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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Sodium-cooled Fast Reactor (SFR)

Economics

Sustainability

Safety

Proliferation resistance

◆ Advantages of SFR

- Reusing the spent fuel efficiently
- Reducing the total volume of high level radioactive waste

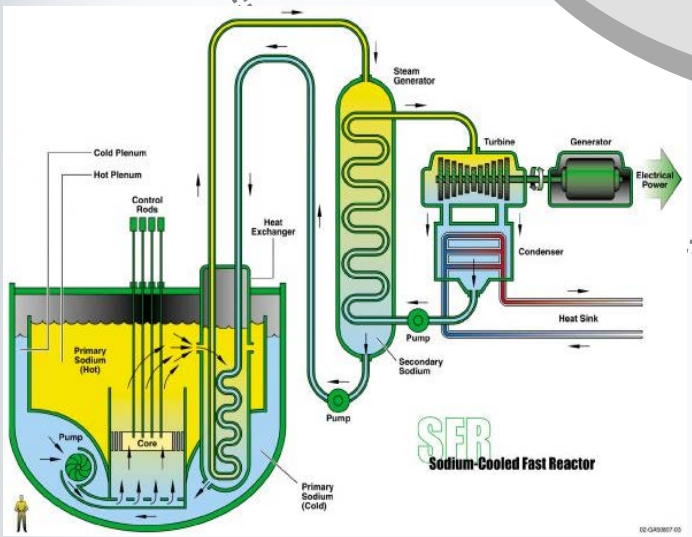
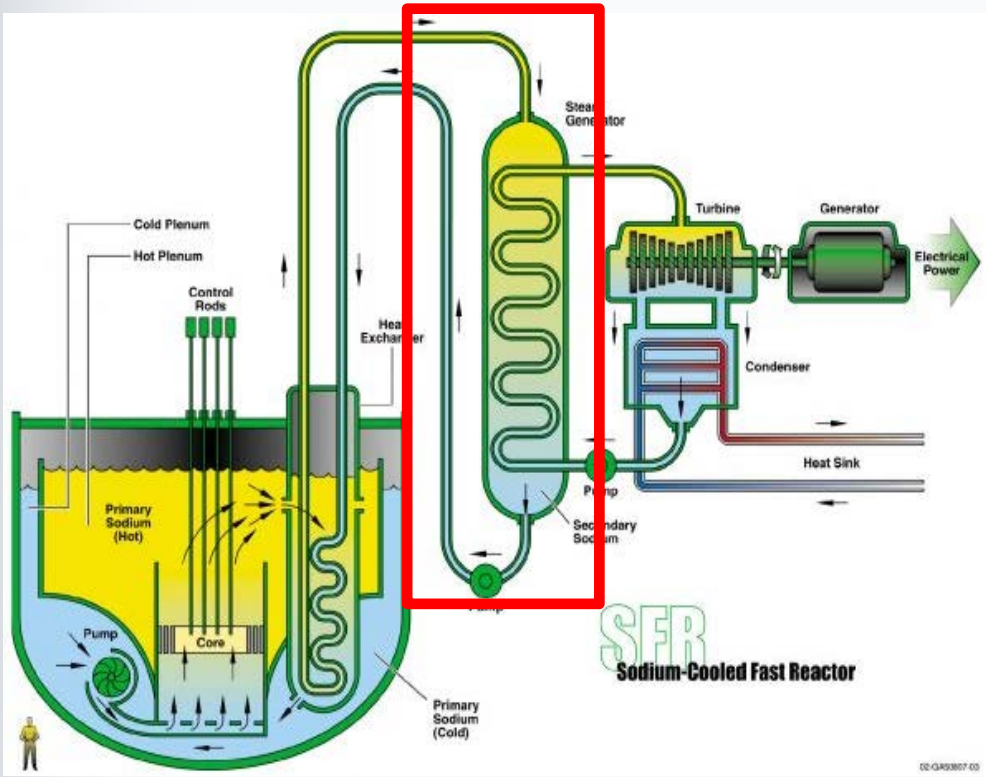


Fig. Pool-type SFR
[http://www.rpi.edu/research/magazine/winter0708/nuclear-3.html]

Technical Challenges of SFR

- Critical issues…
  - Sodium opacity
  - Sodium fire

- Vigorous chemical reactivity of sodium with air or water/steam
  (In the traditional steam Rankine cycle)



$$Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2 - 180\,kJ/mol_{Na}$$

→ Exothermic reaction

→ Extremely high reaction rate

→ Corrosive (NaOH) and explosive (H_2) reaction products

Supercritical CO_2 Brayton Cycle

Advantages of S-CO_2 Brayton Cycle

- High efficiency at relatively low inlet temperature of turbine (500-750 ℃)
- Compact size of turbomachineries and heat exchangers
- Relatively simple layout
- Elimination of sodium-water reaction

