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Preliminary Studies of Na_2CO_3 Cleaning from Na-CO_2 Interaction in S-CO_2 Power Cycle coupled to SFR System

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1. Introduction

The sodium-cooled fast reactor (SFR) has been actively developed in Korea as the future nuclear reactor. SFR has several advantages such as reusing the spent fuel efficiently and reducing the total volume of high level radioactive waste. However, the SFRs have designed and operated with the traditional steam Rankine cycle in the past. Nevertheless, the potential sodium-water reaction (SWR) has been considered unavoidable issue concerning the system safety and integrity due to its vigorous and instantaneous chemical reactivity.

In order to eliminate the SWR, the supercritical CO_2 (S-CO_2) Brayton cycle has been proposed as a design alternative to the steam Rankine cycle due to its improved thermal efficiency, reduced total plant size with compact components (e.g. turbomachinery and heat exchangers) and relatively simplified cycle layout.

Table 1: Review of Na-CO_2 Interaction

Institute/Country	Research works
KAERI/Korea	- Experiment of Na-CO_2 surface reaction [1] - Investigation of wastage phenomenon and self-plugging of narrow flow channel of Na-CO_2 HXs [4]
CEA/France	- Suggestion of the major Na-CO_2 reaction formulas [5] - Investigation of Na-CO_2 interaction with calorimetric studies [2]
JAEA/Japan	- Experiment of reaction behavior of CO_2 with a liquid sodium pool [3]
ANL/USA	- Experiment of Na-CO_2 chemical reaction and kinetics [6]

Even though the S-CO_2 Brayton cycle enables the SFRs to be free from the SWR, several technical challenges are still remaining. CO_2 also reacts with liquid sodium when the pressure boundary of sodium-CO_2 heat exchanger (HX) fails. Thus, further research works have to be done to resolve these issues. As a result, it was defined that the reaction is strongly affected by the reaction temperature and there is the possibility of sodium ignition at very high temperature [1, 2, 3]. And some research works on sodium-CO_2 interaction done in several countries are reviewed in Table 1. However, there are no research works for treatment and removal of reaction products from Na-CO_2 interaction so far.

When the pressure boundary fails, CO_2 will be released to sodium side and the amount of leaked CO_2 will depend on the rupture size. Then, CO_2 gas will react with sodium in the Na-CO_2 HX. The Na-CO_2 interaction results in several significant problems. One of them is an economical problem if the solid reaction products from Na-CO_2 interaction are accumulated in the system or plug a narrow flow channel in PCHE (Printed Circuit Heat Exchanger) used for sodium-CO_2 heat exchanger. Once the flow channel is plugged, to replace the plugged channel, the whole system operation should be stopped or a bypass system is necessary. Therefore, finding a material which can clean up the solid reaction products from Na-CO_2 interaction and the contaminated system with little or no impact on economics can be a valuable research. Hence, a screening process of selecting candidate materials was adopted to find a potential substance which can act as a cleaning agent in the previous study [7].

It is essential to ensure the system economics as well as safety of SFR coupled with S-CO_2 Brayton power conversion system. For this reason, the experiment was conducted to see the possibility of reaction between each selected potential substance and Na_2CO_3, which is the major product of the reaction. Na_2CO_3 does not melt before 856ºC 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, the theoretical background of Na-CO_2 interaction is described and the previous research work to find method for sodium carbonate (Na_2CO_3) cleaning is summarized.

2.1 Review of Sodium-CO_2 Interaction

When the pressure boundary of sodium-CO_2 HX fails, the leaked CO_2 reacts with the liquid sodium. This Na-CO_2 interaction is complex and multiple reactions competitively take place. The major chemical reaction formulas between liquid sodium and CO_2 have been proposed as the following equations from (1) to (4), by the previous experimental and theoretical studies [5].

