Kinetic Study of Sodium-Water Surface Reaction by Differential Thermal Analysis*

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Abstract
In a sodium-cooled fast reactor (SFR), if a heat transfer tube in the steam generator (SG) is failed, high pressurized water vapor blows into the liquid sodium and sodium-water reaction (SWR) takes place. SWR may cause damage to the neighboring heat transfer tubes by thermal and chemical effects. Therefore, it is important to clearly understand the SWR for safety assessment of the SG. From recent study, sodium (Na)–sodium hydroxide (NaOH) reaction as secondary surface reaction of the SWR phenomena in a SFR was identified by ab initio (first-principle) method. However, kinetics of this reaction is a still open question. Thus, it is important to obtain quantitative rate constant of sodium monoxide (Na₂O) generation by Na-NaOH reaction because Na₂O may accelerate the corrosive and erosive effects. Differential thermal analysis (DTA) provides us with the valuable information on the kinetic parameters, including activation energy, pre-exponential factor (frequency factor) and reaction rate constant. In this work, kinetic study of Na–NaOH reaction has been carried out by using DTA technique. Based on the measured reaction temperature, the first-order rate constant of Na₂O generation was obtained by the application of the laws of chemical kinetics. From the estimated rate constant, it was found that Na₂O generation should be considered during SWR. The results can be the basis for developing a chemical reaction model used in a multi-dimensional sodium-water reaction code, SERAPHIM, being developed by the Japan Atomic Energy Agency (JAEA) toward the safety assessment of the SG in a SFR.

Key words: Fast Reactor, Sodium Water Reaction, Chemical Kinetics

1. Introduction
In a SFR, liquid sodium is used as coolant to transfer the energy from the reactor core to the SG system for power generation. If a heat transfer tube in the SG is failed, high pressurized water vapor blows into the liquid sodium and the SWR takes place. The extremely high-temperature reaction jet formed by the SWR may cause damage to the neighboring heat transfer tubes by thermal and chemical effects. Therefore, it is important to clearly understand the SWR for safety assessment of the SG.

In the past, large amount of experiments of the SWR were performed in the former JAEA. However, the SWR is generally complex and the experimental measurement technologies have not been matured enough to unroll the reaction mechanism in detail. With regard to the chemical effect, it was inferred that the reaction products were NaOH, Na₂O, sodium hydride (NaH) and so on from the X-ray diffraction (XRD) analysis of the residues after the experiment (1). However, it was difficult to even identify the major reaction
products and understand the reaction mechanism during the SWR. Thus, to study the reaction mechanism is an integral part of clarification on the SWR.

Currently, the JAEA has been developing a multi-dimensional sodium-water reaction code, SERAPHIM (Sodium-watEr Reaction Analysis PHysics of Interdisciplinary Multi-phase flow) for the analytical evaluation of this reaction (2). In SERAPHIM code, the surface and gas-phase reactions are considered. The water vapor reacts with the liquid sodium, and the reaction occurs at their interface (surface reaction). Subsequently, the chemical reaction heating vaporizes the liquid sodium, causing the gas-phase reaction. Regarding the gas-phase reaction, some works have been reported from both experimental and theoretical sides (2) (3) (4).

On the other hand, the study of the surface reaction is quite scarce, due to the experimental difficulty of the real-time observation of the surface reaction which is extremely-rapid. Thus, the authors recently studied the surface reaction mechanism in the SWR by using \textit{ab initio} calculations (5). Based on the calculation results, we found the reaction pathways in the SWR as follows;

\begin{equation}
\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 \quad (1)
\end{equation}

\begin{equation}
\text{Na} + \text{NaOH} \rightarrow \text{Na}_2\text{O} + \frac{1}{2}\text{H}_2 \quad (2)
\end{equation}

And also, the estimated rate constant of reaction formula (1) was much larger than that of reaction formula (2). However, it is not clear that Na\textsubscript{2}O by reaction formula (2) can be generated during SWR due to unknown quantitative reaction rate. Thus, it is significant to obtain the quantitative rate constant of Na\textsubscript{2}O generation. Because Na\textsubscript{2}O is suspected to accelerate the corrosive and erosive effects, whose phenomenon is so-called wastage.

In this work, we tried to obtain the rate constant of Na\textsubscript{2}O generation as the secondary surface reaction in the SWR by using DTA technique. Based on the reaction temperature at different heating rates, rate constant was estimated by the application of the laws of chemical kinetics. XRD analysis of the residues after the experiment was also performed to identify the reaction products such as Na\textsubscript{2}O for reference data.

