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Citation	Proceedings of 2014 Nuclear Plant Chemistry Conference (NPC 2014), 2014, 9pages.
Text Version	Author Accepted Manuscript
URL	http://jolissrch-inter.tokai-sc.jaea.go.jp/search/servlet/search?5048306
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Revaluation of Hydrogen Generation by Water Radiolysis in SDS Vessels at TMI-2 Accident

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ABSTRACT

Two years after Three Mile Island Unit 2 (TMI-2) loss-of-coolant accident, radioactive contaminated water has been processed by Submerged Demineralizer System (SDS) with two types of zeolite adsorbents to remove radioactive nuclides of Sr-90, Cs-134 and Cs-137. During and after the process, adsorption amount and distribution of nuclides on the zeolites, residual water content and thermal conductivity in the SDS vessels have been measured or estimated for verification of safety in the process, subsequent transportation and disposal. Hydrogen generation has been also evaluated mainly by direct monitoring in the large-scale of vessel after the process. In this work, the revaluation of hydrogen generation was demonstrated on the basis of the open information of vessel, and the latest experimental data obtained in adsorption and radiolysis occurring in small-scale of zeolite-water mixtures.

As a property of the zeolites (UOP IE-96, A-51), adsorption and desorption of water vapour on the zeolites were observed as a function of relative pressure corresponding to relative humidity. 10-20 wt% of water was found to be physically and chemically adsorbed on the zeolites within normal humidity of 20 to 90 %RH, reflecting residual water content absorbed on the dominant zeolites in the dewatering of vessels after the process. Hydrogen generated in the radiolysis of zeolite-water mixtures was further measured to obtain the observed yields of hydrogen as functions of water content in the mixtures and of the height of mixtures. It was found that additional water radiolysis took place through the energy dissipation of radiation to the zeolites, and that liquid depth effect on the yield in water was depressed by adding zeolites to water. Based on these experimental results and further estimations, hydrogen generation dependent on decay heat and water content in the SDS vessel was finally revaluated. The procedure and results in this revaluation would be helpful for the decontamination of radioactive water at Fukushima Daiichi NPS accident.

Keywords: Three Mile Island Unit 2 (TMI-2) accident, Submerged Demineralizer System (SDS) vessel, Zeolite adsorbents, Radioactive nuclides, Energy absorption, Water radiolysis, Hydrogen generation

1. INTRODUCTION

Two years after Three Mile Island Unit 2 (TMI-2) accident in 1979, radioactive contaminated water present in the Reactor Building (Basement), Reactor Coolant Bleed Tank (RCBT) and Reactor Coolant System (RCS) has been processed by Submerged Demineralizer System (SDS) with two types of zeolites set in the spent fuel pool to remove radioactive nuclides of Sr-90, Cs-134 and Cs-137, like the decontamination made for Fukushima Daiichi Nuclear Power Station (NPS) accident in 2011 [1]. After the process, the SDS vessels containing the zeolites adsorbed by the nuclides (their decay heat lower than 300 W) were drained and dewatered by drip (nitrogen gas dewatering) and vacuum drying, and then shipped to carry out two programs of solidifying and burying: zeolite vitrification demonstration program (3 vessels) and dry handling and monitored demonstration program (10). During and after the process, the adsorption of radionuclides on the zeolites, residual water content and thermal conductivity in the vessels have been measured or estimated for verification of safety in the process, subsequent transportation and disposal. Gas generation of hydrogen molecule (H_2) from the radiolysis of residual water by ionizing radiations emitted from the radioactive nuclides has been also evaluated mainly by direct monitoring in the large-scale of vessel after the process, together with other gases such as oxygen, of which the amounts were reported as functions of radioactivity and water content.