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

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

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

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

where (*s*), (*l*) and (*g*) denote the solid, liquid and gas phases, respectively. In all reactions, the reaction heat is generated with the negative value of the standard enthalpy change (ΔH^o). As the solid reaction products, sodium oxides (Na_2O), sodium carbonate (Na_2CO_3), sodium oxalate ($Na_2C_2O_4$) and carbon (C) are formed but they are not highly reactive. And the toxic CO gas is produced. According to the previous studies, Na-CO_2 interaction strongly depends on the temperature [2, 3] and Na_2CO_3 and CO are dominantly produced as temperature increases [1].

2.2 Summary of Previous Research on Na_2CO_3 Cleaning

In the previous study [7], in order to clean sodium carbonate by a chemical means which was initially selected as the primary target, it was determined to inject other sodium-based compound in the liquid state into the failed system. The sodium-based compound was chosen to avoid additional reaction with sodium. The best desired scenario is that Na_2CO_3 reacts with the selected sodium-based compound to produce other liquid reaction products.

On the basis of the chemical information of sodium-based compounds [8], all of them were selected according to several criteria: 1) melting under 400ºC, 2) neither decomposing nor boiling under 600ºC, 3) no H or H_2O in the compound and 4) MSDS (Material Safety Data Sheet). The compounds without information were excluded. The important point of the imposed criteria is that the selected compound should be liquid state in the operating temperature range of SFR, from 400 to 550ºC, without decomposition.

Under the above criteria, sodium bromate ($NaBrO_3$), sodium chlorate ($NaClO_3$) and sodium tetrafluoroborate ($NaBF_4$) were finally selected. However, the boiling point of several materials was not given from the reference. Thus it was planned to check the phase change point experimentally. The chemical information of selected sodium-based compounds and Na_2CO_3 [8] is listed in Table 2.

Table 2: Chemical Information of Selected Sodium-based Compounds and Na_2CO_3 [8]

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

3. Experiment

In order to confirm whether the selected sodium-based compound reacts with Na_2CO_3 or not, both the mixtures of each selected sodium-based compound and Na_2CO_3 with one to one mass ratio and each selected sodium-based compound were analyzed by TGA (Thermogravimetric Analysis) and DTA (Differential Thermal Analysis) methods using SETARAM instrument in Fig.1. TGA measures the weight change of sample varying with the temperature. DTA records the temperature difference between sample and reference while undergoing identical thermal cycles, and the upward and downward peaks of the DTA curves mean that they are respectively exothermic and endothermic. [9]

All experimental cases are listed in Table 3. The TG/DTA studies were recorded under the argon atmosphere in the temperature range of 50~630°C with the heating rate by 5°C/min.

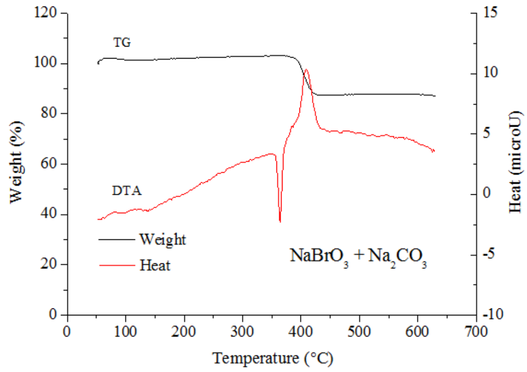
Fig. 1. Photo of TG/DTA.

Table 3: Experimental Cases

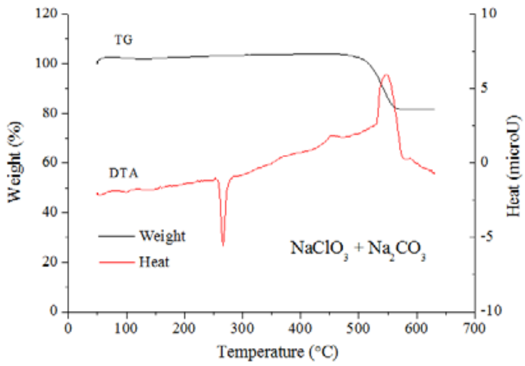
Sample Number	Analyzed Material
1	$NaBrO_3 + Na_2CO_3$
2	$NaClO_3 + Na_2CO_3$
3	$NaBF_4 + Na_2CO_3$
4	$NaBrO_3$
5	$NaClO_3$
6	$NaBF_4$
7	Na_2CO_3

