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DEVELOPMENT OF FAST REACTOR CONTAINMENT SAFETY ANALYSIS CODE, CONTAIN-LMR (3) IMPROVEMENT OF SODIUM-CONCRETE REACTION MODEL

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ABSTRACT

A computer code, CONTAIN-LMR, is an integrated analysis tool to predict the consequence of severe accident in a liquid metal fast reactor. Because a sodium-concrete reaction behavior is one of the most important phenomena in the accident, a Sodium-Limestone Concrete Ablation Model (SLAM) has been developed and installed into the original CONTAIN code at Sandia National Laboratories (SNL) in the U.S.

The SLAM treats chemical reaction kinetics between the sodium and the concrete compositions mechanistically using a three-region model, containing a pool (sodium and reaction debris) region, a dry (boundary layer (B/L) and dehydrated concrete) region, and a wet (hydrated concrete) region, the application is limited to the reaction between sodium and limestone concrete.

In order to apply SLAM to the reaction between sodium and siliceous concrete which is an ordinary structural concrete in Japan, the chemical reaction kinetics model has been improved to consider the new chemical reactions between sodium and silicon dioxide. The improved model was validated to analyze a series of sodium-concrete experiments which were conducted in Japan Atomic Energy Agency (JAEA). It has been found that relatively good agreement between calculation and experimental results is obtained and the CONTAIN-LMR code has been validated with regard to the sodium-concrete reaction phenomena.

1. INTRODUCTION

The CONTAIN-LMR code is an integrated analysis tool to predict the consequence of severe accident in a liquid metal fast reactor, and is incorporated a lot of models analyzing sodium-related phenomena [1]. The sodium-concrete reaction model is important to simulate heat generation and combustible hydrogen gas release which are caused by the reaction in the containment vessel. SLAM has been originally developed at SNL in the U.S. and installed into the CONTAIN-LMR code to analyze the reaction of sodium-limestone concrete [2].

It has been known that the sodium-concrete reaction behavior depends on the concrete type whose aggregate is used [3]. In Japan, siliceous concrete is an ordinary structural concrete and graywacke concrete is similar to siliceous concrete in regard to the compositions. Therefore JAEA conducted the small and middle scale sodium–siliceous concrete reaction experiments under the various conditions such as temperature and concrete size [4-5].

The bulk chemical compositions of a representative limestone and graywacke concrete are shown in Table 1. The limestone concrete mainly consists of about 40 weight percents (wt.%) calcium oxide (CaO) and about 37 wt.% carbon dioxide (CO_2). The graywacke concrete mainly consists of silicon dioxide (SiO_2) whose content is about 75 wt.%. For the difference of these major compositions, it is necessary to introduce the new chemical reaction kinetics model such as Na+SiO_2 and NaOH+SiO_2 reactions in the sodium-siliceous concrete reaction. Therefore the new chemical reaction kinetics equations and parameters have been added in consideration of the original SLAM parameters using the results of the thermal analysis experiments [8-11].

In this study, the chemical reaction kinetics models between sodium and the compositions of the siliceous concrete are discussed. Then, we calculated the series of sodium-siliceous concrete reaction experiments with the improved sodium-concrete reaction model, and compared the calculation and experimental results [6].

Table 1 Bulk chemical compositions of representative limestone and graywacke concrete [3, 7]

Composition	Limestone concrete [wt.%]	Graywacke concrete [wt.%]
CaO	40	9*
MgO	5	1
SiO_2	9	75
CO_2	37	-
Al_2O_3	-	7
NaOH	-	4
KOH	-	3
H_2O	7	1
Inert	2	-

* as CaOH

2. Description of SLAM [2]

The calculation coordinate system of the SLAM in CONTAIN-LMR code is shown in figure 1. There exist three distinct regions; the pool region (1 node), the dry region (27 nodes), and the wet region (23 nodes). In addition, the B/L region (12 nodes) where diffusion and chemical reaction kinetics of the sodium and the concrete compositions are calculated is defined at upper of the dry region. As the hydrated concrete of the wet region is dehydrated by heat-conducting, the node number of the wet region is decreasing gradually. The SLAM solves the conservation equations of three main equations; continuity, energy and momentum equations numerically in each region. For the application to the sodium-siliceous concrete reaction, the B/L is a particularly important region to analyze chemical reaction kinetics between the sodium and the concrete compositions, and the concrete ablation velocity in SLAM.

