Study on chemisorption model of cesium hydroxide onto stainless steel type 304

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Abstract

A large amount of cesium (Cs) chemisorbed onto stainless steel is predicted to be present especially in the upper region of reactor pressure vessel (RPV) during light water reactor severe accident. A chemisorption model was developed for estimation of such amounts of Cs for stainless steel type 304 (SS304) exposed to cesium hydroxide (CsOH) vapor. However, this existing chemisorption model cannot accurately reproduce experimental results and is considered not to be suitable for the estimation of the Cs-chemisorbed amounts under various conditions experienced in Fukushima Dai-ichi nuclear power station. Our recent laboratory study indicated that the surface reaction rate constant used in the existing chemisorption model depended on both of silicon content in SS304 and concentration of gaseous CsOH as well as on temperature. Therefore, in this study, a modified Cs chemisorption model which accounts for these effects was constructed by combining penetration theory for gas-liquid mass transfer with chemical reaction and mass action law for CsOH decomposition at interface between gaseous and solid phases. As a result, it was found that the modified model was able to adequately describe effects on concentration of CsOH in gaseous phase and Si content in SS304 and more accurately reproduce the experimental data than the existing model.

Keywords: Cesium, Chemisorption, Stainless steel, Cesium hydroxide, Silicon, Penetration theory, Mass transfer

1. Introduction

Radioactive cesium (Cs) is one of the principal radiation sources and information on the Cs distribution within reactor pressure vessel (RPV) is of crucial importance to make a reasonable safety assessment for the fuel debris retrieval and the reactor decommissioning at Fukushima Dai-ichi nuclear power station (1F) (NDF, 2016). Especially, a large amount of Cs can be present in the upper region of the RPV by chemical reactions of Cs vapor species with structures, known as chemisorption, since internal structures such as steam-water separator and steam dryer have large surface areas and would experience relatively high temperatures in the 1F accident. Such a chemisorption behavior has been paid attention to since Three Mile Island unit 2 accident (Baston et al., 1985), and laboratory studies started mainly in USA and Europe in 1980’s (Elrick et al., 1984; Elrick and Powers, 1987; Bowsher et al., 1990; Johnson et al., 1989). Through these studies, a chemisorption model was developed (Bowsher et al., 1990) and incorporated into current severe accident (SA) analysis codes (Bixler, 1998; Gauntt et al., 2000; Plys et al., 2017). However, this existing chemisorption model was constructed based on limited experimental data and a simple assumption of a first order reaction rate with respect to Cs vapor species concentration. Therefore, it was considered that this model would not be suitable for estimation of the Cs-chemisorbed amounts under various conditions experienced in the 1F accident. Thus, experimental studies on the Cs chemisorption behavior have started not only to validate the existing model but also to accumulate experimental data on rate of the chemisorption. As the results, our recent laboratory study (Nishioka et al., 2019) indicated that the surface reaction rate constant, which is used in the existing chemisorption model, depended not only on temperature but also on silicon (Si)
content in SS and cesium hydroxide (CsOH) concentration in gaseous phase and it was found that the chemisorption rate did not follow a simple first order reaction with respect to CsOH vapor concentration. Therefore, in this study, a new Cs chemisorption model was constructed by combining penetration theory for gas-liquid mass transfer with chemical reaction (Matsuyama, 1950; Fujita et al., 1954) and mass action law for CsOH decomposed at interface between gaseous and solid phases.

