Preliminary Studies of Na_2CO_3 Elimination from Na/CO_2 Reaction in S-CO_2 Power Cycle coupled to SFR System

Hwa-Young Jung [a,b], Jeong Ik Lee [a*], Myung-Hwan Wi [b]
[a] *Dept. Nuclear & Quantum Eng., KAIST. 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea*
[b] *Div. Fast Reactor Technology Demonstration, KAERI, 1045, Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Republic of Korea*
**Corresponding author: jeongiklee @kaist.ac.kr*

1. Introduction

Among the Generation IV Nuclear Reactors, sodium-cooled fast reactor (SFR) has been actively developed. SFR has an advantage of successfully reusing the spent fuel efficiently and reducing the total volume of high level radioactive waste. In the past, SFRs have operated successfully with the traditional steam Rankine cycle as a power conversion system. However, the potential sodium-water reaction (SWR) whose chemical reactivity is vigorous and instantaneous has been considered as one of the major safety concerns.

In order to avoid the SWR, the supercritical CO_2 (S-CO_2) Brayton cycle was proposed as a design alternative to the steam Rankine cycle. The S-CO_2 Brayton cycle has good features such as 1) improved thermal efficiency, 2) reduced total plant size by having compact turbomachinery and heat exchangers and 3) relatively simplified cycle layout. However, several technical challenges are still remaining for application of S-CO_2 Brayton cycle to SFR. This is because when the pressure boundary in sodium-CO_2 heat exchanger (HX) fails then leaked CO_2 reacts with sodium, although the SWR is eliminated. The reaction between sodium and CO_2 is much milder than SWR but more complex. The reaction is affected by the reaction temperature and there is the possibility of sodium ignition at very high temperature [1].

So far, some research works on Na/CO_2 reaction has been done. The experiments for Na/CO_2 surface reaction [1], wastage phenomenon and self-plugging of narrow flow channel of Na/CO_2 HXs [2] were successfully conducted in KAERI. CEA proposed the major Na/CO_2 reaction formulas [3] and performed the calorimetric studies [4]. JAEA experimentally investigated reaction behavior of CO_2 with a liquid sodium pool [5].

However, any research works for treatment and removal of reaction products from Na/CO_2 reaction has not been done so far. Generally, when the pressure boundary fails CO_2 will be released to sodium side and the amount of leakage will be depending on the rupture size. CO_2 will react with sodium in the sodium-CO_2 HX. It will lead to an economical problem if the channel is plugged by the solid reaction products of Na/CO_2 reaction. Since the whole system operation should be stopped or some sort of bypass system should be applied to replace the plugged channel, which will affect the system economics. Therefore, it needs a material which can clean up the solid reaction products of Na/CO_2 reaction and contaminated system while minimizing the impact on economics. If there is a material that can act as a cleaning agent, it can be injected into the system or channel and clean the residue of Na/CO_2 reaction easily.

In order to ensure the system economics as well as safety of SFR with S-CO_2 Brayton power conversion system, this study was conducted. The final goal is to find some ways to remove the solid reaction products from Na/CO_2 reaction by conducting simple and basic experiments. This study was performed with the collaboration of Korea Atomic Energy Research Institute (KAERI) and Korea Advanced Institute of Science and Technology (KAIST).

2. Review and Research

In this section theoretical background of Na/CO_2 interaction and research to find method to remove the solid reaction products are described.

2.1 Review of Sodium-CO_2 Interaction

As it was mentioned earlier, the major chemical reaction formulas between liquid sodium and CO_2 have been identified as the following equations from (1) to (4). Each reaction occurs competitively.

