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Examination of ^{131}I and ^{137}Cs releases during late phase of Fukushima Daiichi NPP accident by using ^{131}I/^{137}Cs ratio of source terms evaluated reversely by WSPEEDI code with environmental monitoring data

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To investigate what happened in reality during the Fukushima Daiichi Nuclear Power Plant accident, the phenomena within reactor pressure vessel and the discussion of ties with the environmental monitoring measurement are very important. However, the previous study that treats phenomena of the both has not necessarily advanced up to the present time. The source terms predicted by simulation codes such as MELCOR has not yet been consistent with the reverse estimation by WSPEEDI code using environmental measurement data. The present study investigated ^{131}I and ^{137}Cs release behaviors during the late phase of the accident to contribute to such examination using the ^{131}I/^{137}Cs ratio of the new source terms predicted by Katata. The ^{131}I release by the gas-liquid partition from the contaminated water in the 1F2 and 1F3 reactor buildings which was pointed out in the previous study was reevaluated using the new source terms. In addition, paying attention to the similarity of the core conditions between the

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Fukushima accident and the Phébus FPT3 experiment using the B_4C control rods, the release of organic iodine (CH_3I) during the 1F3 suppression pool venting, formation of $CsBO_2$ and its release behavior were examined which have not yet been sufficiently studied so far.

Keywords; Source Term; Fukushima Daiichi NPP Accident; $^{131}I/^{137}Cs$ Ratio; WSPEEDI; MELCOR; Boron Carbide (B_4C); Cesium Metaborate ($CsBO_2$)

1. Introduction

In an evaluation of the Fukushima Daiichi NPP (Nuclear Power Plant) accident, hereafter the Fukushima accident, understanding the phenomena that occurred in the reactor pressure vessel (RPV) and discussing its ties with environmental monitoring measurement are important. Individual studies on the thermo-hydraulic phenomena in the RPV [1] and radiological dispersion in the environment [2] were performed after the accident but a study that treats both phenomena in gross has not necessarily been conducted in the six years after the accident.

Thus far, many examinations of ^{131}I and ^{137}Cs source terms during the Fukushima accident have been conducted, mainly using the two methods. One is estimation from thermo-hydraulic characteristics and analyses of radionuclides release and transport [3] within the RPV and the containment vessel (CV) using severe accident analysis codes such as MELCOR. The other is reverse estimation [4] using an atmospheric dispersion simulation code such as WSPEEDI combined with environmental monitoring data, hereafter WSPEEDI reverse.

The RPV simulation results of past examinations have not yet been adequately consistent with the environmental measurement results. Concerning the cumulative releases of ^{131}I and ^{137}Cs, the results of both methods are in reasonable agreement with each other, as shown in **Fig. 1**. The MELCOR calculation was deemed complete on March 17 because there was no more meaningful release from the core while WSPEEDI reverse evaluated continued release until the beginning of April, leading to a clear difference between the results of both methods.

A study [5] by Hidaka showed that the discrepancy of ^{131}I release during the late phase of the Fukushima accident could be explained mainly by the following reasons. MELCOR did not treat a release model from the accumulated water in the basement of the 1F2 and 1F3 reactor buildings due to gas-liquid partition based on Henry's law and steam generation by decay heat.

In the previous study, ^{131}I and ^{137}Cs source terms prepared by Terada [6] were used. However, "new source terms" were recently published by Katata [2] considering the radionuclide amount delivered by wind blowing from land to sea, which was estimated from sea surface concentration. The new source terms predicted an increase in the total cumulative releases of ^{131}I and ^{137}Cs by 10%-20% compared with those reported by Terada (see **Fig. 1**) and a more detailed ^{131}I/^{137}Cs ratio of their release rates (Bq/hr) (see **Fig. 2)**.

Therefore, in the present study, ^{131}I release from the contaminated water during the late phase (after March 17) was reevaluated using the new source terms. In addition, by paying attention to the similarity of the core conditions between the Fukushima accident and the Phébus FPT3 experiment conducted using B_4C control rods [7], the release of organic iodine, e.g., methyl iodide (CH_3I) during the venting of the 1F3 suppression pool was estimated preliminarily. Further examinations were focused on the chemical form and release behavior of ^{137}Cs during the Fukushima accident, which had not yet been sufficiently studied.

2. ^{131}I/^{137}Cs ratio

The release rates of ^{131}I and ^{137}Cs predicted using WSPEEDI reverse are shown in **Fig. 3** and are equal to the radioactivity, Bq, number actually released to the environment. In the Katata's study, the chemical and physical forms of ^{131}I were assumed to be particulate iodine, gaseous I_2, and gaseous CH_3I, respectively, while no forms were assumed for Cs. When the ^{131}I/^{137}Cs ratio was calculated, the radioactivity levels of the three ^{131}I forms were added up. The ratio of particulate ^{131}I to the gaseous form was determined by the monitoring data at Tokai [8], and the fraction of CH_3I was determined by assuming that 60% of all the gaseous iodine was CH_3I and 40% was I_2.

The ^{131}I/^{137}Cs ratio based on these forms would be approximately equal to 10 just after the accident initiation if the volatility of ^{131}I and ^{137}Cs were assumed to be mostly the same because the core inventory of Cs is larger by about one order of magnitude than that of iodine [9], as given in **Table 1**, while the specific radioactivity of Cs is smaller by about two orders of magnitude than that of iodine.

The ^{131}I/^{137}Cs ratio (see **Fig. 2**) increased temporarily to more than 10 between March 15 and 16. This corresponds to the timing of the 1F3 suppression pool venting. It is considered that the gaseous iodine (CH_3I) formed within the RPV under relatively elevated temperatures could have been released to the environment. The details are discussed in **Chapter 5**.

The ^{131}I/^{137}Cs ratio increased on March 21 and between March 23 and 28. Meanwhile, the state of excess ^{131}I release continued. This excess release could be explained by ^{131}I release from the contaminated water in the basements of 1F2 and 1F3 reactor buildings because of the gas-liquid partition of ^{131}I and steam generation due to evaporation of the accumulated water by decay heat. The details are described in **Chapter 3**.

A decrease in the ^{131}I/^{137}Cs ratio due to excess ^{137}Cs release was found on March 21 and 29. The timing corresponds roughly to the increase in core temperature due to the temporal shortage of core cooling water. This can be explained by the increase in the vapor pressure of $CsBO_2$ at the time of the core temperature increase. The details are described in **Chapter 4**.

After the beginning of April, the ^{131}I/^{137}Cs ratio decreased gradually mainly because of the radioactive decay of ^{131}I (half life: 8.02 days). The broken line in **Fig. 2** shows the ^{131}I/^{137}Cs ratio when the radioactive decay of ^{131}I and ^{137}Cs (half life: 30.17 years) is considered assuming that the release fractions of ^{131}I and ^{137}Cs into the environment over the core inventory are the same. It is impossible to say whether the duration when the ^{131}I/^{137}Cs ratio is larger than the broken line corresponds to excess ^{131}I release because the release rates or volatilities of ^{131}I and ^{137}Cs are not necessarily equal.

3. Reevaluation of ^{131}I release from the contaminated water in the basements of 1F2 and 1F3 reactor buildings

In a previous study[5], the release of ^{131}I from the contaminated water in the basements of the 1F2 and 1F3 reactor buildings was assumed to have started on March 17, while in the present study, this date was changed to March 21 based on the new source terms. This is because the ^{131}I/^{137}Cs ratio of the new source terms increased after

March 21, and the Japanese government's report to IAEA [10] (see pages IV-58 and IV-71) states that the release of grayish smoke from the 1F3 reactor building was witnessed at 15:55 on March 21 and the release of white haze-like smoke from the 1F2 reactor building was also witnessed at 18:20 on March 21. These release times of these smokes are considered the times of commencement of ^{131}I release from the contaminated water.

By contrast, the termination of ^{131}I release from the contaminated water was set to be March 28 based on the ^{131}I/^{137}Cs ratio in the present study because excess ^{131}I release by the new source terms continued up to March 28. Notably, the termination date in the previous study was March 26 because ^{131}I release decreased on that day when the core cooling water in 1F2 was changed from seawater to pure water.

Based on the new source terms, the amount of ^{131}I released from the contaminated water was reevaluated by using **formula (1)**, which is the same method as the previous study [5]. It was assumed that ^{131}I release could occur with the same fractional release rate as ^{137}Cs as a function of core temperature and that the excess ^{131}I release is caused by the release from the contaminated water.

$$\left(\frac{I2}{I1}-\frac{C2}{C1}\right)\times\frac{I1}{IT} \qquad (1)$$

where, $I1$: cumulative release of ^{131}I at the beginning of release from the contaminated water = 1.35 × 10^{17} Bq, $I2$: cumulative release of ^{131}I at the end of release from the contaminated water = 1.49 × 10^{17} Bq, $C1$: cumulative release of ^{137}Cs at the beginning of release from the contaminated water = 1.29 × 10^{16} Bq, $C2$: cumulative release of ^{137}Cs at the end of release from the contaminated water = 1.33 × 10^{16} Bq, and IT: total cumulative release of ^{131}I =

1.51×10^{17} Bq.