In the original SLAM, the following chemical reaction kinetics equations for the major compositions of the limestone concrete are calculated in the B/L region.

(1) $Na + H_2O \rightarrow NaOH + 1/2H_2$
(2) $4Na + CO_2 \rightarrow 2Na_2O + C$
(3) $4Na + 3CaCO_3 \rightarrow 2Na_2CO_3 + 3CaO + C$
(4) $4Na + 3MgCO_3 \rightarrow 2Na_2CO_3 + 3MgO + C$
(5) $2NaOH + CaCO_3 \rightarrow Na_2CO_3 + CaO + H_2O$
(6) $2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$

It is difficult to simulate the complex chemical reaction kinetics process of the sodium-siliceous concrete reaction using the only above equations (1) ~ (6) equations of the original SLAM because of the difference of the major consisting compositions shown in Table 1. The second-order Arrhenius-type reaction rate (k: reaction rate constant [m^3/kmol-s]) is used to simulate temperature and reactant concentrations dependency in the SLAM. In a chemical reaction equation of $aA+bB \rightarrow cC+dD$, the calculated chemical kinetics equation is expressed as;

$$dX/dt=ke^{-\Delta E/RT}(X - \rho_A/aW_A)\ (X - \rho_B/aW_B) \qquad (1)$$

where X [kmol] is the total amount of reactant, $\rho_{A,B}$ [kg/m^3] and $W_{A,B}$ [kg/kmol] are the density and the molar weight of material A or B, and $ke^{-\Delta E/RT}$ is the kinetics rate coefficient of the reaction. ΔE [cal/mol], R [cal/K-mol] and T [K] are the activation energy, the gas constant and the temperature, respectively. The dependency of the reactant concentrations was measured for limestone concrete in the laboratory-scale sodium-carbonate aggregate concrete experiments which were conducted in SNL, and the chemical reaction kinetic parameters were derived from the best correlation with experimental results [7].

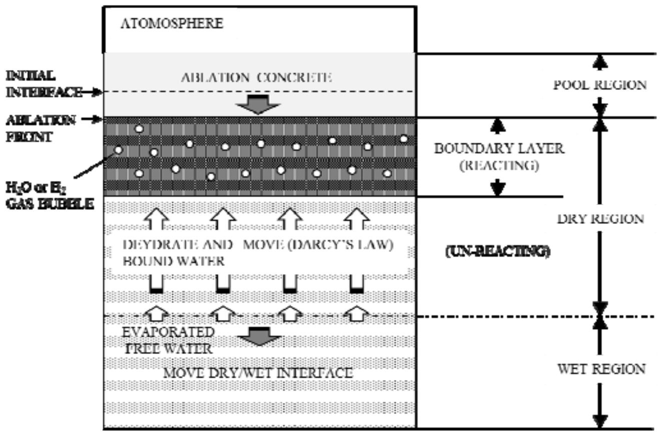

Figure 1 Calculation coordinates system in SLAM

3. THE CHEMICAL REACTION KINETICS PARAMETERS BETWEEN SODIUM-SILICEOUS CONCRETE MATERIALS

The thermal analysis experiments of Na+NaOH, Na+SiO_2, Na+Al_2O_3, NaOH+SiO_2 and NaOH+Al_2O_3 reactions were conducted to investigate these chemical kinetics properties. The several chemical reaction kinetics properties of the threshold temperature, the residual materials after the experiment, and the reaction rate, k [1/s] were reported [8-12]. These past experimental results are indicated in table 2 and table 3.

(1) Na+NaOH reaction:

The thermal analysis experiments in which the mixing ratio of Na : NaOH was 15 mg : 15 mg, 18.4 mg : 16.0 mg and 18.4 mg : 8.0 mg were conducted. The reaction threshold temperature was obtained in the range of 360 ~ 400 deg-C. The residual materials were Na, NaOH and Na_2O after the experiments. The reaction rates were suggested in assumption of the first-order reaction.