2. Experimental apparatus

The experimental apparatus and Na and NaOH samples are illustrated in Figure 1, and the experimental conditions are summarized in Table 1.

2.1 Equipment

All DTA analyses were carried out on a SETARAM model SETSYS Evolution 24 of TG/DTA equipment under a 100 ml/min argon (Ar) flow as a carrier gas, in Tungsten (W) / Rhenium (Re) detector as shown in Fig. 1. The samples can be heated up to the desired temperatures with graphite heater. The obtained data were processed by using SETSYS 2000 software. Data sampling rate was set to 1 point /s.

2.2 Specimen preparation

NaOH (99 wt%, Merk) and Na (99 wt%, Kanto Chemical) were used as samples without further purification. All samples were stored in a glove box under an Ar atmosphere, which is controlled under the pressure of ~2.0 mbar(g) (0.0002 MPa(g)). NaOH samples were prepared by mortar, and Na samples were cut into about 2 mm diameter pieces by paper cutter. Alumina (Al\textsubscript{2}O\textsubscript{3}) of 31.6 mg was used as a reference, whose melting point is about 2327 K, which is sufficiently high against the maximum heating temperature. These samples and reference were put in sample containers made of SUS304L, whose depth and
inner diameter are 7.5 mm and 4.0 mm, respectively.

The preliminary experiment was performed to confirm the behavior of Na and NaOH, including the melting points of Na and NaOH, the phase transition temperature of NaOH and the reactivity of the sample container with Na or NaOH. In this experiment, the mass of Na and NaOH were set to 18.4 mg and 8.0 mg, respectively as shown in Table 1.

On the other hand, with regard to Na-NaOH reaction experiment, the volume fraction of Na:NaOH was set to 4:1 and 2:1, which corresponds to 18.4 mg:8.0 mg and 18.4 mg:16.0 mg, respectively. We put the Na sample underneath the NaOH sample to suppress the evaporation of Na, whose evaporation temperature is around 1156 K as shown in Fig. 1.

### 2.3 DTA analysis

In the preliminary experiment, each sample was subjected to the temperature range of 298-773 K at heating rates of 3, 5, 7 and 10 K/min as shown in Table 1. One of the Na samples was subjected to the temperature range of 298-1073 K to confirm the evaporation of Na. With regard to Na-NaOH reaction experiment, each sample was subjected to the temperature range of 298-773 K at heating rates of 2, 3, 5, 7 and 10 K/min.

In addition, measurement deviation is less than one percent of temperature of measurement materials, which is confirmed by temperature correction test.

### 2.4 X-ray diffraction (XRD) analysis

XRD patterns were obtained by a Rigaku model RINT2500HL diffractometric apparatus in the $2\theta = 5$ to 90° range and scan rate of 0.02°s$^{-1}$. X-ray diffractometer with Cu radiation (50 kV, 250 mA) was used to identify structural/compositional changes. International Centre for Diffraction Data (ICDD) was used to identify the peak from the measured profiles. Each sample was prepared under inert atmosphere of Ar.

| Table 1 Experimental conditions |
|---------------------------------|
|                                |
| **Reaction experiment**         |
|                                |
| Na:NaOH (Volume fraction)      |
| 4:1                            |
| 2:1                            |
| **Preliminary experiment**      |
|                                |
| Na                              |
| NaOH                            |
| Pure                            |
| Pure                            |
| **Pressure in reaction chamber [MPa]** | 0.1 |
| **Na mass (sample) [mg]**       | 18.4  |
| **NaOH mass (sample) [mg]**     | 8.0   |
| **Al$_2$O$_3$ (reference) [mg]** | 31.6  |
| **Sample container material**   | SUS304L |
| **Carrier gas flow rate (Ar) [ml/min]** | 100 |
| **Heating rate [K/min]**        | 2,3,5,7,10 |
| **Temperature range [K]**       | Room temp.~773 (Partially room temp. ~1073) |
3. Theoretical consideration

We have estimated the activation energy and pre-exponential factor (frequency factor) for rate constant of Na-NaOH reaction based on the measured reaction temperature data by using kinetic methods.

3.1 Kissinger method

Kissinger method (6) is one of the derivative kinetic laws based on the Arrhenius equation by using several measured reaction temperatures at different heating rates. The equation of reaction rate is described as follows;

\[ \frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A(1-\alpha)^n \exp \left( -\frac{E_a}{RT} \right) \]  \hspace{1cm} (3)

where \( \beta \), \( A \), \( R \), \( E_a \), \( T \), \( \alpha \), \( n \) are the heating rate, the frequency factor, the gas constant, the activation energy, the temperature, the reacted fraction, and the empirical order of reaction.

