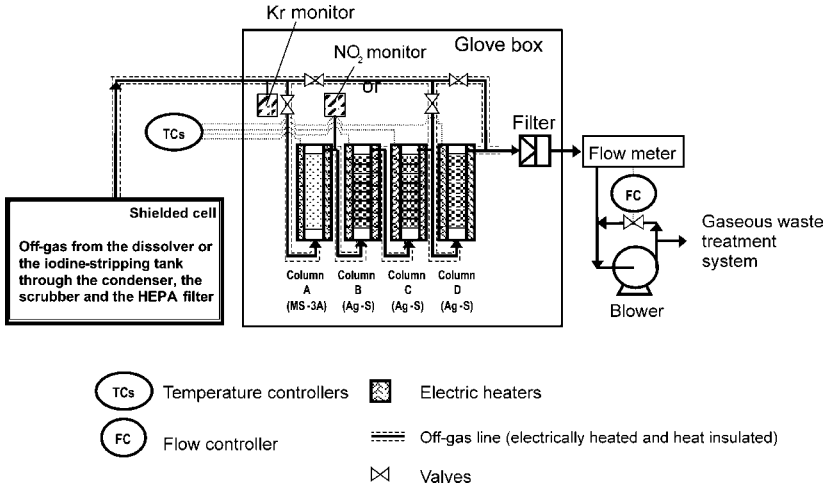

Figure 1. Schematic diagram of adsorption columns.

The adsorbent was supplied as AC6120 from Süd Chemie AG. More than 98% of the adsorbent particles were sized between 1 and 2 mm. The bulk density was about $700\,kg\,m^{-3}$ and its silver content was 12% in weight. The average pore diameter was 10 nm. The porosity inside the Ag-S particle was estimated to be about 0.578. The distribution of Ag inside of an Ag-S particle was observed using a SEM-EDX (Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer, Hitachi). It was confirmed that the Ag atom was dispersed inside the particle. This supports the validity of one of the assumptions in the model, i.e., that silver nitrate is uniformly distributed over an Ag-S particle.

Experimental Condition

The present study used PWR spent fuel with burnups of 8000, 29,000, and $44{,}000\,MWdt^{-1}$. The spent fuel had been cut into short pieces, with a length of 40 mm, before transfer into the cell. Table 1 lists the dissolution conditions employed in the present study. About 400 to 500 g of the spent fuel was used in one batch of dissolution using about 4 or $5\,mol\,l^{-1}$ of nitric acid.

Table 1. Spent fuel dissolution conditions.

Burnup [GWd/t]	Run number	U element (g)	HNO_3 concentration ($mol\,l^{-1}$) [volume (l)]	Temperature (K)	Dissolution time (min)
8	SFD1-1	436.05	5.00 (1.64)	373	200
29	SFD2-1	372.66	5.21 (1.57)	373	220
44	SFD3-1	325.72	5.26 (1.59)	373	220
44	SFD3-2	325.54	4.68 (1.64)	373	220
44	SFD3-3	342.74	3.93 (1.61)	373	220

Dissolution was carried out by elevating the temperature of the dissolver containing the spent fuel and HNO_3 aqueous solution with a designated acidity and volume and holding the temperature for a designated dissolution period.

After the dissolution, the resultant dissolver solution from the dissolution of each burnup of spent fuel was transferred to the iodine-stripping tank, where the remaining iodine in the dissolver solution was expelled into

Table 2. Iodine-stripping operations.

Burnup ($GWdt^{-1}$) (Run number)	Iodine-stripping methods employed		KIO_3 added in the two-step method (g)
8 (SFD1)	Two-steps iodine-stripping method KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min	—-	0.1
29 (SFD2)	Two-step iodine-stripping method KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min	—	0.2
44 (SFD3)	Introduction of NO_2 NO_2 gas, 363 K, 120 min	Two-step iodine-stripping method KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min	0.45

the DOG. Table 2 summarizes the operations of iodine stripping used in the present study. Iodine is contained in the dissolver solution as I_2, IO_3^-, and precipitates (AgI and PdI_2).[16] As shown in the table, two methods were employed in the present study. One is the introduction of NO_2 gas into the dissolver solution. Another method was the two-step stripping.

