DEVELOPMENT OF TREATMENT TECHNOLOGY FOR DISSOLVER OFF-GAS OF SPENT FUEL

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Abstract

Dissolution experiments using unirradiated UO_2 pellets, PWR spent fuels (8, 29 and 44 GWd/t) have been conducted in a bench-scale test rig to investigate the behavior of iodine and carbon-14 during the dissolution of nuclear fuel for reprocessing. Also, a new adsorbent has been under development by cold tests for carbon-14 removal from dissolver off-gas.

The iodine adsorbent column of AGS (silver impregnated silica-gel) could effectively remove the iodine-129 introduced into the column during the spent fuel dissolution at about 373 K where 4 to 5.5 mol l^{-1} of nitric acid was used. The fraction of adsorbed iodine-129 accounted for 62 to 72 % of total amount of iodine-129 estimated by ORIGEN2, which was almost the same fraction as it was determined in the AGS column using iodine-131 as tracer in the dissolution test of unirradiated UO_2 pellets. Iodine stripping using NO_2 could effectively remove the iodine remaining in the dissolver solution. Also, two-steps iodine stripping process using potassium iodate could expel additional iodine from the solution. No significant amount of iodine-129 was found in dissolver solution of spent fuel after the iodine stripping, though the direct measurement of iodine-129 in insoluble residue was not possible because of high radioactivity. In the carbon-14 measurement the release of carbon-14 as carbon dioxide during the dissolution was found to occur when the release of Kr-85. From the measurement, the concentration of nitrogen-14 initially contained in the fuel was estimated to be about 5 ppm.

The adsorbent consisting of hydrogenated-mordenite impregnated with sodium hydroxide showed a capacity to be about 1.4 gCO_2/50g-adsorbent, which was about 4.3 times higher adsorption capacity than that of hydrogenated mordenite for the carbon dioxide. Though the capacity was decreased with the increase in concentration of NOx gas and relative humidity, good repeatability for CO_2 adsorption was obtained in the cold tests.

Introduction

Iodine-129 is a long-lived (1.57×10^7 years), volatile and hazardous radionuclide, which is generated mainly in the dissolution process of spent fuel reprocessing. The nuclide should strictly be controlled and confined within the reprocessing process. There have been a number of studies carried out for the confinement of radioiodine. Various types of adsorbents were developed. Silver impregnated adsorbents such as AGS (silver-impregnated silica gel) could remove both I_2 and organic iodine compounds in gaseous phase, effectively.(1) Therefore, from the viewpoint of the environmental safety, it is expected that iodine be expelled from the dissolver solution to dissolver off-gas (DOG) as much as possible. Sakurai et al. reported that a few percentage of iodine was conveyed to the insoluble residue as colloids (AgI and PdI_2) and some (up to 10 %) of iodine remained in the dissolver solution.(2) And the balance was in the off-gas. They indicated that iodine (I^-) in spent fuel was subject to the oxidation into I_2 by nitric acid, the oxidation into I_2 by nitrous acid arising from NOx and the formation of colloidal iodine. Those two species were the major species in a dissolver solution.(3) The expulsion of colloidal iodine from the solution was difficult using only NOx-gas. Sakurai et al. proposed a method to expel the iodine effectively, which consisted of two-steps of iodine stripping,(3),(4) which other workers showed identical methods, separately.(5) Their study could throw a light on the physicochemical aspect of iodine in the dissolution and iodine stripping process using beaker-scale equipment. Further study using actual spent fuel is necessary to understand the iodine behavior in dissolution and off-gas treatment process of a bench-scale test rig because some difference in the iodine behavior was suggested.(6) It is also important to confirm the capability to confine and control the radioactivity within the process under normal operation. In the present study, therefore, a series of tests have been carried out using PWR spent fuels with burn-ups ranging from 8,000 to 44,000 MWd/t.

Carbon-14 has a half-life of 5.7×10^3 years and is generated from the neutron absorption by nitrogen and oxygen during the irradiation of nuclear fuel, which are an impurity and a constituent of fuel, respectively. Most of carbon-14 is released as carbon dioxide during the dissolution.(7) In the present, carbon-14 is not included in the nuclides that have to be removed in Japan. The nuclide is, however, the largest contributor to the equivalent dose rate of nearby residents,(8) it is important to study behavior of carbon-14 in the dissolution and off-gas treatment processes.

In a future advanced reprocessing process, the confinement of carbon-14 may be required for the environmental safety.(9) A method to capture and stabilize the nuclide is necessary, fulfilling the ALARA principle. Carbon-14 concentration in dissolver off-gas (DOG) is, however, very low and can be estimated to be about 0.1 ppm, if air gas is used as the purge gas of the dissolver, which contains about 340 ppm of carbon dioxide.(8) Therefore, a carbon-14 capturing system should separate carbon dioxide from the DOG unless the system has selectivity for the radionuclide. In some existing reprocessing plants, caustic scrubbing to remove radioactive iodine also absorbs carbon dioxide containing ^{14}C. A dry method was proposed to decompose $^{14}CO_2$ into carbon-14 through its reaction with H_2 using microwave discharge.(8) This method was developed as the treatment of captured $^{14}CO_2$ on an adsorbent. Takeshita et al. (10) and Arai et al. (11) showed a dry method using adsorbents (natural zeolite etc.), which was a combination of chromatographic separation and desorption by temperature elevation to separate carbon dioxide from NOx and H_2O. In the present study, adsorption technique is focused as one of the candidates for the carbon-14 treatment process because of its simplicity and the compatibility in the operation with radioactive iodine capture using AGS adsorbents. Cold tests have been conducted to find relevant adsorbents for the carbon-14 treatment.

This paper describes the behavior of iodine-129 and carbon-14 in the dissolution and off-gas treatment process obtained in the present study using spent fuel. Also, cold test results on the adsorbents for the $^{14}CO_2$ treatment are reported.

Experimental

Dissolution test rig

The dissolution test rig is shown in Figure 1. The dissolution process comprises a dissolver, an iodine stripping tank, a dissolver solution filter, an extraction feed tank, a condenser, a scrubber, iodine adsorbent columns and a blower. The equipment is installed in an alpha-gamma cell except for the iodine adsorbent columns and blower, which have been installed in a glove-box above the cell. The blower is used to maintain the dissolution process under negative pressure for all operating condition.

Following the dissolution, all dissolver solution is transported to the iodine stripping tank where NO_2 gas is purged through the dissolver solution to strip remaining iodine. After iodine stripping operation, the dissolver solution is then filtrated to remove all particulate residue and subsequently adjusted to 3M HNO_3 and 250 g/l uranium concentration as extraction feed solution. Table 1 summarizes dissolution conditions employed for the present study. Unirradiated UO_2 pellet and spent fuel were dissolved in the dissolver with 4 to 5.5 N nitric acid. Unirradiated UO_2 pellet dissolution test employed continuous supply of nitric acid. Spent fuel dissolution was carried out in batch operation.