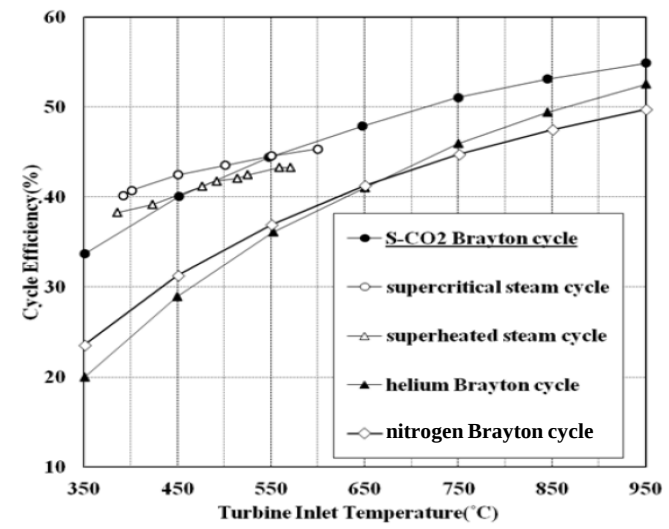


Fig. Cycle efficiency as a function of temperature [Y. H. Ahn et al., 2011]

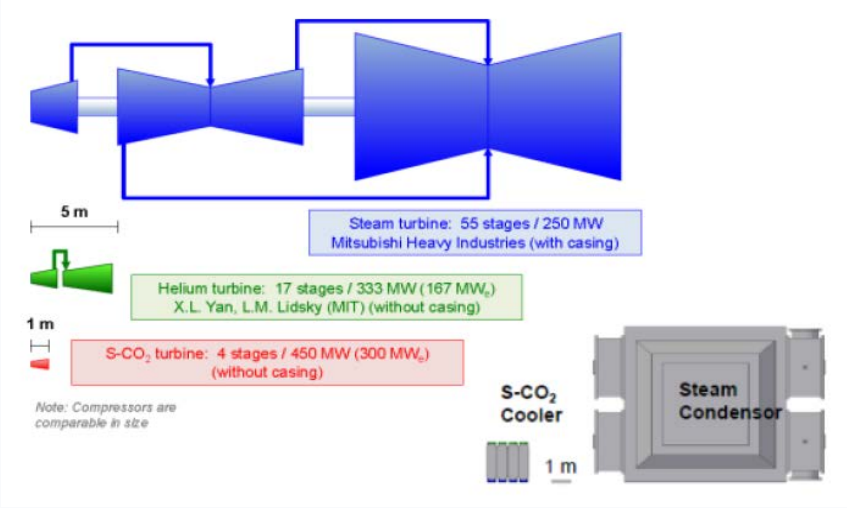
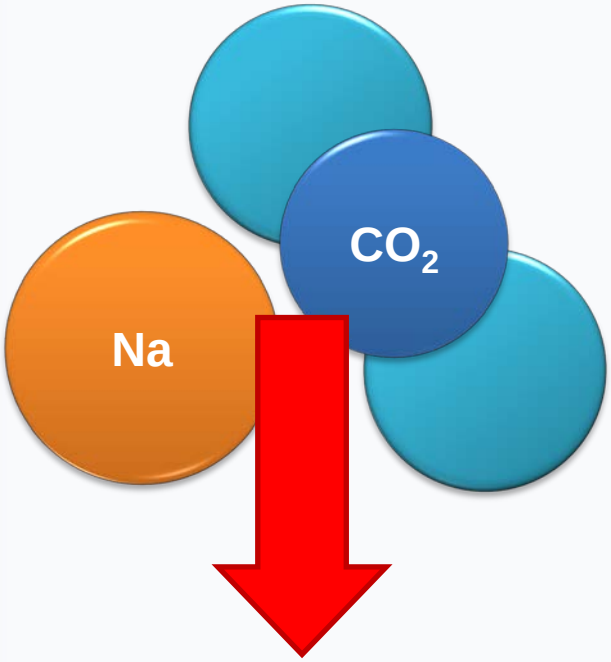


Fig. Comparison of component size with different cycle [S. A. Wright]