These measured and estimated data are now open and available in the reports [2-6] as well as the size and geometry of SDS vessel, different from the case of Fukushima accident for which adsorption behavior of radioactive Cs, radiolytic gas generation and corrosion, and heat and gas transfers have been investigated by using small-scale of columns, vials and vessels [7]. In this work, the revaluation of H_2 generation in the vessel was demonstrated on the basis of the open information of vessel, and of the latest experimental data obtained in adsorption and radiolysis occurring in the small-scale of zeolite-water mixtures.

2. EVALUATION PROCEDURE

2.1 Submerged demineralizer system (SDS) vessel

Table 1 shows the form and size of SDS vessel and zeolite bed in the vessel for the evaluation. Although the form of real vessel was a combination of spherical parts at top and bottom and cylindrical body [2-3], a cylindrical form with the same inner volume and radius was adopted for the sake of simplicity in this work. The loaded volume and weight of dry zeolites were reported to be 227 L (8 ft^3) and 143 kg, respectively, leading to the particle density of 0.63 kg/L. However, the actual density obtained experimentally is higher than 0.63 kg/L as shown later, and then the weight of zeolites was only adopted for the evaluation.

Table 1. Geometry of SDS vessel and zeolite bed for the evaluation in this work

	SDS vessel*	Zeolite bed
Form	Cylinder	
Inner height [mm]	988.0	575.2
Inner radius [mm]	295.3	
Volume [L (ft^3)]	271 (10)	158 (5.6)

* The vessel was made by the plate of SUS (9.5 mm thickness).

Thus the volume and height headspace above the zeolite bed, which is filled with water during the decontamination process, were 113 L and 412.8 mm, respectively.

2.2 Zeolite adsorbents of IE-96 and A-51 in SDS vessel

The two types of zeolite adsorbents of IE-96 for radioactive Cs and A-51 for Sr-90 have been used at their mixing ratios of 1:1, 3:2 and 2:1 [2]. The chemical structures of IE-96 and A-51 are of chabazite (CHA) and Linde type A (LTA), respectively [8]. The chemical formulas of CHA and LTA, important in the estimation of absorption coefficients for ionizing radiations such as mass energy-absorption coefficients, $(\mu/\rho)_{en}$, for photons [9] as mentioned later, were assumed to be the sodium types of $Na_4[Al_4Si_8O_{24}]12H_2O$ and $Na_{12}[Al_{12}Si_{12}O_{48}]27H_2O$, respectively. Their structural data of true and particle densities, and specific surface area and pore volume are necessary for the evaluation and were measured in the followings.

In order to measure the surface structures of zeolites and to clarify the adsorption behaviors of water vapor on the zeolites, adsorbed amounts of water as a function of pressure relative to saturated one at T=298.15 K (adsorption isotherms) were measured at dry and wet conditions through gas adsorption method as shown in **Figure 1** (a) and (b). The relative pressure, P/P_0, in this case corresponds with relative humidity. The dry condition means drying the zeolites *in vacuo* at T>573.15 K for more than three hours before the measurement, while the wet one is drying the zeolites *in vacuo* at T=298.15 K for more than seven hours after the zeolites were exposed to the atmosphere at equilibrium humidity of 79.3 %RH of saturated NH_4Cl solution [10] for more than one week.