The introduction of NO_2 gas is used to reduce iodine in IO_3^- and to expel as I_2 to the DOG, which can be given by the following reaction:

$$2IO_3^- + 10NO_2 + 4H_2O \rightarrow I_2 + 8H^+ + 10NO_3^- \quad (14)$$

The two-step stripping method was proposed by Sakurai et al.[17] In the first-step of the operation, KIO_3 was added to the dissolver solution being heated up at 373 K to decompose the precipitates (AgI and PdI_2) according to the reaction.[15] The solution was maintained at the same temperature for 2 hours. In the second-step of the operation, NO_2 gas was introduced and maintained at 373 K for 2 hours, which is the same as Reaction (14). This enables the reduction and expulsion of iodine that has been oxidized to IO_3^- by nitric acid during the operation using Reaction (15).

$$\begin{aligned} 5AgI + KIO_3 + 6HNO_3 &\rightarrow 3I_2 + KNO_3 + 5AgNO_3 + 3H_2O \\ 5PdI_2 + 2KIO_3 + 12HNO_3 &\rightarrow 6I_2 + 2KNO_3 + 5Pd(NO_3)_2 + 6H_2O \end{aligned} \quad (15)$$

In all experiments, the flow rate of DOG for both dissolution and iodine stripping was maintained at approximately $0.4\,Nm^3\,h^{-1}$.

Analysis

After each operation of dissolution and iodine stripping, the cartridge was removed from the column and the amount of iodine-129 on each cartridge was measured using a multichannel pulse height analyzer (SEIKO EG&G 7700) with a germanium detector (ORTEC LO-AX51370/20-P) for low-energy gamma rays. Each measurement was carried out using whole Ag-S particles contained in each cartridge. A calibration curve for the relationship between the counting rates and iodine-129 amount in an Ag-S cartridge was determined using a procedure similar to that used by Sakurai et al.[18] In the present study, the detection limit of the measurement was about 1 Bq per cartridge. Relative measurement error using the calibration curve was estimated to be about 7%. The low-energy gamma radioactivity measurement for each cartridge was repeated three times and averaged. The relative random error of measurement

was about 3%. Therefore, the total relative measurement error in the present study was estimated to be 7.6%.

RESULTS AND DISCUSSION

Iodine-129 Profiles Measured

Figure 2 shows the profiles of iodine-129 on the Ag-S column (Column B) that were measured in the dissolution and iodine-stripping operations using 44,000 $MWdt^{-1}$ spent fuel. It can be seen from the figure that the adsorbent was not saturated with iodine. The profiles obtained in the dissolution tests were almost identical to each other, though the nitric acid concentration used was different. Table 3 lists the total amount of iodine captured by Ag-S column (Column B) at each dissolution test. The total amount of iodine in one dissolution test series was shown to be almost the same amount, around 5.3×10^{-5} kg. The proposed model has suggested that the iodine profile was determined by the amount of iodine adsorbed under a given operating condition.[7]

In the table, the iodine-stripping operation using NO_2 gas evolved about 2.7×10^{-5} kg of iodine-129. The two-step method removed about 5.9×10^{-6} kg of iodine-129. Those two methods were shown to be effective for iodine stripping. The amounts of iodine-129 adsorbed were

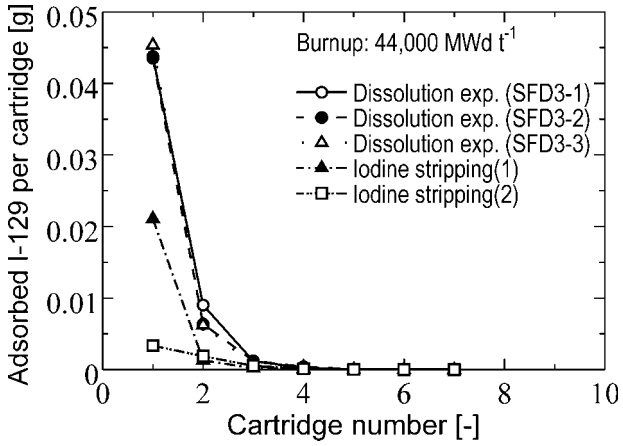

Figure 2. Profiles of iodine-129 obtained in the dissolution and iodine-stripping operation using 44,000 $MWdt^{-1}$ spent fuel.