2. Existing Cs chemisorption model onto stainless steel type 304

In 1980’s, thermodynamic equilibrium calculation (Cubicciotti and Sehgal, 1984) predicted that main chemical forms of Cs vapor species were CsOH and cesium iodide (CsI) and then the Cs chemisorption behavior was investigated between gaseous CsOH or CsI and stainless steel type 304 (SS304) used as a structural material of the RPV internals in 1F. However, experiments performed by Elrick and Powers (Elrick and Powers, 1987) indicated that the chemisorption rate between gaseous CsI and SS304 was less than $3 \times 10^{-5}$ (cm/s) at 1273 K. Thus, our studies have focused on investigation of Cs chemisorption behaviors between gaseous CsOH and stainless steels and development of a more mechanistic model for improvement of the existing chemisorption model (Di Lemma et al., 2016; Di Lemma et al., 2017; Kobata et al., 2018; Nakajima et al., 2018; Nishioka et al., 2019). As other important points we should consider as simulation of the chemisorption behavior during SA, there can be effects of the pre-oxidized layer forming on stainless steels and the irradiation damages. However, Elrick et al. (Elrick et al., 1984) examined the effect of the pre-oxidized layer and there was no clear difference between the Cs-chemisorbed amounts for the as-received samples and those for the pre-oxidized samples, which were prepared at 1070 K for 24 h or at 1270 K for 2h. According to the study investigating Cs diffusion behavior in the oxide layer (Saito et al., 1983), the oxide layer is not protective against the penetration of Cs since the oxide layer forming on stainless steel has numerous defects, which are probably induced by the stress during oxidation. Thus, it is inferred from these experimental results that the oxide layer forming on stainless steel prior to or concurrently with the Cs release during SA would have little effect on the chemisorption rate. As for the irradiation damage, enrichment of Si at grain boundary occurred and the concentration of Si increased with increasing neutron fluence (Kasahara et al., 2018), which can influence on the chemisorption behavior forming Cs silicates. However, it was also found that the Si concentration at the grain boundary decreased with increasing annealing temperature from 723 to 823 K although, in the case of stainless steel type 316 irradiated to 25 dpa in a PWR (Fukuya, et al., 2004). Therefore, such an irradiation damage is expected to be recovered at temperatures higher than 873 K, where the chemisorption occurs, and effect of the irradiation damage would be considered negligible.

As mentioned in the previous section, the existing model was developed by assuming that chemisorption rate of Cs, \( N \), was expressed as a first order reaction with respect to gaseous CsOH concentration, \( C_g \):

\[
N = v_d C_g
\]  

where

- \( N \) = chemisorption rate of Cs per unit time unit area [\( \mu g \text{ Cs/cm}^2\text{/s} \)],
- \( v_d \) = surface reaction rate constant [cm/s], and
- \( C_g \) = concentration of Cs reactant species in gaseous phase [\( \mu g \text{ CsOH/cm}^3 \)].

The \( v_d \) was assumed to have an Arrhenius-type temperature dependence and determined by a regression analysis of the available experimental data (Bowsher et al., 1990). Figure 1 shows comparison of the \( v_d \) between the existing model and the experimental data (Bowsher et al., 1990; Nishioka et al., 2019) in the case of gaseous mixture of argon, hydrogen, and water (Ar-H\(_2\)-H\(_2\)O). As shown in this figure, the existing model cannot reproduce the experimental data well. Furthermore, our recent laboratory study (Nishioka et al., 2019) revealed that the \( v_d \) for the water-insoluble Cs deposit depended on both of Si content in SS304 and CsOH concentration in gaseous phase as well as temperature. Accordingly, another chemisorption model considering these effects had to be developed.
3. Construction of modified chemisorption model

Since there was little experimental data in the region of high concentrations of gaseous CsOH as experienced in the 1F accident (Plys et al., 2017), our recent laboratory study (Nishioka et al., 2019) was conducted not only to confirm the reliability of the existing chemisorption models (Bowsher et al., 1990) but also to accumulate the experimental data. Thus, a lot of experimental data for the \( v_d \) were obtained in the temperature range of 843 to 1273 K, in the Si content range of 0.1 to 4.9 wt.%, and in the gaseous CsOH concentration range of 0.03 to 19.86 \( \mu g/cm^3 \). As the result, it was found that the \( v_d \) for the water-insoluble Cs deposit at temperatures above 1073 K depended not only on temperature but also on both of the Si content and the gaseous CsOH concentration. Furthermore, it was found that the main Cs-chemisorbed compound at temperatures around 873 K changed from Cs silicates, which have already been known to be present (Elrick et al., 1984; Di Lemma et al., 2016; Di Lemma et al., 2017; Kobata et al., 2018), to a Cs ferrate. Therefore, we tried to construct the modified Cs chemisorption model valid above 1073 K where the main Cs-chemisorbed compound was a Cs silicate.