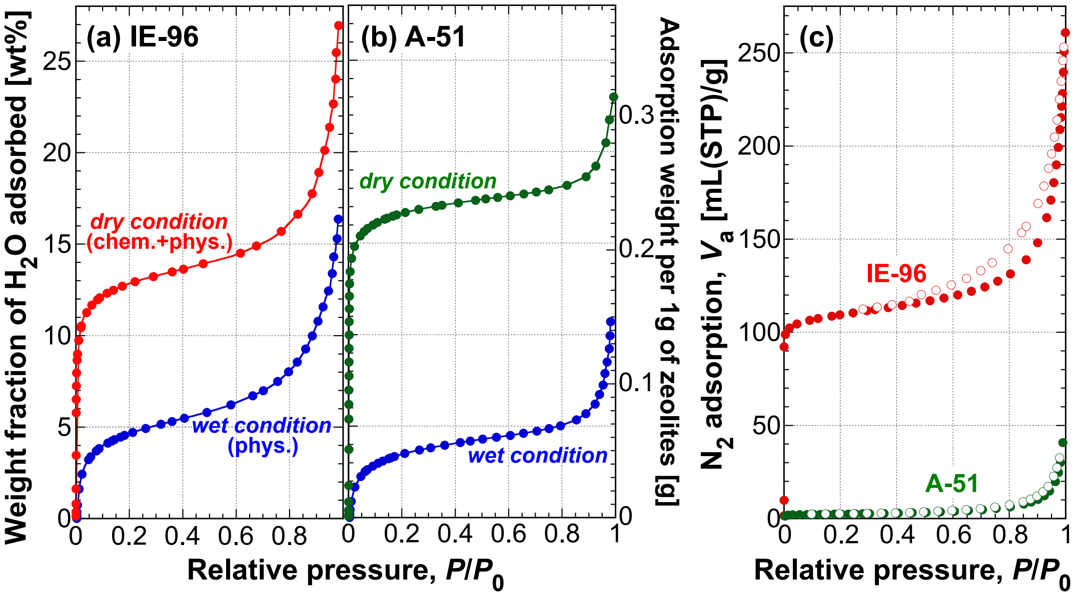

Figure 1. Adsorption isotherms of water vapor on IE-96 (a) and A-51 (b) at T=298.15 K, and their isotherms of nitrogen (c) at T=77 K

Both "chemical" (water loosely bound to the zeolites remained after the vacuum drying without heat [3]) and "physical" (unbound water removed by the drip drying) adsorptions were observed in the isotherms at the dry condition, while only the physical one at the wet condition. Thus the chemical adsorption was observed from the difference between the isotherms at the dry and wet conditions, and followed Langmuir isotherm equation. The rapid increases of adsorptions at the lower P/P_0 in Fig. 1 (a) and (b) indicate that the zeolites have micropores (<2 nm) inside them. Furthermore, when comparing with adsorption isotherms of nitrogen on the zeolites at T=77 K as shown in Fig. 1 (c), the presence of ultra-micropores (<0.7 nm), into which H_2O but not N_2 can invade, was suggested inside the LTA type of A-51. The specific surface areas of zeolites were obtained from the isotherm at P/P_0=0.02-0.1 according to BET absorption one, and the total pore volumes were obtained from the adsorption amounts of water vapor at P/P_0=0.99.

The true and particle densities (ρ_{true}, ρ_{app}), and total pore volume (V_{tot}) of dry mixed zeolites of IE-96 and A-51 were measured as a function of the mixing ratio as shown in **Figure 2** (a). The ρ_{true}, ρ_{app} and V_{tot} were found not to vary so much within the mixing ratio adopted in the SDS vessel [2]. From these three data, the volumes of zeolites (ρ_{app}/ρ_{true}), pores (ρ_{app} V_{tot}) inside the zeolites and inter spaces among the zeolites per unit volume of 1 L can be estimated separately. Then the estimation of densities of damp or submerged zeolites, when the pores and/or inter spaces are filled with water, is important not only in the heat and gas transfers but also in the energy absorption and gas generation in the vessel.