Fuels dissolved

The unirradiated UO_2 pellet used in these experiments included some non-radioactive fission products elements to simulate real spent fuel. The composition of used unirradiated fuel is listed in Table 2. Full detail was given in the literature(12). Based on the ORIGEN-II calculation for the spent fuel of 45GWd/t burn-up, eleven elements were selected for the inclusion: Sr, Zr, Mo, Ru, Rh, Ba, La, Ce, Pr, Nd and Sm. Given that Cs is a volatile species and Tc is a radioactive element difficult to fabricate, these two fission products were not included. In addition, it should be noted that Ag and Pd were added to the simulated fuel since the behavior of iodine was found to be greatly influenced by these two elements. All pellets were loaded into the dissolver with zircaloy hulls.

PWR spent fuel with burn-ups of 8, 29 and 44 GWd/t were used in the present study. Those fuels had been sheared into short pieces with a length of 40 mm, before the transportation to the alpha-gamma cell. Burn-up of each spent fuel was determined by measuring the concentration ratio of Cs-134 to Cs-137 in the respective dissolver solution and the irradiation history of each spent fuel.

Table 3 summarizes iodine-stripping operations used in the present study. In the case of unirradiated UO_2 pellet dissolution, all of the dissolver solution was transferred to the iodine stripping vessel, where NO_2 gas was purged through the solution for 2 hours at 363 K. In the experiments of spent fuel, iodine-stripping is carried out in two-steps operation, which has been developed.(4) In the first step of the operation, KIO_3 is added to all dissolver solution collected in the iodine stripping tank heated up at 373 K and then the solution is maintained at the same temperature for two hours. In the second step of the operation 50% NO_2 (+50% N_2) gas is introduced at a flow rate of 170 l/h and maintained at 373 K for two hours. It was reported that the first step of this method decomposed precipitates: AgI and PdI_2, by the following reactions.

$$5AgI + HIO_3 + 5HNO_3 \rightarrow 3I_2 + 5AgNO_3 + 3H_2O$$
$$5PdI_2 + 2HIO_3 + 10HNO_3 \rightarrow 6I_2 + 5Pd(NO_3)_2 + 6H_2O$$

Iodine-129 measurement

Dissolver off-gas and iodine stripping off-gas via the scrubber pass through the HEPA filter and then into the glove-box located above the cell where iodine is collected by the adsorbent columns which are installed in the glovebox as illustrated in Figure 2. A Kr monitor (NaI detector) and an NO_2 monitor were also attached to the off-gas line in the glovebox. In order to reduce the adhesion of the iodine to the piping associated with the off-gas treatment system in the glovebox, the piping is maintained at 323 K. The first column (Column A) was maintained at 333 K and contains 130 g of MS-3A to remove H_2O contained in the off-gas. Other three columns heated up at 423 K contain AGS particles. The first two of those three columns (Columns B and C) have seven cartridges respectively and each cartridge (25 mm i.d. and 9 mm in length) accommodates 3.4 g of AGS. The fourth column (Column D) also contains AGS in one large cartridge. The AGS 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 719 kgm^{-3} and its silver content was 12 %. The off-gas flow rate was approximately 0.4 Nm^3h^{-1}.

The amount of iodine-129 on each cartridge was measured using a Ge detector for low-energy gamma ray with the method shown by Sakurai et al. (13) Iodine-129 remained in the dissolver solution of 29 GWd/t was analyzed using the method shown by Castleman et al. (14)

Iodine distribution measurement

In the unirradiated UO_2 fuel experiment, potassium iodide (KI) aqueous solution containing I-131 tracer was periodically directly injected into the dissolver. The required amount of iodine to be injected was obtained from the ORIGEN-II calculation. Tracer iodine (iodine-131) was analyzed in the dissolver solution, residue, circulation water of a scrubber, a HEPA filter and iodine adsorbent in the column cartridge, so that the behavior of the iodine in the dissolution could be determined. In order to examine the adhesion behavior of iodine to stainless steel, test pieces were inserted at 3 places: in the water phase of the dissolver, the vapor phase of dissolver and vapor phase of scrubber. Trace I-131 was analyzed on each sample to determine the adhesion.

Carbon-14 measurement

Measurement of carbon-14 during the spent fuel dissolution is carried out using a carbon dioxide trap containing 2 mol/l potassium hydroxide aqueous solution shown in Figure 3, which is connected to a bypass line located between the Column C and D. Periodical sampling was carried out from the trap. Carbon-14 in each sample was measured using a beta liquid scintillation counter. The off-gas flow rate in the trap was about $6x10^{-3}$ m^3h^{-1}. The effect of NO_2 gas contained on the efficiency of carbon dioxide capturing was checked prior to the experiment. It was necessary to reduce the NO_2 concentration less than 1 % to avoid the adverse effect. During the spent fuel dissolution tests the concentration of NO_2 was maintained at low level by the scrubber and was found to be less than 0.1 %.

Cold test on adsorbents for carbon dioxide

In the present study, natural zeolite (Itado, Japan), hydrogenated mordenite (H-M) and modified-hydrogenated mordenite were used. In addition, MS-13X was also employed. The hydrogenated mordenite was prepared from the natural zeolite.(15) Three types of modified-H-M were prepared by the process where aqueous solutions of NaOH, KOH and $CaCl_2$ were respectively introduced into the column containing the above hydrogenated mordenite and each resultant adsorbent (Na-HM, K-HM and Ca-HM) was washed with H_2O and heated at 673 K for one hour to remove H_2O.

The composition of adsorbent Na-HM and mordenite is listed in Table 4, which was analyzed using an ICP-AES. In the table, for example, "2M" means that 2 mol/liter of NaOH aq. was used in the above procedure of the modification of hydrogenated mordenite. Si and Al are constituents of matrix of mordenite and their molar ratio Si/Al was reported to be five. (16) In the present study the ratio was about 4.7 close to the value. The ratio Si/Al of H-M was high and reported to be about 27.6.(15) The ratio of Si to Al of 2M-Na-HM was found to be 21 which compared well with the H-M. This could imply that the matrix of H-M was not affected by the modification very much, which was confirmed by the comparison of XRD(X-ray diffractometry) patterns.

Figure 4 shows a schematic diagram of experimental apparatus used. The apparatus consists of a cylindrical column (28 mm i.d. 300 mm in length), gas flow controllers, valves and a GC-MS. Because the dissolver off-gas contains about 340 ppm of CO_2, CO_2 in this study was supplied from a gas cylinder of dry air containing 350 ppm of CO_2. In addition, NO gas with concentrations ranging between 0.05 and 1.0 % was added as NOx gas to the air to study its effect on the adsorption capacity. The CO_2 adsorption capacity was evaluated by the measurements of breakthrough curves from column experiments. Breakthrough curves were obtained by measuring CO_2 concentration by a GC-MS at the outlet of a cylindrical column filled with 50 g of absorbent. Typical superficial gas velocity in the cylindrical column was 0.0434 m/s and temperature was 293 K.