Although many studies on gas-solid reaction system have been presented as represented by “unreacted core models” (Szekely et al., 1976), there are scarce theoretical studies for mass transfer accompanied by a chemical reaction. On the other hand, there are many similar studies in gas-liquid system as represented by “Hatta number” (Sherwood et al., 1975). Then, it was considered that a theoretical model used in gas-liquid system was more suitable for development of a modified Cs chemisorption model.

Theoretical studies on rate of gas absorption with chemical reaction in gas-liquid system are roughly classified as the steady state diffusion and the unsteady state diffusion. As representative theoretical study for the steady state diffusion, there is a double film theory where the physical mass transfer coefficient in liquid phase, \( k_L \), is expressed as the following equation:

\[
k_L = \frac{D_L}{\delta_L}
\]

where \( D_L \) and \( \delta_L \) are the diffusion coefficient and the film thickness in liquid phase, respectively. However, since the film thickness in solid phase cannot be fully developed and can change with time due to a slow diffusion of reactant in solid phase, the film thickness in solid phase cannot be defined as in the case of liquid phase in the double film theory. Hence, the double film theory based on the steady state diffusion is not applicable for modeling the Cs chemisorption. On the other hand, a gas-liquid mass transfer related to the steady state diffusion is a penetration theory where the physical mass transfer coefficient in liquid phase is expressed as functions of diffusion coefficient and heating time, \( t \):
Thus, mass transfer coefficient in solid phase can be defined and the penetration theory for gas-liquid mass transfer was preferred to construct the Cs chemisorption model. Figure 2 shows image for concentration of Cs reactant species around the interface between gaseous and solid phases.

Fig. 2 Image of reactant Cs concentration around the gas-solid interface. $C_g$ is bulk concentration of gaseous CsOH, $C_w$ concentration of gaseous CsOH at the interface between the gas phase and solid phase, $C_i$ concentration of Cs reactant species in the solid phase.

Based on mass transfer theory, the absorption rate in gaseous phase can be expressed as the following equation:

$$N = k_G (C_g - C_w)$$

(4)

where

- $k_G =$ mass transfer coefficient of Cs reactant species in gaseous phase [cm/s], and
- $C_w =$ concentration of Cs reactant species in gaseous phase at the interface [$\mu$g CsOH/cm$^3$].

On the other hand, based on the penetration theory accompanied with chemical reaction (Sherwood et al., 1975), the absorption rate in solid phase can be expressed as the following equation:

$$N = \beta k_s (C_i - 0) = \beta k_s C_i$$

(5)

where

- $\beta =$ Hatta number [-],
- $C_i =$ concentration of Cs reactant species in solid phase at the interface [$\mu$g Cs/cm$^3$], and
- $k_s =$ mass-transfer-like coefficient of Cs reactant species in solid phase defined as the following equation [cm/s]:

$$k_s = \frac{2}{\sqrt{\pi}} \sqrt{\frac{D_s}{T}}$$

(6)

where

- $D_s =$ diffusion coefficient of Cs reactant species in solid phase [cm$^2$/s], and
- $t =$ heating time [s].

Strictly speaking, mass transfer coefficient cannot be defined in solid phase. However, in this study, the $k_s$ expressed as Eq. (6) is defined as the mass-transfer-like coefficient of Cs reactant species in solid phase.

Next, the solubility coefficient, $H$, is defined as the following equation:

$$C_i = H C_w$$

(7)
Hence, the following relation can be obtained from Eqs. (4), (5), and (7) by deleting $C_w$ and $C_i$.

$$N = \frac{1}{k_G H B S} C_g$$  \hspace{1cm} (8)

Thus, the surface reaction rate constant, $v_d$, used in the existing model can be expressed as the following equation:

$$v_d = \frac{1}{k_G H B S}$$  \hspace{1cm} (9)

Furthermore, since values of the $k_G$, which can be estimated from the test condition as mentioned later, were found to be much greater than those of the experimental $v_d$, the $v_d$ in Eq. (9) can be approximated as the following equation:

$$v_d \cong H B k_S$$  \hspace{1cm} (10)

In order to derive expression of the $\beta$, the following fundamental equation was considered (Matsuyama, 1950; Fujita et al., 1954):

$$\frac{dc}{dt} = D_S \frac{d^2c}{dx^2} - k''C_B C$$  \hspace{1cm} (11)

where

$C =$ concentration of Cs reactant species in solid phase $[\mu g Cs/cm^3]$

$x =$ depth (distance) from the interface between gaseous and solid phases $[cm]$

$k'' =$ second order chemical reaction rate constant $[1/s/wt.% Si]$

$C_B =$ Si content in SS304 $[wt.% Si]$.