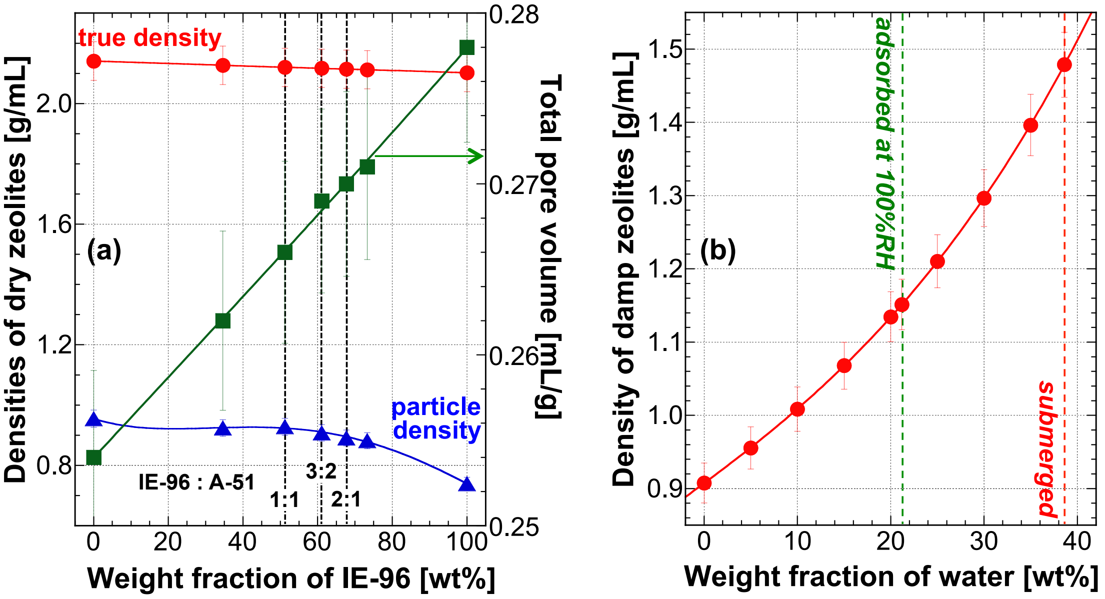

Figure 2. Densities and total pore volume of dry mixed zeolites of IE-96 and A-51 (a), and the densities of damp or submerged zeolites at their mixing ratio of 3:2 (b)

Fig. 2 (b) illustrates the increase of density at the mixing ratio of 3:2 with increasing weight fraction of water, in which 21.1 wt% indicates the pores filled with water at 100 %RH (the damp condition of zeolites) and 38.6 wt% both the pores and inter spaces filled with water (the submerged condition). In the report [3], the weights of components in the SDS vessel have been described separately when the vessel has been filled with water completely: 143 kg (bone dry zeolite), 122 kg (loose water), 45 kg (unbound water) and 45 kg (loosely bound water). The loose, unbound and loosely bound water indicate the volume of headspace above the zeolite bed, and the adsorbed volumes of water on the physical and chemical sites of mixed zeolites, respectively, leading to the suitability of size data of vessel adopted for the revaluation.

2.3 Estimation of energy absorption and H_2 generation in SDS vessel

The radioactivity and decay heat of radioactive nuclides adsorbed in the SDS vessel are available in the reports [2-3]. The activity has been described as those of radioactive Cs, Sr and daughters, of which the main nuclides have been reported to be Cs-137 and Sr-90. Therefore, Cs-137 (half life time: 30.17 years), Cs-134 (2.062), Sr-90 (28.79) and its daughter of Y-90, which emit γ- and/or β-rays, are considered to be present in the vessel as shown in **Table 2**, where the conversion ratio means recoverable averaged energy excluding neutrino (Q_{rec}) per unit decay from the nuclide [11]. Assuming that secular equilibrium between Sr-90 and Y-90 has attained when the activity has been measured, the activity of Cs-134 was much lower than that of Cs-137 (<1/20), different from the activity ratio of Cs-134 (≈1) just after the Fukushima Daiichi NPS accident [1].

Table 2. Gamma and beta rays emitted from radioactive nuclides in SDS vessel

	Cs-137*		Cs-134		Sr-90		Y-90	
	γ-ray	β-ray	γ-ray	β-ray	γ-ray	β-ray	γ-ray	β-ray
Averaged energy [keV]	662	188	698	157	-	196	-	934
Energy emission [%]	75.0	25.0	90.8	9.2	-	100	-	100
Conversion [MeV/Bq]	0.787		1.719		0.196		0.934	

* The γ-ray is from the daughter nuclide of Ba-137m.