Adsorption and desorption test was also conducted using about 20 g of adsorbent. In the test desorption and the measurement of adsorbed CO_2 amount was carried out with the following procedure:

1) Reduce the pressure in the adsorbent column to expel the gas retained at the inner surface of column and piping,
2) Heated up the adsorbent at 673 K to the adsorbed carbon dioxide and trap the gas in a bottle with a known volume cooled by liquid nitrogen,
3) Measure the pressure of carbon dioxide in the bottle by a Burdon tube gage,
4) Use the adsorbent in the adsorption test as described above.

Results and discussion

Iodine-131 distribution

The iodine remaining in the dissolver solution of unirradiated UO_2 pellet before iodine-stripping operation was 5.06% of total iodine. Iodine concentration and nitrous acid concentration in the stripping process are shown in Figure 5. The nitrous acid concentration is very high because NO_2 gas was purged through the dissolver solution. Hence, the iodine concentration gradually decreased, and 92.62% of remaining iodine in the dissolver was discharged. Only 7.38 % remained which corresponds to 0.37% of the total addition iodine. From this data, it is clear that the iodine stripping operation was effective.

The distribution of iodine after stripping is listed in Table 5. The iodine collected in the AGS columns was 74.06% of the total iodine, that collected in the HEPA filter was 11.33%, and that which remained in the scrubber was 0.10%. The iodine adhered to the piping-surface in the vapor phase was estimated to be 1.58% from analysis of the stainless steel test pieces. Thus total iodine released to the off-gas is 87.07%, and therefore, most iodine seems to transfer to the off-gas from dissolver solution. With regard to safety evaluation, HEPA filters were not considered efficient for retaining iodine. However results have shown 11.33% of total iodine is collected by the filter, which implies there is a large safety margin concerning present iodine discharge.

For the iodine which was not transferred to the off-gas, 0.37% remained in the dissolver solution and 1.49% transferred to the precipitation product in the dissolver, 0.57% adhered to the stainless steel test piece surface in the dissolver solution, and 0.05% adhered to the dissolution bucket and hull surface. The precipitation product observed in the dissolver was found to be zirconium molybdate $ZrMo_2O_7(OH)_2(H_2O)_2$ by X-ray diffractometry. This precipitation appeared to incorporate AgI and PdI_2 which were generated in the dissolver solution. This precipitation also adhered to the dissolution bucket and hull surface.

The chemical states of iodine after the dissolution and stripping showed that most iodine from the dissolution stage was in the form of IO_3^-, although this seemed to decrease when NO_2 was injected as Sakurai et al. reported.(3) After stripping the dominant iodine species was not IO_3^- but other forms, possibly colloidal iodine.(2),(17)

In the present study, the total balance of iodine was not found to be 100%. It is possible that this imbalance is due to an underestimate of the amount of iodine adheres to the stainless steel piping associated with the dissolver off-gas. It appeared that 10% of the remaining iodine adhered to the surface of the process equipment.

Iodine-129 measurement etc.

Profiles of iodine-129 in the AGS column were illustrated in Figure 6, which were obtained in the dissolution of 29 GWd/t spent fuel. It can be seen in Figure 7 that most of the iodine was captured in the first and second cartridges in the upstream AGS column (Column C). Table 6 shows the amount of iodine-129 captured by the AGS column during the dissolution and iodine stripping, which accounted for 62, 69, 72 % of total amount of iodine-129 estimated by ORIGEN II calculation for respective spent fuels (8, 29 and 44 GWd/t). Those fractions of iodine collected in the columns are supposed to be in the range of reasonable amount, comparing with the result of the above test using iodine-131 in the same test rig. Rest of iodine-129 was supposed to adhere to the piping and HEPA filter.

As shown in Table 3, two methods were used for iodine stripping. A method using NO_2 gas at 363 K expelled iodine-129 from dissolver solution of 44 GWd/t spent fuel, effectively. In the study, expelled iodine-129 by the method accounted for about 9.1 % of total amount of iodine-129 estimated by ORIGEN II calculation. Another method, the two-steps process mentioned above, removed additional iodine-129 into off-gas, of which amount accounted for about 2.1 %. This fraction is supposed to be the iodine-129 fraction existed as precipitates, and the fraction is comparable to the iodine-131 transferred to the precipitates as listed in Table 5 (=1.49%). Sakurai et al. reported that a few percentage of iodine was conveyed to the insoluble residue as colloids (AgI and PdI_2) and some (up to 10 %) of iodine remained in the dissolver solution.(2)

In the iodine-stripping operation for 29 GWd/t disslover solution, iodine species in the solution was analyzed, using Castleman's method. Applying this method to the actual spent fuel solution was extreme difficult because of high background level due to high radioactivity of other nuclides and low-gamma energy of iodine-129. Figure 8 shows change in $^{129}I_2$ concentration obtained by the method. It can be seen that the concentration leveled off during the first step of iodine-stripping for 4.74 liter of dissolver solution in the tank. $^{129}IO_3^-$ was once detected as shown in the figure, of which concentration was comparable to the concentration of $^{129}I_2$.

In the iodine-129 measurement of each cartridge, iodine-131 was also detected, which was generated from spontaneous fission, mainly from curium-244. The profiles of iodine-131 in the AGS column were plotted in Figure 9. It was found that the gradient of the profile was similar to that of iodine-129. This could mean the chemical form of iodine-131 in the dissolver off-gas was same as that of iodine-129, mainly I_2.

Carbon-14 measurement in dissolution

Table 7 lists the results from carbon-14 measurement using 29GWd/t spent fuel. The nuclide was measured also in the MS-3A column. Most of carbon-14 in the dissolver solution was released during the dissolution. From the results, concentration of nitrogen-14 initially contained in fuels as impurity was estimated to be about 5 ppm by ORIGEN II calculation for both 8 and 29 GWd/t spent fuels, which could compare well with the reported concentration of nitrogen in other PWR fresh fuels ranging between 5 and 20 ppm.(18)

Figures 10 shows change in beta radioactivity by carbon-14 measured in the sample, which was obtained in the dissolution of 29 GWd/t spent fuel. Kr-monitor reading was also plotted in the same figure. It was found that release of carbon-14 as CO_2 into dissolver off-gas occurred when gaseous radionuclides such as Kr-85 were released. It seems that the release of $^{14}CO_2$ delayed when the concentration of nitric acid was low. Chemical form of the carbon is not well known. It may present as free element or as traces of metal carbide.(7) $^{14}CO_2$ in spent fuel is produced by oxidation of carbon-14 during spent fuel dissolution. Further kinetic study on the CO_2 release from dissolver solution is necessary.

