Research Article

Chemical Forms of Important Fission Products in Primary Circuit of HTR-PM under Conditions of Normal Operation and Overpressure and Water Ingress Accidents: A Study with a Chemical Thermodynamics Approach

Chuan Li,^{1,2,3} Wenqian Li ,^{1,2,3} Lifeng Sun,⁴ Haoyu Xing,^{1,2,3} and Chao Fang ^{1,2,3,5}

¹Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

²Collaborative Innovation Center of Advanced Nuclear Energy Technology, Beijing 100084, China

³The Key Laboratory of Advanced Reactor Engineering and Safety, Ministry of Education, Beijing 100084, China

⁴CNNC High Energy Equipment (Tianjin) Co., Ltd., Tianjin 300300, China

⁵Lab for High Technology, Tsinghua University, Beijing 100084, China

Correspondence should be addressed to Chao Fang; fangchao@tsinghua.edu.cn

Received 20 March 2019; Accepted 18 June 2019; Published 25 July 2019

Academic Editor: Arkady Serikov

Copyright © 2019 Chuan Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The chemical forms of important fission products (FPs) in the primary circuit are essential to the source term analysis of high-temperature gas-cooled reactors because the volatility, transfer, and diffusion of these radionuclides are significantly influenced by their chemical forms. Through chemical reactions with gaseous impurities in the primary circuit, these FPs exist in diverse chemical forms, which vary under different operational conditions. In this paper, the chemical forms of cesium (Cs), strontium (Sr), silver (Ag), iodine (I), and tritium in the primary circuit of the Chinese pebble-bed modular high-temperature gas-cooled reactor (HTR-PM) under normal conditions and accident conditions (overpressure and water ingress accident) are studied with chemical thermodynamics. The results under normal conditions show that Cs exists mainly in the form of Cs_2CO_3 at 250°C and gaseous form at 750°C, and for I and Ag, Ag_3I_3 and Ag convert to gaseous CsI and AgO , respectively, with increasing temperature, while SrCO_3 is the only main kind of compound for Sr. It is also observed that new compounds are generated under accidents: I exists in HI form when a water ingress accident occurs. Regarding tritium, the chemical forms of FPs change little, but compounds need higher temperature to convert. Furthermore, hazard of some FPs in different chemical forms is also discussed comprehensively in this paper. This study is significant for understanding the chemical reaction mechanisms of FPs in an HTR-PM, and furthermore it may provide a new point of view to analyze the interaction between FPs and structural materials in reactor as well as their hazards.

1. Introduction

Modular determining the chemical forms of fission products (FPs) in the primary circuit of a high-temperature gas-cooled reactor (HTGR) is important because they significantly influence the volatility, transfer, and diffusion of FPs [1]. Previous works [2, 3] and the Phenomena Identification and Ranking Tables (PIRTs) of the Next Generation Nuclear Plant (NGNP) Project [4] indicated that studying the chemical forms of radionuclides is essential for source term analyses of the primary circuit of HTGRs under normal and accident

conditions. This is because the interactions between radionuclides and reactor materials (e.g., adsorption, desorption, and corrosion) depend on the chemical forms. However, few related works have been thoroughly studied on this topic. In an HTGR, cesium (Cs), strontium (Sr), silver (Ag), iodine (I), and tritium (^3H) are important FPs for source term analysis. To comprehensively understand their microscopic behaviors, the chemical forms of these radionuclides need to be studied in depth.

Early studies on the chemical forms of Cs, Sr, Ag, I, and ^3H in nuclear reactors have found that some compounds

that threaten the safety of the reactor may accumulate through chemical reactions. HI and CsOH directly influence the primary circuit through their causticity and can be generated in reactions between Cs, I, H₂, and H₂O [5]. Other compounds affect reactors indirectly. Park et al. showed that carbonation in concrete enhances the Cs adsorption capacity through a negative charge [6]. Wu proved that CsCO₃ has a similar effect and increases the thermal expansion coefficient of concrete [7]. It should be pointed out that only in the accident can Cs escape and then react with the concrete. Nishikawa studied the chemical forms of ³H and showed that most of ³H is released in form of HTO [8]. Perriot showed that the tendency of FPs to form metallic and oxide second-phase inclusions influences their diffusivity [9]. The above results clearly show that chemical reactions vary under different conditions. It indicates that the final stable chemical forms of the FPs can be diverse under different operating conditions, even if the amounts and types of FPs remain the same.