Strictly speaking, the $C_B$ changes with reaction progress. However, the $C_B$ is assumed to be constant by supposing $C << C_B$ in this study. Thus, Eq. (11) can be solved under the following boundary conditions:

$C = C_i$ at $x = 0$,

$C = 0$ at $t = 0$,

$C = 0$ at $x = \infty$,

and the $C$ is obtained as the following equation (Matsuyama, 1950):

$$C = C_i \left[ e^{-\frac{4\pi k'' C_B x^2}{4D_S t + u^2}} - \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-\frac{(4\pi k'' C_B u^2 + u^2)}{4D_S t}} du \right]$$  \hspace{1cm} (12)

Since the $N$ can be derived by averaging the absorption rate at the interface over a time interval from 0 to $t$:

$$N = \frac{1}{t} \int_0^t \left( \frac{dc}{dx} \right)_{x=0} \, dt$$  \hspace{1cm} (13)

the $N$ is ultimately obtained as the following equation (Matsuyama, 1950):

$$N = C_i \left[ \sqrt{k'' C_B D_S} + \frac{1}{t} \sqrt{\frac{D_S}{k'' C_B}} \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-\frac{(4\pi k'' C_B u^2 + u^2)}{4D_S t}} du \right]$$  \hspace{1cm} (14)

Thus, since Eq.(14) can be rearranged as the following equation:

$$N = \frac{2}{\sqrt{\pi}} \sqrt{\frac{D_S}{t}} C_i \left[ \sqrt{\frac{\pi}{2}} \sqrt{k'' C_B t} + \frac{\pi}{2^{3/2}} \sqrt{\frac{1}{k'' C_B}} \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-\frac{(4\pi k'' C_B u^2 + u^2)}{4D_S t}} du \right]$$  \hspace{1cm} (15)

the $\beta$ can be obtained as the following equation (Fujita et al., 1954):
\[ \beta = \gamma + \frac{\pi}{4\gamma} \text{erf} \left( \frac{2\gamma}{\sqrt{\pi}} \right) \]  

(16)

where

\[ \gamma = \frac{\sqrt{\pi}}{2} \sqrt{k'' C_B t} \]  

(17)

Now, our recent laboratory study (Nishioka et al., 2019) indicates that the \( v_d \) is independent of heating time. Hence, it was inferred from this experimental fact that the \( \gamma \) should be great enough to approximate the \( \beta \) with the \( \gamma \), because the time-independent \( v_d \) can be obtained as follows:

\[ v_d \approx H \gamma k_S = H \sqrt{k'' D_S C_B} \]  

(18)

In this study, this expression for the \( v_d \) was used as a new equation for the modified Cs chemisorption model. Normally, diffusion coefficient, reaction rate constant, and solubility coefficient can be assumed to have an Arrhenius-type temperature dependence. Thus, this modified model can consider not only the Arrhenius-type temperature dependence but also Si content in SS304 since Eq. (17) can be expressed as a function of the \( C_B \). However, as mentioned above, our recent laboratory study (Nishioka et al., 2019) also indicates that the \( v_d \) depends on the \( C_g \). Hence, application of mass action law at the interface between gaseous and solid phases was considered to obtain the \( C_g \)-dependent solubility coefficient. Namely, for instance, when the following dissociation of the gaseous CsOH at the gas-solid interface is assumed to occur:

\[ \text{CsOH(g)} = \text{Cs}^+ \text{in solid phase} + \text{OH}^- \text{in solid phase} \]  