$$4Na(l) + CO_2(g) \rightarrow 2Na_2O(s) + C(s) + \Delta H^\circ \qquad \Delta H^\circ = -442.3kJ/mol \tag{1}$$

$$4Na(l) + 3CO_2(g) \rightarrow 2Na_2CO_3(s) + C(s) + \Delta H^\circ \qquad \Delta H^\circ = -1081.1kJ/mol \tag{2}$$

$$2Na(l) + 2CO_2(g) \rightarrow Na_2CO_3(s) + CO(g) + \Delta H^\circ \qquad \Delta H^\circ = -454.5kJ/mol \tag{3}$$

$$\begin{aligned} &4Na(l) + 4CO_2(g) \\ &\quad \rightarrow Na_2C_2O_4(s) + CO(g) + Na_2CO_3(s) + \Delta H^\circ \\ &\qquad \Delta H^\circ = -980.1kJ/mol \end{aligned} \tag{4}$$

(*s*), (*l*) and (*g*) denote the solid, liquid and gas phases, respectively. All reactions are exothermic with the negative value of the standard enthalpy change (*ΔH°*).

Sodium oxides, sodium carbonate, sodium oxalate and carbon are produced as the solid reaction products but these reaction products are not highly reactive. According to the previous studies, Na/CO_2 interaction strongly depends on the temperature [4] and Eq. (3) becomes dominant in a high temperature reaction condition [1].

2.2 Research on the solid reaction products elimination

The main objective of this research is to eliminate the solid reaction products, mainly sodium carbonate (Na_2CO_3) by a chemical mean. Since Na_2CO_3 is mainly produced from Na/CO_2 interaction as the reaction temperature increases [1], it was initially selected as the primary target to be removed. Method to eliminate Na_2CO_3 was determined to inject other sodium-based compound in the liquid state to the system. The reason for the choice of sodium-based compound is to avoid additional reaction with sodium. The best expected scenario is that Na_2CO_3 dissolves in the selected sodium-based compound or produces other reaction products in the liquid state by reacting with sodium-based compound.

On the basis of the chemical information of sodium-based compounds [6], all of them were classified under the following criteria listed in Table 1.

By setting these criteria, several sodium-based compounds were finally selected and chemical information is listed in Table 2. Actually, there is no information about the boiling point of several materials in the reference. Therefore, this will have to be checked experimentally.

Since there is no information as well as related research works on this study, we cannot know whether these compounds will react with or dissolve Na_2CO_3. Thus, each experiment with selected compounds will be performed in the near future.

Table 1: Criteria for Classification and Reason

	Criteria	Reason
1	Melting point under 400℃ (Except compounds without information)	Compound should be in liquid state over 400℃ to consider the general operating temperature of SFR.
2	No decomposition and boiling under 600℃	Decomposition and boiling of a compound can be critical. The general operating temperature of a SFR was considered.
3	No H or H_2O in the compound	Compound containing H or H_2O can react with sodium and produce H_2.
4	Consideration of MSDS	Compound threatening environment or health cannot be used.

3. Summary and Further Works

When the pressure boundary of sodium-CO_2 HX fails, leaked CO_2 will react with sodium then the solid reaction products will be formed. Even though some research works on investigating Na/CO_2 interaction has been performed, the research on elimination or treatment of reaction products generated from Na/CO_2 interaction was not performed previously. In order to improve system economics by reducing the cleanup process cost after the reaction between sodium and CO_2 occurs, this study will be important for guaranteeing high economics of SFR with S-CO_2 cycle.

Table 2: Chemical Information of Selected Sodium-based Compounds [6]

Name	Sodium bromate	Sodium chlorate	Sodium tetrafluoroborate	Sodium carbonate
Formula	$NaBrO_3$	$NaClO_3$	$NaBF_4$	Na_2CO_3
Mol. weight	150.892	106.441	109.795	105.989
Physical form	Colorless cubic crystals	Colorless cubic crystals	White orthorhombic prisms	White powder
Melting point (℃)	381	248	384	856
Boiling point (℃)	-	630 (Decomposing)	-	-
Density (g/cm^3)	3.34	2.5	2.47	2.54
Solubility ($g/100g\ H_2O$ at 25℃)	39.4	100	108	30.7
Qualitative solubility	Insoluble in ethanol	Slightly soluble in ethanol	Slightly soluble in ethanol	Insoluble in ethanol

ACKNOWLEDGEMENT

This research was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning.

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