In previous work [1], the chemical forms of the Cs–Sr–Ag–I–O five-component system in the primary circuit of a 200 MW modular pebble-bed high-temperature gas-cooled reactor (HTR-PM) were studied with the core under the equilibrium condition. Although the obtained conclusions were constructive, the results were still insufficient to describe the chemical forms of FPs in the primary circuit environment. Some work focusing on the impurities in helium (He) that participate in chemical reactions indicated that these impurities should not be ignored [9–11]. The chemical reactions between radionuclides and gaseous impurities in the primary circuit should be clearly considered, and these radionuclides vary under different operating conditions. In the present study, the impurities in the He coolant in the primary circuit of the HTR-PM were considered, and the chemical forms of Cs, Sr, Ag, I, and ³H were examined through a chemical thermodynamics approach. The variation tendencies for the chemical forms of the radionuclides under different conditions were also evaluated comprehensively. The findings of this study are significant for understanding the chemical reaction mechanism of FPs in an HTR-PM and may provide a new viewpoint for analyzing the interactions between FPs and structural materials in reactors, such as the effects of compounds on the properties of concrete and hazards from the causticity of some compounds.

2. Methodology

There are three steps to determine the concentration of each nuclide in order to calculate the chemical forms of FPs in the HTR-PM primary circuit: first, calculating the inventory of FPs in the reactor core; second, calculating the release fraction of FPs from the core to the primary circuit; third, calculating the chemical forms of FPs at a certain temperature and pressure according to chemical thermodynamics approaches. Figure 1 shows a flowchart for the methodology used in this study.

First, to obtain the species and amounts of FPs, the inventory of FPs in the core should be calculated. The

FIGURE 1: The flowchart of the methodology.

FIGURE 2: The structures of the fuel element and fuel particle.

radioactivity of each kind of nuclide in the reactor core can be calculated as follows [12]:

$$\frac{dX_i}{dt_i} = \sum_{j=1}^N l_{ij} \lambda_j X_j + \Phi \sum_{k=1}^N f_{ik} \sigma_k X_k - (\lambda_i + \Phi \sigma_i) X_i \quad (1)$$

$$i = 1, 2, \dots, N$$

where i , j , and k indicate different types of nuclides; X , λ , and σ are the atomic concentration, decay constant, and average neutron absorption cross-section, respectively; and l and k are fractions from one nuclide converting to the other through decay and absorbing neutrons. Equation (1) was calculated with the KORIGEN code in this study.

In the second step, the release fraction of FPs to the primary circuit needs to be determined. The structures of the fuel element and fuel particle are shown in Figure 2. FPs can release from intact coated particles, broken coated particles, and contaminated heavy metals (mainly uranium pollution) in graphite. Fick's laws of diffusion can be used to obtain the concentration c of FPs according to their diffusive transport in the fuel materials as follows:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c}{\partial r} \right) + Q - \lambda c \quad (2)$$

where Q is the production rate of FPs and D is the diffusion coefficient. Besides, the boundary condition of mass transfer from boundary layer into the coolant can be expressed as follows:

$$-D \frac{\partial c}{\partial r} \Big|_{r=r_p} = \beta (C_{rp} - C_{gr}) \quad (3)$$

where β is the mass transfer coefficient, r_p is the radius of fuel element, and C_{rp}/C_{gr} are the concentrations of FPs

on the surface of the fuel element or in the He outside the fuel element. Equations (2) and (3) were calculated with the German computer model FRESKO-II in this study [13].