Cold tests for CO_2 adsorbent

Figure 11 shows the breakthrough curves obtained in the adsorption tests using MS-13X, mordenite (Itado, Japan), hydrogenated mordenite (H-M), hydrogenated mordenite impregnated with NaOH (Na-HM), KOH (K-HM) and $CaCl_2$ (Ca-HM). H-M and MS-13X showed a relatively low capacity among the adsorbents. Each adsorption capacity of K-HM and Ca-HM was improved, but was not as high as the mordenite. Highest adsorption capacity was shown by 2M-Na-HM. The capacity was about 1.4 gCO_2/50g-adsorbent, which was 4.2 times higher than that of H-M and was 1.4 times higher than that of the mordenite. Adsorption capacity of natural mordenite increases with the abundance of Na_2O in the adsorbent.(19) The breakthrough time of each adsorbent used in the present study was plotted in Figure 12 as a function of sodium concentration in the adsorbent. It can be seen that the breakthrough time was increased with sodium content. Impregnation with potassium hydroxide and calcium hydroxide also increase the capacity. Those hydroxides are not effective for the improvement of the capacity.

The effect of NOx contained in the feed gas on the adsorption capacity of each adsorbent was also tested. No significant effect was detected when NO gas, which was a feed for NOx, was introduced at 0.05 vol% into the air. When NO gas concentration was 1.0 vol%, the capacity was decreased. It was also shown that humidity had a large effect.

Test on adsorption/desorption was conducted using 2M-Na-HM adsorbent. Table 8 show the result obtained so far. It was found that almost the same amount of carbon dioxide was repeatedly adsorbed. From those results, it is expected that the adsorbent 2M-Na-HM can be applied for a carbon-dioxide capturing process where adsorption/desorption is conducted by changing the temperature of adsorption column of 2M-Na-HM with a removal system for NOx and humidity as pretreatment of dissolver off gas.

Conclusions

A series of dissolution tests using unirradiated UO_2 pellets and spent fuels with burn-ups of 8, 29 and 44 GWd/t have been carried out in order to investigate the behavior of iodine over the dissolution and off-gas treatment process of a bench-scale test rig.

1. Iodine-129 and iodine-131

(1) Using iodine-131 in the test as tracer, it was found that more than 85 % of the iodine was transferred to the off-gas from the dissolver solution.

(2) Large amount of iodine was retained by piping and HEPA filter. Iodine-131 trapped by the AGS column accounted for about 74 % of total iodine-131 fed during the dissolution.

(3) Spent fuel dissolution test showed the fraction of iodine trapped in the AGS column ranged from 62 to 72 % of total iodine-129 estimated by ORIGEN calculation, which was found to be comparable to the results by iodine-131.

(4) Two-steps iodine stripping process using potassium iodate KIO_3 could expel additional iodine from the solution.

(5) No significant amount of iodine-129 was found in dissolver solution of spent fuel after the iodine stripping, though the direct measurement of iodine-129 in insoluble residue was not possible because of high radioactivity.

(6) Iodine-131 was detected in the AGS column capturing iodine-129, which was generated by spontaneous fission. It is likely that the chemical form of iodine-131 was similar to iodine-129 because the profiles were comparable.

2. Carbon-14

(1) In the carbon-14 measurement the release of carbon-14 as carbon dioxide during the dissolution was found to occur when the release of Kr-85. From the measurement, the concentration of nitrogen-14 initially contained in the fuel was estimated to be about 5 ppm.

(2) The adsorbent consisting of hydrogenated-mordenite impregnated with sodium hydroxide was found to have a capacity to be about 1.4 gCO_2/50g-adsorbent, which was about 4.3 times higher adsorption capacity than that of hydrogenated mordenite for the carbon dioxide. Though the capacity was decreased with the increase in concentration of NOx gas and relative humidity, good repeatability for CO_2 adsorption was obtained in the cold tests.

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References

1. Wilhelm, J.G., Furrer, J., and Schultes, E., "Head-End Iodine Removal from a Reprocessing Plant with a Solid Sorbent," *Proc. the 14th ERDA Air Cleaning Conference, CONF-760822*, 447(1976).
2. Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., Ohnuki, M., and Adachi, T., "The Iodine Species and their Behavior in the Dissolution of Spent-Fuel Specimens," *Nucl. Technol.*, **99**, 70(1992).
3. Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., "The Behavior of Iodine in a Simulated Spent-Fuel Solution," *Nucl. Technol.*, **85**, 206(1989).
4. Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., Ohnuki, M., and Kato, K., "A Study on the Expulsion of Iodine from Spent-Fuel Solutions," *Proc. the 23rd DOE/NRC Nuclear Air Cleaning and Treatment Conference, NUREG/CP-0141, CONF-940738*, 321(1994).
5. Boukis, N., Henrich, E., "Two-Step Procedure for the Iodine Removal from Nuclear Fuel Solutions," *Radiochimica Acta*, **55**, 37(1991).
6. Sakurai, T., Komatsu, K., Takahashi, K., "Behavior of Iodine in the Dissolution of Spent Nuclear Fuels," *Proc. the 24th DOR/NRC Nuclear Air Cleaning and Treatment Conference, NUREG/CP-0153, CONF-960715*, 550(1996).
7. Bush, R.P., Smith, G.M., White, I,F., nuclear science and technology, Carbon-14 waste management, *EUR-8749EN*, (1984).
8. Sakurai, T., Yagi, T., Takahashi, A., "A Method of Decomposing Carbon Dioxide for Fixation of Carbon-14," *J. Nucl. Sci., Technol.*, **35**, 76(1998).
9. Fujine, S., Uchiyama, G., Kihara, T., Asakura, T., Maeda, M., Sakurai, T., "Development of Process Technology for Reprocessing which Reduces the Environmental Impact," *Proc. the 10th Pacific Basin Nuclear Conference*, Vol.2, 1125(1996).
10. Takeshita, K., Nakano, Y., Kumagai, M., Takashima, Y., "Development of Natural-Zeolite adsorption process for recovery of 14C," *Proc. the Fall Meeting of Atomic Energy Society of Japan*, K42(1997), (Japanese).
11. Arai, T., Wang, Z.M.Y., Kumagai, M., Tamura, T., Takashima, Y., "A study on Removal of 14CO2 from Dissolver Off-Gas of Reprocessing Plant -Construction of a two-step adsorption separation process-," *Proc. the Fall Meeting of Atomic Energy Society of Japan*, K6(1998), (Japanese)
12. Kihara, T., Sakurai, T., Nakano, Y., and Fujine, S., "Iodine Behavior during Dissolution Process with NUCEF-BECKY," *Proc. the 5th international Conference on Nuclear Fuel Reprocessing and Waste Management (RECOD'98)*, (1998).
13. Sakurai, T., Takahashi, A., Ming-lu, Y.E., Kihara, T., Fujine, S., "Trapping and Measuring Radioiodine (Iodine-129) in

Cartrige Filters," *J. Nucl. Sci. Technol.*, **34**, 211(1997).