Table 3. Amount of Iodine-129 adsorbed by the Ag-S column (Column B).

Burnup ($GWdt^{-1}$)	SFD3-1 (kg)	SFD3-2 (kg)	SFD3-3 (kg)	SFD3 iodine stripping (1) (kg)	SFD3 iodine stripping (2) (kg)
44	5.44×10^{-5}	5.16×10^{-5}	5.23×10^{-5}	2.27×10^{-5}	5.87×10^{-6}

smaller than in the dissolution test. It was, therefore, expected that the iodine profiles were different from those obtained in dissolution tests. Figure 3 shows reduced profiles of iodine-129 adsorbed in the tests, in order to enhance the difference. A smaller amount of adsorbed iodine-129 would show a larger gradient in the profile, which can be confirmed by the comparing of the profile obtained in the iodine-stripping operation using NO_2 with the profiles obtained in the dissolution. The profile obtained in the iodine-stripping operation using the two-step method had, however, the smaller gradient, though the adsorbed iodine-129 amount was much smaller. The two-step method employs KIO_3, which contains nonradioactive iodine. The profile was, therefore, affected by not only the iodine-129 amount but also the iodine amount from KIO_3. In the present

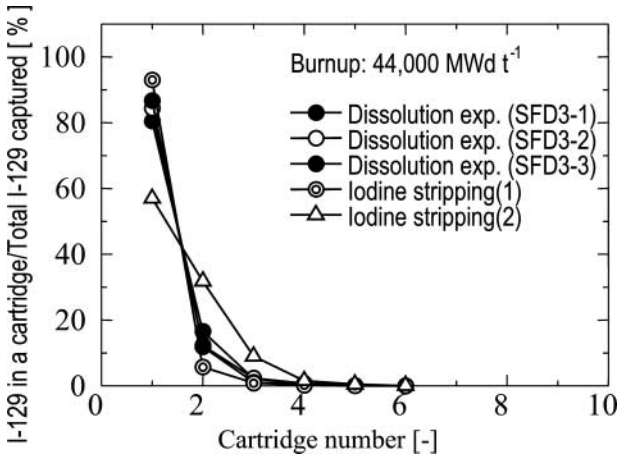

Figure 3. Reduced profiles of iodine-129 obtained in the dissolution and iodine-stripping operation using 44,000 $MWdt^{-1}$ spent fuel.

study, about 450 mg of KIO_3 was added to the dissolver solution of 44,000 $MWdt^{-1}$ spent fuel, containing about 267 mg of iodine, which is much larger than the iodine evolved in each dissolution test. Consequently, the reduced profile was different from other results and the gradient was small.

Procedure to Compare Iodine Profiles

Using the iodine-129 profiles obtained in the dissolution and iodine-stripping operations, the validity of the model was examined. It was necessary to develop the following procedure for the comparison of the predicted iodine profiles with the experimentally obtained data since the dissolver off-gas contains other iodine isotopes as well as iodine-129. Iodine-127 was the major isotope, which amounted to almost 30% iodine-129 according to the calculation result by ORIGEN2.

1. Calculation of the ratio of iodine-129 mass to total iodine mass using ORIGEN2,
2. Estimation of total iodine introduced into the Ag-S column,
3. Prediction of the profile of total iodine in the Ag-S column by proposed model applying the amount of the total iodine obtained in 2,
4. Prediction of iodine-129 profile using the results 1 and 3,
5. Comparison between the prediction and experimental result.

In the second procedure just described, the total iodine introduced into an Ag-S column can be estimated by the ORIGEN2 calculation for a given amount of spent fuel. The estimation, however, needs the assumption that all the iodine were expelled during the dissolution and released into DOG were brought into the Ag-S column. Previous studies reported that some percentage of iodine remained in dissolver solution after a dissolution operation.[16] Iodine in DOG could adhere to the surface of the inner wall of off-gas piping, which is not heated up.[19] In the present study, about 70% of the total I-129 estimated by ORIGEN2 calculation was found in the Ag-S columns after the iodine-stripping operation.[15,20] It was, however, not possible to calculate total amount of iodine introduced into an Ag-S column directly from the ORIGEN2 calculation for each dissolution and iodine-stripping operation. In the present study, therefore, total amount of iodine introduced was estimated by:

2-1. Calculation of total iodine-129 measured in a column.
2-2. Estimation of total iodine introduced into the column using the result of the procedure 2-1 and the ratio of iodine-129 mass to total iodine mass obtained in procedure 1.