(19)

and concentration of the Cs reactant species at the interface, \( C_i \), is assumed to be equal to concentrations of dissociated Cs ion, \([\text{Cs}^+]\) and \([\text{OH}^-]\), at the interface:

\[ [\text{Cs}^+] = [\text{OH}^-] = C_i \]

equilibrium constant, \( K \), of the above dissociation can be expressed as follows:

\[ K = \frac{[\text{Cs}^+][\text{OH}^-]}{C_w} = \frac{C_i^2}{C_w} \]  

(20)

Thus, the following relation for the \( H \) can be obtained assuming that the \( C_w \) is proportional to the \( C_g \):

\[ H = \frac{C_i}{C_w} = \sqrt{K} \propto \sqrt{\frac{K}{C_g}} \]  

(21)

Consequently, in this study, since the \( K \) can be also assumed to have an Arrhenius-type temperature dependence, the following equation was considered as the modified Cs chemisorption model:

\[ v_d = \frac{A(k'' D_S K)}{C_w^{C_{(HD)}}} \sqrt{C_B \exp \left(- \frac{B(k'' D_S K)}{T} \right)} \]  

(22)

where \( A(k'' D_S K) \), \( B(k'' D_S K) \), and \( C(H) \) are fitting parameters which should be determined from the experimental \( v_d \).

### 4. Determination of mass transfer coefficient of gaseous CsOH in gaseous phase

The gas-side mass transfer coefficient, \( k_G \), was determined from the test condition using correlations for parallel flow on a flat plate. In the case of a forced convective carrier gas flow in the laminar flow regime, the following empirical relation can hold (Sherwood et al., 1975):
where \( Sh \) is the Sherwood number, \( Sc \) is the Schmidt number, and \( Re \) is the Reynolds number. These dimensionless numbers can be expressed by using representative length, \( L \), diffusion coefficient of Cs reactant species in the mixture of all other gaseous species, \( D_{mix} \), viscosity of the mixture, \( \mu_{mix} \), density of the mixture, \( \rho_{mix} \), and velocity of the mixture, \( v_{mix} \), as follows:

\[
Sh = \frac{k_{GL}}{D_{mix}} \quad (24)
\]

\[
Sc = \frac{\mu_{mix}}{\rho_{mix}D_{mix}} \quad (25)
\]

\[
Re = \frac{L}{v_{mix}D_{mix}} \quad (26)
\]

In this study, the \( L \) is regarded as length of the test species, and the \( D_{mix} \) and the \( \mu_{mix} \) were calculated based on Chapman-Enskog kinetic theory described below (Poling et al., 2004).

Binary diffusion coefficient of gaseous species \( i \) in gaseous species \( j \) is expressed as the following equation:

\[
D_{ij} = 0.00266 \frac{T^{3/2}}{1.01325 \sqrt{T/M_{i}^{0.51+0.91 \sigma_{i}}/2} \Omega_{D_{ij}}} \quad (27)
\]

where

- \( D_{ij} \) = binary diffusion coefficient of gaseous species \( i \) diffusing through gaseous species \( j \) [cm²/s],
- \( T \) = temperature [K],
- \( M_{i} \) = mass number for species \( i \) [g/mol],
- \( \sigma_{i} \) = Lennard-Jones parameter for characteristic diameter of species \( i \) [Å], and
- \( \Omega_{D_{ij}} \) = collision integral for diffusion in a binary mixture of \( i \) and \( j \) expressed as the following equation [-]:

\[
\Omega_{D_{ij}} = \frac{1.06036}{T^{0.35636}} + \frac{0.19300}{\exp(0.47635T)} + \frac{1.03507}{\exp(1.52996T)} + \frac{1.76474}{\exp(3.89411T)} \quad (28)
\]

where

\[
T^* = kT/\sqrt{\varepsilon_i \varepsilon_j} \quad (29)
\]

- \( k \) = Boltzmann constant [J/K/molecules], and
- \( \varepsilon_i \) = Lennard-Jones parameter for characteristic energy of self-interaction for species \( i \) [J/molecules].