4. Results and Discussion

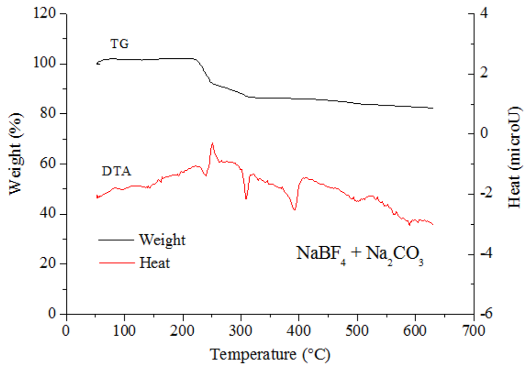
First, the three different mixtures, sample 1~3, were analyzed. And the TG/DTA curves for them are shown in Fig. 2. From each DTA curve of samples 1 and 2, the endothermic peak of each sample at about 365 and 266°C indicates the melting point of $NaBrO_3$ and $NaClO_3$. The difference is within 20°C from the reference data in Table 2. The exothermic peak with the weight loss is also observed in both samples at about 410 and 550°C, respectively. However, each compound had to be additionally analyzed in order to clarify whether the reaction in mixtures takes place or one of them decomposes due to lack of boiling point information. In case of the sample 3, the continuous weight loss is observed in TG curve after 220°C with the frequent endothermic and exothermic peaks.



[Sample 1]



[Sample 2]



[Sample 3]

Fig. 2. TG/DTA curves for sample 1, 2, and 3.

As the analysis results of four sodium-based compounds, the TG/DTA curves are shown in Fig. 3. The endothermic and exothermic peaks in DTA curve for samples 4 and 5 are observed at the points almost the same as those in sample 1 and 2. This means the decomposition with weight loss occurred at around 425 and 570ºC, respectively. These results are consistent with the results for decomposition of $NaBrO_3$ and $NaClO_3$ in the previous research [10, 11]. $NaBrO_3$ in samples 1 and 4 and $NaClO_3$ in samples 2 and 5 decompose respectively at 323~430 and 600ºC.

$$NaBrO_3 \rightarrow NaBr + 3/2O_2 \qquad (5)$$

$$NaClO_3 \rightarrow NaCl + 3/2O_2 \qquad (6)$$

$$NaBF_4 \rightarrow NaB + BF_3 \qquad (7)$$

On the other hand, in the DTA curves of both samples 3 and 6, an endothermic peak is observed at around 384ºC which is given as the melting point from the reference data in Table 2. According to the literature [12], $NaBF_4$ decomposes to sodium fluoride (NaF) and boron trifluoride (BF_3) under heating upto its melting point and the decomposition follows the chemical equation (7). Even though the TG/DTA curves of sample 6 differ from those of sample 3, it is sure that $NaBF_4$ decomposes because there is a weight loss observed from the TG curve of sample 6. In addition, it is confirmed that Na_2CO_3 in sample 7 does not melt before 630ºC (its melting point is 856ºC). Thus, it is concluded that above three selected sodium-based compound decomposes and do not react with sodium carbonate as the authors have intended originally.

4. Summary and Further Works

Liquid sodium and CO_2 gas would react then produce the solid reaction products when the pressure boundary of sodium-CO_2 heat exchanger fails. The solid reaction products are possible to plug the narrow flow channel of PCHE and this concerns the system economics. Thus, it is necessary to search a method for cleaning the solid reaction products which is mainly Na_2CO_3. From the preliminary study, some sodium-based compounds were selected and the mixtures of several sodium-based compounds with Na_2CO_3 were thermally analyzed by the TG/DTA studies.