In the prediction for the iodine-stripping operation, the same procedure was employed. It should be noted that the mass of nonradioactive iodine added as KIO_3 in iodine-stripping operation was also taken into account, assuming that 70% of the iodine added was introduced into the Ag-S column and that the isotopic composition of iodine was uniform in the column.

Verification of the Model

Previous work determined the values of D_{ea} and K to be $5.60 \times 10^{-7}\,m^2\,s^{-1}$ and $1.0 \times 10^5\,m^3\,kg^{-1}$, respectively, which agreed fairly well with the iodine profiles obtained in the experiments using radioiodine as tracer.[7] In using those D_{ea} and K values, iodine profiles were respectively predicted for the dissolution of spent fuel with different burnups. In the calculation, q_0 was estimated to be $9.879 \times 10^{-2}\,kg\,kg^{-1}$, which was the same value used in the previous work for Ag-S adsorbent with Ag content of 12%.[7] Table 4 shows the parameter values used. In the calculation, an Ag-S column consisting of 10 Ag-S cartridges was divided into 50 cells in an axial direction and an Ag-S particle was divided into 50 shells in a radial direction.

Table 4. Values used for calculation.

Parameter	Ag-S size (mm)	Bulk density ($kg\,m^{-3}$)	Porosity (-)	Pore size (nm)	Ag content (wt%)	Ag utilization efficiency (%)	q_0 ($kg\,kg^{-1}$)
Values reported	1–2	About 700	0.578	10 Max. 20–40	12	60–80	—
Values used in the calculation	1.5	700	0.578	10	12	70	9.879×10^{-2}[a]

[a] The value of q_0 can be obtained from the Ag content, Ag utilization efficiency and stoichiometrical relationship between silver and iodine based on Eqs (1) and (2).

The amount of iodine captured by one Ag-S cartridge used in the present study was obtained from the integration of calculation results of five cells.

The comparison of the predicted profile with the corresponding experimentally obtained profile is shown in Fig. 4. About 0.4 to 0.5 kg of spent fuels with 8000, 29,000, and 44,000 $MWdt^{-1}$ were dissolved at 373 K using about 5 $mol\,l^{-1}$ nitric acid. As can be seen in the figure, fairly good agreement was found in each comparison of profiles.

Figures 5 and 6 compare the predicted iodine-129 profile with the profiles obtained in the iodine-stripping operation. The two-step method was employed in the iodine-stripping operation for dissolver solution of 8000 and 29,000 $MWdt^{-1}$ spent fuel. The introduction of NO_2 gas and the two-step method was employed for the 44,000 $MWdt^{-1}$ spent fuel. As exhibited in Fig. 5, the predicted profiles for 8000 and 29,000 $MWdt^{-1}$ spent fuels agree very well. Also, in Fig. 6, the predicted iodine profiles for 44,000 $MWdt^{-1}$ spent fuel shows good agreement.

Applicable Range of Parameters Used

It was envisaged that the NO_2 contained in DOG would affect the iodine adsorption behavior and would require different values of parameters for the prediction. In the present study, however, the prediction using the same

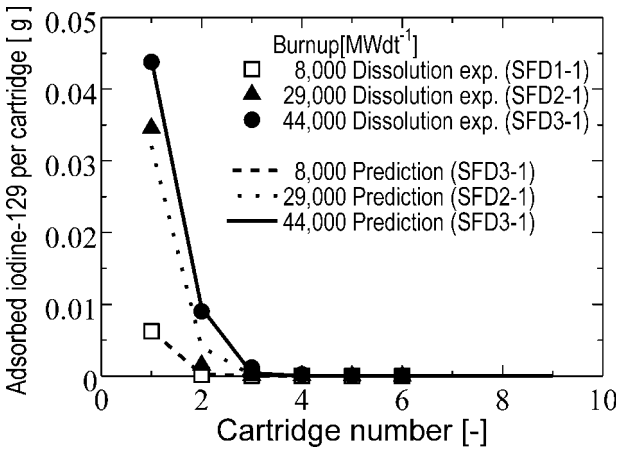

Figure 4. Comparison of predicted iodine-129 profile with experimental data obtained in the dissolution of spent fuels.