Reevaluation showed that about 6.5% of the total ^{131}I source term could be attributed to the release from the contaminated water although the previous study evaluated it to be about 35%. Uncertainties included in the present study may be larger than those in the previous study because the differences in the cumulative releases of ^{131}I and ^{137}Cs between the two dates are smaller than those in the previous study.

Possible reasons for the smaller estimate than that of the previous study are as follows: 1) Onset of ^{131}I release from the reactor buildings which originated from the contaminated water was delayed by four days compared with that in the previous study, and some amount of ^{131}I released from the contaminated water for four days could be deposited onto the basement wall or be dissolved again in the water, and 2) Comparing the new source terms with those by Terada or other researchers [11], the new source terms led to higher estimates of ^{131}I and ^{137}Cs release rates between March 17 and 19 when the wind blew from land to sea (see **Fig. 3**). By contrast, the new source terms led to lower estimates of ^{131}I and ^{137}Cs release rates between March 21 and 28. Therefore, the present reevaluation may have estimated lower ^{131}I release from the contaminated water than the previous study. The prediction accuracy of the new source terms when the wind blows from land to sea is discussed in **Chapter 5**.

4. $CsBO_2$ release

4.1 Decay heat and heat removal by core cooling water

The decrease in the ^{131}I/^{137}Cs ratio, which is the excess of ^{137}Cs release, predicted on March 21 and March 31 is examined in this chapter.

After the cooling down of the 1F1, 1F2, and 1F3 reactor cores on March 16, TEPCO operators tried to find the appropriate amount of water injection by changing the flow rate while controlling the increase in the contaminated water. However, this unexpectedly resulted in a temporal shortage of the core cooling water and an increase in the core temperature of the 1F3 RPV shell flange up to 832 K from March 21 to 23 [12]. Owing to the same reason, the measured temperature of the 1F1 safety valve exhaust reached 673 K from March 21 to 23, and the measured temperature of the 1F2 upper CRD housing increased up to 835 K from March 28 to 30.

TEPCO conducted measurements at about 10 points of the core regions at 1F1, 1F2 and 1F3, respectively [12]. The maximum core temperature is plotted in **Fig. 4** to understand the rough trends in the core temperatures, and its digital values are listed in **Table 2**. Generally, the temperature at the same point should be used, but this is not the case in the present study owing to considerable malfunction in the measurement and the lack of availability of some of the digital values.

The increase in core temperature from March 21 to 23 and from March 28 to 31 can be explained by a comparison between the decay heat of each reactor and heat removal by the flow rate of core cooling water. For simplicity, heat removal by cooling water was assumed equal to the heat necessary for evaporation of water injected into the core.

The decay heat was calculated using the Borst-Wheeler correlation given in **formula (2)**.

$$Q_d = 0.0622 \times \left(t^{-0.2} - (t_0 + t)^{-0.2} \right) \times Q_0 \tag{2}$$

where Q_d: decay heat (W), t: time after reactor shutdown (s); t_0: duration of operation (s); and Q_0: rated thermal power (W).

The parameter values used in the calculation are listed in **Table 1**. Heat removal was calculated from the heat of evaporation, 2,256,900 (J/kg) multiplied by flow rate of the water injected into the core. It should be noted that all water could not be necessarily used for heat removal from the core because the core configuration could become complex after melting. Accordingly, the present estimation could provide the minimum core cooling flow rate, and the actual minimum core cooling flow rate could be slightly larger than the value obtained in the present calculation.

A comparison between the decay heats of 1F1, 1F2, and 1F3 and heat removal from them by the injected core cooling water [13] is shown in **Figs. 5-7**. These results coincide with the results obtained by Tanabe [14]. Heat removal from 1F1 and 1F3 was lower than the corresponding decay heats from March 21 to 23. Heat removal from 1F2 was lower than the decay heat from March 28 to 31. These periods correspond to the increases in the core temperatures.

The temperature of the 1F2 core also increased from April 11 to 13 despite higher heat removal by cooling water than the decay heat. A probable reason is that the core was not cooled sufficiently due its complex shape after melting.

4.2 Formation of $CsBO_2$ and release

The control rods of the 1F1, 1F2, and 1F3 reactors were composed of the B_4C powder-coated with stainless steel (SS) and were arranged in cruciate. If B_4C comes into contacts with SS, the rods would be liquefied by the resulting eutectic reaction at about 1500 K [15], which is lower than the melting point of B_4C or SS. Therefore, B_4C could be oxidized easily under severe accident conditions and/or could react chemically with ^{131}I and ^{137}Cs.

When a severe accident occurs in a PWR with silver-indium-cadmium (SIC) control rods, the molybdenum (Mo) generated by nuclear fission could react with Cs, and the formation of Cs_2MoO_4 would enhance Cs deposition onto reactor coolant system (RCS). Thereafter, Cs_2MoO_4 could react with water and change to CsOH [16], which was considered the representative chemical form of Cs in previous studies.

By contrast, in the case of a severe accident in a PWR with B_4C control rods, as in the Phébus FPT3 test, Cs could be consumed by the formation of $CsBO_2$, resulting in the formation of a lower amount of Cs_2MoO_4 formation [17]. Notably, the possibility of $CsBO_2$ formation under various LWR severe accident conditions with B_4C absorbers has been confirmed already by many thermochemical equilibrium calculations based on the minimization of Gibbs free energy [18] and other experiments [19].

The possible chemical reactions are as follows [20]. The physical property data of the related chemical compounds and alloy are given in **Table 3**. The standard reaction enthalpies, ΔH_r in **formulas (3)–(15)**, were calculated from the standard formation enthalpies, ΔH_f, of chemical compounds [21], [22] which are given in **Table 4**.

$$B_4C(s) + 7H_2O(g) \rightarrow 2B_2O_3 + CO(g) + 7H_2(g) \qquad \Delta H_r = -890\,kJ/mol \tag{3}$$

$$B_4C(s) + 8H_2O(g) \rightarrow 2B_2O_3 + CO_2(g) + 8H_2(g) \qquad \Delta H_r = -931\,kJ/mol \tag{4}$$

$$B_4C(s) + 6H_2O(g) \rightarrow 2B_2O_3 + CH_4(g) + 4H_2(g) \qquad \Delta H_r = -1097\,kJ/mol \tag{5}$$

Then, boron oxide (B_2O_3) can react with CsOH or CsI [23], which are the most probable chemical forms of ^{131}I and ^{137}Cs in an RPV or a CV during severe accidents, to form cesium metaborate ($CsBO_2$) [24].

$$2CsOH(g) + B_2O_3(g) \rightarrow 2CsBO_2 + H_2O(g) \qquad \Delta H_r = 151\,kJ/mol \qquad (6)$$

$$2CsI(g) + B_2O_3(g) + 0.5O_2(g) \rightarrow 2CsBO_2 + I_2(g) \qquad \Delta H_r = 249\,kJ/mol \qquad (7)$$

$$2CsI(g) + B_2O_3(g) + H_2O(g) \rightarrow 2CsBO_2 + HI(g) \qquad \Delta H_r = 482\,kJ/mol \qquad (8)$$

$$2HI(g) \rightarrow H_2(g)) + I_2(g) \qquad \Delta H_r = 10\,kJ/mol \qquad (9)$$

Between the reactions given by **formulas (7) and (8)**, that of **formula (8)** is more promising because there could be little oxygen in the steam atmosphere within an RPV under severe accident conditions. By contrast, although **formulas (6) and (8)** represent endothermic reactions, **formula (6)** is more promising because the endothermic energy of **formula (6)** is smaller than that of **formula (8)**. That is, $CsBO_2$ would be likely formed by the reaction with CsOH rather than that with CsI.

When the temperature rises to over 1500 K, B_4C, B_2O_3 or $CsBO_2$ could melt and relocate downward under the condition that a part of it is taken in the molten stainless steel (SS) and is immediately cooled and solidified in the lower part of the RPV [25]. Boron oxide (B_2O_3) would change to a boric acid such as metabolic acid (HBO_2) below 573 K and orthoboric acid (H_3BO_3) below 373 K.

$$B_2O_3(g) + H_2O(g) \rightarrow 2HBO_2(g) \qquad \Delta H_r = 387\,kJ/mol \qquad (10)$$

$$B_2O_3(g)+3H_2O(g)\rightarrow 2H_3BO_3(g) \qquad \Delta H_r=-11kJ/mol \qquad (11)$$

The formation of H_3BO_3 under severe accident conditions has also been confirmed experimentally [26]. When the core temperature increases again by several hundred Kelvin after cooling of the cores, as in the Fukushima accident, additional $CsBO_2$ may be generated according to the following chemical reactions.

$$CsI(g)+HBO_2(g)\rightarrow CsBO_2(g)+HI(g) \qquad \Delta H_r=47kJ/mol \qquad (12)$$

$$CsI(g)+H_3BO_3(g)\rightarrow CsBO_2(g)+HI(g)+H_2O(g) \qquad \Delta H_r=246kJ/mol \qquad (13)$$

$$CsOH(g)+HBO_2(g)\rightarrow CsBO_2(g)+H_2O(g) \qquad \Delta H_r=-118kJ/mol \qquad (14)$$

$$CsOH(g)+H_3BO_3(g)\rightarrow CsBO_2(g)+2H_2O(g) \qquad \Delta H_r=-81kJ/mol \qquad (15)$$

The exothermic reactions of **formulas (14) and (15)** are more promising than the endothermic reactions of **formulas (12) and (13)**. This suggests that at the time of re-ascension of the core temperature, additional $CsBO_2$ would likely be generated by the reaction of HBO_2 or H_3BO_3 with CsOH rather than with CsI.