If the temperature rises during the reaction, the reaction rate \( d\alpha/dt \) will rise to a maximum value, then return to zero as the reactant is exhausted. The maximum rate occurs when \( d(d\alpha/dt)/dt \) is zero. If the temperature rises at a constant heating rate \( \beta \), then by differentiation of Equation (3), we obtain

\[ \frac{d}{dt} \left( \frac{d\alpha}{dt} \right) = \frac{d\alpha}{dt} \left[ \frac{E_a\beta}{RT^2} - An(1-\alpha)^{-1} \exp \left( -\frac{E_a}{RT} \right) \right] \]  \hspace{1cm} (4)

The maximum rate occurs at a temperature \( T_m \) defined by setting Equation (4) equal to zero. Then, we obtain

\[ \frac{E_a\beta}{RT_m} = An(1-\alpha)_m^{-1} \exp \left( -\frac{E_a}{RT_m} \right) \]  \hspace{1cm} (5)
When the empirical order of reaction is one, Equation (5) is expressed as follows:

\[ \frac{E_a \beta}{RT_w} = A \exp \left( -\frac{E_a}{RT_w} \right) \]  

(6)

With data collected in a series of measurements performed with the different heating rates \( \beta \), it ensues from the above equation that the dependence \( \ln(\beta/T_w^m) \) vs \( 1/T_w \) will be linear with a slope \( m_\beta = -E_a/R \) and the intercept as frequency factor, whose plot is so-called Kissinger plot. Then, from this plot, activation energy is obtained as follows:

\[ E_a = -m_\beta R \]  

(7)

### 3.2 Ozawa method

In order to validate the estimated activation energy by Kissinger method, we also evaluated the kinetics by using Ozawa method (7) which is one of the integrated kinetic law shown as follows:

\[ \log \beta = \log \frac{AE_a}{f(\alpha)} - 2.315 - 0.4567 \frac{E_a}{R} \left( \frac{1}{T_m} \right) \]  

(8)

where \( \beta \), \( A \), \( R \), \( E_a \), \( T_m \), \( \alpha \), \( f(\alpha) \) are the heating rate, the frequency factor, the gas constant, the activation energy, the reaction temperature, the reacted fraction, and the kinetic function.

With data collected in a series of measurements performed with the different heating rates \( \beta \), it ensues from the above equation that the dependence \( \log \beta \) vs \( 1/T_m \) will be linear with a slope \( m_\beta = -0.4567E_a/R \), whose plot is so-called Ozawa plot. Then, from this plot, activation energy is obtained as follows:

\[ E_a = -\frac{m_\beta R}{0.4567} \]  

(9)

### 4. Results and discussion

#### 4.1 Preliminary experiment

##### 4.1.1 Evaporation of pure Na sample

Figure 2 shows thermogravity (TG) profile of pure Na sample with the temperature range of 298-1073 K at a heating rate of 10 K/min. TG profile shows the drastic decrease on the amount of Na from about 873 K. It is indicated that Na starts evaporating at this temperature. Therefore, it is important that maximum heating temperature should be less than about 873 K. In light of this result, we adapted the temperature range of 298-773 K to suppress the evaporation of Na.

##### 4.1.2 Pure Na and NaOH samples testing

DTA curves of pure Na and NaOH samples at around phase change are shown in Figures 3 and 4, respectively, and the peaks measured at different heating rates are summarized in Table 2. In the thermal analysis such as DTA, physical properties on phase change, including melting point, freezing point and phase transition temperature are not top of the peaks but onset points. On the other hand, reaction temperature \( T_m \) becomes top of the peak from Eq. (5) as mentioned before.

In the DTA curves of pure Na samples, for each heating rate, the endothermic peaks (onset points) at around 371-374 K were identified, which nearly correspond to the melting point according to JANAF data (8). And with regard to the DTA curves of pure NaOH
samples, two endothermic peaks (onset points) at around 563 K and 589 K were identified, which are consistent with the phase transition temperature and the melting point, respectively (9).

Besides, there were no outstanding endothermic and exothermic peaks in the DTA curves with temperature range of 298-773 K, which indicates no reaction between the sample containers made of SUS304L and Na or NaOH samples. From this result, we confirmed the applicability of the sample containers against strong corrosive materials such as Na and NaOH.