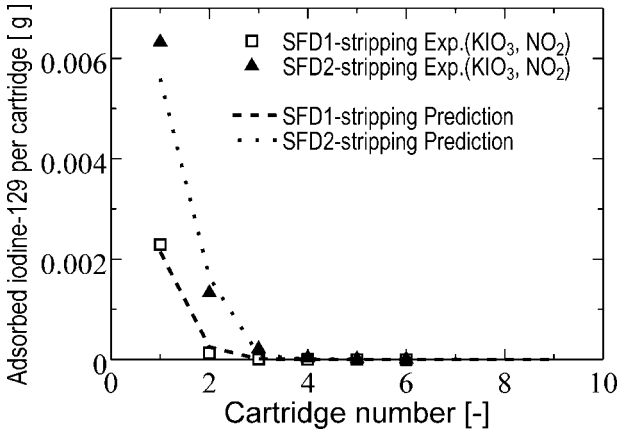

Figure 5. Comparison of predicted iodine-129 profile with experimental data obtained in the iodine-stripping operations for 8000 and 29,000 $MWdt^{-1}$ spent fuels.

parameter values as the previous work showed good agreement. This suggests that the effect of NO_2 was very small. It has been reported that no systematic influence of NO_2 concentration on the removal efficiency was observed in the concentration range up to 5% of NO_2 at 423 K.[3] Hattori et al showed that no significant change in the iodine profile was detected at 423 K, under

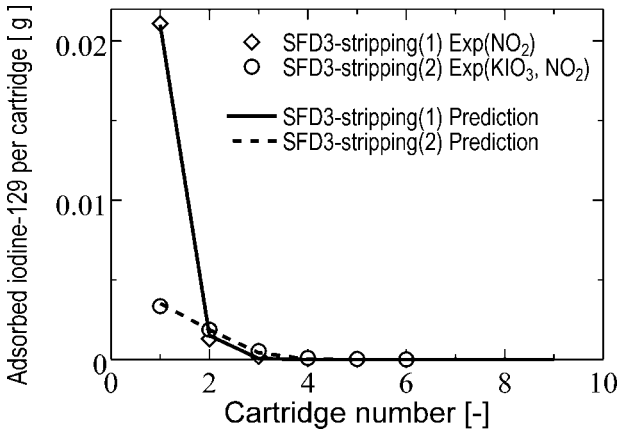

Figure 6. Comparison of predicted iodine-129 profile with experimental data obtained in the iodine-stripping operations for 44,000 $MWdt^{-1}$ spent fuel.

the presence of NO_2 with a volumetric concentration of 1%.[2] In the present study, the NO_2 monitor showed the concentration during dissolution tests to be less than 0.1%, which was lower than the studies described. Conversely, it can be suggested that the proposed model would be applicable to predict iodine profile using the parameters values of D_{ea} and K under the presence of NO_2 with a volumetric concentration of up to 1%, provided that the condensation of water is avoided by keeping the operation temperature around 423 K.

Discussion of the Proposed Model

The effective diffusion coefficient of iodine in an Ag-S particle can be related by the following equation, applying the parallel pore model[21]:

$$D_{ea} = \frac{\varepsilon_a}{\tau}\left(\frac{1}{1/D_{ea} + 1/D_{ab}}\right) \tag{16}$$

where D_{ka}, D_{ab}, ε_a, and τ denote the Knudsen diffusion coefficient, molecular diffusion coefficient, the porosity of adsorbent, and the tortuosity factor. D_{ka} and D_{ab} can be estimated to be $6.262 \times 10^{-7}\,m^2\,s^{-1}$ and $6.877 \times 10^{-7}\,m^2\,s^{-1}$, respectively. The porosity of adsorbent is 0.578. As the previous study showed, when the inverse of adsorbent porosity was used as the tortuosity factor, D_{ea} was calculated to be $1.92 \times 10^{-7}\,m^2\,s^{-1}$. It is clear that the best estimated D_{ea} in the previous study ($= 5.60 \times 10^{-7}\,m^2\,s^{-1}$) has similar order of magnitude to the calculated value of D_{ea} and is reasonable. It should, however, be noted that the value of the tortuosity factor was calculated to be less than unity using the equation, when the values of D_{ea}, D_{ka}, D_{ab}, and ϵ_a were $5.60 \times 10^{-7}\,m^2\,s^{-1}$, $6.262 \times 10^{-7}\,m^2\,s^{-1}$, $6.877 \times 10^{-7}\,m^2\,s^{-1}$, and 0.578, respectively. This could mean that it may be necessary to introduce other factors to increase the diffusion rate (such as the surface diffusion effect).