(2) Na+SiO_2 reaction:

The thermal analysis experiments in which the mixing ratio of Na : SiO_2 was 20 mg : 10 mg and 18.4 mg : 36 mg were conducted. The reaction threshold temperature was obtained in the range of 500 ~ 540 deg-C, which was the same as that of the sodium-siliceous concrete. The residual materials were Na, SiO_2 and Na_2SiO_3 after the experiments. The reaction rate was suggested in assumption of the first-order reaction. The thermal analysis experiment of Na+aggregate reaction was conducted, and the reaction properties were reported to be similar to those of Na+SiO_2 reaction although the aggregate includes the other materials.

(3) NaOH+SiO_2 reaction:

The thermal analysis experiments in which the mixing ratio of NaOH : SiO_2 was 20 mg : 10 mg and 32 mg : 24 mg were conducted. The reaction threshold temperature was obtained in the range of 313 ~ 330 deg-C. The past experimental results were reported that the reaction rate was extremely fast since the reaction temperature was invalid though the heating rate was increased.

(4) Na+Al_2O_3 and NaOH+Al_2O_3 reaction:

The thermal analysis experiments in which the mixing ratio of Na : Al_2O_3 and NaOH : Al_2O_3 was 20 mg : 11 mg and 20 mg : 20 mg were conducted. These reaction threshold temperatures were similar to those of Na+SiO_2 and NaOH+SiO_2 reactions. The residual materials were Na, Al_2O_3 and $NaAl_2O_3$ after the experiments.

The reaction rates of Na+NaOH, Na+SiO_2 and Na+aggregate reactions are shown in figure 2. The black solid lines show the values of the improved model, and the dotted colored lines show the experimental results in table 2 and 3.

Table 2 Summary of chemical reaction properties between Na and NaOH

Na	✧ NaOH[8] ・Na:NaOH=15mg:15mg ・ER in about 360deg-C ・residual material: Na_2O ✧ NaOH[10] ・Na:NaOH=18.4mg:8.0mg ・ER in 391deg-C ・$k=3.2*10^{13}exp(-48.2*10^3/RT)$ ✧ NaOH[11] ・Na:NaOH=18.4mg:16.0mg ・ER in 401deg-C ・residual materials: Na_2O, Na, NaOH ・$k=1.2*10^{10}exp(-38.5*10^3/RT)$

ER: Exothermic reaction

Table 3 Summary of chemical reaction properties between Na, NaOH and SiO_2, aggregate, Al_2O_3.

Na	✧ SiO_2[8] ・Na:SiO_2=20mg:10mg ・ER in 520 ~ 540 deg-C ・residual materials: Na_2SiO_3,Si ✧ SiO_2[9] ・Na:SiO_2=18.4mg:36.0mg ・ER in 504 ~ 531 deg-C ・residual materials: Na_2SiO_3, Na_2SiO_2, Na ・$k=7*10^{12}exp(-55.2*10^3/RT)$ ✧ Aggregate[9] ・Na:aggregate=18.4mg:36.0mg ・ER in 503 ~ 523 deg-C ・residual materials: Na_2SiO_3, Na_2SiO_2, Na ・$k=6*10^{14}exp(-61.6*10^3/RT)$	✧ Al_2O_3[8] ・Na: Al_2O_3=20mg:11mg ・ER in 500 ~ 520 deg-C ・residual material: $NaAlO_2$
NaOH	✧ SiO_2[8] ・NaOH:SiO_2=20mg:10mg ・ER in about 330 deg-C ✧ SiO_2[12] ・NaOH:SiO_2=32mg:24mg ・ER in about 313 deg-C ✧ Aggregate[12] ・NaOH:aggregate=32mg:24mg ・ER in about 313 deg-C	✧ Al_2O_3[8] ・NaOH: Al_2O_3=20mg:20mg ・ER in about 330 deg-C ・residual materials: $NaAlO_2$, Al