The ^{131}I release rate increased from March 23 to 24 and from March 30 to 31, similar to the increase in the ^{137}Cs release rate (see **Fig. 3**). This could be due to the release of CsI, which has a similar vapor pressure as that of $CsBO_2$ (see **Fig. 8)**. However, the decrease in the ^{131}I/^{137}Cs ratio on those days cannot be explained only by the release of CsI. The release of Cs compounds without iodine such as $CsBO_2$ or CsOH could lead to decrease in the ^{131}I/^{137}Cs ratio. It is noted that the release of $CsBO_2$ may be more promising than that of CsOH because most of CsOH in the RPV had been vaporized and transported to outside of the RPV between March 11 and March 16 due to the high vapor pressure, Alternatively, it may have been dissolved in the water in the RPV owing to its high solubility and released to the CV and/or the reactor buildings.

The equilibrium vapor pressures of $CsBO_2$ calculated from formula (16) [27] at the maximum temperatures measured in each core region are shown in **Fig. 9**

$$P_{CsBO2}(Pa) = \exp\left(\frac{-(14159)}{T_S} + 15.537 \right) \qquad (16)$$

Figure 9 shows that the timings of the increase in the equilibrium vapor pressure of $CsBO_2$ mostly agree with those of excess ^{137}Cs release (decrease in ^{131}I/^{137}Cs ratio). It is inferred that the excess ^{137}Cs release from March 23 to 24 was caused by the release of $CsBO_2$ from 1F1 and 1F3, while that on March 31 was caused by the release of $CsBO_2$ from 1F2.

If all the ^{137}Cs release after March 19 is assumed to be caused by the re-ascension of the core temperature, the ratio of the amount of ^{137}Cs released after March 19 to the total cumulative release of ^{137}Cs reaches about 28% when calculated using the new source terms and about 50% when calculated using Terada's source terms.

4.3 Comparison with environmental radiation monitoring data

As a response to the Fukushima accident, the environmental radiation, such as ambient radiation dose rates, radioactivity concentrations in air and in fallout, and meteorological observations, was monitored from March 11 to May 31, 2011, at the Nuclear Fuel Cycle Engineering Laboratories, JAEA, in Tokai. According to the report [28], gaseous ^{137}Cs was measured until March 29 but not after March 30. It is noted that the concentration of particulate ^{137}Cs drastically increased after March 30.

In this monitoring operation, radionuclide sampling was performed using a HE-40T filter paper measuring 50 mm in diameter (for floating dust sampling in atmosphere) in combination with a CHC-50 charcoal filter (for sampling gaseous iodine sampling in atmosphere). HE-40T can collect the particulates measuring about >0.1 μm in diameter, while CHC-50 can collect gaseous iodine or hygroscopic moisture passing through the HE-40T filter paper.

The concentrations of gaseous or particulate ^{137}Cs and ^{131}I in atmosphere measured in Tokai are shown in **Figs. 10** and **11**, respectively. The ^{131}I/^{137}Cs ratio in the fallout measured in the environmental radiation monitoring operation is shown in **Fig. 12**. The trends agree reasonably with the ^{131}I/^{137}Cs ratios predicted using the new source terms, and the environmental radiation monitoring data can be considered to have adequate precision for examining the present issues. The drastic change from gaseous ^{137}Cs to the particulate on March 30 and the abrupt increase in the particulate concentration suggest that some kinds of phenomena occurred within the NPPs.

CsOH could be easily dissolved in water and contained in hygroscopic moisture. By contrast, $CsBO_2$ could likely become particulate in atmosphere compared with CsOH because of the lower vapor pressure of $CsBO_2$ than that of CsOH. Although the vapor pressure of CsI is almost the same as that of $CsBO_2$ as shown in **Fig. 7**, CsI could be easily dissolved in water and change to Cs^+ and I^- while $CsBO_2$ is not soluble to the same extent.

Therefore, the gaseous ^{137}Cs measured before March 29 is considered to be CsOH or CsI which was dissolved in hygroscopic moisture. On the contrary, the particulate ^{137}Cs measured after March 30 is considered to be $CsBO_2$ particulate or the particulate which $CsBO_2$ became the nucleus, and the nucleus growth occurred by deposition of other radionuclide onto the nucleus surface. Unfortunately, the elemental composition data of the measured ^{137}Cs particulates are not available but the measured increase in ^{137}Cs particulate concentration after March 30 supports the release of $CsBO_2$.

The decrease in the ^{131}I/^{137}Cs ratio (increase in ^{137}Cs release) on March 30 can be explained not by CsI release but by $CsBO_2$ release. The trend of ^{137}Cs release after April 2 reverted to the overall trend that follows the decay of radioactive ^{131}I because the dominant chemical form was changed from $CsBO_2$ generated in the RPV to CsI generated in the CV or the reactor buildings owing to, for example, re-suspension.

4.4 Possible reason for termination of gaseous ^{137}Cs release on March 29

When the core temperature increases again after cool down, as in the Fukushima accident, $CsBO_2$ formed under high temperatures and solidified at the bottom of the RPV after melt down could be re-vaporized (see **chapter 4.2**).

The release of ^{137}Cs from fuel would occur continuously from the lower temperatures to temperature higher than about 1500 K, at which B_4C oxidation occurs [29]. Therefore, all ^{137}Cs released from the fuel cannot react with B_2O_3 and some of ^{137}Cs would exist as CsOH. However, if the core temperature increases again after pausing for a while after cooling, it is possible that HBO_2, H_3BO_3 or B_2O_3 could react with almost of all remaining CsOH or CsI based on **formulas (14) and (15)**, and $CsBO_2$ would be newly formed. Otherwise CsOH would be deposited onto the surface of particulate $CsBO_2$ formed by re-vaporization.

The measurement of gaseous ^{137}Cs was continued until March 29 possibly because the release of CsOH from 1F2 continued up to March 29 because there was no-re-ascension of the 1F2 core temperature between March 16 and 29. By contrast, re-ascension of the 1F1 and 1F3 core temperatures began on around March 20 and CsOH release from them decreased thereafter. However, re-ascension of the 1F2 core temperature started at last on March 29, and CsOH release from 1F2 also decreased, as in the cases of 1F1 and 1F3. Therefore, gaseous ^{137}Cs release was not observed after March 30. In this way, the series of observation results can be explained.

5. Discussions

5.1 Amount of CH_3I released from 1F3 during Fukushima accident

It is important to know the source term of organic iodine such as CH_3I, during severe accidents because most of CH_3I does not dissolve in water and cannot be removed easily by using an aerosol filter. The Phébus FPT3 experiment with B_4C control rods showed an enhancement of CH_3I [7] (about 8% [25] of iodine inventory), which was never observed in the experiments with SIC control rods used in typical PWRs. Therefore, in the present study, we attempted to estimate CH_3I release during the Fukushima accident.

The increase in the $^{131}I/^{137}Cs$ ratio from March 15 to 16 corresponds mostly to the timing of suppression pool venting at 1F3, as shown in **Fig. 2**. The Japanese government report [10] describes that the venting was initiated at 16:05 on March 15.

Most of iodine compounds such as CsI or I_2, with the exception of organic iodine (CH_3I), can be removed by pool scrubbing during their passage through the suppression pool. Although I_2 has a gaseous form and the solubility of I_2 in water is very weak (see **Table 3**), about 99% of I_2 is soluble in water in the chemical form of I^-. It has also been reported that the decontamination factor of the pool scrubbing could decrease in the case of the saturated water[30], which may have also occurred in the Fukushima accident. However, in that case, it is guessed that both of ^{131}I removal and ^{137}Cs removal are affected and the $^{131}I/^{137}Cs$ ratio does not change considerably.

Therefore, the excess ^{131}I release from March 15 to 16 can be attributed to the release of CH_3I formed by the reaction of iodine with CO, CO_2, or CH_4 that are generated by oxidation of the absorber material B_4C as described in **Chapter 4.2** or the reaction of iodine and the paint on the CV wall [31].