The previous studies showed that the release of iodine was not detected in the air flowing through a column of Ag-S particles at temperatures lower than 673 K.[22,23] Therefore, Reactions (1) and (2) are supposed to be irreversible and the iodine will be retained in Ag-S particles after the iodine supply is stopped. The proposed model employs a Langmuir-type equation. Although the amount, Q_p, will not change very much under a wide range of C_p, thanks to the large value of K ($= 1.0 \times 10^5\,m^3\,kg^{-1}$), it is clear that Q_p will decrease when C_p decreases, which may not occur in irreversible reaction systems. Therefore, it is necessary for the proposed model to assume that the bulk concentration of

iodine is constant. In the actual dissolution step of a reprocessing plant, the change in iodine concentration in dissolver off-gas would depend on the dissolution mode. When the continuous dissolution mode is employed, the iodine concentration will increase initially and will be kept at a constant value during the operation. As for the batch-wise dissolution, the concentration change just after the dissolver will have a peak, as observed in WAK.[24] However, because there are several locations along the off-gas line where the trapping and release of iodine must occur, such as scrubbers and inner surfaces of pipe works, the concentration change at the entrance of adsorbent column will be significantly moderated. Also, a series of batch-wise dissolutions showed the iodine concentration to increase and become constant in a commercial-scale reprocessing plant.[23] Those reports could imply that it is practically reasonable to assume the iodine concentration in the bulk is constant.

Thus, it can be suggested that the proposed model is simple and useful to predict iodine profiles in a column when the total amount of iodine introduced into the column is given. However, further studies are required, particularly on the adsorption reaction mechanism including a rate-limiting step, so that more accurate modeling for iodine adsorption on Ag-S particles can be established. In addition, it is required that the total amount of iodine introduced into the column during spent fuel dissolution and iodine stripping operations be determined, which depends on the extent of iodine evolution from dissolver solution and is affected by the adsorption to the off-gas piping. It is necessary to develop the model to estimate the total iodine amount.

CONCLUSION

The validity of a simple adsorption model proposed to predict the iodine profile in an Ag-S adsorbent column was examined using data obtained in dissolution and iodine-stripping operations of spent fuels burned up to 44,000 $MWdt^{-1}$. It was found that the model could well predict the iodine profiles, using the parameter values obtained in previous work. In addition, it was suggested that the parameter values are applicable in the presence of NO_2 gas, with a volumetric concentration up to 1% in the off-gas. It was shown that the proposed model was simple and would be useful to predict the iodine profiles in Ag-S adsorbent columns under actual spent fuel operations, when the total amount of iodine introduced into the column was given.

NOMENCLATURE

av	outer surface area of adsorbent per unit volume of adsorbent $m^2\,m^{-3}$
C_G	iodine concentration in bulk, $kg\,m^{-3}$
C_P	iodine concentration in pores of adsorbent denote, $kg\,m^{-3}$
C_{PS}	iodine concentration at the surface of adsorbent particle, $kg\,m^{-3}$
D_{ea}	effective diffusion coefficient, $m^2\,s^{-1}$
D_{ka}	Knudsen diffusion coefficient, $m^2\,s^{-1}$
D_{ab}	molecular diffusion coefficient, $m^2\,s^{-1}$
k_f	mass transfer coefficient, $m\,s^{-1}$
K	Langmuir coefficient, $m^3\,kg^{-1}$
q_0	saturated weight of adsorbed iodine per unit weight of adsorbent, $kg\,kg^{-1}$
Q_P	weight of adsorbed iodine per unit weight of adsorbent at a radius r in an Ag-S particle, $kg\,kg^{-1}$
$\bar{Q}_p$	average weight of adsorbed iodine per unit weight of adsorbent particles in an adsorbent column, $kg\,kg^{-1}$
r	radial position inside of Ag-S particle, m
R_a	radius of Ag-S particles, m
u	superficial gas velocity, $m\,s^{-1}$
z	axial position in adsorption column, m
Z	adsorption column length, m
ϵ_a	porosity of adsorbent, −
ϵ_b	void fraction of adsorbent column, −
ρ_b	weight of Ag-S particle per unit volume of adsorption column, $kg\,m^{-3}$
ρ_s	particle density, $kg\,m^{-3}$
τ	tortuosity factor, −

