Evaluation of the *Na-CO₂* chemical reaction and its consequences for a SFR system employing a supercritical *CO₂ Brayton cycle*

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1. Introduction

The supercritical *CO₂ Brayton cycle* option for an effective energy conversion of a sodium-cooled fast reactor (SFR) has been highlighted recently due to its high thermal efficiency and its potential compactness of the BOP equipments (small-sized turbo-machineries). Moreover, the proposed option is very attractive from the aspect that it can achieve a more reliable system design completely free from an essential risk of the sodium-water reaction (SWR) phenomena possibly occurring in a conventional Rankine cycle energy conversion system.

Although this advanced option may have many advantages for its plant design, basic concerns regarding the potential tube rupture of a *Na-CO₂* heat exchanger that would initiate a high-pressure blowdown of *CO₂* gas into the shell-side liquid sodium should be considered. In a previous study, Latge et al. [1] claimed that the chemical interaction between a supercritical *CO₂* and liquid sodium has less serious potential risks than those of a SWR. However, the consequences of this chemical interaction between supercritical *CO₂* and liquid sodium need to be evaluated to achieve a more feasible and reliable system design.
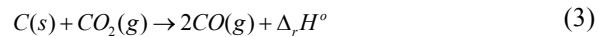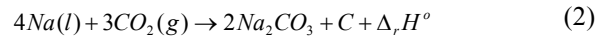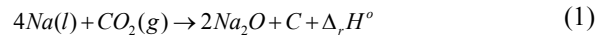
In this study, a detailed chemical reaction model and related system models to simulate the extremely complex thermodynamic behaviors coupled with this chemical reaction were developed and a computer code, STASCOR (System Transient Analyzer for Sodium and Carbon-diOxide Reaction) was formulated by implementing the developed analysis models. Overall long-term behaviors of the *Na-CO₂* chemical reaction and its consequences which lead to a system pressure transient during a tube rupture event were also evaluated for the KALIMER-600[2] employing a supercritical *CO₂ Brayton cycle*.
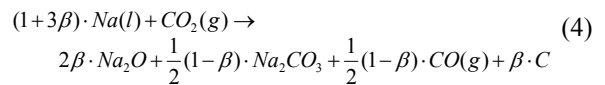
2. Analysis model description

2.1 Basic chemical reaction model

When superitical *CO₂* is injected into the shell-side liquid sodium during a tube rupture event occurring at a *Na-CO₂* heat exchanger, various intermediate or elementary chemical reactions should be taken into account. In order to model these complex chemical reaction phenomena, major reactions for the *Na-CO₂* interactions were obtained by using chemical equilibrium calculations [3]. As a result, the following reactions are generally accepted as representing the *Na-CO₂* interaction for an excessive sodium environment.

$$4Na(l) + CO_2(g) \rightarrow 2Na_2O + C + \Delta_r H^o \qquad (1)$$

$$4Na(l) + 3CO_2(g) \rightarrow 2Na_2CO_3 + C + \Delta_r H^o \qquad (2)$$

$$C(s) + CO_2(g) \rightarrow 2CO(g) + \Delta_r H^o \qquad (3)$$

Eqns (1) and (2) are the spontaneous and exothermic reactions, but Eqn.(3) is an endothermic reaction. The major reaction products are commonly *Na₂O*, *Na₂CO₃*, *C* and *CO*. At lower temperature conditions below 450 ~ 500ºC, *Na₂O* is dominantly produced but *Na₂CO₃* and carbon are usually extracted above 500ºC. As a secondary reaction, Eqn.(3) could occur and produce *CO* gas for a higher temperature range above 1000ºC. Therefore the representative reactions could be combined with a reaction frequency coeff. as follows

$$(1+3\beta) \cdot Na(l) + CO_2(g) \rightarrow$$
$$2\beta \cdot Na_2O + \frac{1}{2}(1-\beta) \cdot Na_2CO_3 + \frac{1}{2}(1-\beta) \cdot CO(g) + \beta \cdot C \qquad (4)$$

The reaction frequency coefficient, β is not a constant but it was obtained by using the results of the chemical equilibrium calculations as a function of the temperature.

2.2 Exothermic heat generation model

The exothermic reaction heat generation for the *Na-CO₂* interaction was also modeled since it is one of the most significant sources for a system transient during a tube rupture accident. Since a heat of reaction generally depicts enthalpy changes between the given initial and final states of chemical reaction, they may be calculated for any convenient path concerning the following two states of a postulated cooling process from the temperature T(K) to 298K (standard state) and a postulated heat-up process from 298K to T(K).

$$\Delta H_T^o = \Delta H_{298}^o + \sum_{i=products} \left(n_i \int_{298}^{T} C_{P,i}^o dT \right) - \sum_{i=reactants} \left(n_i \int_{298}^{T} C_{P,i}^o dT \right) \qquad (5)$$

Concerning the generation rate of gaseous products (e.g. carbon monoxide), the mass conversion ratio (ξ_{CO}) was obtained from the stoichiometric relations given in the combined reaction of Eqn.(4). From this, the rate of the reaction heat could be obtained as the following equation by reflecting the temperature effect provided in Eqn.(5) for an actual chemical reaction process;

$$Q_R = \xi_{CO} \cdot \dot{m}_{CO_2}^{leak} \cdot \left(\frac{\Delta H_T^o}{M_{CO}} \right) \qquad (6)$$

,where ξ_{CO} and M_{CO} mean the *CO* mass conversion ratio per unit mole of CO_2 and the molecular weight of carbon monoxide, respectively.