Owing to the reasons described above, the amount of CH_3I released from 1F3 during venting can be estimated based on the $^{131}I/^{137}Cs$ ratio, and ^{131}I release rate and release duration, and it becomes equal to 1.31×10^{16} Bq (1.85×10^{16} Bq on March 11). Details of the calculations are described in **Table 5**. The new source terms originally predicted the gross CH_3I release rate from 1F1, 1F2, and 1F3 assuming 60% of all gaseous iodine is CH_3I and the rest is I_2 based on the method of RASCAL 4.0 [32]. The prediction results are also given in **Table 5**. The present estimation based on the phenomena in the RPV is considered more reliable than the prediction by Katata.

From **Table 5**, the ratio of CH_3I release during the venting to the ^{131}I inventory in 1F3 is equal to about 0.8% and is larger than the descriptions of NUREG/CR-5732 [23] in which 0.15% of the total iodine released to the CV is in the form of CH_3I. On the contrary, the hypothetical accident in the Japanese review guides for site evaluation [33] and safety assessment [34] prepared by the previous Nuclear Safety Commission assumes that 5% of the total iodine core inventory is organic iodine (CH_3I). The present study supports the assertion that the review guides were prepared based on a conservative assumption compared with the Fukushima accident.

5.2 Delay of increase in source terms by WSPEEDI reverse compared with simulation codes before March 16

Comparing the increase in cumulative ^{131}I and ^{137}Cs release from March 12 to 16 obtained by WSPEEDI reverse and those obtained by simulation codes such as MELCOR (see **Fig. 1**), WSPEEDI reverse clearly predicted a slower increase in release than MELCOR. The simulation codes usually treat the condensation of gaseous radionuclides or the deposition of particulates onto the inside wall of BWR reactor building, RCS, and CV, while WSPEEDI reverse considers the time for transportation of radionuclides along with the flow of air current to the monitoring points.

A possible reason for the difference is that during the transportation of radionuclides from the outside of the reactor building to the monitoring points, condensation or deposition of radionuclides onto the outside structures of the reactor building or the land near the NPPs and re-vaporization or re-suspension from there could have occurred repeatedly, and this could have caused a delay in the increase in source terms that are not considered by both methods. This issue needs to be investigated further.

5.3 Prediction accuracy of new source terms when the wind blows from land to sea

The release rates of ^{131}I and ^{137}Cs obtained using the new source terms decreased gradually after March 16 but they increased temporarily on March 18 (see **Fig. 3**). This trend was not predicted by Terada. Since the reactor cores of 1F1, 1F2, and 1F3 were cooled sufficiently on March 18 (see **Figs. 5-7**), it is difficult to think that the core temperature increased on that day.

On March 18, the wind blew from land to sea and the source terms were predicted from the measured sea surface concentration using an estimation grid of 80 km over the ocean [2], which is larger by about one order of magnitude than the estimation grid over land. It cannot be denied that some uncertainties were included in the estimation. It is expected that this examination be performed continuously in future.

Similarly, the new source terms did not predict the decrease in the ^{131}I release rate on March 26. This decrease was predicted by Terada and may have been caused by the decrease in the ^{131}I release rate from the contaminated water by covering of the surface by pure water, when the 1F2 core cooling water was changed from seawater to pure water on that day [5]. Since the wind also blew from land to sea on March 26 as well, further investigation may be needed.

6. Conclusions

The present study investigated ^{131}I and ^{137}Cs release behaviors during the late phase of the Fukushima accident based on the ^{131}I/^{137}Cs ratio of the source terms put forth by Katata, which were recently evaluated backward by using the WSPEEDI code based on environmental monitoring data.

Even after March 17, the core temperatures of 1F1 and 1F3 increased temporarily by several hundred Kelvin from March 21 to 23, and that of 1F2 increased on March 31 when TEPCO operators were optimizing the core cooling flow rate. The evaluation by WSPEEDI reverse showed that the excess release of ^{131}I over ^{137}Cs occurred on March 21 and from March 23 to 29, and that of ^{137}Cs over ^{131}I occurred on March 22 and from March 30 to 31.

The excess of ^{131}I release can be explained by the ^{131}I gas-liquid partition on the surface of the contaminated water accumulated in the basements of the 1F2 and the 1F3 reactor buildings. ^{131}I release from the contaminated water was reevaluated based on the new source terms. In addition, organic iodine (CH_3I) release during venting of the 1F3 suppression pool was estimated based preliminarily on the ^{131}I/^{137}Cs ratio obtained using the new source terms. The fractions of ^{131}I and ^{137}Cs released due to the specific mechanisms to their total cumulative releases predicted by the present study are summarized in **Table 6.**

The excess of ^{137}Cs release can be explained by re-vaporization of $CsBO_2$ from solidified materials relocated to the lower part of the RPV after reactions of Cs with B_4C or additional formation by reaction of CsOH with boric acid when the core temperature re-ascended owing to slight shortage of cooling water. Environmental radiation monitoring performed in Tokai showed that gaseous ^{137}Cs was measured up to March 29 but not after March 30. These findings could also be explained by the change from CsOH in hygroscopic moisture to particulate $CsBO_2$ on that day.

There remain substantial differences in the source terms during the Fukushima accident between simulation codes such as MELCOR and WSPEEDI reverse. The main reasons for these differences are that the present simulation codes do not treat the releases of ^{131}I and ^{137}Cs, especially the $CsBO_2$ generated due to the re-ascension of core temperature owing to slight shortage of core cooling water. In addition, the codes do not model the ^{131}I gas-liquid partition on the surface of the contaminated water accumulated in the basements of reactor buildings during the late phases of the Fukushima accident.

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Table lists

Figure captions

Table 1 Plant parameters and inventories for 1F1, 1F2 and 1F3

	1F1	1F2	1F3
Rated thermal power (W)	1.380×10^{9}	2.381×10^{9}	2.381×10^{9}
Operation duration (s) [9]	5.49×10^{7}	5.87×10^{7}	5.61×10^{7}
^{131}I inventory on March 11 (Bq) [9]	1.35×10^{18}	2.34×10^{18}	2.33×10^{18}
^{137}Cs inventory on March 11 (Bq) [9]	2.02×10^{17}	2.55×10^{17}	2.41×10^{17}

Table 2 Maximum temperatures measured at core region at 1F1, 1F2 and 1F3

	1F1 (K)	1F2 (K)	1F3 (K)		1F1 (K)	1F2 (K)	1F3 (K)
Mar.19	—	—	625	April 2	535	533	439
Mar.20	661	423	666	April 3	530	532	430
Mar.21	663	423	**832**	April 4	516	530	431
Mar.22	**673**	419	**806**	April 5	511	536	441
Mar.23	**673**	413	**777**	April 6	495	535	428
Mar.24	566	411	621	April 7	490	562	470
Mar.25	512	410	540	April 8	498	550	418
Mar.26	536	424	447	April 9	534	541	456
Mar.27	559	424	473	April 10	515	538	433
Mar.28	605	449	447	April 11	502	**767**	486
Mar.29	605	477	436	April 12	497	**838**	444
Mar.30	559	501	445	April 13	493	**838**	482
Mar.31	531	**835**	437	April 14	477	692	530
April 1	531	557	432	April 15	471	596	538

Table 3 Physical properties of chemical compounds and alloy

	Melting point (K)	Boiling point (K)	Solubility to water
B_4C	2620	3773	—
Stainless steel (SS)	1673～1723	—	—
$CsBO_2$	987.3	～1200 [18]	—
CsI	894.15	1550.15	44g/100cm^3 (273K)
B_2O_3	753.15	1953.15	2.2g/100g
CsOH	545.45	1263.15	395g/100cm^3（288K）
HBO_2	449	—	—
H_3BO_3	444.0	573	37.9g/100cm^3 (373K)
I_2	386.9	457.4	0.03g/100cm^3 (293K)
CH_3I	206.7	315.6	1.4g/100cm^3 (293K)
HI	184.55	273.79	—

Table 4 Standard formation enthalpy of chemical compounds [21], [22]

	$\varDelta H_f$		$\varDelta H_f$
B_4C (s)	-71.13 kJ/mol	H_3BO_3 (g)	-1004.30 kJ/mol
CO (g)	-110.54 kJ/mol	B_2O_3 (s)	-835.96 kJ/mol
O_2 (g)	0 kJ/mol	B_2O_3 (g)	-1271.94 kJ/mol
CH_4 (g)	-74.87 kJ/mol	CsOH (g)	-257.00 kJ/mol
$CsBO_2$ (g)	-696.80 kJ/mol	CsOH (s,l)	-416.40 kJ/mol
$CsBO_2$ (s,l)	-976.80 kJ/mol	CsI (g)	-154.30 kJ/mol
H_2 (g)	0 kJ/mol	CsI (s,l)	-348.13 kJ/mol
H_2O (g)	-241.83 kJ/mol	HI (g)	26.40 kJ/mol
HBO_2 (g)	-563.20 kJ/mol	I_2 (g)	62.42 kJ/mol
CO_2 (g)	-393.5 kJ/mol	I_2 (s,l)	0 kJ/mol