The penetration and attenuation of ionizing radiations of γ- and β-rays in the vessel were estimated by calculating those in the small area of vessel after the cylindrical vessel was divided into every 10 mm (1 cm) in the axial and radial directions. And then the energy (dose) absorbed in the vessel could be evaluated in the axial direction. For the γ-rays of 662 and 698 keV, the linear attenuation coefficients, μ_{tot}, of water, stainless steel (SUS) and mixed zeolites were obtained from the product of mass attenuation coefficients, μ_{tot}/ρ, [9] and densities, ρ, as shown in **Table 3**, where the μ_{tot}/ρ of dry mixed zeolites was estimated on the basis of the above chemical formulas of zeolites and their mixing ratio. In the case of penetration of γ-rays with incident intensity of I_0 through media with length of L, the intensity of I after the penetration can be expressed in the following equation of penetrated fraction of γ-rays (I/I_0), and the fraction of 1-I/I_0 was assumed to be that of γ-rays absorbed within the media in this study. For example, the fractions of γ-ray of Cs-137 penetrated through 10 mm of the damp and submerged zeolites were 92.3 and 89.8 %, respectively. The plate of SUS as the building material of SDS vessel had constant thickness of 9.5 mm, and then the fraction penetrated through the plate became 57.6 %.

$$I/I_0 = \exp[-(\mu_{tot}/\rho)\ X] = \exp(-\mu_{tot}\ L), \quad X\text{: mass thickness} \qquad (1)$$

Table 3. Linear energy-absorption (μ_{en}) and attenuation (μ_{tot}) coefficients for gamma ray emitted from Cs-137

		Water	SUS	Mixed zeolite (IE-96 : A-51 = 3:2)		
				Dry 0 wt%	Damp* 21.2 wt%	Submerged 38.6 wt%
Coefficient $\times 10^2$ cm^{-1}	μ_{en}	3.300	21.97	2.718	3.522	4.603
	μ_{tot}	8.443	57.95	5.983	8.040	10.81

* The "Damp" means the zeolite only having adsorbed H_2O at 100 %RH.

For the β-rays of 150-1000 keV, depth-dose curve (energy-deposition distribution) of fast electrons in semi-infinite media was estimated by using "Electron-Material Interaction Database" (EMID) [12] to obtain the relation between incident energy, E_0, of electron beams and extrapolated range, R_{ex}, in the media of water, SUS, IE-96 and A-51 with their effective atomic number (Z_{eff}) and weight (A_{eff}): H_2O (Z_{eff}=6.60, A_{eff}=11.89), SUS (25.82, 55.41), IE-96 (10.21, 19.52), A-51 (10.31, 19.50). The R_{ex} increased linearly with increasing E_0, and was found to be within 10 mm in water and the zeolites even at E_0=2000 keV, corresponding to the maximum energy of β-ray from Y-90 (2.28 MeV). Therefore, the β-rays emitted from the radioactive nuclides adsorbed in the above small area were assumed to be absorbed within the area.

After the absorbed dose (energy) in the small area was evaluated, the amount of H_2 generation by water radiolysis could be obtained from the product of dose and observed yield, $G(H_2)$, of H_2 in the following equation.

$$P \text{ (mol/g)} = G \text{ (mol/J)} \times D \text{ (J/g)} \qquad (2)$$

Where the absorbed dose in the small area is proportional to the mass energy-absorption coefficient of $(\mu/\rho)_{en}$ in the area [9]. In general, the $G(H_2)$ would depend on the weight fraction of water and kinds of zeolites in the area. In order to obtain the observed yields of H_2 generated in the radiolysis of zeolite-water mixtures, the radiolysis experiments were conducted by using Co-60 γ-ray with its averaged energy of 1.25 MeV. It can be noted that results on water radiolysis obtained by irradiating Co-60 γ-ray are comparable to those by irradiating γ- and β-rays (including photons and electron beams) with energies of 0.1-20 MeV. In this study, the $G(H_2)$ for the damp and submerged zeolites are important in evaluating the H_2 generation in the SDS vessel. **Figure 3** shows the H_2 generation from the zeolite-water mixtures of IE-96 (a) and A-51 (b) at room temperature, aerated condition and sample height of 1 cm. The amount of H_2 increased linearly with increasing the absorbed dose, leading to the determination of $G(H_2)$ from the slope of line according to the equation (2).