Table 2 Endothermic peaks in Na and NaOH samples testing

| Heating rate [K/min] | 3     | 5     | 7     | 10    |
|----------------------|-------|-------|-------|-------|
| Endo.peak of Na testing [K] | 371.0 | 371.2 | 372.5 | 374.0 |
| 1st endo.peak of NaOH testing [K] | 563.9 | 564.3 | 563.4 | 563.4 |
| 2nd endo.peak of NaOH testing [K] | 589.8 | 590.0 | 588.2 | 589.4 |

Fig. 2 TG profile of pure Na up to 1073K at 10 K/min

Fig. 3 DTA curves of pure Na samples
4.2 Na-NaOH reaction experiment

In cases of Na:NaOH=4:1 and 2:1, DTA curves of Na-NaOH reaction with the temperature range of 298-773 K at a heating rate of 5 K/min are shown in Figures 5 and 6, respectively. In both DTA curves, melting point of Na and NaOH, and phase transition temperature of NaOH were identified at 371, 584, and around 563 K, respectively as well as the results of the preliminary experiment. The melting point of NaOH is lower than that of pure NaOH sample testing because purity of NaOH is suspected to be lower by mixing up with Na. In addition to physical properties on phase change, including melting points and phase transition temperature, one endothermic peak and one exothermic peak were observed in both cases. In Figs. 5 and 6, endothermic peaks were around 685 K. It is inferred that the endothermic peaks are chemical decomposition of NaH as shown in reaction formula (10), whose temperature is consistent with about 685 K from some previous works \(^{(10)}\) \(^{(11)}\).

\[
\text{NaH} \rightarrow \text{Na} + \frac{1}{2} \text{H}_2 \quad (T > 685 \text{ K}) \quad (10)
\]

On the other hand, exothermic peaks at the same heating rate were around 664 K and 674 K in Figs. 5 and 6, respectively. Na-NaOH reaction is exothermic over the melting point of NaOH according to JANAF data. Thus, these exothermic peaks are considered as reaction temperature. As mentioned before, Na\(_2\)O could be generated by overall reaction formula (2). However, from thermal analysis, NaH generation should be considered below its decomposition temperature as well as Na\(_2\)O generation. Therefore, overall reaction is considered as follows;

\[
2\text{Na}^+ + \text{NaOH} \rightarrow \text{Na}_2\text{O} + \text{NaH} \quad (T < 685 \text{ K}) \quad (11)
\]

Variation of exothermic peaks at the same heating rate was identified from Figs. 5 and 6. In general, peaks of DTA curve at constant heating rate appear at higher temperature if reaction rate is slower. Because, it takes a certain time to return to the baseline from the onset of reaction in the DTA curve. Thus, it is assumed that reaction rate is slower in case of lower volume fraction of Na against NaOH.

DTA curves around the exothermic peak in cases of Na:NaOH=4:1 and 2:1, are shown in Figures 7 and 8, respectively. And the exothermic peaks, which were measured four times in each heating rate, are summarized in Table 3. From both DTA curves, it is observed that increasing heating rates shift the exothermic peaks to higher temperature. From Table 3, in case of Na:NaOH=4:1, exothermic peaks appeared from heating rate of 10K/min. However, in case of Na:NaOH=2:1, exothermic peaks appeared from heating rate of 5K/min. In thermal analysis, we should arrange appropriate heating rate against reaction phenomena. Otherwise, it is impossible to measure the reaction temperature when reaction rate is slow in...
comparison with heating rate. From Table 3, heating rate is too high for the case of Na:NaOH=2:1 to measure the reaction temperature at 7 or 10 K/min. This indicates that reaction rate in case of Na:NaOH=2:1 is slower than that of Na:NaOH=4:1 as shown in the exothermic peaks at 10 K/min. In light of these results, it is considered that reaction rate is slower in case of lower volume fraction of Na against NaOH as well as finding from Figs. 5 and 6. As for decomposition temperature, there was little change on values at different heating rates in both cases. It is inferred that the reaction rate on decomposition of NaH is quite rapid.