14. Castleman, A.W., Jr., Tang, I.N., and Mulkelwits, H.R.,"The Chemical States of Fission-Product Iodine Emanating into a High Temperature Aqueous Environment," *J. Inorg. Nucl. Chem.*, **30**, 5(1968).
15. Fumoto, H., Sato, S., Ito, W., Tamura, T., Yoshiki, N., Kobayashi, Y., "A Study of Mineral Zeolite as a Nitrogen Oxides Adsorbent for Dissolver Off-gas Treatment," *Nucl. Technol.*, **75**, 96(1986).
16. Kyu-chaku Gijutu Handobukku (Adsorption Technology Handbook), H. Shimizu (eds.), Enu Tii Esu, (1993), (Japanese).
17. Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., "The Interaction of Iodine with Insoluble Residue in the Dissolution of Simulated Spent-Fuel Pellets," Nucl. Technol.,
18. Japan Nuclear Fuel Ltd. et al., "Behavior of Radionuclides in a Reprocessing Facility," *JNFS R-91-001* (2nd ed.), (1996).
19. Minato, H., Watanabe, M., "Adsorption of CO_2 and N_2 Gases on Natural Zeolites and its Theoretical Interpretation," *Sci. Pap. Coll. Gen. Edu., Univ. Tokyo*, 28(1), 135(1978).

Table 1 Dissolution conditions

Burn-up [GWd/t]	Run No	U element [g]	HNO_3 Concentration [N] (volume [l])	Temperature [K]	Dissolution time [min]
Unirradiated	-	305.90	5.5 (2.2) : 150 ml/h	373	300
8	SFD1-1	436.05	5 (1.7)	373	200
8	SFD1-2	443.01	5 (1.7)	373	200
8	SFD1-3	439.90	4.5 (1.7)	373	260
29	SFD2-1	372.66	5 (1.5)	373	220
29	SFD2-2	283.95	4 (1.3)	373	160
29	SFD2-3	274.36	4 (1.3)	373	140
44	SFD3-1	325.72	5 (1.5)	373	220
44	SFD3-2	325.54	5 (1.5)	373	220
44	SFD3-3	342.74	4 (1.4)	373	220

Table 2 The Composition of the Simulated Spent Fuel

Element	Contents [%]
Sr	0.098
Zr	0.477
Mo	0.455
Ru	0.318
Rh	0.057
Pd	0.230
Ag	0.012
Ba	0.245
La	0.165
Ce	0.322
Pr	0.150
Nd	0.547
Sm	0.104
U	96.82

note: **The composition was determined by ORIGEN-II calculations for 45,000MWd/t.**

Table 3 Iodine-stripping operations employed

Burn-up [GWd/t]	Iodine-stripping operations	
Unirradiated	NO_2 gas, 363 K, 120 min	-
8	KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min	-
29	KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min	-
44	NO_2 gas, 363 K, 120 min	KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min

Table 4 Composition of CO_2 adsorbents

Adsorbent	Na [wt%]	K [wt%]	Al [wt%]	Mg [wt%]	Ca [wt%]	Si [wt%]	Si/Al [mol/mol]
Mordenite	1.08	0.70	6.31	0.14	1.77	30.99	4.735
2 M-Na-H-M*	1.98	0.13	1.24	0.01	0.33	27.1	21.1

Table 5 Iodine Distribution in the Dissolver Process

Place	Migration Ratio [%]
Iodine Adsorbent Columns	74.06
HEPA Filter	11.33
Scrubber	0.10
Dissolver Solution	0.37
Surface of Stainless Steel Test Piece in Dissolver Solution	0.57
Surface of Stainless Steel Test Piece in Dissolver Off-gas	1.58
Surface of Bucket and Hull	0.05
Precipitation Product	1.49
Total	89.55

Table 6 Amount of iodine-129 adsorbed by the columns

Burn-up [GWd/t]	Dissolution No.1 [x10^5Bq]	Dissolution No.2 [x10^5Bq]	Dissolution No.3 [x10^5Bq]	Iodine stripping (1) [x10^5Bq]	Iodine stripping (2) [x10^5Bq]	Total amount of iodine-129 adsorbed by columns [x10^5Bq]	Total amount of iodine-129 estimated by ORIGEN II [x10^5Bq]
8	0.4436*	0.8518*	0.5878*	0.1931*	-	2.107**	3.375
29**	2.478	1.935	1.867	0.553	-	6.834	9.867
44**	3.706	3.591	3.304	1.580	0.3999	12.58	17.37

*: Sum of iodine-129 on Columns B and C
**: Sum of iodine-129 on Columns A, B, C and D

Table 7 Amount of carbon-14 captured (29GWd/t spent fuel)

Dissolution No.1 [x10^5Bq]	Dissolution No.1 [x10^5Bq]	Dissolution No.1 [x10^5Bq]	Iodine stripping (1) [x10^5Bq]	Total [x10^5Bq]
30.00	20.00	17.61	2.602	70.21

note: Values are sum of carbon-14 captured by the trap and MS3A column (Column A)