Table 5 Estimation of CH_3I release during the 1F3 suppression pool venting

Time	Venting	Release duration (hr)	$^{131}I/^{137}Cs$ ratio (A)	^{131}I release (Bq/hr) (B)	CH_3I release by present study (Bq/hr)$^{*1)}$	CH_3I release by Katata (Bq/hr)$^{*2)}$
15/3 18:00		2	9.91	2.18×10^{15}	—	6.5×10^{14}
15/3 20:00	○	2	29.9	2.27×10^{15}	1.5×10^{15}	9.5×10^{14}
15/3 22:00	○	1	29.4	1.00×10^{16}	6.6×10^{15}	4.2×10^{15}
15/3 23:00	○	1	30.3	2.21×10^{15}	1.5×10^{15}	9.3×10^{14}
16/3 0:00	○	1	30.0	1.95×10^{15}	1.3×10^{15}	6.7×10^{14}
16/3 1:00	○	5	29.9	2.00×10^{14}	1.3×10^{14}	8.4×10^{13}
16/3 6:00		3	10.0	2.00×10^{14}	—	6.0×10^{13}
CH_3I release amount (Bq)		—	—	—	1.3×10^{16}	8.1×10^{15}

*1) (B)×((A)-10.0)/(A),

*2) Constant 60% of gaseous iodine release (method of RASCAL 4.0 [32])

Table 6 Fractions of ^{131}I and ^{137}Cs released due to specific mechanisms to their total cumulative releases

^{131}I or ^{137}Cs release due to specific mechanisms	Katata source term[2]	Terada source term[6]
^{131}I release from the contaminated water	6.5%	35%
CH_3I release from 1F3 during 1F3 venting (present study)	0.8%$^{*1)}$	—
Gross CH_3I release during 1F3 venting (Katata original)	0.2%$^{*2)}$	—
^{137}Cs release by re-ascension of core temp. after Mar.19	28%	50%

*1) Ratio to 1F3 inventory, *2) Ratio to 1F1+1F2+1F3 inventories

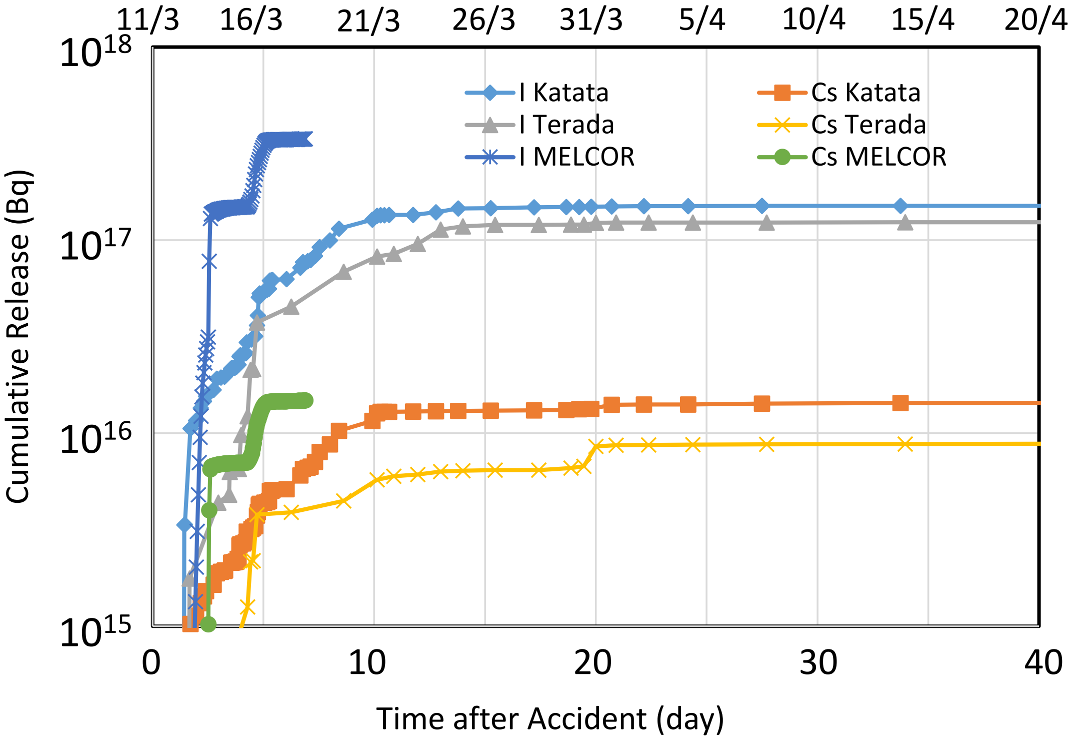

Fig. 1 Comparison of source terms for the Fukushima accident predicted by various methods

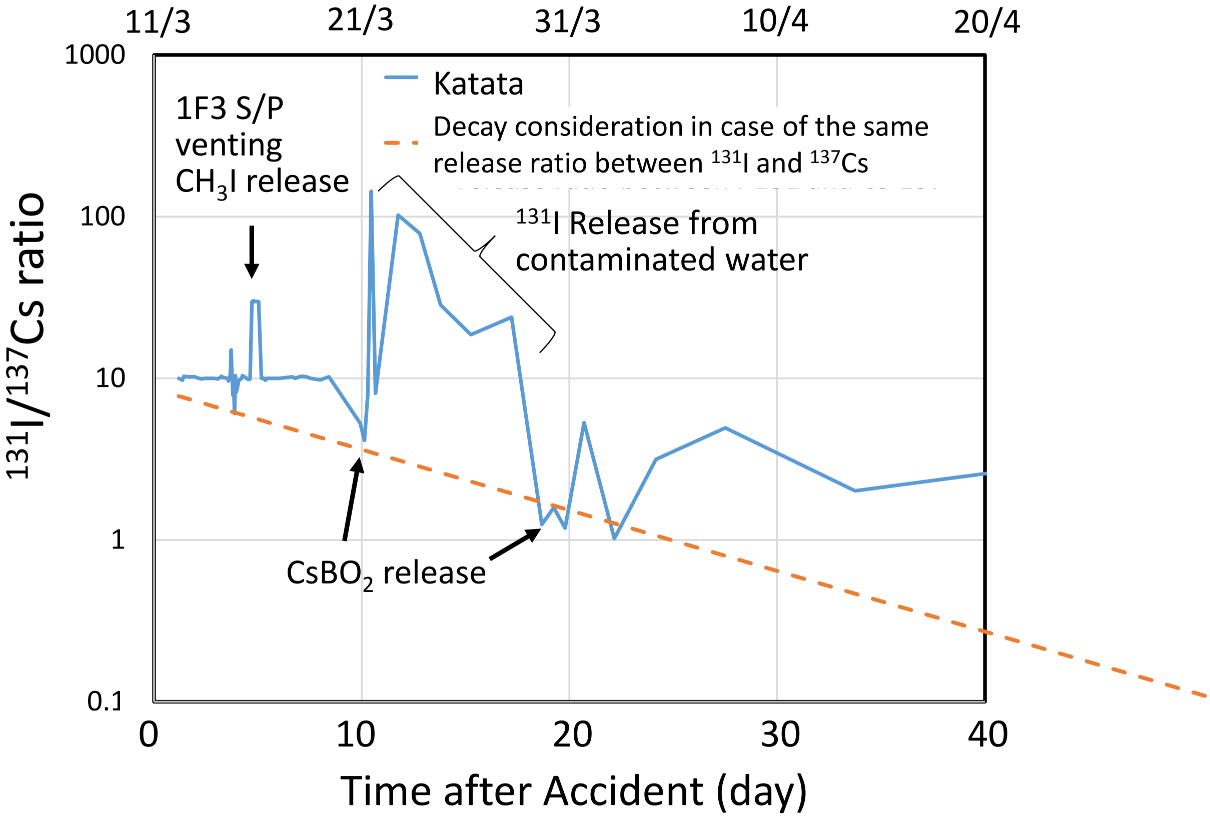

Fig. 2 $^{131}I/^{137}Cs$ ratio during the Fukushima accident predicted by the new source terms