Table 3 Exothermic peaks in Na-NaOH reaction experiment

| Heating rate  | 2  | 3  | 5  | 7  | 10 |
|---------------|----|----|----|----|----|
| Na:NaOH=4:1   | 656.8 | 663.4 | 669.3 | 676.2 |
|               | 656.2 | 664.5 | 669.5 | 678.0 |
|               | 655.9 | 664.6 | 670.1 | 676.0 |
| Na:NaOH=2:1   | 654.8 | 664.3 | 669.6 | 677.1 |
|               | 654.4 | 662.7 | 672.6 | -    |
|               | 656.1 | 660.3 | 673.9 | -    |
|               | 653.0 | 661.2 | 673.9 | -    |
|               | 655.5 | 662.1 | 674.5 | -    |

Fig. 5 DTA curve up to 773K at 5K/min (Na:NaOH=4:1)

Fig. 6 DTA curve up to 773K at 5K/min (Na:NaOH=2:1)
4.3 XRD analysis

The X-ray diffraction (XRD) patterns for the residues after Na-NaOH reaction are shown in Figures 9 and 10. Na, NaOH and Na₂O as major chemical species were observed from XRD analysis except NaH. Combined with the DTA results, it is assumed that NaH will be decomposed around 685 K just after Na-NaOH reaction as shown in reaction formula (10), though both Na₂O and NaH initially can be generated by Na-NaOH reaction as shown in reaction formula (11). Therefore, it is inferred that only Na₂O will be identified as reaction product at higher temperature reaction zone caused by SWR. Though it is impossible to define the yield of Na₂O from the results of XRD, it is considered that the rate of Na-NaOH reaction is less than 100% at least from residual Na and NaOH.

In addition, the broad peaks such as A and B can be identified in Figs. 9 and 10. It is believed that these peaks are originated from a sample holder made of glass and silicon grease for sample fixing, which are amorphous not a crystal structure.

In cases of Na:NaOH=4:1 and 2:1, the DTA curves of Na-NaOH reaction with the temperature range of 298-773 K at a heating and cooling rate of 5 K/min are shown in Figures 11 and 12, respectively. In both Figures, freezing points of Na and phase transition temperature of NaOH are observed at the cooling process. These results indicate that there are some residual Na and NaOH, which is consistent with the results of XRD analysis as mentioned before. Besides, it was found that the reaction temperature and recombination to NaH were not identified at the cooling process, which indicates that the reaction might be irreversible.
Fig. 9 XRD analysis (Na:NaOH=4:1)

Fig. 10 XRD analysis (Na:NaOH=2:1)

(a) Heating process
(b) Cooling process

Fig. 11 DTA curves (5K/min, Na:NaOH=4:1)

(a) Heating process

(b) Cooling process

Fig. 12 DTA curves (5K/min, Na:NaOH=2:1)
4.4 Rate constant

Kissinger plot and Ozawa plot with the temperature range of 298-773 K at several heating rates from 2 to 10 K/min in cases of Na:NaOH of 4:1 and 2:1 are shown in the Figures 13 and 14, respectively. We used the least squares method for approximation of these plots. Based on these liner plots, kinetic parameters such as activation energy $E_a$ and frequency factor $A$ were estimated by using Kissinger method as shown in Table 4. In case of Na:NaOH=4:1, the activation energy and frequency factor were 202 kJ/mol and $3.2\times10^{13}$ s$^{-1}$, respectively. And in case of Na:NaOH=2:1, the activation energy and frequency factor were 161 kJ/mol and $1.2\times10^{10}$ s$^{-1}$, respectively.

![Fig. 13 Kissinger plot (Na:NaOH=4:1 and 2:1)](image)

![Fig. 14 Ozawa plot (Na:NaOH=4:1 and 2:1)](image)

| Parameters for Arrhenius equation | Na:NaOH (Volume fraction) |
|-----------------------------------|---------------------------|
|                                   | 4:1                       | 2:1                       |
| $E_a$ [kJ/mol]                    | 202 (202*)                | 161 (164*)                |
| $A$ [s$^{-1}$]                    | $3.2\times10^{13}$        | $1.2\times10^{10}$        |

*value estimated by Ozawa method
We also estimated the activation energy by using Ozawa method. As a result, the activation energy came to 202 kJ/mol and 164 kJ/mol in cases of Na:NaOH=4:1 and 2:1, respectively. These are in good agreement with the values estimated by Kissinger method. In light of these results, both activation energy and frequency factor are smaller when volume fraction of Na against NaOH is getting lower.

Table 5 shows the first-order rate constant of Na₂O generation by Na-NaOH reaction at the temperature of 773 K. At present, there is limited knowledge on the rate constant of Na₂O generation. Kong et al., investigated the kinetics of NaOH decomposition under the environment of the liquid sodium in the MEPHYSTO experiment (12). Here, we referred to the Kong’s correlation equation for Na₂O generation, whose frequency factor $A$ and activation energy $E_a$ have been reported to be $2.1 \times 10^4$ s⁻¹ and 51.5 kJ/mol, respectively.