In the third step, when the concentrations of FPs in the primary circuit are obtained, the chemical forms of FPs in the primary circuit under certain temperature and pressure conditions can be analyzed according to the Gibbs free energy criterion. According to the van 't Hoff equation, the molar Gibbs free energy change $\Delta_r G_{m,T}$ of a chemical reaction in a nonstandard state conforms to

$$\Delta_r G_{m,T} = \Delta_r G_{m,T}^\theta + RT \cdot \ln Q \quad (4)$$

where Q is the activity quotient, R is the ideal gas constant [J/(mol·K)], T is the temperature of the environment (K), and $\Delta_r G_{m,T}^\theta$ is the standard molar Gibbs free energy change at a certain temperature. This can be derived from the standard molar free energy of formation $\Delta_f G_{m,T}^\theta$:

$$\Delta_r G_{m,T}^\theta = \sum_B \nu_B \Delta_f G_{m,T}^\theta(B) - \sum_A \nu_A \Delta_f G_{m,T}^\theta(A) \quad (5)$$

where the subscripts A and B represent reactants and products, respectively. ν is the corresponding coefficient that satisfies the relation with Q and activity a of the reactant/product:

$$Q = \frac{\prod_B a^{v_B}}{\prod_A a^{v_A}} \quad (6)$$

A chemical reaction occurs spontaneously when the Gibbs free energy is greater than 0 and nonspontaneously when it is less than 0. When the reaction reaches equilibrium, $\Delta_r G_{m,T}$ is zero, so Q can be calculated as follows:

$$Q = \exp\left(\frac{-\Delta_r G_{m,T}^\theta}{RT}\right) \quad (7)$$

This relation can be used to obtain the chemical forms of elements that participate in reactions.

The concentrations of Cs, Sr, Ag, and I in the primary circuit can be calculated with the above methods, and the detailed process is described in the authors' previous work. Equations (6) and (7) were used with the HSC software [14] to calculate the chemical forms of FPs under certain temperature and pressure conditions in this study.

^3H is produced differently from other nuclides. Besides the fission reaction, ^3H is also produced by neutron-activation reactions. Four source terms contribute to the accumulation of ^3H in the primary circuit [15]: (1) the ternary fission reaction of heavy nuclides (U-235, Pu-239, Pu-241), (2) the activation reaction of He-3 in the coolant, (3) the activation reaction of Li-6 in the matrix graphite of the fuel elements, and (4) the activation reaction of Li-6 in the graphite of the reflector layer. The amount of ^3H generated per unit of time can be determined by successively calculating

$$\frac{dN_X}{dt} = \frac{P \cdot f \cdot y}{g} \quad (8)$$

$$\begin{aligned} \frac{dN_{\text{He-3}}^T}{dt} &= \sigma_{\text{He-3}} \cdot \phi \cdot N_{\text{He-3}}^0 \\ &\cdot \left(\frac{\sigma_{\text{He-3}} \phi}{L + \sigma_{\text{He-3}} \phi} \cdot e^{-(L + \sigma_{\text{He-3}} \phi)t} + \frac{L}{L + \sigma_{\text{He-3}} \phi} \right) \end{aligned} \quad (9)$$

$$\frac{dN_{\text{Li-6}}^T(1)}{dt} = N_F \frac{\int_{t=0}^{t=T} \sigma_{\text{Li-6}} \phi \cdot n_{\text{Li-6}}^0 \cdot e^{-\sigma_{\text{Li-6}} \phi t} dt}{T} \quad (10)$$

$$\frac{dN_{\text{Li-6}}^T(2)}{dt} = \sigma_{\text{Li-6}} \phi N_{\text{Li-6}}^0 \cdot e^{-\sigma_{\text{Li-6}} \phi t} \quad (11)$$

where X is the species of fission nuclides, P is the reactor power (MW), f is the proportion of the nuclide X , y is the yield of the light nuclide, g is the energy released from each fission reaction, $\sigma_{\text{He-3}}$ is the cross-section of the reaction He-3 (n, p) ^3H (barn), ϕ is the thermal neutron fluence rate in the reactor core ($\text{cm}^{-2}\text{s}^{-1}$), $N_{\text{He-3}}^0$ is the initial number of He-3, L is the leakage rate of He in the coolant (s^{-1}), $\sigma_{\text{Li-6}}$ is the cross-section of the reaction Li-6 (n, α) ^3H (barn), $n_{\text{Li-6}}^0$ is the initial number of Li-6 in one fuel sphere, and N_F is the number of fuel spheres (420,000 for the HTR-PM). $N_{\text{Li-6}}^T(1)$ and $N_{\text{Li-6}}^T(2)$ are the production of ^3H due to the activation reaction of Li-6 in the matrix graphite of the fuel elements and the reflector layer, respectively.