ACKNOWLEDGMENTS

A portion of the study was carried out by Japan Atomic Energy Research Institute under the auspices of the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors are indebted to Messrs. Y. Nakano, T. Iijima, S. Kimura, M. Sawada, T. Yagi, T. Kashimura, and M. Sato for their effort to carry out the spent-fuel dissolution tests and analysis. The authors express their appreciation to Messrs. T. Kihara, A. Takahashi, and T. Yagi for their effort in the earlier stage of the study, and also

to Messrs. A. Maeda, S. Kurobane, T. Tsuboi, N. Sano, and O. Shimizu for their cooperation during the tests at the Nuclear Fuel Cycle Engineering Research Facility (NUCEF) of Japan Atomic Energy Research Institute.

REFERENCES

1. Holladay, D.W. *A Literature Survey Methods for the Removal of Iodine Species from Off-Gases and Liquid Waste Streams of Nuclear Power and Nuclear Fuel Reprocessing Plants, with Emphasis on Solid Sorbents*; Report ORNL/TM-6350 Oak Ridge National Laboratory: Oak Ridge, Tennessee, USA, 1979.
2. Hattori, S.; Kobayashi, Y.; Ozawa, Y.; Kunikata, M. Removal of iodine from off-gas of nuclear fuel reprocessing plants with silver impregnated adsorbents. Proceedings of the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, Maryland, USA, August 13–16, 1984; 1343–1360.
3. Wilhelm, J.G.; Furrer, J.; Schultes, E. Head-end iodine removal from a reprocessing plant with a solid sorbent. Proceedings of the 14th ERDA Air Cleaning Conference, Sun Valley, Idaho, USA, August 2–4, 1976; 447–477.
4. Herrmann, F.J.; Herrmann, B.; Hoeflich, V.; Beyer, Ch. Removal efficiency of silver impregnated filter materials and performance of iodine filters in the off-gases of karlsruhe reprocessing plant WAK. Proceedings of the 24th DOE/NRC Nuclear Air Cleaning and Treatment Conference, Portland, Oregon, USA, July, 15–18, 1996; 609–617.
5. Wilhelm, J.G.; Schüttelkopf, H. An inorganic adsorber material for off-gas cleaning in fuel reprocessing. Proceedings of the 12th AEC Air Cleaning Conference, Oak Ridge, Tennessee, USA, August 28–31, 1972; 540–550.
6. Furrer, J.; Kaempffer, R.; Wilhelm, J.G. Iodine removal at reprocessing plants by means of AC-6120 sorption material and determination of its leaching resistance to Brine. In *Management Modes for Iodine-129*; Hebel, W., Cottone, G., Eds.; Radioactive Waste Management, A Series of Monographs and Tracts, Harwood Academic Publishers, 1982; Vol. 7, 277–290.
7. Mineo, H.; Gotoh, M.; Iizuka, M.; Fujisaki, S.; Uchiyama, G. A simple model predicting iodine profile in a packed bed of silica-gel impregnated with silver nitrate. J. Nucl. Sci Technol. **2002**, *39* (3), 241–247.