In both cases of Na:NaOH=4:1 and 2:1, the order of the rate constants are smaller than the values estimated by Kong’s correlation equation. With regard to Kong’s experiment, NaOH was injected in the liquid sodium with velocity of about 1 m/s. On the other hand, nature of thermal analysis is more static in comparison with Kong’s experiment. Thus, agitation effect in the Kong’s experiment is suspected to affect rate constant by increasing collisions of the amount of reactants. In case of Na:NaOH=2:1, the rate constant is slightly smaller than that of Na:NaOH=4:1. However, the order of the rate constant is $10^{-1}$ at the temperature of 773 K. As timeframe of SWR is over several tens of seconds, this result indicates high possibility of Na₂O generation during SWR. Besides, it is assumed that the rate constant of Na₂O generation is getting large in accordance with Arrhenius equation when the temperature is raised over 773 K.

| Temperature [K] | Na:NaOH (Volume fraction) | Kong’s experiment (12) |
|----------------|---------------------------|------------------------|
| 773            | 4:1 7.8×10⁻¹              | 7.1                    |
|                | 2:1 1.5×10⁻¹              |                        |

4.5 Proposal of chemical reaction model

Based on the results of thermal analysis and XRD analysis, chemical reaction model for Na₂O generation should be considered. According to the result of thermal analysis, NaH and Na₂O initially could be generated during Na-NaOH reaction as shown in reaction formula (11). However, combined with the result of XRD analysis, NaH will be decomposed at around 685 K just after Na-NaOH reaction from DTA curves as shown in reaction formula (10). It is assumed that NaH will be decomposed in the SG of a SFR, whose operation temperature of sodium side is over 773 K. Therefore, initial overall reaction is expressed as reaction formula (11).

It is better to simplify the chemical reaction model in terms of installing the present SERAPHIM code. The rate of reaction formula (11) is expressed in Equation (12) due to the second-order reaction.

$$\frac{d[Na_2O]}{dt} = k[NaOH][Na]^2$$  \hspace{1cm} (12) 

where $\frac{d[Na_2O]}{dt}$, $k$, $[NaOH]$, $[Na]$ are the generation rate of Na₂O, rate constant, concentrations of NaOH and Na, respectively.

However, rate constant estimated from thermal analysis is the basis of the first-order reaction. Now, considering actual SWR environment, amount of Na is much larger than those of water and reaction product such as NaOH by SWR. Thus, we assumed the pseudo first-order reaction approximation as follows;

$$\frac{d[Na_2O]}{dt} = k[NaOH]$$  \hspace{1cm} (13)

In light of assumption, first-order of Arrhenius type rate constant for Na-NaOH reaction
model was employed in SERAPHIM code. For kinetic parameters, frequency factor $A$ and activation energy $E_a$ in case of Na:NaOH=2:1 would be considered based on the molar fraction of overall reaction formula (11).

5. Conclusions

In this work, we studied the kinetics of Na–NaOH reaction as secondary surface reaction in the SWR by using DTA technique. Melting points of Na and NaOH, phase transition temperature of NaOH, Na–NaOH reaction temperature, and the decomposition temperature of NaH were identified from DTA curves. Na, NaOH, and Na$_2$O as major chemical species were identified from the XRD analysis of the residues after the DTA experiment. It was inferred that Na$_2$O could be generated as Na-NaOH reaction product.

Based on the measured reaction temperature, the first-order Arrhenius type rate constant of Na$_2$O generation and these related kinetic parameters were obtained by the application of kinetic laws. According to this kinetic study, it was found that Na$_2$O generation should be considered during SWR.

These results can be the basis for the surface reaction model in developing SERAPHIM code. It is expected that this improved reaction model allows more reasonable safety assessment of the steam generator by reproducing more realistic wastage environment and its affected area.

Nomenclature

\[ \begin{align*}
\beta &: \text{ heating rate, [K/s]} \\
A &: \text{ frequency factor, [s}^{-1}] \\
R &: \text{ gas constant, [kJ/mol \cdot K]} \\
E_a &: \text{ activation energy [kJ/mol]} \\
T &: \text{ temperature, [K]} \\
\alpha &: \text{ reacted fraction, [-]} \\
k &: \text{ rate constant, [s}^{-1}] \\
\end{align*} \]

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