2.2 CO_2 leak model

The CO_2 from the ruptured heat exchanger tube is assumed to be promptly blowdown, and the mass flux of CO_2 during this blowdown may or may not be chocked, depending upon the critical pressure ratio (P^*/P_{CO2}). By assuming an ideal gas behavior of CO_2, the following relations govern the mass flux from the failed heat transfer tube of a *Na-CO_2* heat exchanger.

$$G''(t) = \begin{cases} \sqrt{k_c \rho_0 P_0} \cdot \left(\frac{2}{k_c+1} \right)^{\frac{k_c+1}{2(k_c-1)}} & for \left(\frac{P^*}{P_0} \right) \le \left(\frac{2}{k_c+1} \right)^{\frac{k_c}{k_c-1}} \quad (a) \\[3mm] \sqrt{k_c \rho_0 P_0} \cdot \sqrt{ \left(\frac{P^*}{P_0} \right)^{\frac{2}{k_c}} - \left(\frac{P^*}{P_0} \right)^{\frac{k_c+1}{k_c}} } & for \left(\frac{P^*}{P_0} \right) > \left(\frac{2}{k_c+1} \right)^{\frac{k_c}{k_c-1}} \quad (b) \end{cases} \qquad (7)$$

where $G''(t)$ is the mass flowrate per unit area with the dimension of [$kg\text{-}sec^{-1}\text{-}m^{-2}$]. The tube-side CO_2 pressure is assumed to be constant over the course of the calculation. Eqn.(7-a) is used to evaluate the blowdown mass flux when the flow is not chocked, while Eqn.(7-b) is applicable for the chocked flow condition. By reflecting the design criterion related the number of guillotine tube breaks, the nominal mass flow rate of the ruptured tube could be determined by using Eqn. (8).

$$\dot{m}_{leak} = N_{DEGB} \times (2 \times A_{leak}) \cdot G''_{crit} \qquad (8)$$

3. Evaluation of the HX tube rupture event

The system temperature and pressure transients including the pressure relief system are shown in **Fig. 1**. The system pressure gradually increases until a rupture disk (R/D) break, and it promptly decreases to the normal system pressure range with some pressure oscillations. The rupture disk break time is about 17.4 sec after a leak initiation.
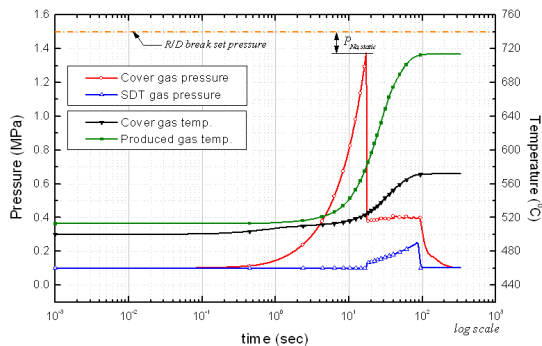

Fig. 1 Temperature and Pressure transient during the tube rupture event

The sodium drain tank (SDT) pressure remains at the initial gas pressure of 0.1 MPa before the rupture disk break, and it slowly rises corresponding to the vented sodium volume increase from the *Na-CO_2* heat exchanger, just after the rupture disk break. However, the pressure increase is relatively small when compared to the system depressurization because the free volume of the inert gas in the SDT is sufficiently large enough to accommodate the entire sodium volume of the IHTS loop including the shell-side *Na-CO_2* heat exchanger. At the end of the reaction period, about 3 minutes after the leak initiation, the shell-side sodium is almost drained and the pressure difference between the system and the SDT becomes very small. The cover gas temperature also gradually increases up to the rupture disk bursting time because its volume is fixed before the rupture disk break. In other words, since the rigid boundary condition is applied to the cover gas region and the exothermic reaction energy flows into the fixed volume with the mass inflow of the gaseous reaction product, the compressible cover gas experiences a drastic pressure and temperature transient. However, after the rupture disk break, the cover gas volume is expanded and a moving boundary condition is applied to the region, so the temperature increment appears to be very slow or almost diminishes due to the net effects between the energy term added by the gaseous reaction product generation and the volume expansion term for an adiabatic system.

3. Conclusions

For the evaluation of the *Na-CO_2* chemical reaction possibly occurring at the *Na-CO_2* heat exchanger of KALIMER-600 employing a supercritical CO_2 Brayton cycle, the computer code STASCOR was developed by reflecting detailed chemical reaction processes and various system models. The design characteristics of the pressure relief system and R/D performance were evaluated, and it was demonstrated that the numerical method developed in the present study is practicable for simulating the complex phenomena of the *Na-CO_2* interaction in an advanced SFR energy conversion system.

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