8. Patil, K.C.; Rao, C.N.R.; Lacksonen, J.W.; Dryden, C.E. The silver nitrate–iodine reaction: iodine nitrate as the reaction intermediate. J. Inorg. Nucl. Chem. **1967**, *29*, 407–412.
9. Leslie, J.C.; Dryden, C.E. An Integrated System of Tracer Techniques for Studying Gas-Solid Reactions. Chem. Eng. Prog. Symp. Ser. **1966**, *62*(68), 121–134.
10. Schon, T. *Chemisches Vorhalten von Jod-129 bei der Abfallkonditionierung*; Report JUEL-2834 Forschungszentrum Jülich GmbH: Germany, 1993, (in German).
11. Szkely, J.; Evans, J.W.; Sohn, H.Y. *Gas–Solid Reactions*; Academic Press: New York, San Francisco, London, 1976.
12. Tang, J.; Ye, M-L.; Wao, Y.; Lu, S.; Tang, Z.; Guo, Z. Removal of radioiodine from nuclear-fuel-reprocessing off-gases with silver-nitrate-impregnated silica gel. J. Radioanal. Nucl. Chem. Lett. **1987**, *119* (2), 109–118.
13. Carberry, J.J. A boundary-layer model of fluid-particle mass transfer in fixed beds. AIChE J. **1960**, *6* (3), 460–463.
14. Fumoto, H.; Sato, S.; Ito, W.; Tamura, T. A study of mineral zeolite as a nitrogen oxides adsorbent for dissolver off-gas treatment. Nucl. Technol. **1986**, *75*, 96–108.
15. Mineo, H.; Iizuka, M.; Fujisaki, S.; Hotoku, S.; Asakura, T.; Uchiyama, G. Study on gaseous effluent treatment for dissolution step of spent nuclear fuel reprocessing. Proceedings of Waste Management 2002, Tucson, Arizona, USA, February 24–28, 2002.
16. Sakurai, T.; Takahashi, A.; Ishikawa, N.; Komaki, Y.; Ohnuki, M.; Adachi, T. The iodine species and their behavior in the dissolution of spent-fuel specimens. Nucl. Technol. **1992**, *99*, 70–79.
17. Sakurai, T.; Takahashi, A.; Ishikawa, N.; Komaki, Y. The behavior of iodine in a simulated spent-fuel solution. Nucl. Technol. **1989**, *85*, 206–212.
18. Sakurai, T.; Takahashi, A.; Ming-lu, Y.E.; Kihara, T.; Fujine, S. Trapping and measuring radioiodine (Iodine-129) in cartridge filters. J. Nucl. Sci. Technol. **1997**, *34* (2), 211–216.
19. Herrmann, F.J.; Herrmann, B.; Kuhn, K.D.; van Schoor, A.; Weishaupt, M. Control of radio-iodine at the german reprocessing plant WAK during operation and after Shutdown. Proceedings of the 24th DOE/NRC Nuclear Air Cleaning and Treatment Conference, Portland, Oregon, USA, July 15–18, 1996; 618–628.
20. Kihara, T.; Sakurai, T.; Nakano, Y.; Fujine, S. Iodine behavior during dissolution process with NUCEF-BECKY. Proceedings of the 5th International Conference on Nuclear Fuel Reprocessing and Waste

Management (RECOD'98), Nice, France, October 25–28, 1998; 830–837.

21. Hashimoto, K. *Han-nou-kogaku*; Baihu-kan: Tokyo, Japan, 1991, in Japanese.
22. Sugimoto, Y.; Kondo, Y.; Hirose, Y.; Fukasawa, T.; Furrer, J.; Herrmann, F.J.; Knoch, W. The development of Ag-A for radioactive iondine removal from nuclear fuel reprocessing. Proceedings of the 3rd Int. Conf. on Nuclear Fuel Reprocessing and Waste Management (RECOD'91), Sendai, Japan, April 14–18, 1991; Vol. 1, 236–240.
23. Inami, S.; Kawasaki, M.; Tachihara, T.; Okamoto, H. Development of iodine removal technology at the tokai reprocessing plant. Proceedings of the 3rd Int. Conf. on Nuclear Fuel Reprocessing and Waste Management (RECOD'91), Sendai, Japan, April 14–18, 1991; Vol. 1, 230–235.
24. Furrer, J.; Wilhelm, J.G.; Jannakosm K. Aerosol and iodine removal system for the dissolver off-gas in a large fuel reprocessing plant. Proceedings of the 15th DOE/NRC Nuclear Air Cleaning and Treatment Conference, Boston, Massachusetts, USA, August 7–10, 1978; 494–511.

Received May 2002
Revised December 2002