Considering the equilibrium process, ^3H in the primary circuit is removed in four ways: (1) decay of ^3H , (2) leakage of coolant, (3) purification of coolant, and (4) diffusion of ^3H to the secondary circuit. Equation (12) shows the variation in the amount of ^3H in the primary circuit:

$$\begin{aligned} \frac{dN^T}{dt} &= k \cdot \frac{dN_X^T}{dt} + \frac{dN_{\text{He-3}}^T}{dt} + \frac{dN_{\text{Li-6}}^T(1)}{dt} \\ &+ \frac{dN_{\text{Li-6}}^T(2)}{dt} - (L + P_{\text{ur}} + \lambda) \cdot N^T - P_{\text{er}} \end{aligned} \quad (12)$$

where k is the damage proportion of fuel elements, P_{ur} is the purification rate of He (1/s), and P_{er} is the diffusion rate of ^3H to the secondary circuit (1/s).

The above equations can be used to determine the concentration of ^3H in the primary circuit. Obviously, the amount of ^3H is much smaller than that of H, so the impact from ^3H with H would be irrelevant. On this basis, the concentration of Hydrogen Isotopes can be approximately equal to the concentration of H during the analysis of the chemical forms. The differences in the types of chemical forms and variations are focused.

3. Input Data for Studying Chemical Forms of Radionuclides under Normal and Accident Conditions

3.1. Related Design Parameters of HTR-PM. First, the inventory of FPs was calculated in order to analyze the reaction

TABLE 1: Design parameters of HTR-PM.

Parameter	Data
Thermal power of HTR-PM	250 MW
Temperature of Heat inlet	250°C
Temperature of Heat outlet	750°C
Maximum temperature of fuel element	900°C
Pressure of He in primary circuit	7.0 MPa
Fresh fuel enrichment in the equilibrium core	8.5%
Average residence time of fuel elements in core	1056.8 day
Thermal neutron flux in equilibrium core	$6.57 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$
Resonance neutron flux in equilibrium core	$7.68 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$
Fast neutron flux in equilibrium core	$8.98 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$
Amount of Helium in HTR-PM	3000 kg

TABLE 2: Parameters of fuel particles.

Parameter	Normal data
Diameter of fuel particle	500 μm
Thickness of buffer layer	95 μm
Thickness of OPyC	40 μm
Thickness of iPyC	40 μm
Thickness of SiC layer	35 μm
Failure fraction of TRISO at objective burn-up	2.00E-04
Natural uranium contamination of fuel elements	7.00E-07

products in the primary circuit. Thus, the parameters of HTR-PM were required; these are presented in Table 1. The inventories in the core were determined with these parameters by using the method introduced in Section 2. According to Table 1, the temperatures of the He gas at the outlet and inlet are 750 and 250°C, respectively, under normal conditions, and the He gas pressure in the primary circuit is 7 MPa [1].

The parameters of the fuel particle were required to calculate the release fraction from diffusion and are presented in Table 2. The amount of gas impurities in the primary circuit was calculated according to the design level of gas impurities in He, as presented in Table 3 and the design level in Table 3 describes the quality proportion of gas impurities in He under normal conditions.

Considering that the concentration of ^3H was $1.19 \times 10^8 \text{ Bq/m}^3$ in the balanced state and the volume of the primary circuit was 425 m^3 [16], the amount of ^3H in the primary circuit was $4.69 \times 10^{-5} \text{ mol}$. This means that the analysis method for ^3H is reasonable because the amount of ^3H was negligible compared to H_2 .

3.2. Accident Conditions and Related Parameters. Analyzing the accident conditions is important because the safety design requires predicting what would happen in the event of accidents. In this study, overpressure and water ingress were considered as two types of representative accident scenarios during operation.

Under overpressure accidents, the pressure in the primary circuit increases when heat fails to be removed and triggers

TABLE 3: Parameters of gas impurities in Helium (industrial quality follows Chinese National Standard GB/T 4884).

Species of impurity	Quality proportion (vppm)	Total amount in HTR-PM (mol)
H_2	7	0.00525
H_2O	1	0.0075
CO	7	0.00525
CO_2	1	0.0075
CH_4	3	0.00225
N_2	2	0.0015
O_2	1	0.00075

the safety valve (pilot-operated relief valve) [17] to open upon reaching the critical value (7.9MPa). During the overpressure accident, the pressure in the primary circuit rapidly increases to the critical value while the other parameters vary little.