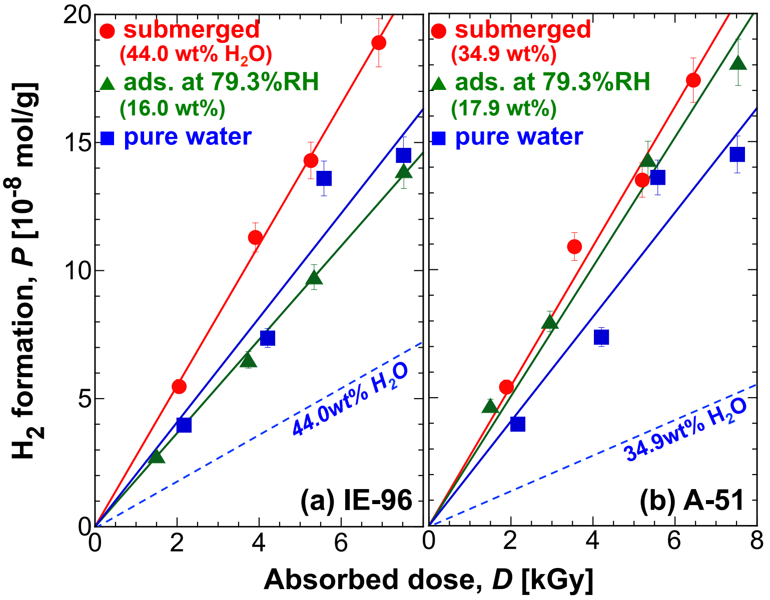

Figure 3. H_2 generation from zeolite-water mixtures of IE-96 (a) and A-51 (b) by water radiolysis at room temperature, aerated condition and sample height of 1 cm

The $G(H_2)$ for the damp and submerged zeolites could not be explained only by the radiolysis of water contained in the mixtures as shown as dashed lines in Fig. 3. This suggests that the water radiolysis to generate H_2 took place not only through the energy dissipation of radiation to water but also through that to the zeolites. The $G(H_2)$ for the submerged zeolites but not for the damp ones were dependent on the height of zeolite-water mixtures (liquid (sample) depth effect [13]), and found to be expressed by the single power of height [7]. When the submerged height in the vessel was higher than 10 mm in evaluating the H_2 generation, the liquid depth effect was applied to the $G(H_2)$ for the submerged zeolites.

3. RESULTS AND DISCUSSION

There are a lot of parameters in the revaluation of H_2 generation: mainly the decay heat (the amount of radioactive nuclides), the composition (time course after the accident) and distribution of nuclides, the residual water content, and the mixing ratio of two types of zeolites in the zeolite bed inside the SDS vessel. In the present paper, the revaluation was demonstrated for the vessel number of D10011, which has been used to obtain SDS vessel burial data [6]. The mixing ratio of IE-96 and A-51 in the D10011 vessel was 3:2 [2], and the decay heat 225W [3], which was assumed to be the sum of 188 (Cs-137), 23 (Cs-134) and 14 W (Sr-90 & Y-90) as the composition of nuclides in the revaluation. The typical axial distribution of Cs-137 activity in the SDS vessel has been measured from the top to bottom of zeolite bed by a remote γ-scanning system in the zeolite vitrification demonstration program [4] as shown in **Figure 4** (a). The typical distribution was assumed to correspond with the absorption one not only of the radioactive Cs but also of Sr-90 in the vessel, and then applied to the revaluation, together with constant distribution for comparison as shown as a dashed line in Fig. 4 (a).