ER: Exothermic reaction

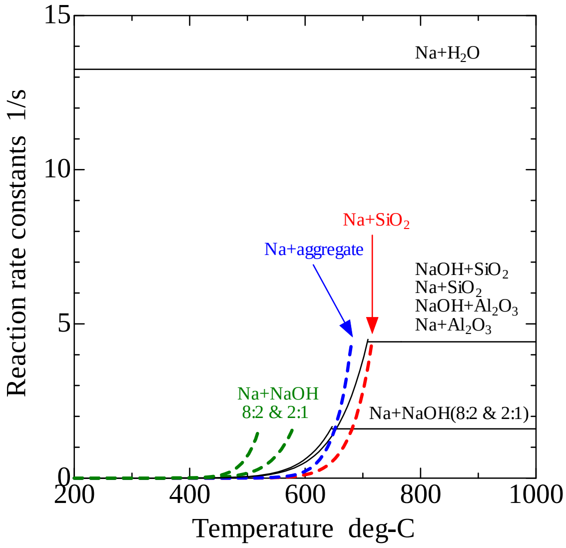

Figure 2 Reaction rates between the sodium and the siliceous concrete compositions

4. COMPARISON BETWEEN CONTAIN-LMR CALCULATION AND EXPERIMENTAL RESULTS

JAEA conducted a lot of the systematic sodium-siliceous concrete reaction experiments and collected the various experimental data [3-5, 13]. In their experiments, the sizes of the siliceous concrete were that ϕ=203 mm in diameter and H=300, 450, 600 and 900 mm in height. In the experiments, the hydrogen release rate was measured, and the total released hydrogen was calculated by integrating the measured hydrogen release rate with time. Several thermocouples were set in the concrete at the position of 20, 40, 70, 150 and 250 mm from the initial concrete surface. The ablation times which indicate the reaching time of the ablation front at the thermocouples were estimated from the threshold temperatures of 530 deg-C to the temperature peaks caused by the heat of chemical reaction. The results of the JAEA's experiments suggested some important knowledge such as following (1) ~ (5);

(1) Reaction threshold temperature: the concrete ablation was unremarkable less than 530 deg-C. The ablation and the released hydrogen were occurred over 530 deg-C.

(2) Concrete ablation: the concrete ablation behavior was like one-dimensional, and the ablation depth was 70 ~ 90 mm for the concrete of 300 and 450 mm in height, and 150 ~ 220 mm for the concrete of 600 and 900 mm in height. The concrete ablation terminated naturally within 24 hours.

(3) Released hydrogen: the containing water in the concrete transferred to the reaction region by heating, reacted with the sodium, and released to the atmosphere as hydrogen. The amount of released hydrogen was about 0.15 kg for the concrete of 300 mm in height and 0.17 ~ 0.22 kg for the concrete of 450, 600 and 900 mm in height.

(4) Temperature: the concrete temperature rose suddenly by the heat of the chemical reaction near the ablation front.

(5) Reaction products: some sodium silicates such as Na_2SiO_3 or Na_4SiO_4 were measured with X-ray diffraction (XRD) technique as the main products in the pool and the ablated concrete region.

The results of the sodium-siliceous concrete reaction experiments were arranged by the concrete heights. We simulated the representative experimental cases of I-8M test (the concrete height: 300 mm), III-1M test (the concrete height: 600 mm), III-3M test (the concrete height: 900 mm) and IV-1M test (the concrete height: 450 mm and the experimental duration: 24 hours) by using the improved SLAM, and compared between the experimental and the calculation results. The main experimental conditions are shown in table 4. Their conditions were reflected to the calculation, and the experimental sodium temperature was used as the boundary condition.

Table 4 Experimental conditions of I-8M, III-1M, III-3M and IV-1M test

Test	I-8M	III-1M	III-3M	IV-1M*
Na mass [kg]	7.6	16	24	25
Duration [hours]	8	8	8	24
Concrete type	Graywacke concrete			
Concrete size	ϕ 203 mm× 300 mmH	ϕ 203 mm× 600 mmH	ϕ 203 mm× 900 mmH	ϕ 203 mm× 450 mmH
Concrete compositions [wt.%]	SiO_2: 73 MgO: 1 CaO: 7 Na_2O: 3 K_2O: 3 Al_2O_3: 7 H_2O: 7			