Water ingress occurs when a steam generator tube breaks during operation [18]. This causes liquid and gaseous water to enter the primary circuit, owing to the much higher pressure of the secondary circuit, and enter the core alone with He. Such an abnormality increases the reactivity of the reactor by affecting the behavior of neutrons. Water vapor also has a corrosion reaction with graphite, which generates water gas. An increase in gas can also trigger overpressure. Drastic changes occurred during the water ingress accident. The temperature and thermal power initially increases rapidly, while the pressure in the primary circuit increases reaching 7.9 MPa after about 23 h, which finally triggers the safety valve to open. After that, the pressure drops very quickly within 1 h [19]. Table 4 presents the typical pressure data during the water ingress accident.

Because of water entering the primary circuit and the temperature increasing up to 900°C, the amounts of gases (CO , CO_2 , H_2 , and H_2O) and FPs also change. The main changes are presented in Table 5. As shown in Table 5, all the four gases were generated rapidly after accident occurs due to water entering and temperature increasing, while amounts of H_2O , H_2 , and CO decreased a lot after safety valve opened since pressure in the primary circuit became

TABLE 4: Variation in pressure during a water ingress accident.

Time into the accident(h)	Pressure (MPa)
0	7.0
8	7.7
23 (safety valve opens)	7.9
24 (safety valve closes)	6.9

TABLE 5: Amounts of gases at different times after a water ingress accident.

Time (h)	CO (kmol)	CO ₂ (kmol)	H ₂ (kmol)	H ₂ O (kmol)
0	0	0	0.01	0
8	2.5	6	14.5	32
23	2	9	20	32
24	0	9	9	23

much higher. The amount of CO₂ changed little because of graphite's corrosion reaction and air circulation (especially O₂).

3.3. Amount of FPs in the HTR-PM Primary Circuit during Normal Operation and Accidents. Section 2 presented the methodology to calculate the concentrations of FPs. The related parameters were introduced in Section 3.1. Table 6 presents the inventories of Cs, Sr, Ag, and I in the equilibrium reactor core. The total amounts of Cs, Sr, Ag, and I are 46.00, 29.86, 0.73, and 0.57 mol, respectively. Their accumulations in the primary circuit were solved and are presented in Table 7. The inventories in the core and amounts in the primary circuit under accident conditions were solved similarly. For overpressure accident, it is assumed that the pressure in the primary circuit increases rapidly to reach 7.9MPa, and therefore the additional release of FPs due to rising temperature of the core can be approximately neglected. As a result, the calculation results for the overpressure accident were the same as those under normal conditions.

When the water ingress occurs, both the temperature and pressure change. According to the safety analysis, the reactor power increases by 20% in 20 s when the accident occurs, so the inventories of radionuclides increased by 20% [20]. This means that the initial amount of FPs (i.e., 8 h after the accident) was 1.2 times greater than that under normal conditions, which is presented in Table 8. Some of the FPs will be released to the environment after the safety valve is opened until it closes after 1 h. The amounts of FPs in the primary circuit 23 and 24 h after the accident were calculated and are presented in Tables 9 and 10, respectively.

4. Results and Discussion

4.1. Chemical Forms of Cs, Sr, Ag, and I considering Impurities in He. The chemical forms of Cs, Sr, Ag, and I and the variations in the amounts of their different compounds at 250–750°C were calculated. The main forms are presented in Table 11. Forms of Cs include Cs₂CO₃, CsHCO₃, and gaseous

CsOH. I exists in Ag₃I₃ and gaseous CsI, while Ag exists in gaseous AgO and the elementary substance. Sr mainly exists in SrCO₃.

Figure 3(a) shows the result for Cs. Among these compounds, Cs has more complex forms than the other FPs. At 250°C, the amount of CsHCO₃ reaches the maximum of 4.73×10^{-9} mol. At 350°C, the amount of Cs₂CO₃ reaches the maximum of 1.42×10^{-8} mol. Both of them reach their minimums at 750°C. In contrast, the amount of gaseous CsOH is negligible at 250°C, while it reaches its maximum at 750°C (2.51×10^{-8} mol). In a word, Cs₂CO₃ is the main form of the Cs compounds at low temperatures (<600°C), while gaseous CsOH is the main form above 750°C. SrCO₃ is almost the only main chemical form of Sr, as shown in Figure 3(b), and Figures 3(c) and 3(d) showed the results for Ag and I, which are very similar in the shape of the curve. At low temperatures, Ag existed as simple substance, while I exists in the form of gaseous Ag₃I₃. At higher temperatures, SrCO₃ and CsI are the principle forms. In conclusion, Ag and I both converted from one compound to another as the temperature increases.