Based on the above assumptions, at fast, the rates of absorbed energy and dose in the vessel were estimated as a function of weight fraction of water, w_{H2O}, from the damp zeolite bed at 100 %RH to the submerged one as shown in Fig. 4 (b). The energy rate increased with increasing w_{H2O}, while the dose rate (~3 kGy/h), which divides the energy rate at the whole weight of zeolite bed, decreased with increasing the weight (w_{H2O}).

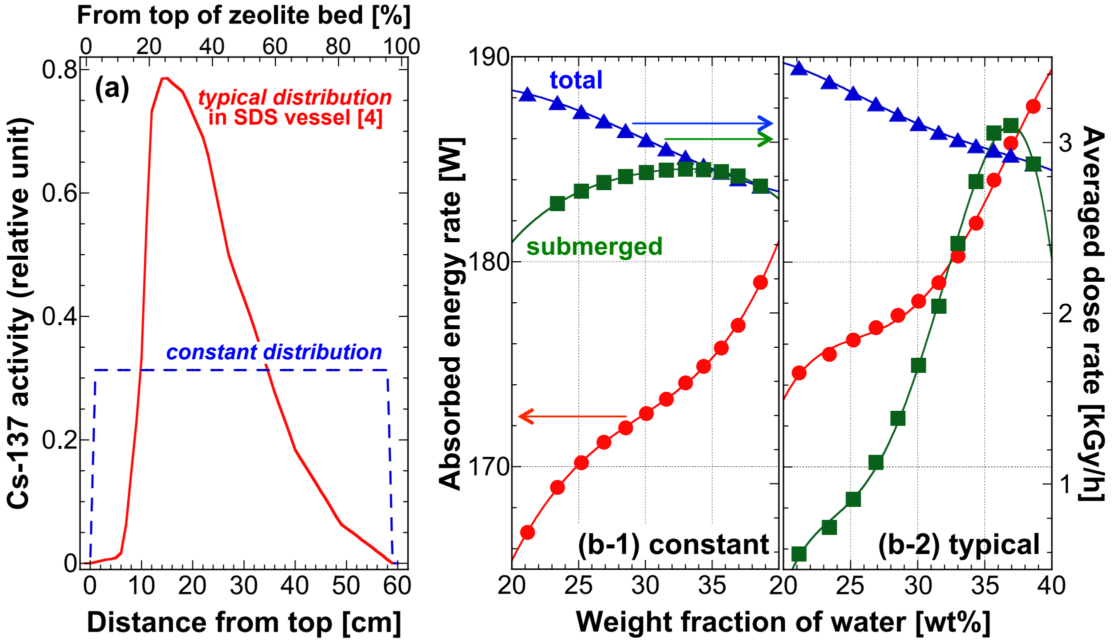

Figure 4. Axial distribution of adsorbed nuclides used for the evaluation (a) and dependence of absorbed energy and dose rates on residual water content (b) in SDS vessel with decay heat of 225 W

The absorbed energy rate in the vessel was also found to be 74-84 % of the decay heat, of which the rest was given to SUS and leakage out of the vessel. The dose rate at the submerged part of zeolite bed was almost constant regardless of w_{H2O} in the constant distribution of adsorbed nuclides (b-1), while it increased with increasing w_{H2O} in the typical distribution (b-2).

From the above absorbed dose rate, finally, the H_2 generation rate in the vessel was estimated as a function of w_{H2O} from the damp zeolite bed at 100 %RH to the submerged one as shown in **Figure 5**, where STP indicates standard condition of temperature (273.15 K) and pressure (1 atm), and the total rate in the case of no liquid depth effect on $G(H_2)$ is also inserted as dashed lines. The generation rate at the submerged part of zeolite bed increased irrespective of the liquid depth effect with increasing w_{H2O}, while the total rate decreased by the liquid depth effect although the total rate without the effect increased. Therefore, the total generation rate became maximum in the damp zeolite bed at 100 %RH inside the SDS vessel, different from the case of zeolite-seawater mixtures just after the decontamination of radioactive water has started for the Fukushima Daiichi NPS accident [7].