Remaining Issues



Potential Na-CO_2 Interaction

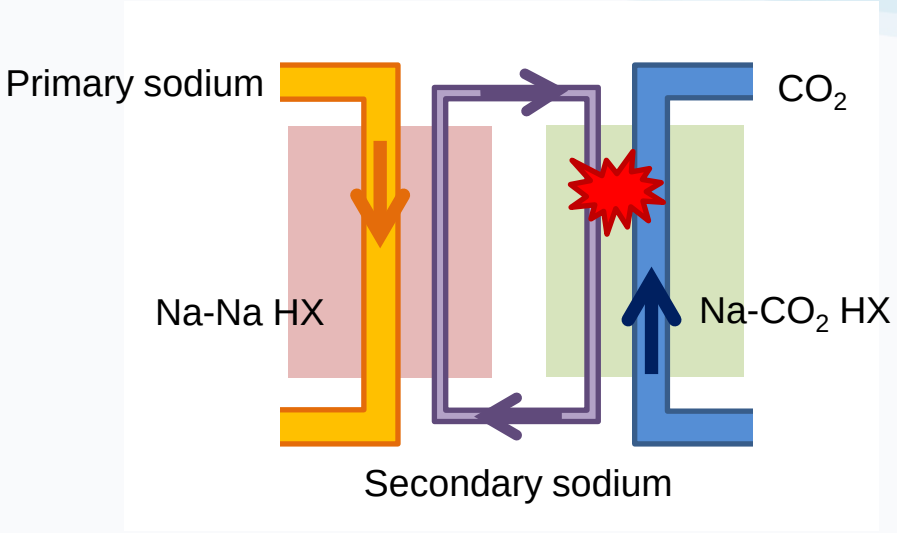


Fig. SFR system coupled with S-CO_2 Brayton cycle with general coolant loops

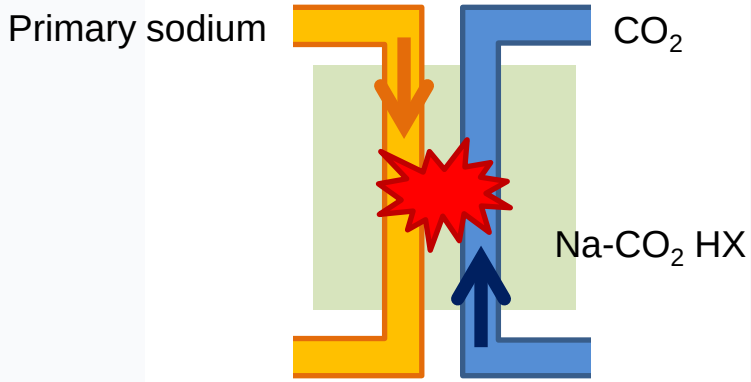


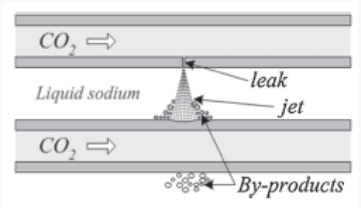
Fig. SFR system coupled with S-CO_2 Brayton cycle without the secondary sodium loop

Research Status at Home and Abroad

Pressure boundary failure → CO_2 leakage → Na-CO_2 interaction → Consequence of Na-CO_2 interaction

Fig. Sequence of possible events in Na-CO_2 heat exchanger

Fig. CO_2-gas jet at 0.75MPa into water [D. Vivaldi et al., 2013]



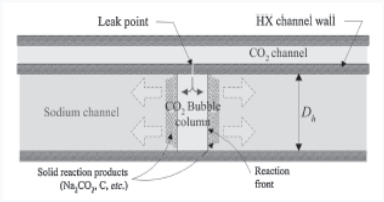


Fig. General wastage mechanism
& Typical channel-plugging mechanism with a Na-CO_2 interaction [J. H. Eoh et al., 2010]

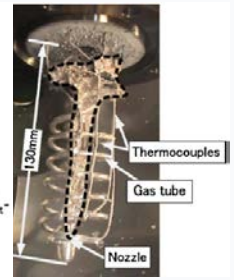


Fig. Reaction behavior of Na and CO_2 (T_{Na} ~ 600℃)
& The state of inner structure with solid reaction product [S. Miyahara et al., 2011]

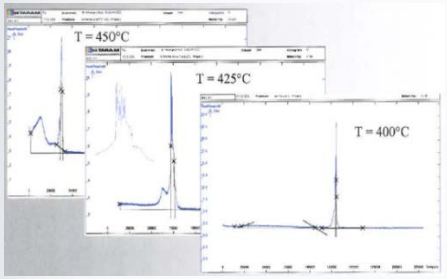


Fig. Calorimetric study results of Na-CO_2 system with calorimeter [N. Simon et al., 2007]

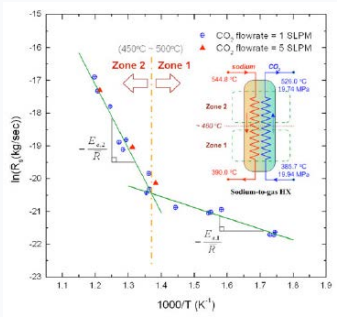


Fig. Two-zone reaction model with the threshold temperature [J. H. Eoh et al., 2011]

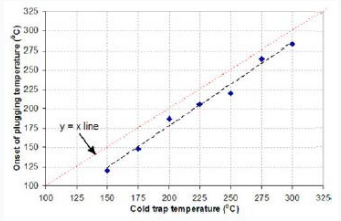


Fig. Onset of plugging temperature as a function of cold trap temperature [Y. Momozaki et al., 2010]

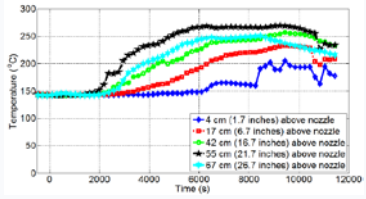


Fig. Temperature variation by the position above the nozzle [C. Gerardi, 2014]

Research Status at Home and Abroad

Table. Performed studies on Na-CO_2 interaction in several countries

Institute/Country	Res works
KAER	- Ex Na-C 2011] lugging of 2010]
	tudies
JAEA/Japan	quid sodium pool
ANL/USA	- Exp f narrow hannel plugging sodium oxide [Y. M et al., 2010] - Expe t of Na-CO_2 che cal reaction and kinetics [Gera t al., 2014]