Table 8 Adsorption/desorption test

Run No.	CO_2 amount at room temperature, 1 atm [ml]
1	258
2	258
3	286

Adsorbent: 2M-Na-HM
Weight of adsorbent: 20 g

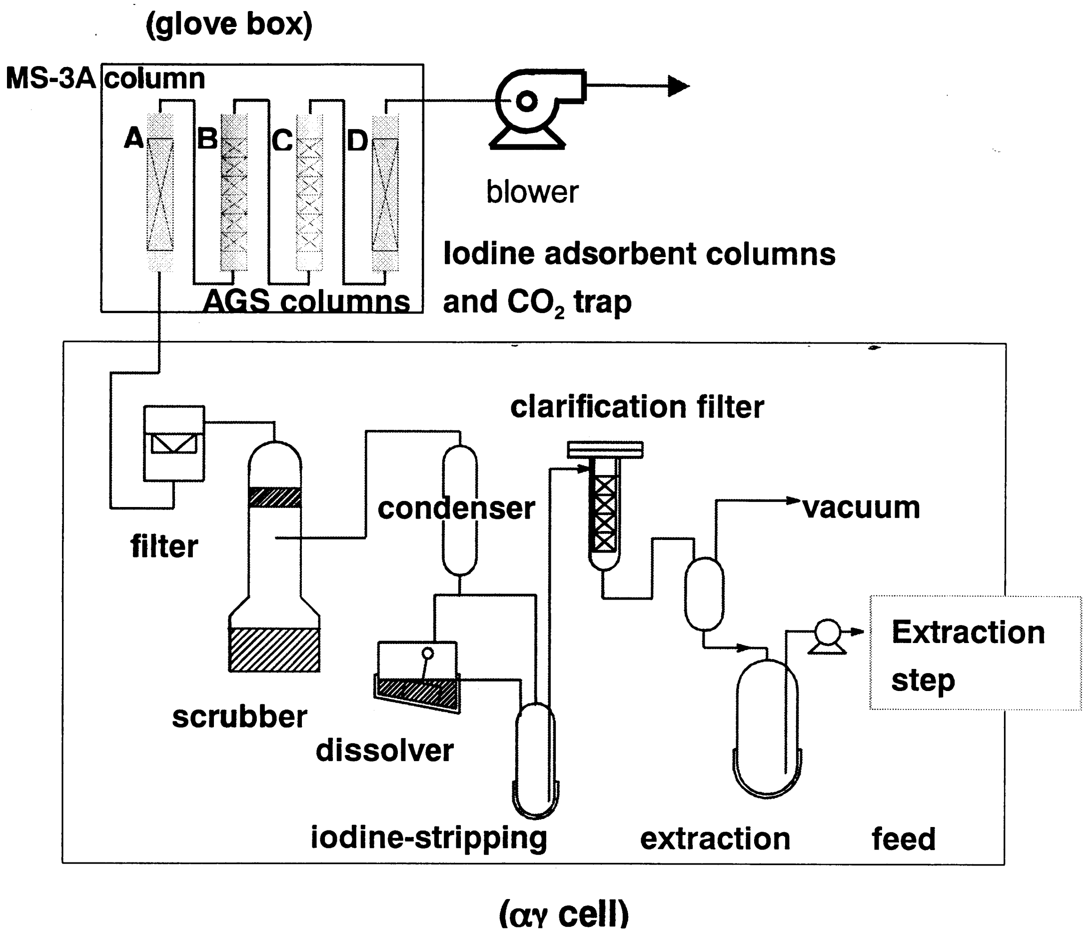

Figure 1 Schematic diagram of dissolution test rig

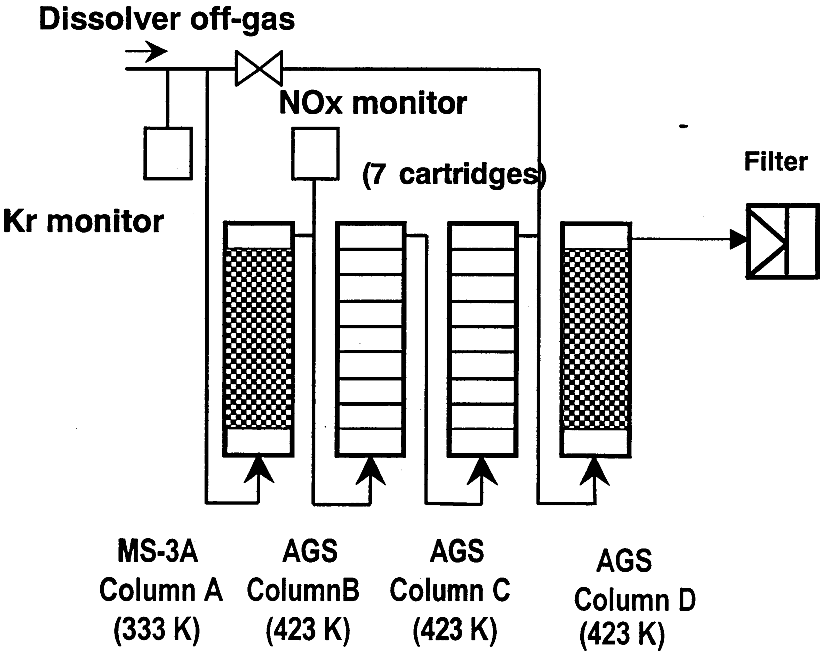

Figure 2 Iodine adsorptoin columns

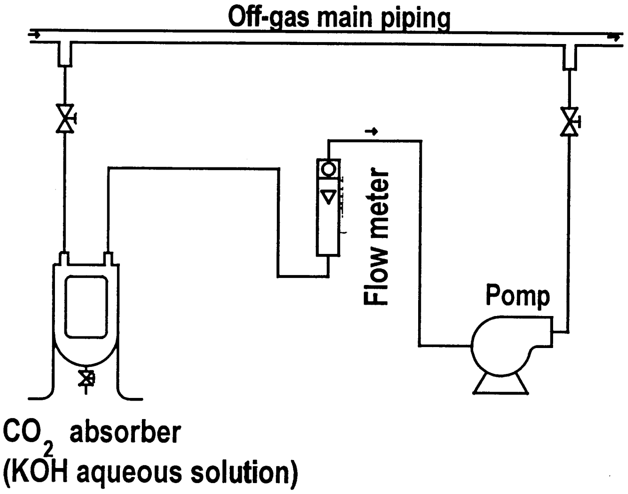

Figure 3 Schematic diagram of a CO_2 trap (The apparatus was set between Columns C and D)