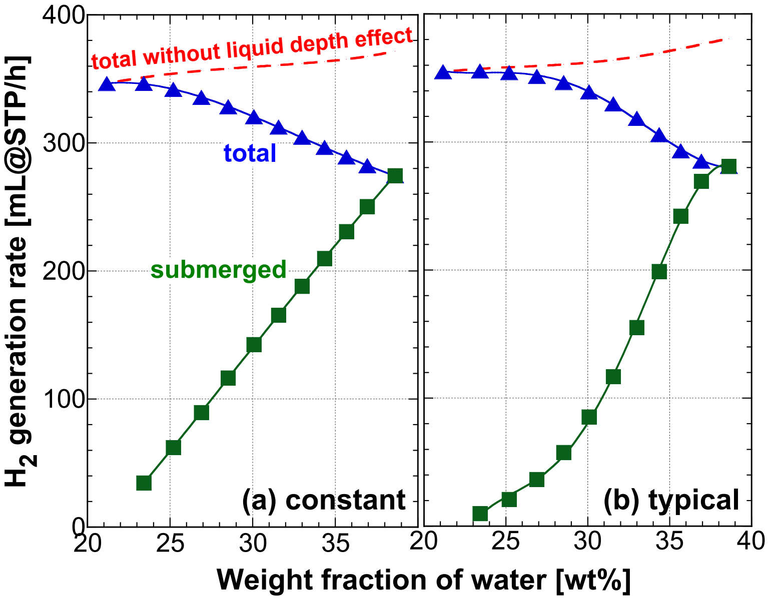

Figure 5. Dependence of H_2 generation rate on residual water content in SDS vessel with decay heat of 225 W at T=298.15 K

In the D10011 vessel [3], the whole generation rate of radiolytic H_2 and O_2 at $w_{H2O} \approx 40$ wt%, where the zeolite bed was almost submerged, has been measured as about 380 mL/h, in which 73 % of H_2 and 27 % of O_2 were present. This indicates that the H_2 generation rate was 254 mL@STP/h, close to the estimated data in Fig. 5. The decrease of total rate at $w_{H2O} < 30$ wt% by the liquid depth effect in the typical distribution of radioactive nuclides (b) was shown to be lower than that in the constant distribution (a), because in the typical distribution, the dose rate at the bottom of zeolite bed was quite low as shown in Fig. 4 (b-2).

4. CONCLUSIONS

In this work, the H_2 generation in the SDS vessel was revaluated on the basis of the open information of vessel and of the latest experimental and estimation data on adsorption and radiolysis obtained in the small-scale of zeolite-water mixtures, and then the evaluated data was found to be comparable with the reported data obtained in the large-scale of real vessel.

In order to estimate the H_2 generation rate more strictly, temperature distribution and radiolytic O_2 generation in the vessel have to be taken into account. The area of temperature higher than 383.15 K, at which any H_2O cannot adsorb on zeolites, has been reported to exist at the center of vessel [6], and at temperature higher than room one (298.15 K), the $G(H_2)$ and its liquid depth effect for the submerged zeolites would increase and decrease, respectively. The O_2 has been observed in the vessel with its amount smaller than the half of H_2 amount [3] mainly due to thermal and/or catalytic decomposition of hydrogen peroxide (H_2O_2) as a radiolysis product of water [14], although O_2 is not generated directly by water radiolysis, different from electrolysis of water (H_2O -> H_2 + 1/2 O_2). The analysis of heat transfer leading to the temperature distribution in the vessel, and the radiolysis experiments on the H_2 and O_2 generation in zeolite-water mixtures are continued at present.

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