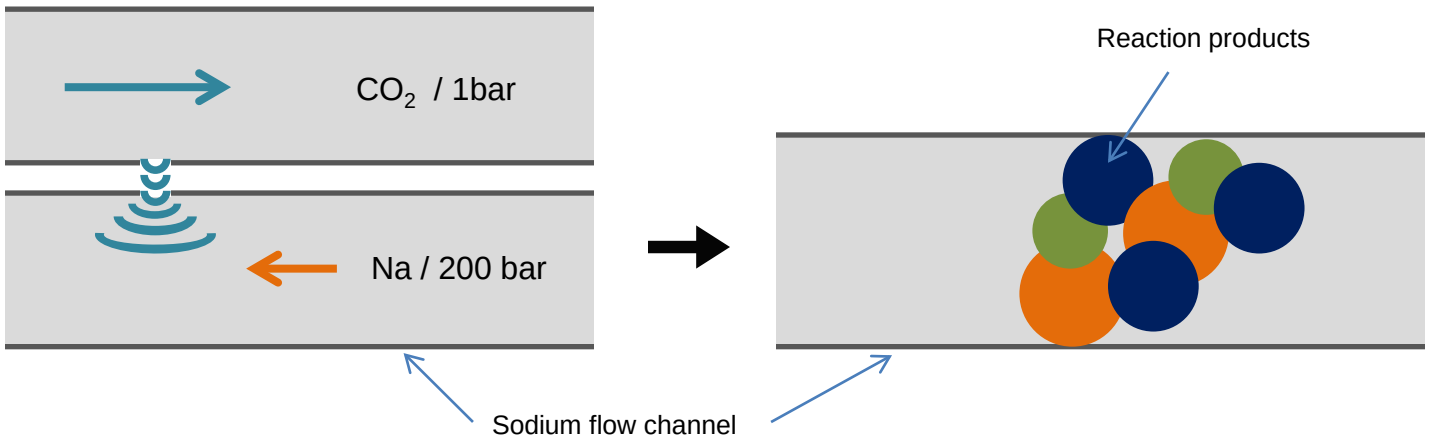
No method for cleaning

the residue of Na-CO_2 interaction

Research Objectives

Study of Na-CO_2 interaction byproduct cleaning agent

- Search potential substances to clean Na-CO_2 interaction byproducts (To minimize the impact on economics)



If the channel is plugged ?

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Review of Sodium-CO_2 Interaction

- Major sodium-CO_2 reaction formulas [C. Latge et al. 2005]

(1) $\mathrm{Na(l)} + \frac{1}{4}\mathrm{CO_2(g)} \rightarrow \frac{1}{2}\mathrm{Na_2O} + \frac{1}{4}\mathrm{C} - 110.6\mathrm{kJ/mol_{Na}}$

(2) $\mathrm{Na(l)} + \frac{3}{4}\mathrm{CO_2(g)} \rightarrow \frac{1}{2}\mathrm{Na_2CO_3} + \frac{1}{4}\mathrm{C} - 270.3\mathrm{kJ/mol_{Na}}$

(3) $\mathrm{Na(l)} + \mathrm{CO_2(g)} \rightarrow \frac{1}{2}\mathrm{Na_2CO_3} + \frac{1}{2}\mathrm{CO(g)} - 227.3\mathrm{kJ/mol_{Na}}$

(4) $\mathrm{Na(l)} + \mathrm{CO_2(g)} \rightarrow \frac{1}{4}\mathrm{Na_2CO_3} + \frac{1}{4}\mathrm{CO(g)} + \frac{1}{4}\mathrm{Na_2C_2O_4} - 245\mathrm{kJ/mol_{Na}}$

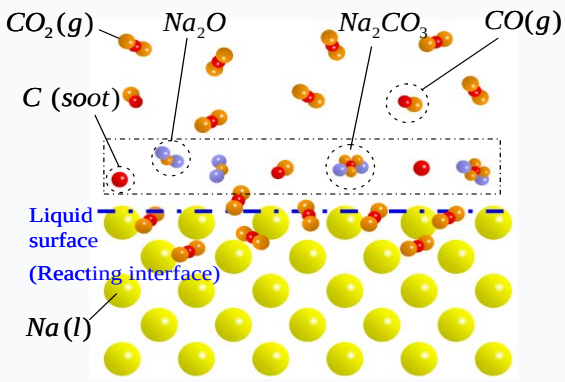

Fig. Typical sodium-CO_2 interaction phenomena [J. H. Eoh et al., 2008]

- Sodium-CO_2 reaction compared with sodium-water reaction (SWR) [L. Gicquel, 2010]

(5) $\mathrm{Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2 - 180\,kJ/mol_{Na}}$

Sodium-CO_2 Interaction	**Sodium-Water Reaction**
- Less vigorous - Not instantaneous	- Vigorous - Instantaneous
- Very complex reaction - Each reaction occurs competitively.	- Less complex reaction
- Non-toxic solid reaction products - Toxic gas reaction product (CO)	- Corrosive (NaOH) and explosive (H_2) reaction products

Review of Sodium-CO_2 Interaction

- Major sodium-CO_2 reaction formulas [C. Latge et al. 2005]

(1) $Na(l) + \frac{1}{4}CO_2(g) \rightarrow \frac{1}{2}Na_2O + \frac{1}{4}C - 110.6kJ/mol_{Na}$

(2) $Na(l) + \frac{3}{4}CO_2(g) \rightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{4}C - 270.3kJ/mol_{Na}$

(3) $Na(l) + CO_2(g) \rightarrow \frac{1}{2}Na_2CO_3 + \frac{1}{2}CO(g) - 227.3kJ/mol_{Na}$