* Measured H_2O content was 6.2 wt.%

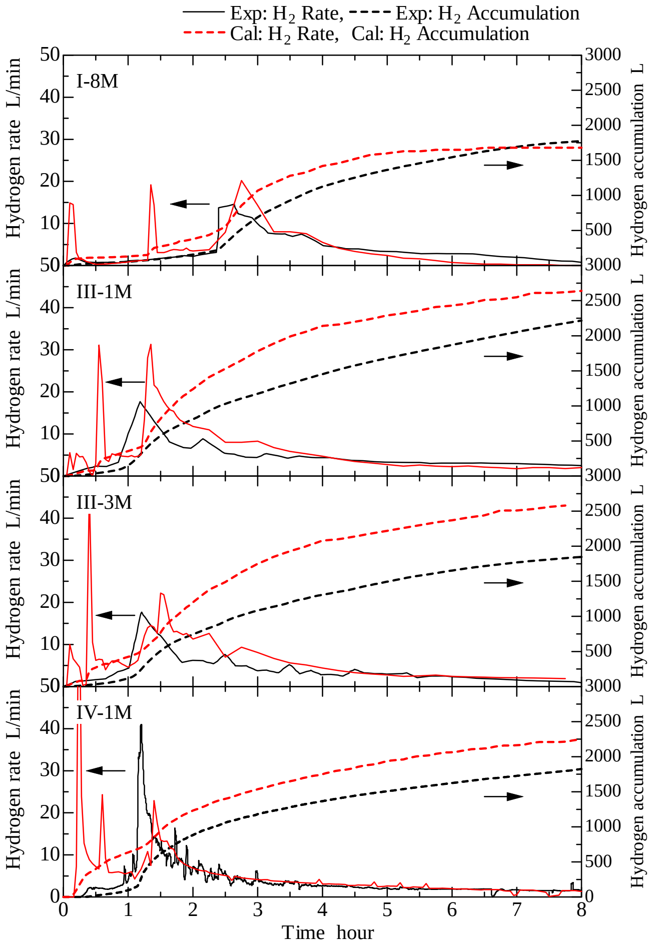

Figure 3 Released hydrogen behaviors in I-8M, III-1M, III-3M and IV-1M test

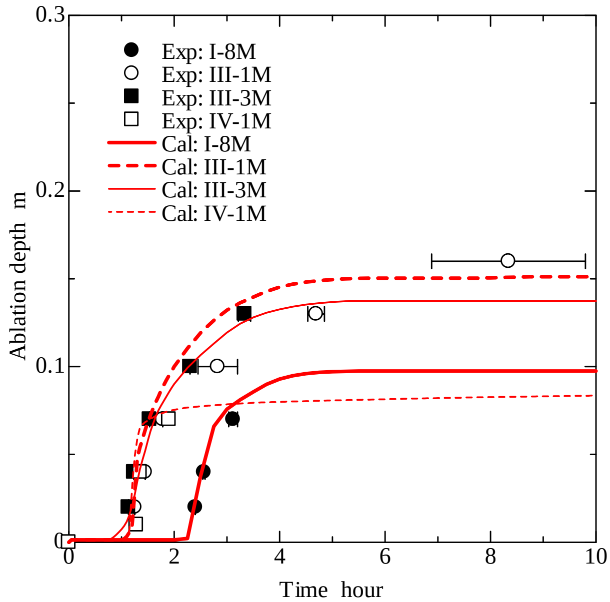

Figure 4 Concrete ablation depth in I-8M, III-1M, III-3M and IV-1M test

Figure 3 and 4 show the experimental and calculation results of the released hydrogen rates and the accumulation, and the concrete ablation depths within 8 hours, respectively.

Figure 5 and 6 show those of IV-1M test within 24 hours. The black solid and dotted lines show the experimental results, and the red ones show the calculation results in the figure 3 ~ 6. The experimental ablation times of the thermocouples were shown by the black points and error bars in the figure 4 and 6. The calculation results gave relatively good agreement with the tendency of the experimental results of all cases.