While, viscosity of gaseous species \( i \) is expressed as the following equation:

\[
\mu_{i} = 26.69 \times 10^{-6} \frac{\sqrt{M_{i}}}{\sigma_{i}^{2} \Omega_{\mu_{i}}} \quad (30)
\]

where

- \( \mu_{i} \) = viscosity for species \( i \) [g/cm/s], and
- \( \Omega_{\mu_{i}} \) = viscosity collision integral for species \( i \) [-]:

\[
\Omega_{\mu_{i}} = \frac{1.16145}{T^{4.96444T}} + \frac{0.52487}{\exp(0.77320T)} + \frac{2.16178}{\exp(2.43378T)} \quad (31)
\]

where

\[
T^* = kT/\varepsilon_{1} \quad (32)
\]
In this study, the Lennard-Jones parameters for CsOH were estimated by using the following equations (Bird et al., 1960):

\[ \sigma = 1.166 V_b^{1/3} \]
\[ \frac{\varepsilon}{k} = 1.15 T_b \]

where

- \( V_b \) = molar liquid volume at normal boiling point [cm\(^3\)/mol], and
- \( T_b \) = normal boiling point [K].

The \( V_b \) for CsOH was estimated by the Le Bas method where the \( V_b \) for compounds can be calculated by a summation of the volume increments for the individual atoms making up the compounds. The volume increment, \( \Delta V_b \) for Cs was obtained from the following empirical equation (Lewis et al., 1998):

\[ \Delta V_b = -0.3196 M_{Cs} + 2.734 (\ln(M_{Cs}))^2 + 0.0008479 M_{Cs}^2 \]

The \( \Delta V_b \) for hydrogen and for oxygen are available from the Le Bas’s structure data (Lewis et al., 1998), which are 3.7 and 7.4, respectively. Consequently, the diffusion coefficient of CsOH in the gaseous mixture of Ar-H\(_2\)-H\(_2\)O-CsOH, \( D_{mix} \), was calculated from the following relation (Wilke, 1950a):

\[ \frac{1 - x_{CsOH}}{D_{mix}} = \frac{x_{Ar} D_{CsOH,Ar}}{x_{Ar} + x_{H2} D_{CsOH,H2} + x_{H2O} D_{CsOH,H2O}} \]

where

- \( x_i \) = molar fraction of species \( i \) in the gaseous mixture of Ar-H\(_2\)-H\(_2\)O-CsOH [-].

While, the viscosity of the gaseous mixture of Ar-H\(_2\)-H\(_2\)O-CsOH, \( \mu_{mix} \), was calculated from the following relation (Wilke, 1950b):

\[ \mu_{mix} = \frac{x_{Ar} \mu_{Ar}}{x_{Ar} + x_{H2} \phi_{Ar,H2} + x_{H2O} \phi_{Ar,H2O} + x_{CsOH} \phi_{Ar,CsOH}} \]
\[ + \frac{x_{H2} \mu_{H2}}{x_{H2} + x_{H2O} \phi_{H2,H2O} + x_{CsOH} \phi_{H2,CsOH}} \]
\[ + \frac{x_{H2O} \mu_{H2O}}{x_{H2O} + x_{CsOH} \phi_{H2O,CsOH}} \]

\[ + \frac{x_{CsOH} \mu_{CsOH}}{x_{CsOH} + x_{H2} \phi_{CsOH,H2} + x_{H2O} \phi_{CsOH,H2O} + x_{CsOH}} \]

where

\[ \phi_{ij} = \left[ 1 + \left( \frac{M_i}{M_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^{1/2} \]

Figure 3 shows comparison results of the values of the \( v_d \) measured by the recent laboratory study (Nishioka et al., 2019) and the \( k_G \) determined from the test conditions by using the empirical relation of Eq. (23) and the \( k_G \) was found to be much greater than the \( v_d \). Therefore, Eq. (9) can be approximated to Eq. (10).
5. Comparison of Cs chemisorption model

The fitting parameters of Eq. (22) were determined from the experimental \( v_d \) and the following equation was obtained as the modified Cs chemisorption model:

\[
    v_d = \frac{7.027\pm 2.794}{C_g^{0.5225\pm 0.0597}} \sqrt{C_B^{6552\pm1197}} \exp \left( -\frac{6552\pm1197}{T} \right)
\]  

(39)

Figures 4 and 5 show comparison of the experimental and calculated \( v_d \) by using the above equation at around 1073K and 1273 K, respectively.
Fig. 5 Comparison of the experimental surface reaction rate constant, \( v_d \) and the calculated \( v_d \) obtained by the modified model at around 1273 K.