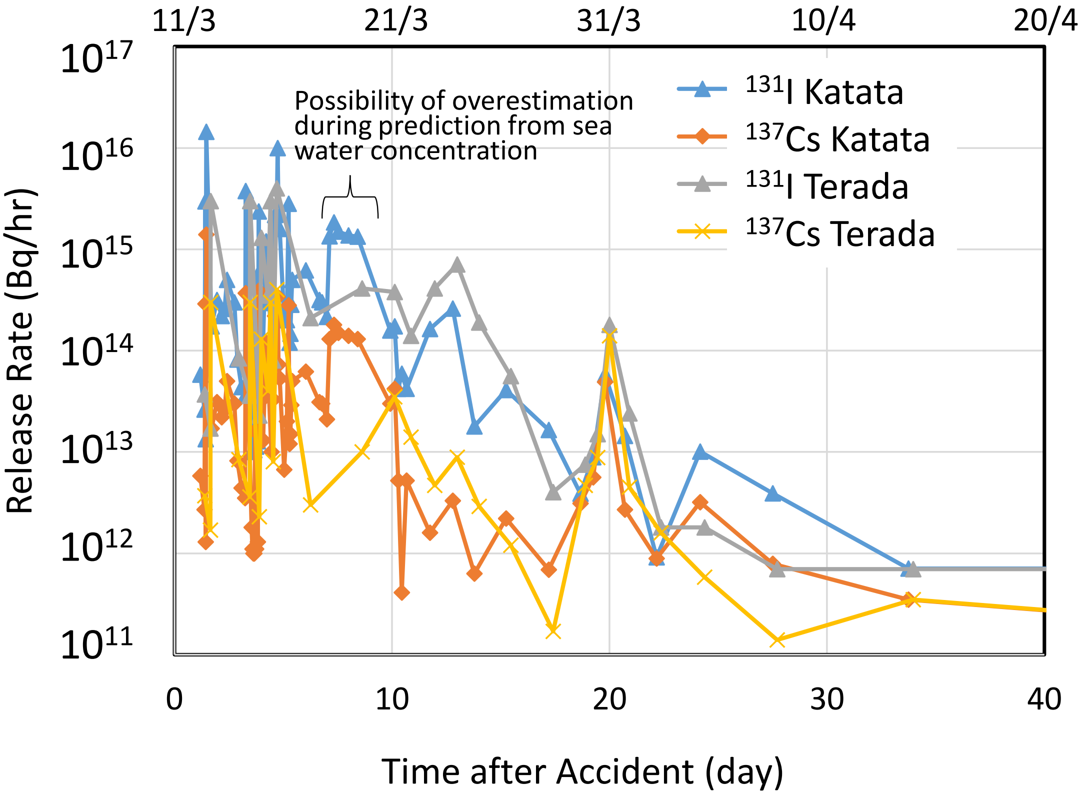

Fig. 3 Release rates of ^{131}I and ^{137}Cs predicted by WSPEEDI reverse

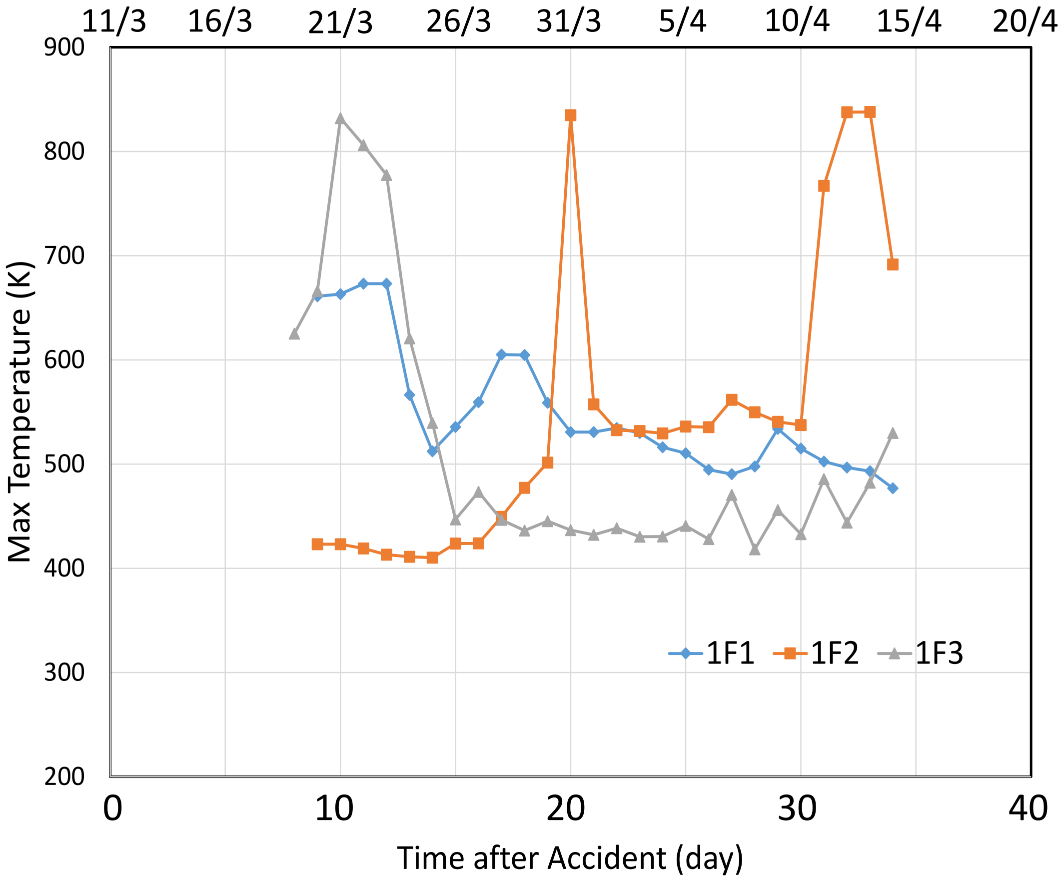

Fig. 4 Maximum temperature measured at core regions during the late phase of the Fukushima accident