(4) $Na(l) + CO_2(g) \rightarrow \frac{1}{4}Na_2CO_3 + \frac{1}{4}CO(g) + \frac{1}{4}Na_2C_2O_4 - 245kJ/mol_{Na}$

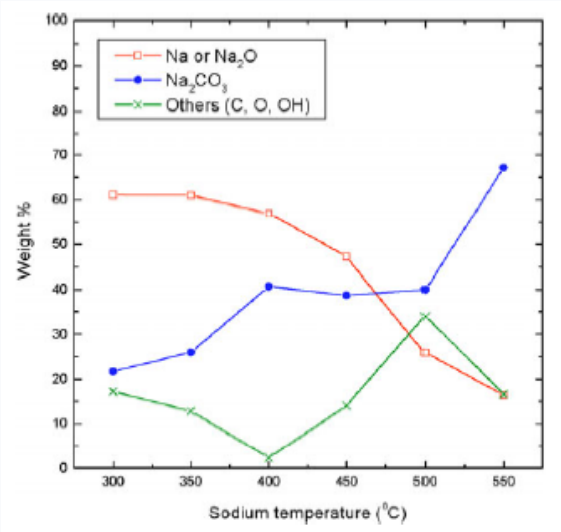

Fig. Results of the solid product analysis [J. H. Eoh et al., 2011]

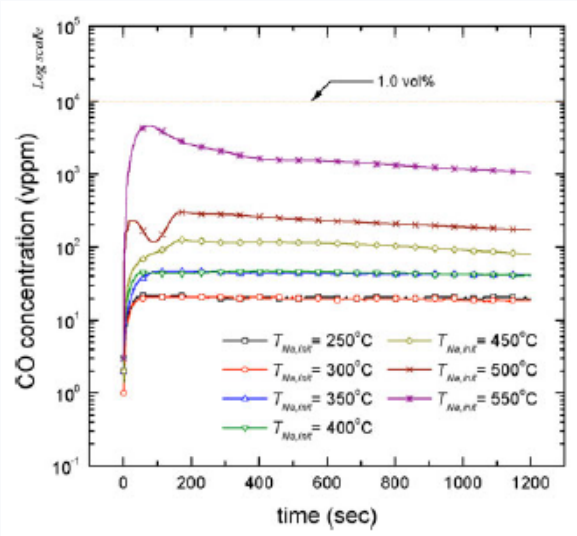

Fig. Variations in CO concentration [J. H. Eoh et al., 2011]

$Na\text{-}CO_2$ Interaction Byproduct (Na_2CO_3) Cleaning Agent Study

- **Objective: Search potential substances to clean $Na\text{-}CO_2$ interaction byproduct, mainly Na_2CO_3**
  → Minimize the impact on economics

Criteria for Classification
Sodium-based compounds to avoid the collateral reaction with sodium
1) Melting below 400ºC 2) Neither decomposing nor boiling below 600ºC 3) No H or H_2O in the compound 4) Consideration of MSDS (Material Safety Data Sheet)

Na-CO_2 Interaction Byproduct (Na_2CO_3) Cleaning Agent Study

Table. Chemical information of selected sodium-based compounds and Na_2CO_3
[CRC Handbook of Chemistry and Physics, 2010]