Since determined value of the C(H) in Eq. (22) was nearly equal to 0.5, similar dissociation of gaseous CsOH expressed by Eq. (19) might occur at the gas-solid interface. Figures 6 and 7 show comparisons of the experimental \( v_d \) and the calculated \( v_d \) for the modified model and for the existing model (Bowsher, 1990), respectively. Regarding the existing model, all of the calculated \( v_d \)s have a same value if their corresponding experimental \( v_d \)s are obtained at a same temperature. Then, for example, there are only two values of the calculated \( v_d \) for the existing model corresponding to our experimental data (Nishioka et al., 2019) since they are obtained at 1073 K and 1273 K. Twofold standard deviations of logarithm of the \( v_d \), \( 2\sigma \), for the modified model and for the existing model were 0.513 and 1.43, respectively. Therefore, it was found that uncertainty of the modified model was nearly one order of magnitude smaller than that of the existing model since the modified model considered effects not only on temperature but also on CsOH concentration in the gaseous phase and Si content in SS304.

Fig. 6 Comparison of the surface reaction rate constant, \( v_d \text{(cal.)} \), calculated by the modified Cs chemisorption model with the experimental \( v_d \text{(exp.)} \) in the case of Ar-H\(_2\)-H\(_2\)O mixed gas atmosphere for stainless steel type 304 exposed to CsOH vapor.
Fig. 7 Comparison of the surface reaction rate constant, $v_d$ (cal.), calculated by the existing Cs chemisorption model with the experimental $v_d$ (exp.) in the case of Ar-H$_2$-H$_2$O mixed gas atmosphere for stainless steel type 304 exposed to CsOH vapor.

The ratios of the $v_d$ calculated by the existing model (Bixler, 1998; Gauntt et al., 2000) to that calculated by the modified model were also examined to investigate effects of the $C_g$ and the $C_B$. The results in the cases of 1073 K and 1273 K are plotted in Figs. 8 and 9, respectively.

Fig. 8 Dependences of CsOH concentration in gaseous phase, $C_g$, and Si content in stainless steel type 304 for ratio of the surface reaction rate constant, $v_d$ (exist.), calculated by the existing Cs chemisorption model to the $v_d$ (mod.), calculated by the modified Cs chemisorption model at 1073 K.
Fig. 9 Dependences of CsOH concentration in gaseous phase, $C_g$, and Si content in stainless steel type 304 for ratio of the surface reaction rate constant, $v_d$ (exist.), calculated by the existing Cs chemisorption model to the $v_d$ (mod.), calculated by the modified Cs chemisorption model at 1273 K.

It was found from these figures that the $v_d$ of the existing model almost agreed with that of the modified model if both of the $C_g$ and the $C_B$ were approximately equal to 1 $\mu$/cm$^3$ and 1 wt.%, respectively. However, the $v_d$ of the existing model was found to become overestimated with the $C_g$ increasing from 1 $\mu$/cm$^3$ and with the $C_B$ decreasing from 1 wt.%. 

6. Conclusions

Our recent laboratory study indicated that the surface reaction rate constant for the water-insoluble Cs deposit, which is used in the existing chemisorption model incorporated into current severe accident analysis codes, depended not only on temperature but also on both of the Si content in SS304 and the CsOH concentration in the gaseous mixture of Ar-H$_2$-H$_2$O at temperatures above 1073 K. Therefore, the surface reaction rate constant valid above 1073 K was modified based on a penetration theory for gas-liquid mass transfer with chemical reaction and mass action law for CsOH decomposition at interface between gaseous and solid phases. As the result, the surface reaction rate constant was able to be expressed as a function of not only temperature but also the Si content and gaseous CsOH concentration in the gaseous mixture of Ar-H$_2$-H$_2$O. It was found that uncertainty of the modified model was considerably reduced compared with that of the existing model since the modified model was able to adequately describe effects on CsOH concentration in the gaseous phase and Si content in SS304.

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