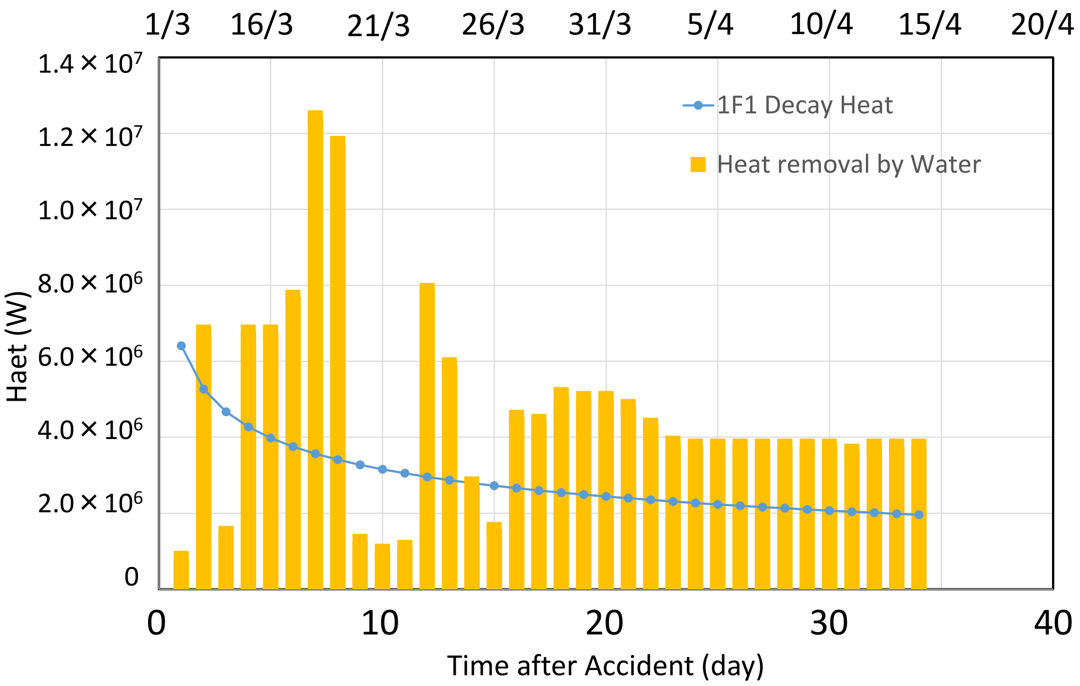

Fig. 5 Comparison between 1F1 decay heat and heat removal by core cooling water

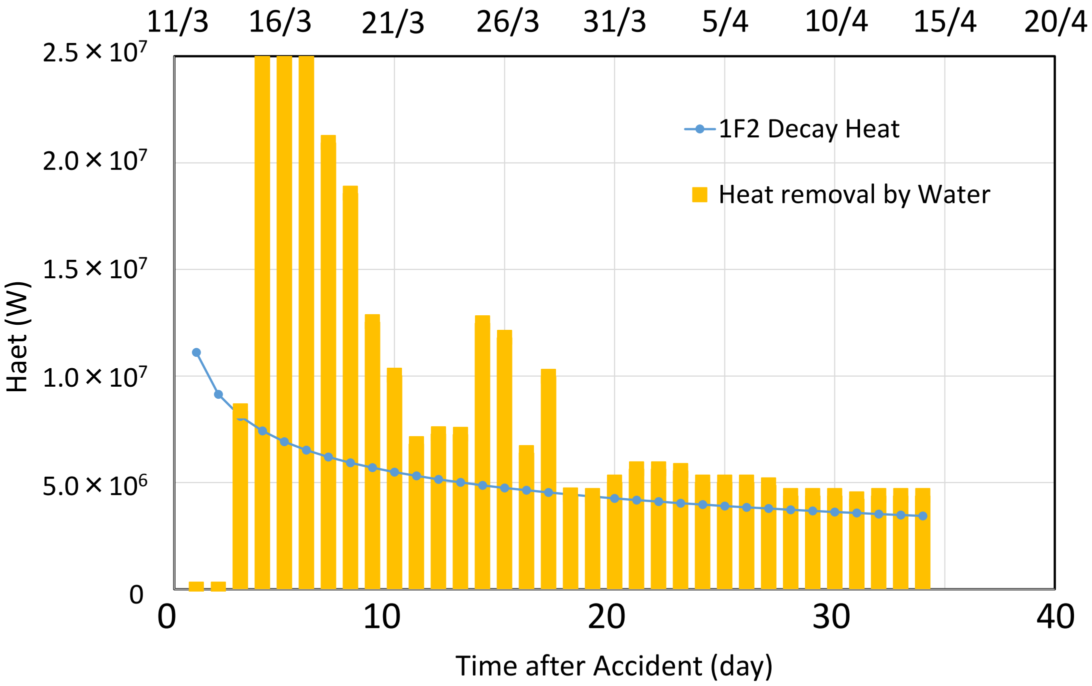

Fig. 6 Comparison between 1F2 decay heat and heat removal by core cooling water

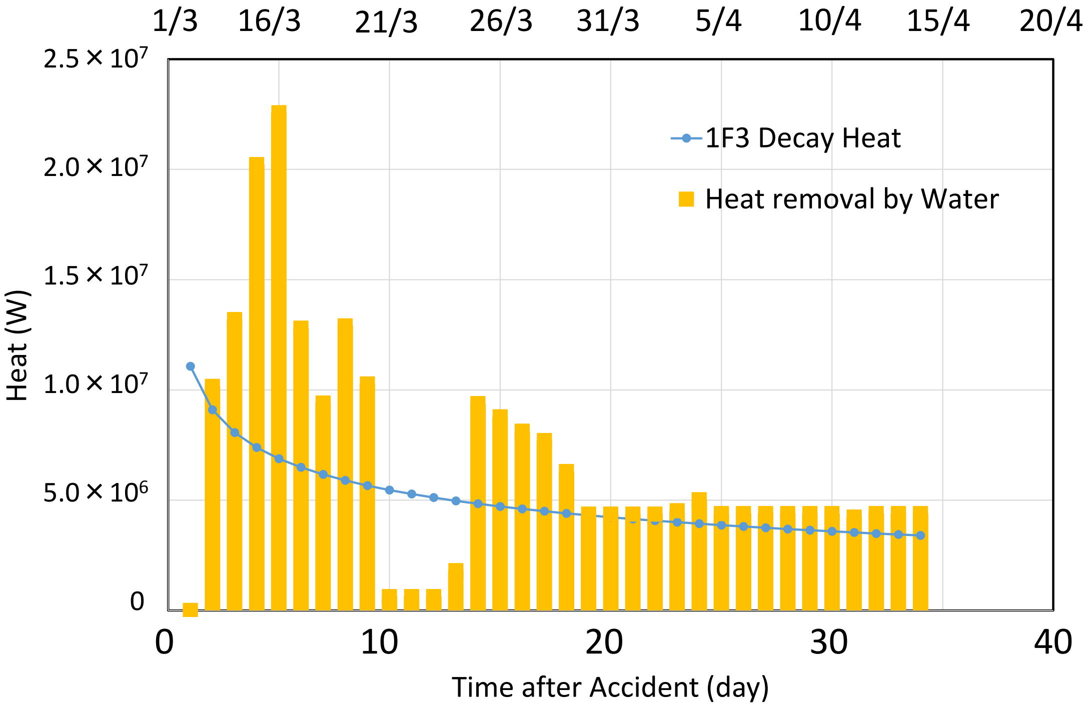

Fig. 7 Comparison between 1F3 decay heat and heat removal by core cooling water

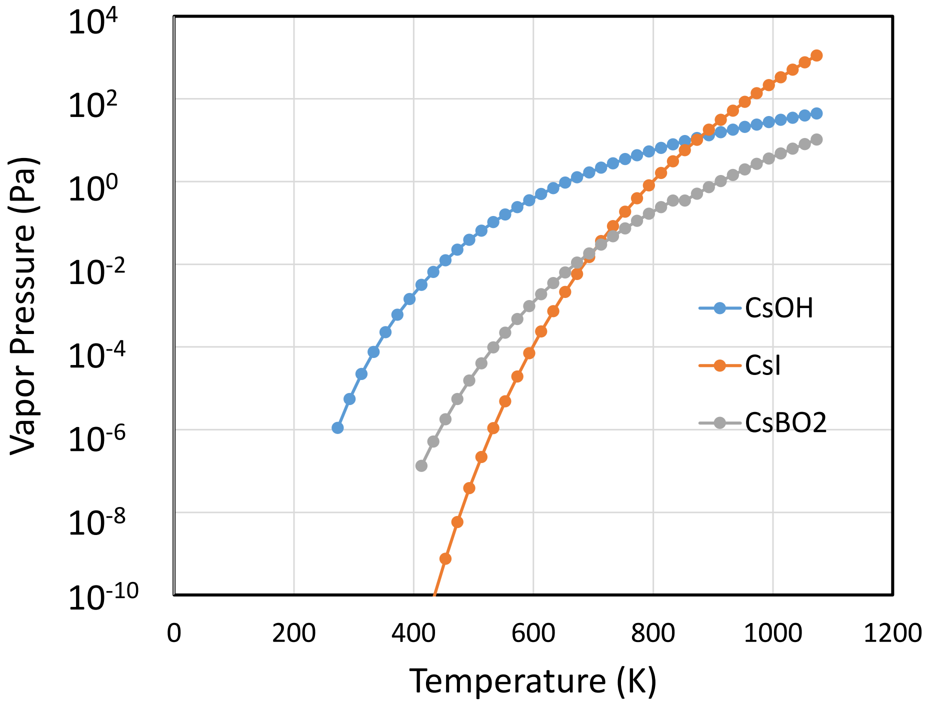

Fig. 8 Comparison of vapor pressures of representative Cs compounds
(Although the vapor pressure of $CsBO_2$ are applicable between 867K and 1087K [27], the pressure below 867K was extrapolated in this figure.)

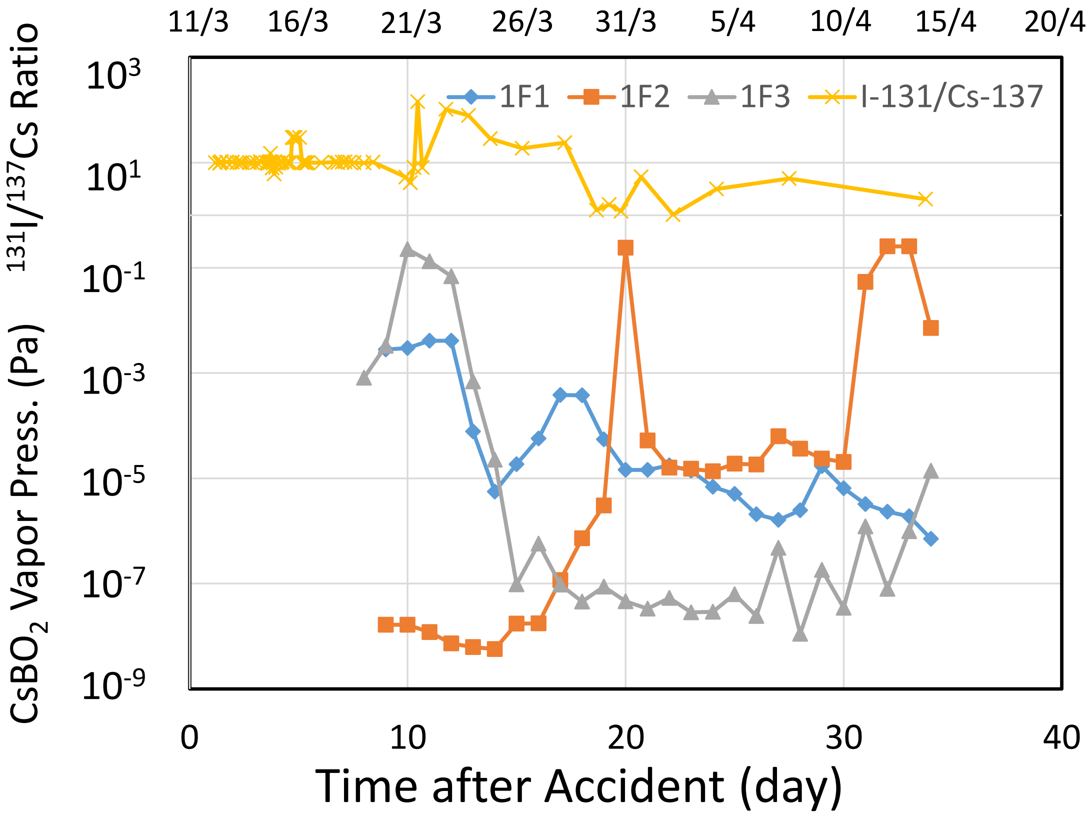

Fig. 9 Vapor pressure of $CsBO_2$ at measured maximum temperature and $^{131}I/^{137}Cs$ ratio