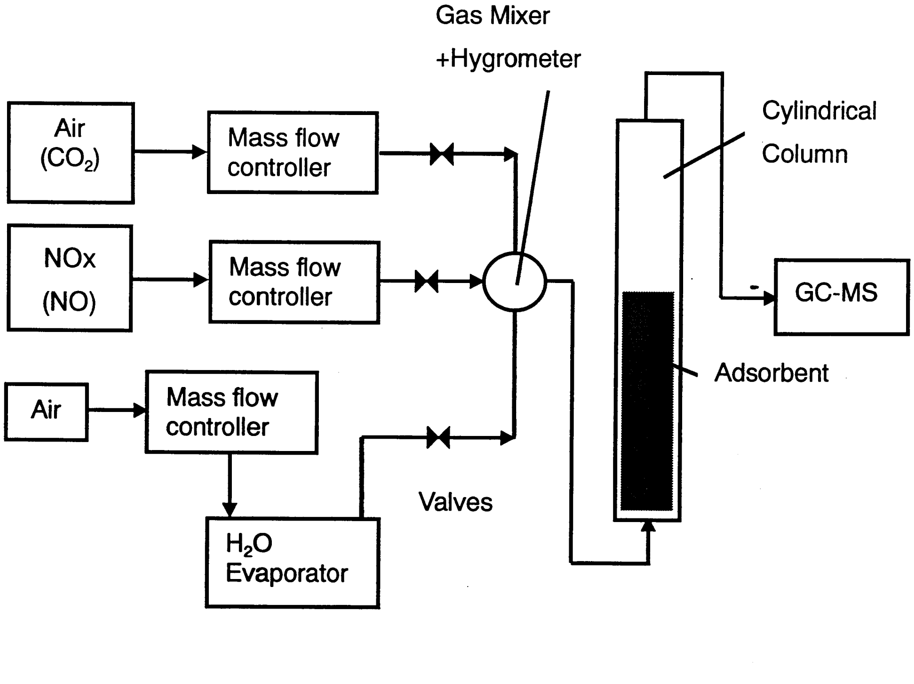

Figure 4 Schematic diagram of a test rig for the cold test of CO_2 adsorbents

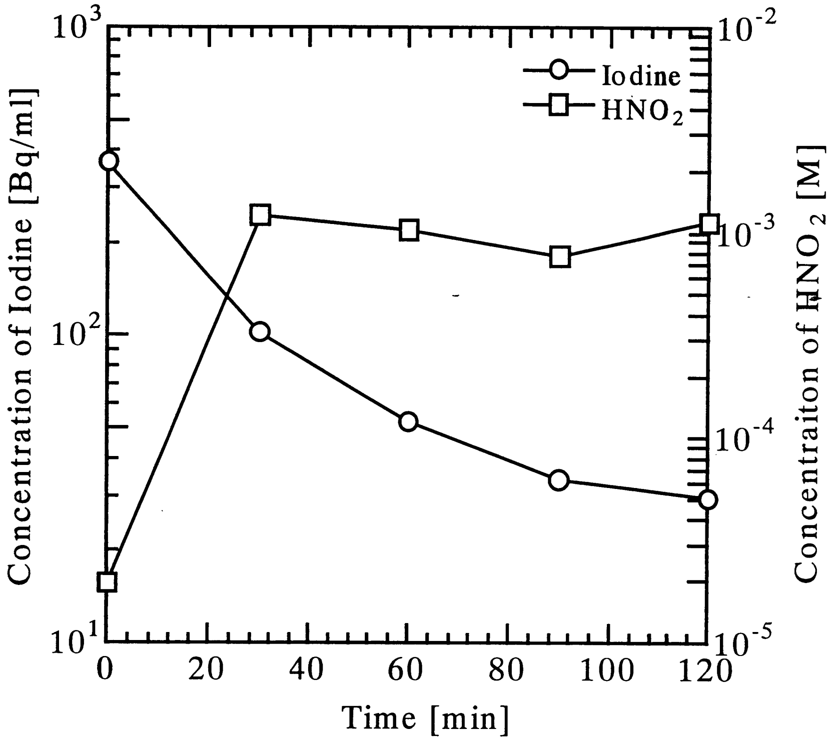

Figure 5 Concentration of iodine-131 and nitrous acid during iodine stripping

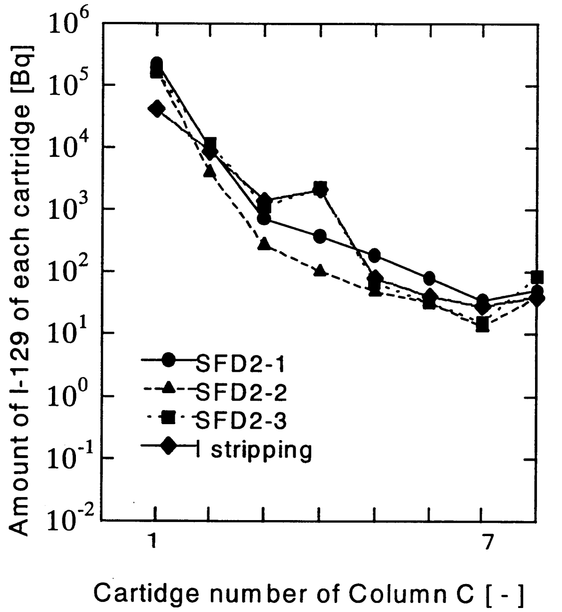

Figure 6 Profiles of iodine-129 in Column C (29 GWd/t SF)

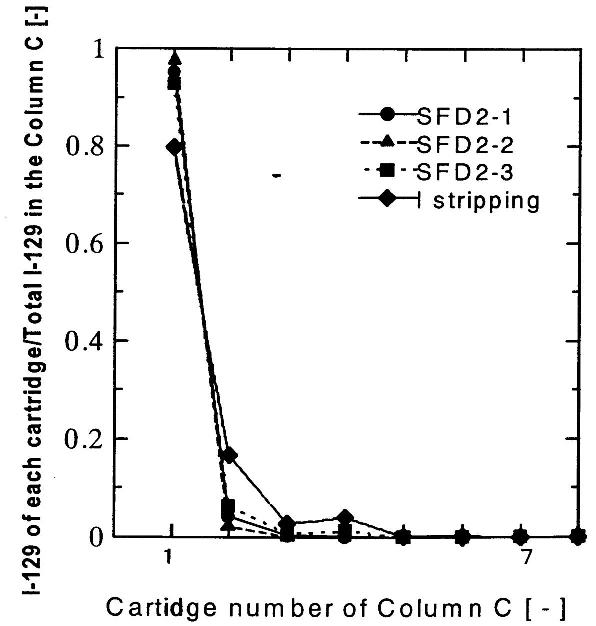

Figure 7 Fraction of captured iodine in each cartridge (29 GWd/t SF)

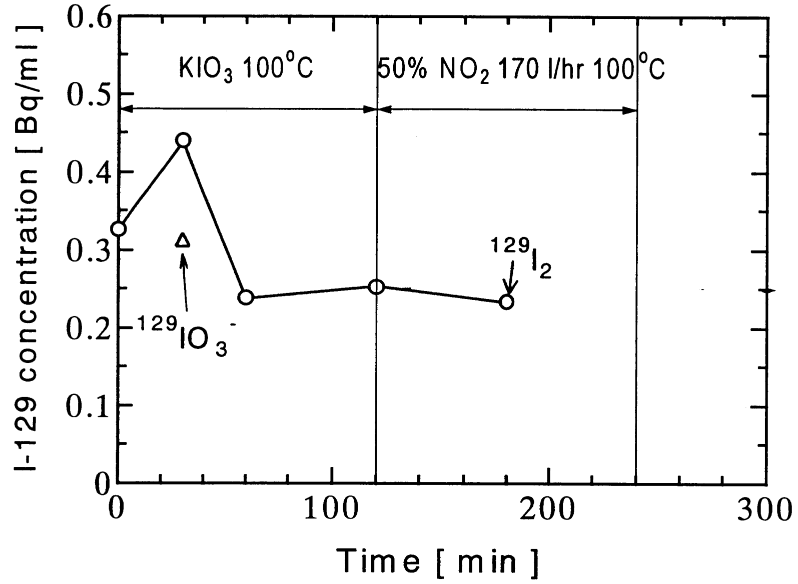

Figure 8 Iodine-129 in dissolver solution during two-step iodine stripping (29 GWd/t SF)

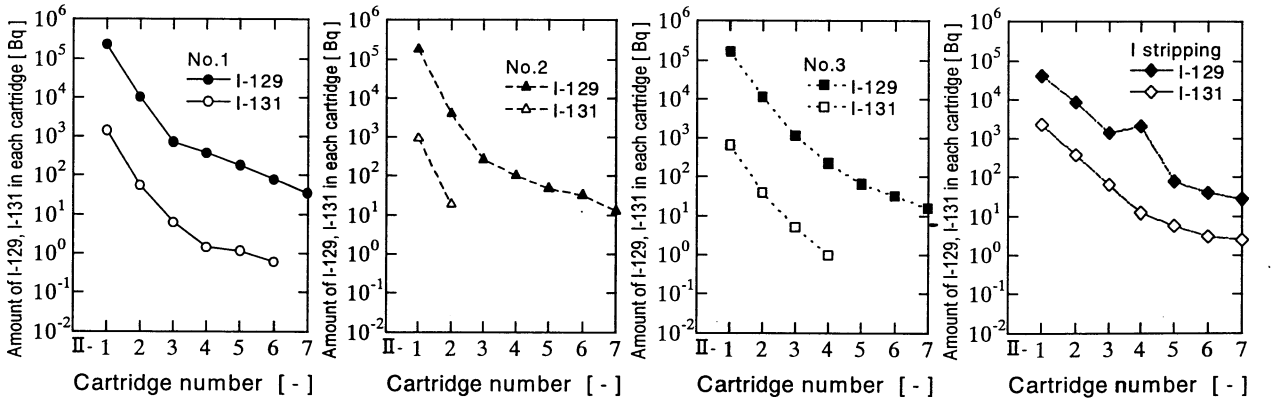

Figure 9 Comparison of profiles of iodine-129 and iodine-131 (29 GWd/t SF)