4.2. Chemical Forms of FPs considering Impurities in He and ³H. Section 2 discussed the effect of ³H. As calculated in Section 3.1, the amount of ³H in the primary circuit is 4.69×10^{-5} mol. This is much smaller than the amount of H in He. Figure 4 displays the results for the four elements. The results are not the same compared with those in Section 4.1. In particular, the chemical forms of Cs no longer include CsHCO₃. However, the results for Sr, Ag, and I are similar to those described in Section 4.1. As stated previously, this study is focused on the differences in the types of chemical forms and variation. When ³H was included rather than H, the chemical forms of Cs become simpler. The performances of Sr, Ag, and I change inconspicuously, but Ag needs a higher temperature to convert to AgO, so does Ag₃I₃.

4.3. Chemical Forms of FPs during an Overpressure Accident. During an overpressure accident, the pressure of the primary circuit rapidly increases to 7.9 MPa, but the temperature remains the same as under normal conditions. The results for Cs/Sr/Ag/I are shown in Figure 5. The results during the overpressure accident were very similar to those under normal conditions. The chemical forms of Cs, Sr, Ag, and I changes little, but compounds need higher temperature to convert.

4.4. Chemical Forms of FPs during a Water Ingress Accident. During water ingress accident, the temperature reaches up to 900°C, while the lowest temperature is 400°C. The other required parameters were presented in Section 3.

4.4.1. Chemical Forms of FPs 8 h after Water Ingress. The calculation results of 8h after water ingress accident are shown in Figure 6. Cs exists as CsOH and Cs₂CO₃, while I exists as CsI, HI, and Ag₃I₃. Sr exists in the same chemical forms as under normal conditions, while Ag exists only as

FIGURE 3: Variations in the amounts of each kind of compound: (a) Cs, (b) Sr, (c) Ag, (d) I.

TABLE 6: Amounts of important FPs in the equilibrium core.

Nuclide	Amount (mol)	Nuclide	Amount (mol)
^{134}Cs	2.38E+00	$^{110\text{m}}\text{Ag}$	1.32E-02
$^{134\text{m}}\text{Cs}$	1.43E-04	^{111}Ag	1.54E-02
^{136}Cs	2.15E-02	^{112}Ag	1.20E-04
^{137}Cs	4.36E+01	^{113}Ag	1.45E-04
^{89}Sr	2.63E+00	^{131}I	4.55E-01
^{90}Sr	2.72E+01	^{132}I	7.32E-03
^{91}Sr	2.38E-02	^{133}I	8.18E-02
^{92}Sr	6.62E-03	^{135}I	2.17E-02
^{110}Ag	6.98E-01

FIGURE 4: Variations in the chemical forms: (a) Cs, (b) Sr, (c) Ag, and (d) I.

TABLE 7: Accumulation of Cs/Sr/Ag/I in the primary circuit.

FPS	Amount in primary circuit (mol)
Cs	2.84E-05
Sr	3.57E-07
Ag	1.00E-06
I	8.77E-09

gaseous AgO because of the higher temperature. Compared with the normal conditions, the chemical forms of Cs and I clearly change when water ingress occurs. Because of the unbalanced temperature in the primary circuit, I exists as HI below 900°C, which was scarce under normal conditions.

TABLE 8: Accumulation of Cs/Sr/Ag/I in the primary circuit 8 h after beginning of the accident.

FPS	Amount in primary circuit (mol)
Cs	3.41E-05
Sr	4.28E-07
Ag	1.20E-06
I	1.05E-08

4.4.2. Chemical Forms of FPS 23 h after Water Ingress. The calculation results of 23h after water ingress accident are shown in Figure 7. It is found that the chemical forms of Cs and I change little compared with the results in Section 4.4.1. Meanwhile, Sr exists as SrCO₃ from low temperatures to high

FIGURE 5: Variations in the chemical forms during an overpressure accident: (a) Cs, (b) Sr, (c) Ag, and (d) I.