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

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Analysis

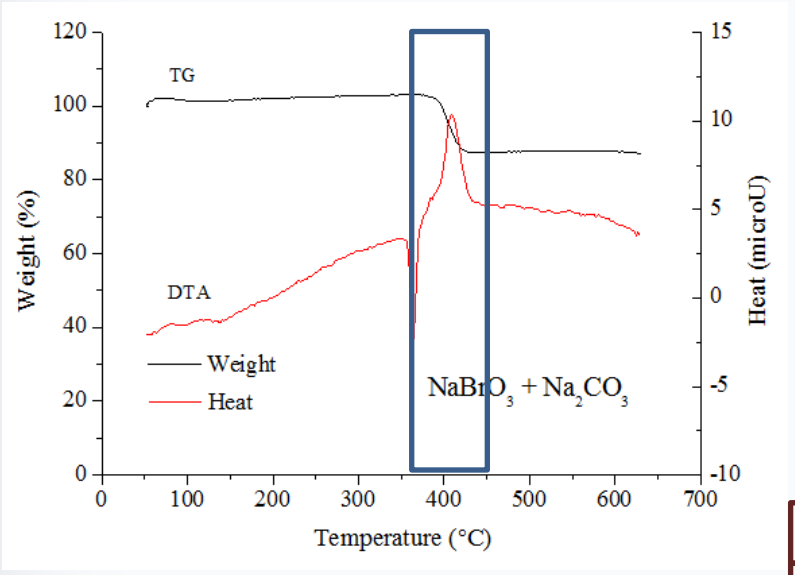
Fig. Photo of TG/DTA*

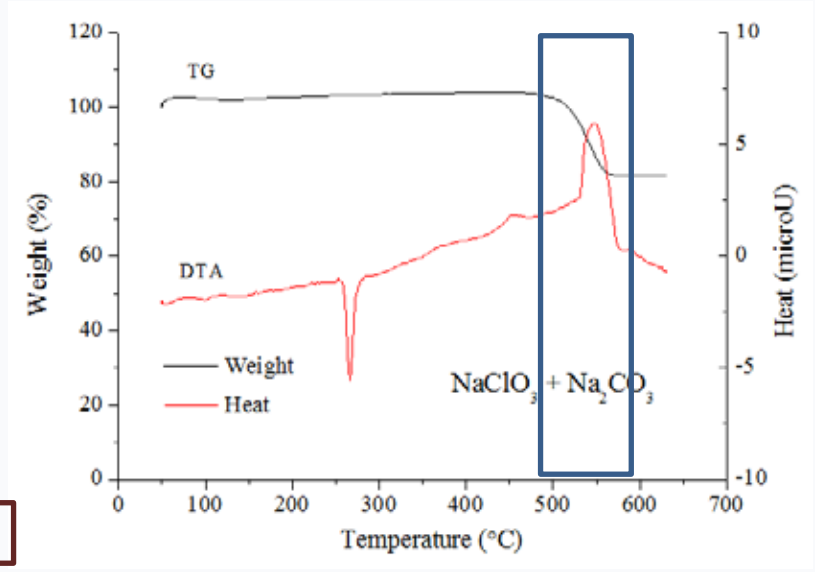
*TGA: Thermogravimetric Analysis
*DTA: Differential Thermal Analysis

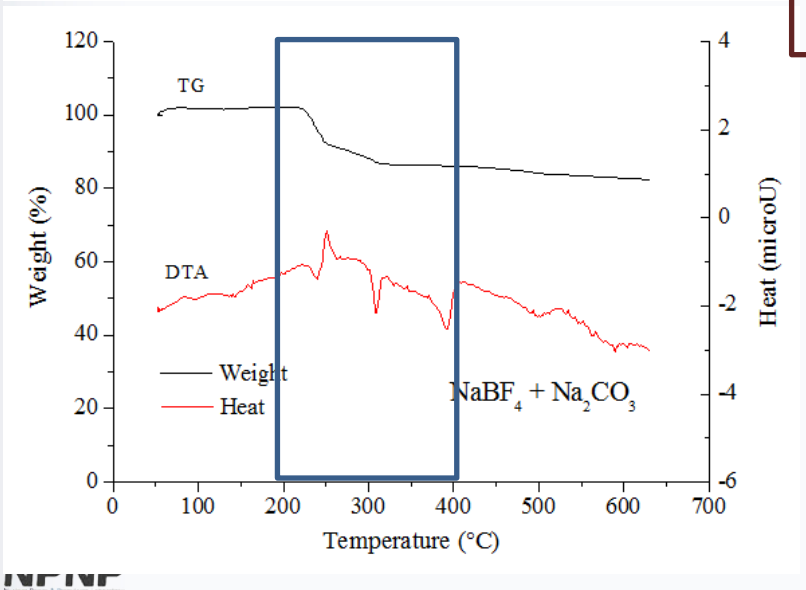
Experimental Conditions
1:1 mass ratio of each substance and Na_2CO_3
Argon atmosphere
Temperature range: 50~630ºC
Heating rate: 5ºC/min

