Experiments on the Sodium-Carbon Dioxide Reaction in a Capsule

J. H. Choi¹, S. D. Suk¹, D. Cho², J. M. Kim¹, D. Hahn¹ and J. H. Cahalan² *1. Korea Atomic Energy Research Institute 2. Argonne National Laboratory*

1. Introduction

This study was performed to provide baseline data on the sodium-carbon dioxide (Na- CO_2) reaction. A small-scale capsule test has been conducted to explore the basic nature and extent of the Na- CO_2 chemical reaction.

Four batches of experiments were performed based on the temperatures of 200, 300, 400 and 600°C. After one batch, the test capsule was taken out for an analysis of the solid products. The amount of sodium used for one batch was about 30g. Quantitative analysis of the gas sample was carried out by a Gas Chromatograph (GC) for each initial pressure condition. The quantitative as well as qualitative analyses of the solid sample were carried out by an acid-base titration, X-ray diffraction (XRD) and Electron probe micro-analysis (EPMA).

2. Experiment

As shown in Figure 1, the test apparatus consisted of a test capsule and associated components: sodium storage tank, vapor trap, gas supply system, instrumentation and gas sampling system.



Figure 1. Flow diagram of the capsule test.

Experiments were carried out for twenty nine cases with the sodium temperature ranging from 200°C up to 600°C, with an operating pressure of up to 40 kg/cm², and with a changing flow rate from 25 scc/min to 100 scc/min.

3. Result and Discussion

Figure 2 shows the results of the reaction between sodium and CO_2 at the temperature of $300^{\circ}C$ representatively. Numbers in the yellow circles are the experimental case numbers. In the case-14 experiment (flow-rate; 25 scc/min, pressure; 30 kg/cm²), a violent temperature variation occurred for a few seconds, 35 minutes after a gas injection. At this time the temperature fluctuated very fast with a maximum sodium temperature of 1110 °C and the thermocouple measuring the gas zone failed for about 3 minutes and then it re-operated, and the body of the test capsule became red-hot. The pressure decreased slowly for about five minutes and then it showed a sharp fall with a fluctuation of the temperature and the gas flow rate. Due to a plugging of the gas injection nozzle, the gas was fed no more and the pressure was maintained near zero. The accumulated amount of CO2 till 35 minutes after a gas injection was about 16 scc.

In reference [1], it is stated that F. Beguin et R. Setton have analyzed in greater detail the reactions involved with all the alkalines. The reaction is at first slow up to 200°C. At about 220 °C it accelerates; and at 260 °C it is reported to be almost complete after several hours. In an experiment of different contact modes to this experiment, H. Ishikawa, S. Miyahara and Y. Yoshizawa [2] have studied a CO_2 gas bubbling through a sodium pool. They observed the following results : below 873 K, CO_2 reacted in the first few seconds then the reaction was stopped. When the initial temperature was higher than 888 K, the reaction occurred continuously.





Figure 2. (a) Flow-pressure data and (b) Thermometry data at 300° C with CO₂ (Case No. : 13~18)

Quantitative analysis of the gas sample was carried out on-line for five minutes by a Gas Chromatograph (GC) after each set of pressure experiments (29 cases). Before the analysis, the GC was calibrated with a standard gas (CO; 1, CO_2 ; 5 mol%/mol).

The experimental results are shown in Tables 1, 2 and Figure 3. Table 1 shows the results of the gas analysis. The content of the carbon monoxide increased with an increase of the gas flow-rate and temperature. Table 2 and Figure 3 show the results of the solid product analysis. The content of the sodium carbonate (Na₂CO₃) was above 74% at the sodium temperature of 200°C and it increased to about 96% at 600 °C. From these, it was confirmed that the carbon dioxide reacted readily with the liquid sodium under these experimental conditions.

| Coco | Gas | Gas Supply | CO contents (vol%) | | | | |
|------|-----------|------------|--------------------|---------|---------|---------|--|
| No | Flow Rate | ture (°C) | | | | | |
| 140. | (scc/min) | (kg/cm²) | 200 | 300 | 400 | 600 | |
| 1 | | 10 | 0.08262 | 0.14584 | 8.49827 | 8.69213 | |
| 2 | 25 | 30 | 0.10209 | 5.37306 | 6.94972 | - | |
| 3 | | 40 | 0.45310 | 4.92466 | 4.80964 | - | |
| 4 | 50 | 10 | 0.09058 | - | - | - | |
| 5 | | 30 | 0.20858 | - | - | 6.33725 | |
| 6 | | 40 | 0.17188 | 4.95063 | 3.40218 | - | |
| 7 | 75 | 10 | 0.34406 | - | - | - | |
| 8 | | 30 | 0.30192 | - | - | - | |
| 9 | | 40 | 1.69037 | 5.00810 | 3.45914 | 4.80339 | |
| 10 | | 10 | 0.60454 | - | - | - | |
| 11 | 100 | 30 | 0.47354 | - | - | - | |
| 12 | | 40 | 2.04488 | 5.12130 | 3,44083 | 4.04666 | |

Table 1. Result of the gas analysis

Table 2. Result of the solid analysis

| J | | | | | | | | | |
|---------------------|---------------------------|-----------------|-------------------------|----------------------------|--|--|--|--|--|
| Temperature (°C) | Na or Na₂O (wt%) | Na₂CO₃ (wt%) | Others (C etc) (wt%) | Non water-soluble (wt%) | | | | | |
| | Acid-base titration & XRD | | EPMA | EDS & SEM | | | | | |
| 200 | 15.5 ± 0.6 | 74.3 ± 0.2 | 10.2 ± 0.5 | trace | | | | | |
| 300 | 7.7 ± 1.8 | 89.2 ± 1.2 | 3.1 ± 0.7 | 1.41 | | | | | |
| 400 | not detected | 93.9 ± 1.5 | 6.1 ± 1.5 | 3.61 | | | | | |
| 600 | not detected | 95.9 ± 0.9 | 4.1 ± 0.9 | 3.21 | | | | | |



Figure 3. Result of the solid product analysis.

4. Conclusion

The sodium-carbon dioxide reaction has been studied experimentally with a small-scale experimental apparatus by using 30g of sodium. Four batches of experiments were performed based on the temperatures of 200, 300, 400 and 600°C. But here only the results of the reaction between sodium and CO₂ at the temperature of 300°C were shown representatively. The results show that the carbon dioxide reacted readily with the liquid sodium under these experimental conditions. It seems that the interaction reaction of Na-CO₂ was slow at the sodium temperature of 200°C and it became very faster above 300 °C. The reaction phenomena at 300°C and 400°C were similar. In the case of 600°C, the reaction of Na-CO₂ occurred very fast.

Acknowledgement

This work was performed under 'the Long-Term Nuclear Energy Research and Development Program' sponsored by the Ministry of Science and Technology of the Republic of Korea.

The chemical analysis of the solid products was performed by the team in Chemical Analysis and Test Division in KAERI.

REFERENCES

[1] C. Latge, G. Rodriguez and N. Simon, Supercritical CO_2 Brayton Cycle for SFR : Na- CO_2 interaction and consequences on design and operation, GLOBAL 2005, Oct. 9-13, 2005.

[2] H. Ishikawa, S. Miyahara and Y. Yoshizawa, Experimental Study of Sodium-Carbon dioxide Reaction, Proceedings of ICAPP '05, Paper 5688, pp., 2005.