TABLE 9: Accumulation of Cs/Sr/Ag/I in the primary circuit 23 h after beginning of the accident.

FPS	Amount in primary circuit (mol)
Cs	2.28E-04
Sr	1.24E-04
Ag	9.38E-06
I	2.31E-06

temperatures. Ag existed as a simple substance below 400°C, which is also different from the results in Section 4.4.1.

4.4.3. Chemical Forms of FPS 24 h after Water Ingress. The calculation results of 24h after water ingress accident are shown in Figure 8. Compared with the results in Section 4.4.2, the

TABLE 10: Accumulation of FPS in the primary circuit 24 h after an accident.

FPS	Amount in primary circuit (mol)
Cs	1.99E-04
Sr	1.08E-04
Ag	8.19E-06
I	1.86E-06

TABLE 11: Main forms of Cs, Sr, Ag, and I.

Gaseous	AgO, CsOH, CsI
Nongaseous	Ag, Cs ₂ CO ₃ , CsHCO ₃ , SrCO ₃ , Ag ₃ I ₃

chemical forms of Cs, Sr, Ag, and I are very similar. This means that the release of FPS through the open safety valve

FIGURE 6: Variations in the chemical forms of 8h after water ingress accident: (a) Cs, (b) Sr, (c) Ag, and (d) I.

does not affect their chemical forms in the primary circuit. Under different conditions, some compounds that accumulated in the primary circuit affect the normal operation of the reactor. In the overpressure scenario, the accumulation of SrO increases in the primary circuit. I exists as HI below 900°C with water ingress, which is considered a hazard to the metallic material used in an HTGR because HI is the most unstable compound among hydrogen halides with strong causticity. Cs and Sr were determined to exist as carbonates, and these compounds can enter concrete through the safety valve at low temperatures in the event of water ingress with the average release rate of about 5E-12mol/h and 6E-14mol/h, respectively. This can affect the thermal expansion coefficient and absorptive capacity for FPs of concrete.

5. Conclusion and Remarks

In this study, the chemical forms of Cs, Sr, Ag, and I under different conditions were analyzed according to chemical thermodynamics. The inventory in the core was calculated first. Then, the concentrations of FPs in the primary circuit were confirmed. Finally, the chemical forms of the FPs were obtained. Under normal conditions, Cs exists as Cs_2CO_3 , CsHCO_3 (at low temperatures), and gaseous CsOH (at high temperatures). Sr exists as SrCO_3 , Ag exists as a simple substance and AgO, and I exists as gaseous CsI and Ag_3I_3 . When an accident occurs, other compounds start to form, especially at high temperatures. HI becomes the most common chemical form of I in the event of water ingress. Some compounds threaten the safety of the reactor because of

FIGURE 7: Variations in the chemical forms of 23h after water ingress accident: (a) Cs, (b) Sr, (c) Ag, and (d) I.

their causticity, such as HI. Some compounds have indirect influence, such as Cs₂CO₃ and SrCO₃. The influence of ³H was also examined. When ³H is considered, the chemical forms of FPs change little.

This study proves that the safety assessment of a reactor requires analyzing the chemical forms of FPs in the primary circuit. Although chemical forms of FPs do not affect the inventories of radioactive isotopes, which means the source terms are not affected, the properties of FPs are affected by their chemical forms. During the operation of reactors, especially when accidents occur, variations in chemical forms could threaten the safety of reactors. Further research is necessary since only two kinds of accidents are analyzed in this article, and FPs may exist in other forms under accident conditions. These findings can help with the safety analysis of HTGRs from a new perspective.

Data Availability

The tables, figures, and references data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the National S&T Major Project (grant 2018ZX06902013).

FIGURE 8: Variations in the chemical forms of 24h after water ingress accident: (a) Cs, (b) Sr, (c) Ag, and (d) I.