Experimental Cases	
# 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

Results & Discussion





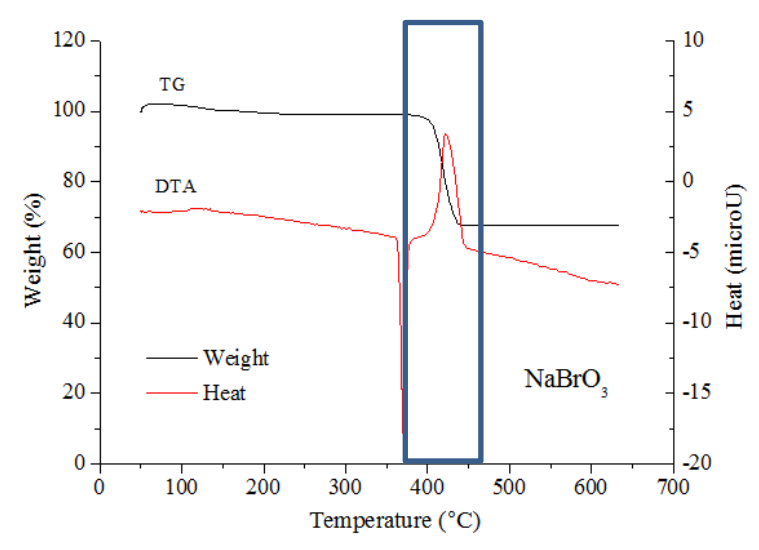


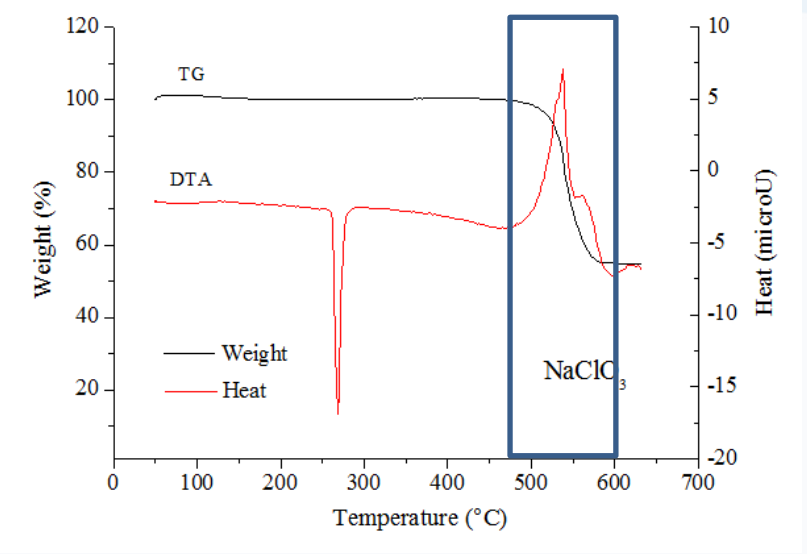
1 2
3

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

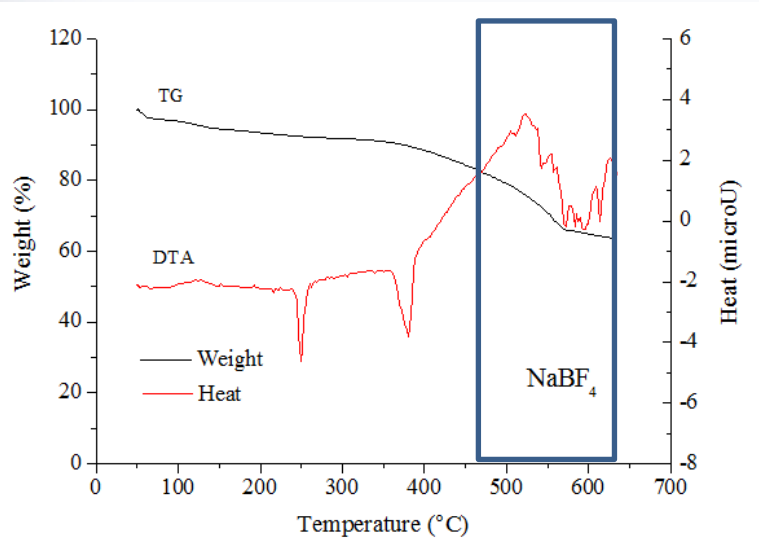
- The meaning of minima and maxima
  - Endothermic phenomenon
  - Exothermic phenomenon

Results & Discussion





4	5
6	7



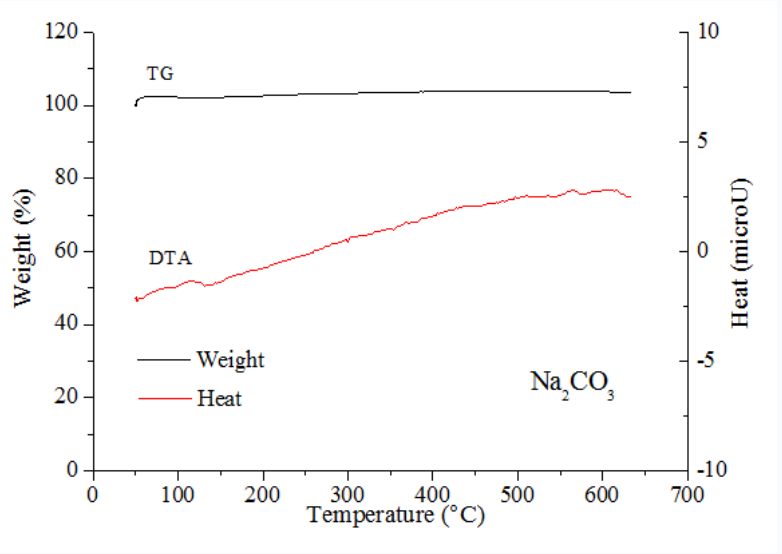
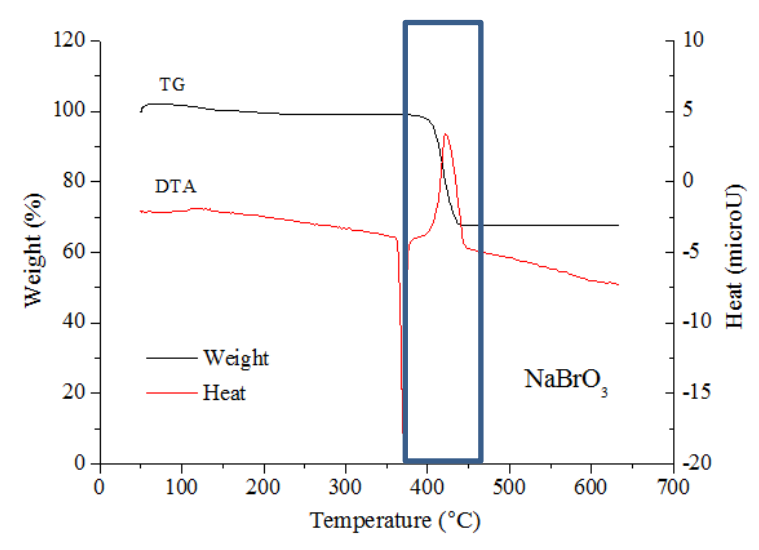
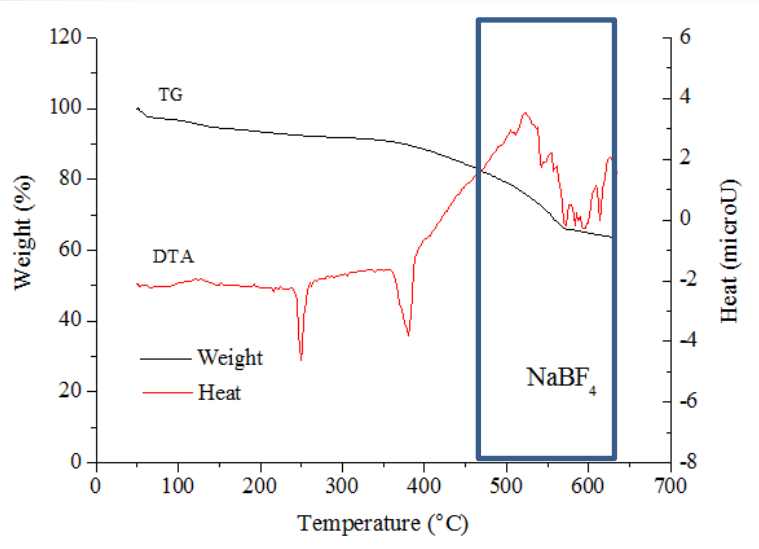