Unfortunately, the selected sodium-based compounds, $NaBrO_3$, $NaClO_3$ and $NaBF_4$, decomposed before 600ºC and did not react with Na_2CO_3.

In the near future, further research will be performed to search other compounds for cleaning the solid reaction products. Other methods like searching material to lower the melting point of sodium-CO_2 reaction product by forming eutectic will be studied also. This study will have importance of ensuring the system economics of SFR with S-CO_2 cycle.

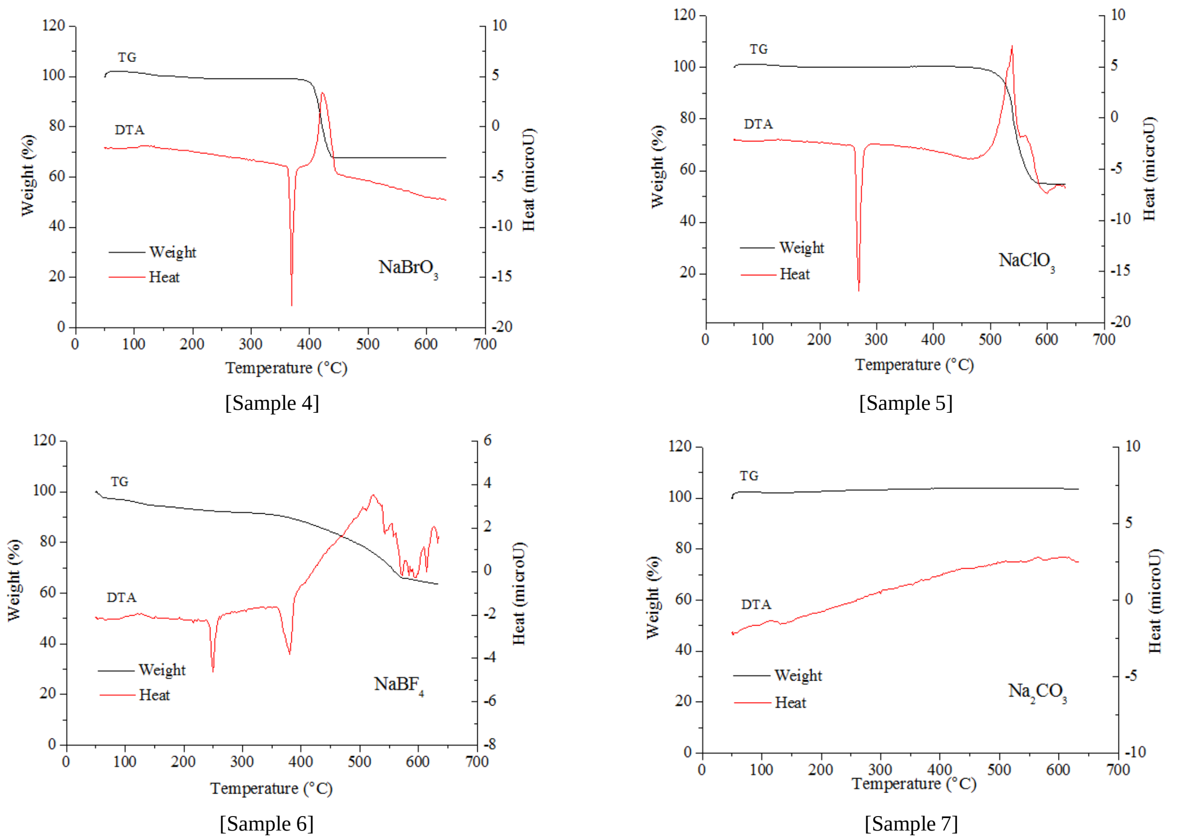


Fig. 3. TG/DTA curves for sample 4, 5, 6, and 7.

ACKNOWLEDGEMENT

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