References

- [1] C. Li, J. Zhang, and C. Fang, "Chemical forms of important fission products in the primary circuit of HTR-PM under the condition of equilibrium core: from methodology to preliminary results," *Nuclear Technology*, vol. 200, no. 1, pp. 45–53, 2017.
- [2] R. De Boer and E. H. P. Cordfunke, "The chemical forms of fission product tellurium during reactor accident conditions," *Journal of Nuclear Materials*, vol. 240, no. 2, pp. 124–130, 1997.
- [3] S. M. Mirza, M. J. Iqbal, and N. M. Mirza, "Effect of flow rate transients on fission product activity in primary coolant of PWRs," *Progress in Nuclear Energy*, vol. 49, no. 2, pp. 120–129, 2007.
- [4] R. N. Morris, "Next Generation Nuclear Plant Phenomena Identification and Ranking Tables (PIRTs), Volume 3: Fission-Product Transport and Dose PIRTs," 2007.
- [5] L. Liu, R. Liu, and X. Tao, "Method for determination of cesium hydroxide in work place air by flame atomic absorption spectrometry," *Chinese Journal of Health Laboratory Technology*, vol. 19, article no 9, 2009.
- [6] S. Park and J. Jang, "Carbonation-induced weathering effect on cesium retention of cement paste," *Journal of Nuclear Materials*, vol. 505, pp. 159–164, 2018.
- [7] Y. Wu and S. Wang, "Research Progress of Barium Carbonate," *Inner Mongolia Petrochemical Industry*, vol. 7, 2008.
- [8] M. Nishikawa, T. Kinjo, and Y. Nishida, "Chemical forms of tritium released from solid breeder materials," *Journal of Nuclear Materials*, vol. 325, no. 2-3, pp. 87–93, 2004.
- [9] R. Perriot, X. Liu, C. Stanek, and D. Andersson, "Diffusion of Zr, Ru, Ce, Y, La, Sr and Ba fission products in UO_2 ," *Journal of Nuclear Materials*, vol. 459, pp. 90–96, 2015.

- [10] J. Zhu and Z. Li, "Research on quality of helium gas in primary system of 10 MW high-temperature gas-cooling reactor," *Atomic Energy Science and Technology*, vol. 44, 2010.
- [11] D. Tochio, A. Shimizu, S. Hamamoto, and N. Sakaba, "Helium leak and chemical impurities control technology in HTTR," *Journal of Nuclear Science and Technology*, vol. 51, no. 11-12, pp. 1407–1412, 2014.
- [12] Z. C. Qian and J. Z. Cao, "Calculation of total radioactivity inventory in HTR-PM reactor core," *Scientific and Technical Review*, vol. 28, no. 11, pp. 19–23, 2010.
- [13] H. Krohn and R. Finken, "FRESCO-II: Ein Rechenprogramm zur Berechnung der Spaltprodukt freisetzung aus Kugelförmigen HTR-Brennelementen in Bestrahlungs- und Ausheizexperimenten," Jül-Spez-212, Jülich Research Center, 1983.
- [14] A. Roine, "Chemical reaction and equilibrium software with extensive thermochemical database and flowsheet simulation," *Outokumpu Research Oy*, 2006, Outokumpu Research Oy.
- [15] "Fuel performance and fission product behaviour in gas cooled reactors," IAEA-TECDOC-978, International Atomic Energy Agency, 1997.
- [16] Y. Wu and J. Cao, "Analysis of tritium production and distribution in HTR-PM," in *Proceedings of the 18th International Conference on Nuclear Engineering*, Xian, China, May 2010.
- [17] F. Forscher and W. M. Bland, "Pilot-operated relief valve design and performance," *Progress in Nuclear Energy*, vol. 6, no. 1-3, pp. 239–325, 1980.
- [18] Y. Zheng, L. Shi, and Y. Wang, "Water-ingress analysis for the 200 MWe pebble-bed modular high temperature gas-cooled reactor," *Nuclear Engineering and Design*, vol. 240, no. 10, pp. 3095–3107, 2010.
- [19] R.-D. Zhang, X.-M. Sun, and Y.-J. Dong, "Hydrogen behavior after water-ingress accident of HTR-PM," *Yuanzineng Kexue Jishu/Atomic Energy Science and Technology*, vol. 50, no. 5, pp. 841–845, 2016.
- [20] Y. Z. Liu and J. Z. Cao, "Accident radioactive release and environmental impact for HTR-10 high temperature gas cooled experimental reactor," *Journal of Radiological Protection*, vol. 15, no. 4, 1995.