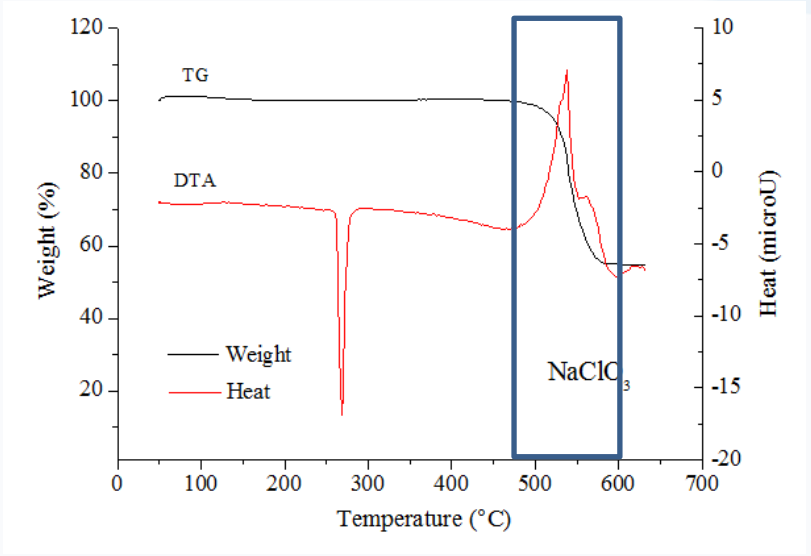
Fig. TG/DTA curves for sample 4, 5, 6, and 7

Conclusions





4	5
6	



$$NaBrO_3 \rightarrow NaBr + 3/2O_2$$ [J. Jach, 1963]

$$NaClO_3 \rightarrow NaCl + 3/2O_2$$ [A. Sweetly et al., 2012]

$$NaBF_4 \rightarrow NaB + BF_3$$ [R. J. Lewis et al., 2008]

$NaBrO_3$, $NaClO_3$, and $NaBF_4$ decompose before 600ºC and do not react with Na_2CO_3.
→ Search other substances or other methods.

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

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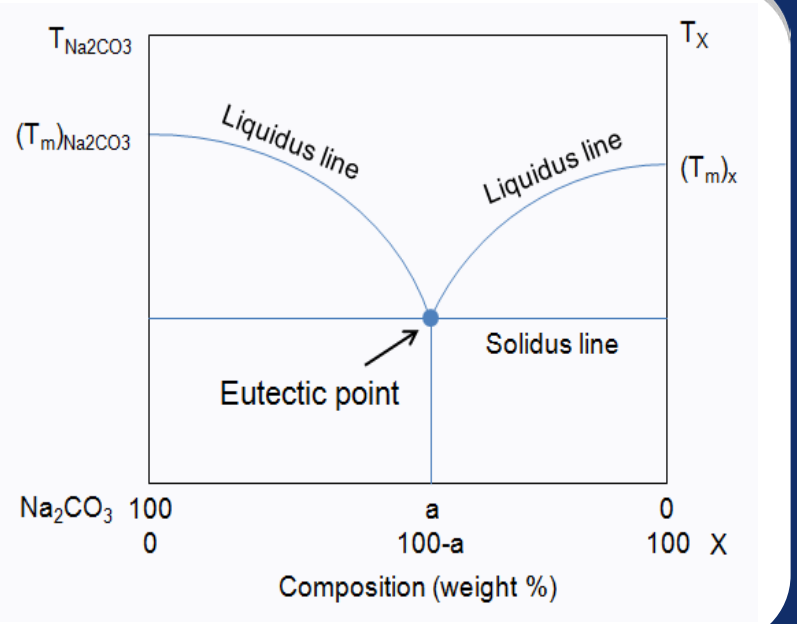
Summary & Future Plans

Na_2CO_3 Cleaning Agent Study

- To search the potential substances to clean Na-CO_2 interaction byproducts, several sodium-based compounds were selected and analyzed.
- $NaBrO_3$, $NaClO_3$, and $NaBF_4$ decompose before 600ºC and do not react with Na_2CO_3.

Future Plans



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THANK YOU

Eutectic Point