The calculation results of the released hydrogen rates show the two peaks in the figure 3. The first peak was caused by a heat-conducting concrete and evaporating and transferring the containing water. The second peak was caused mainly by the concrete ablation. The first one was overestimated in comparison with the experiments; the calculated concrete temperatures became comparatively higher than those of the experiments. After the second peak, the released hydrogen rates calculation were reproduced comparatively well.

In the figure 4, the concrete ablation was unremarkable until the concrete temperature reached to the reaction threshold temperature of 530 deg-C, however once the temperature reached to the reaction threshold temperature, the ablation velocity increased suddenly. This reason was that although their chemical reactions rarely happened at the ablation front under the condition of the less than threshold temperature, once the chemical reactions happened actively, and the heat of the chemical reactions heated strongly the B/L region. As the results the reaction rates and the ablation velocity increased suddenly in reaching the threshold temperature. As the time passed, the ablation velocity decreased gradually, and terminated naturally due to the initial concrete heights. The concrete ablation of the experiment and the calculation terminated at about 0.085 m in IV test.

The amount of released hydrogen was overestimated in the early time for the first peak, but the final amount of the released hydrogen shows relatively good agreement with the experiment in the figure 5. The amount of the released hydrogen is almost equivalent to the containing water in the concrete. This reason was why the calculated concrete temperature of the final state became proper. Although it is necessary to improve the release velocity model of the hydrogen in the SLAM for the best-estimation of the transient, the amount of the released hydrogen was able to be performed at the almost same levels of the experiments. In the long-time analysis of 24 hours, the calculation shows relatively good agreement with the experiment.

Figure 7 shows the concentration distribution of the major components which were calculated by the improved SLAM in CONTAIN-LMR code and referred to the experimental data in IV test [13]. The chemical reaction products were distributed at the whole of the pool and the ablated concrete region. These reaction products were sampled and analyzed with XRD technique. The XRD results showed the main reaction products were not the sodium aluminate but the sodium silicates such as Na_2SiO_3 and Na_4SiO_4 in the all samples. These results suggested $Na+SiO_2$ and $NaOH+SiO_2$ reactions were dominant, either. Further SiO_2 was observed as a main component at the ablation front. The liquid sodium wasn't able to transfer to the ablation front, and the concrete ablation terminated naturally for the sedimentation effect of the reaction products. As a fact, the sodium concentration decreased rapidly in the B/L layer. The improved SLAM in CONTAIN-LMR code simulated these diffusional behaviors, and reproduced the termination of the concrete ablation.