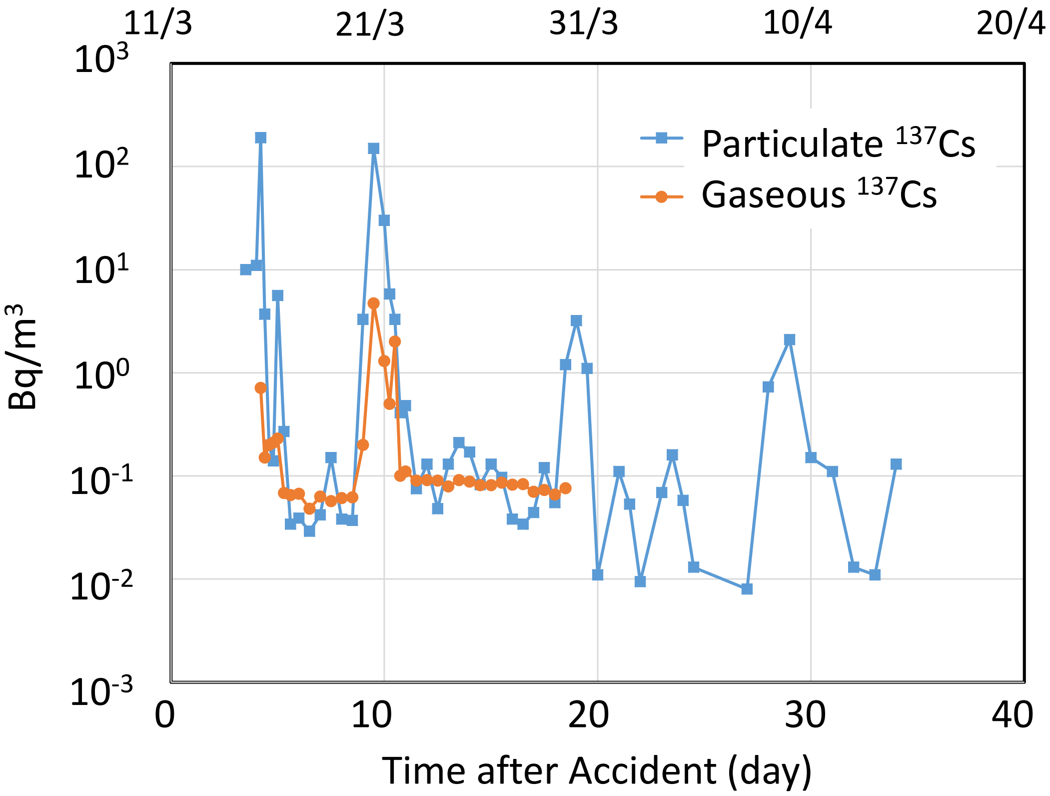

Fig. 10 Concentrations of gaseous or particulate ^{137}Cs in atmosphere measured in Tokai

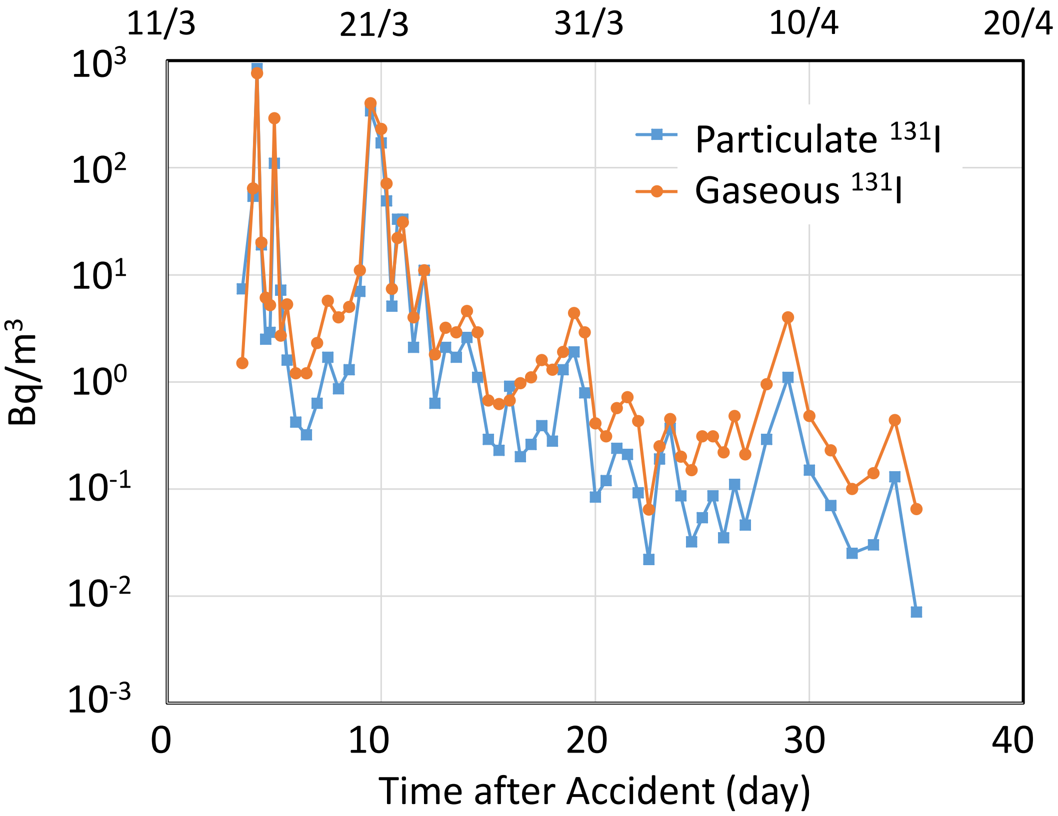

Fig. 11 Concentrations of gaseous or particulate ^{131}I in atmosphere measured in Tokai

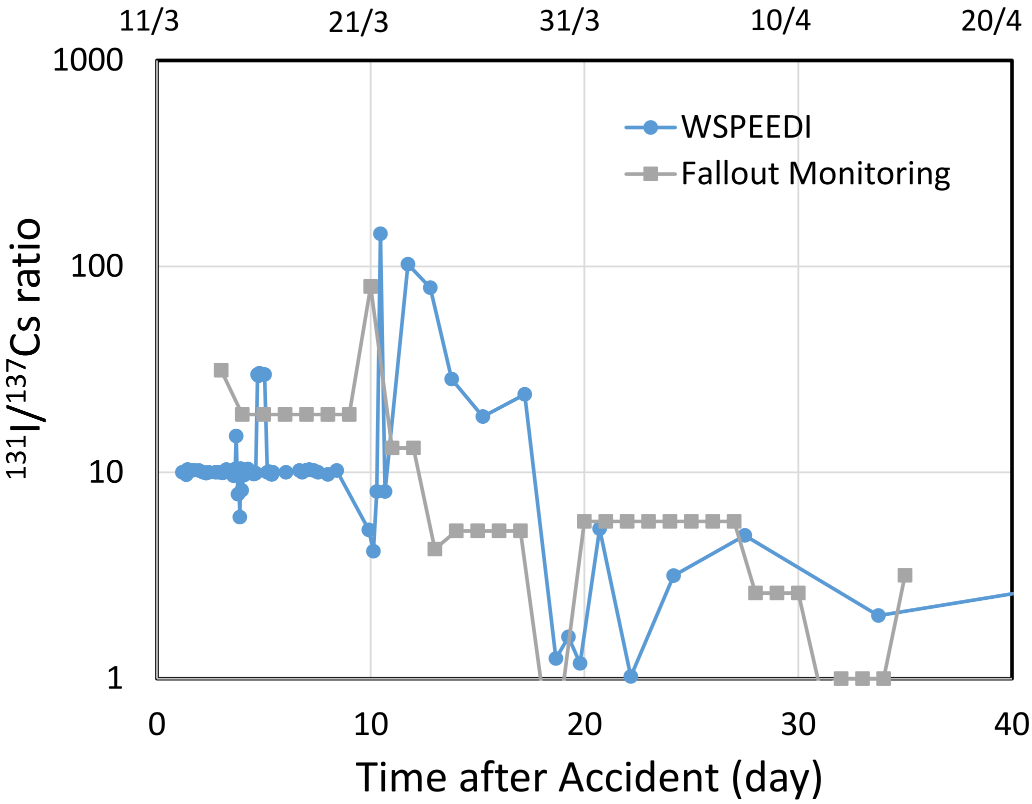

Fig. 12 Comparison of $^{131}I/^{137}Cs$ ratio between the new source terms and fallout measured in environmental radiation monitoring operation