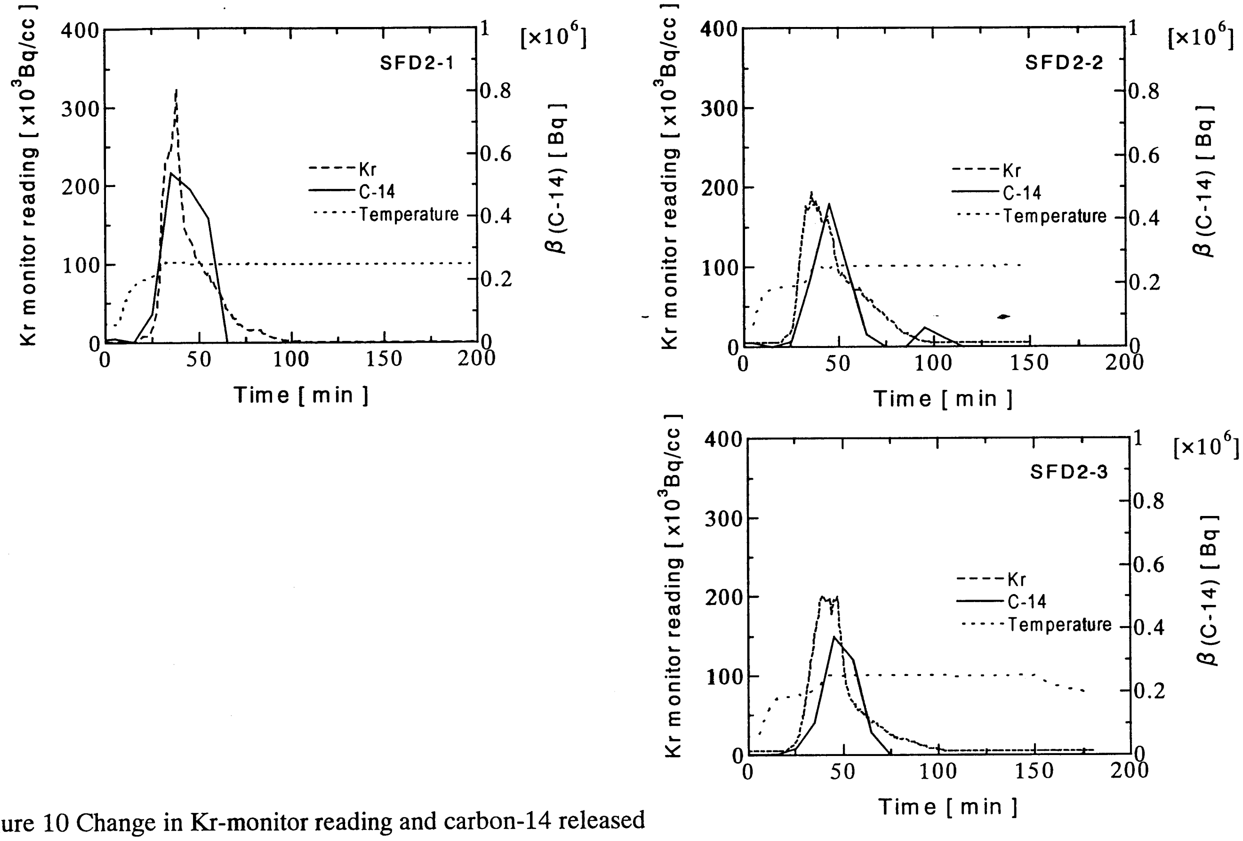

Figure 10 Change in Kr-monitor reading and carbon-14 released during dissolution (29 GWd/t SF)

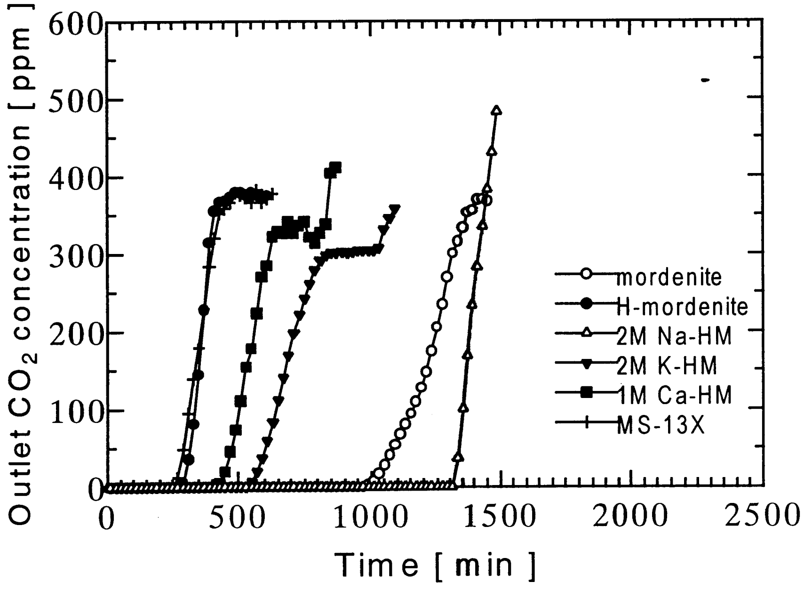

Figure 11 Breakthrough curves of adsorbents tested

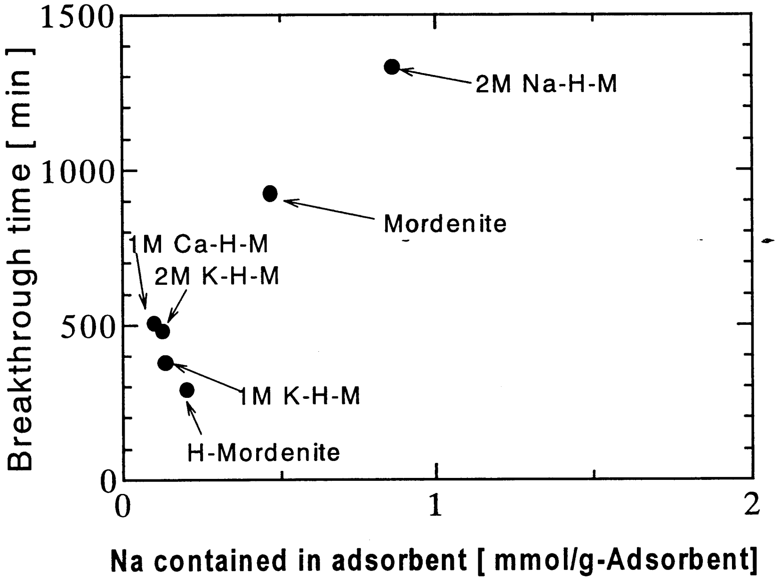

Figure 12 Effect of Na concentration on breakthrough time of adsorbent