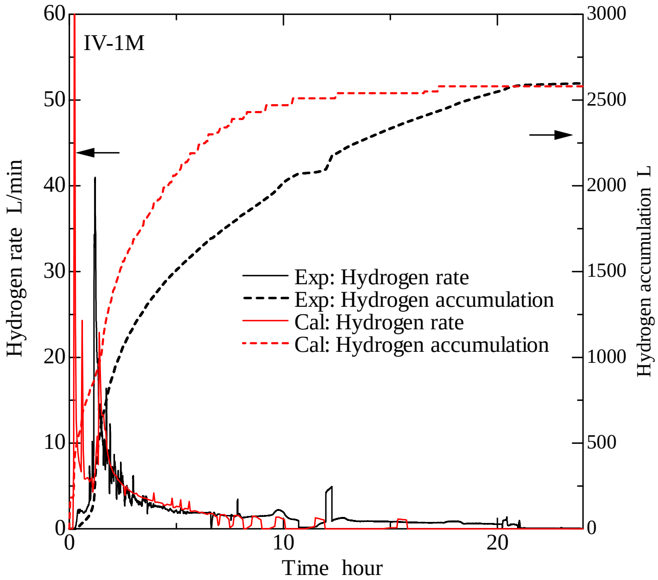

Figure 5 Released hydrogen behaviors in IV-1M test

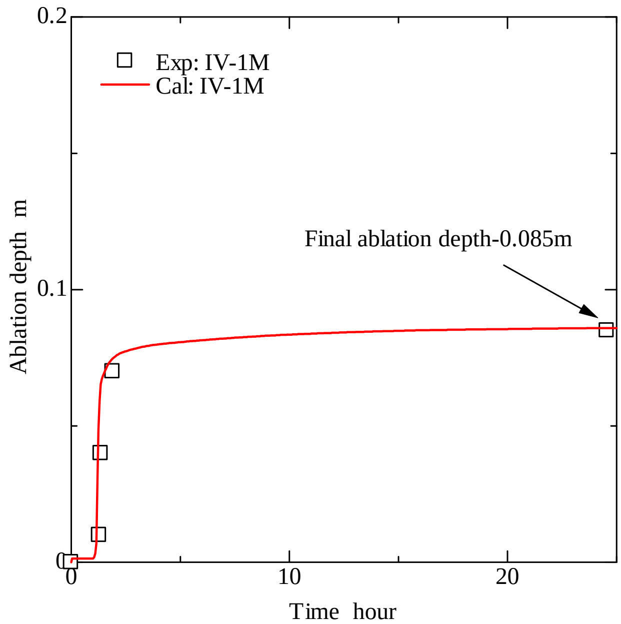

Figure 6 Concrete ablation depth in IV-1M test

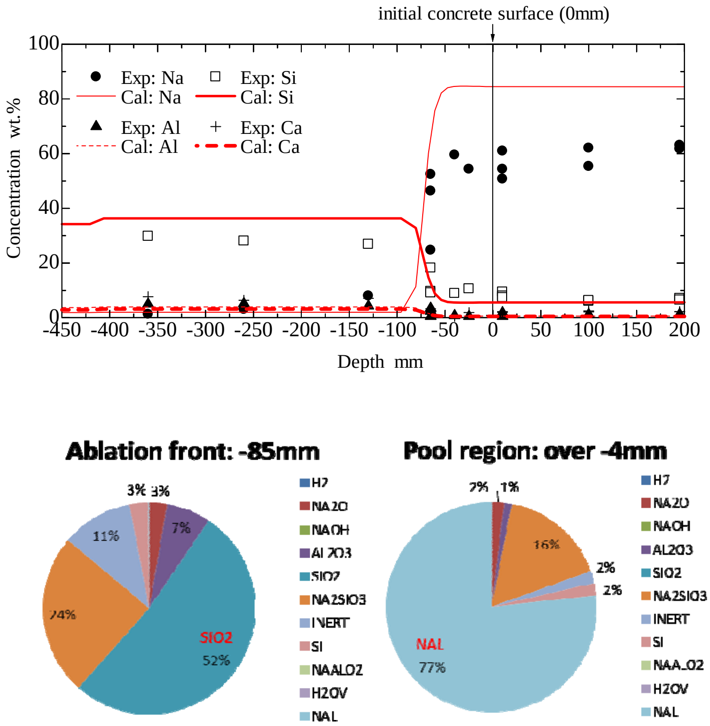

Figure 7 Calculation results of the materials distribution in IV-1M test after 24 hours

6. CONCLUSIONS

A computer code, CONTAIN-LMR, is an integrated analysis tool to predict the consequence of severe accident in liquid metal fast reactors. A sodium-concrete reaction behavior is one of the most important phenomena in the accident. The installed original SLAM application is limited to the reaction between sodium and limestone concrete. For the difference of the main composition between the limestone and siliceous concrete, JAEA has been collecting the experimental data and improving the SLAM such as adding the proper chemical reactions kinetics equations in consideration of the original SLAM parameters and the results of the thermal analysis experiments.

In this study, the chemical reaction kinetics models between sodium and the compositions of the siliceous concrete are discussed to apply the SLAM to the siliceous concrete. Furthermore, we calculated the series of sodium-siliceous concrete reaction experiments which were conducted in JAEA by using the improved SLAM, compared the calculation results and the experimental results.

The calculated concrete ablation behaviors showed relatively good agreement with the experimental results. Especially the long-time behavior terminated the naturally at the approximately 85 mm of the experiment within 24 hours. Although it is necessary to improve the released hydrogen velocity model of the SLAM for the best-estimation of the transient, the amount of the released hydrogen was able to be performed at the almost same levels of the experiments. As a whole it has been found that relatively good agreement between analysis and experimental results is obtained and the CONTAIN-LMR code has been validated with regard to sodium-concrete reaction phenomena.

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