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Investigation of sodium – carbon dioxide interactions with calorimetric studies.

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Abstract – The Supercritical CO_2 Brayton Cycle could be a promising option to enhance the competitiveness of future Sodium Fast Reactors. This cycle has been studied due to its high thermodynamic efficiency. Furthermore, it may suppress the difficulties of the sodium-water reaction. Nevertheless, it is highly necessary to get thermodynamic and kinetics information on the potential sodium-CO_2 chemical reaction and its potential consequences, to compare both of the systems. Calorimetric studies were performed and put into evidence that Na-CO_2 reaction is characterized by an induction time for temperature lower than 500°C, due to CO formation and a consecutive reaction between CO and Na. At higher temperature, a fast global reaction occurs.

I. INTRODUCTION

Within the framework of the Sodium Fast Reactor development, the Supercritical CO_2 Brayton Cycle option for the energy conversion has been considered because of its high thermodynamic efficiency (over 40%) and its potential compactness. Nevertheless, it assumes the hypothesis that the (Supercritical carbon dioxide – sodium) interaction has less serious consequences than the (water-sodium) reaction or may be mitigated easily.

The study of such a reaction is necessary to get the knowledge of both thermodynamic aspects (knowledge of the reaction products, measurement of the heat of the reaction, ...) and kinetics phenomena to check the possible occurrence of a wastage event in case of a leak. It is also of a great importance to get information on the behaviour of the reaction products in the reaction medium - literature cited the formation of Na_2CO_3, $Na_2C_2O_4$, CO,...- which may react themselves with sodium.
Previous studies have been performed in the sixties and seventies by Setton [1], Beguin et al [2] and Cordfunke et al [3] who claimed for the formation of NaC_2O_4, NaC_2O_3, C, CO(g) as reaction products. Some equations of reactions have been proposed. More recently, Ishikawa et al. [4] studied this reaction and investigated the influence of temperature, pre-heating of CO_2 and moisture. They concluded that with temperature lower than 873K, reaction was unsatisfactorily, for temperature higher than 888K, the reaction proceeded with a flame. Choi and coll. [5] suggested a slow reaction under 200°C, faster above 300°C and immediate at 600°C.
A recent literature review has been written [6].

This paper deals with our initial studies of the interaction between Na and CO_2 interaction via calorimetric methods. Such methods are able to point out exothermic/endothermic phenomena and to measure heat of chemical reactions.

II. EXPERIMENTAL SECTION

Sodium metal was provided by Métaux Spéciaux (nuclear purity), CO_2 gas was provided by Air Liquide with a purity of 99.998% (H_2O < 3 ppm). Anhydrous Na_2CO_3 (99.999%) and $Na_2C_2O_4$ (99.8%) come from Aldrich.

Differential calorimetry

Differential Thermal Analysis was carried out with Setaram DSC-111 instruments at a heating rate of 2 or

10°C.min^{-1}, depending on the experiments, for the temperature scans. Solid sodium was introduced in crucibles at ambient temperature in an argon glove-box. Then, CO_2 was cooled until we got pellets of solid CO_2, then was introduced in the crucible with a scoopula, at last we sealed the crucible fast. Mass of sodium and CO_2 were known by weighting.

Vent Sizing Package experiments

A pressure compensated calorimeter for adiabatic experiments has been developed by DIERS (Design Institute for Emergency Relief Systems) in order to keep the Φ-factor (proportion of the heat capacity : $\Phi = C_P(\text{vessel+sample})/C_P\text{sample}$) as small as possible. The ideal value of Φ is 1. A scheme is illustrated in the figure 1. A low Φ-factor thin wall test cell is placed in a pressure vessel. The test cell contains a magnetic stir bar. The apparatus measures sample temperature (T1), pressure (P1), external temperature (T2) and containment vessel pressure (P2). The pressure in the containment vessel is controlled to balance the test cell pressure and to avoid it to crash.

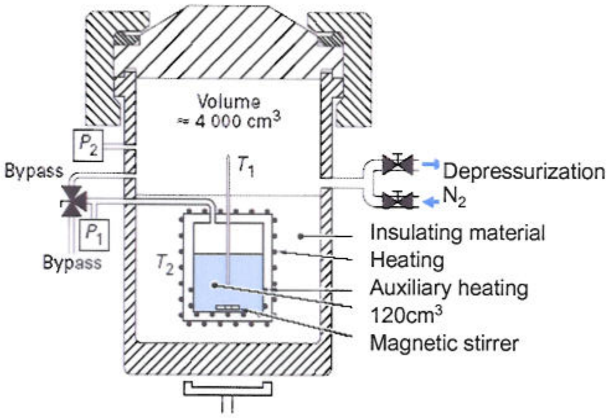

Figure 1 : Vent Sizing Package system [7]

II.A. Na-CO_2 DSC calorimetric studies

Temperature scans

Figure 2 and figure 3 show results of calorimetry temperature exposure scans for Na-CO_2 mixture.

In the first one, temperature scans were carried out from ambient temperature to 400°C. Four successive scans were performed with the same sample. The presence of sodium was controlled by its fusion endothermic peak. We noted an exothermicity from 70°C to 300°C which disappeared from the second scan (may be due to an impurity), and a second exothermicity above 300°C. The corresponding reaction consumed sodium and during the following exposure we pointed out both sodium fusion endothermicity and second exothermicity decreasing.

In the second experiment reported in the figure 3, temperature scans were carried out up to 700°C. Two cycles were performed. During heating, the previous peak appeared, as one expected it, above 300°C and a new important exothermic event occurred from 500°C, exhibiting a fast and significant reaction. The first cooling pointed out two exothermicities, one corresponding to sodium crystallisation, the other exhibiting the crystallisation of a new product (exothermicity between 530°C and 435°C), previously formed during temperature increasing scan, due to sodium/CO_2 reaction. During the second scan, CO_2 was totally consumed (Na/CO_2 ratio = 1.67), and we observed the fusions of sodium and of the resulting reaction product.

Isothermal studies

We realized constant temperature exposures using DSC111. An example of results is reported in the figure 4 for an isotherm at 400°C. As we increased the temperature, we observed the expected exothermicity above 300°C. During the isothermal time, a fast and highly exothermic reaction was obtained on the DSC thermogram. This thermogram exhibited a dissymmetric and very complex shape, as the one observed in temperature increasing above 500°C. The detected Na/CO_2 chemical reaction is so characterized by an induction time.

II.B. study of the possible autocatalytic features

According to our first investigations, the dissymmetric shape of the DSC thermograms obtained at about 500°C, by a temperature scan, may be explained by an autocatalytic behaviour of the Na/CO_2 reaction. Such a reaction is a reaction which produces its own controlling reactant. So it can accelerate at a constant temperature due to chemical features. It will appear after some induction time at a constant temperature exposure.

According to kinetic theory, the induction time τ in logarithmic scale would be an increasing linear function of the reciprocal temperature according to the law :

$$\tau = \frac{e^{(E/RT)}}{k_0} * \int_{\alpha=0}^{\alpha_{\max}} \frac{d\alpha}{f(\alpha)}$$

On the contrary, the heat flux decreases linearly with the reciprocal temperature as indicated in the figure 5.

The figure 6 gathers examples of constant temperature exposures using DSC 111. The isothermal induction time was measured using temperatures : 375°C, 400°C, 425°C, 450°C, to obtain the plot of the induction time versus the temperature. At 500°C, the reaction became instantaneous.

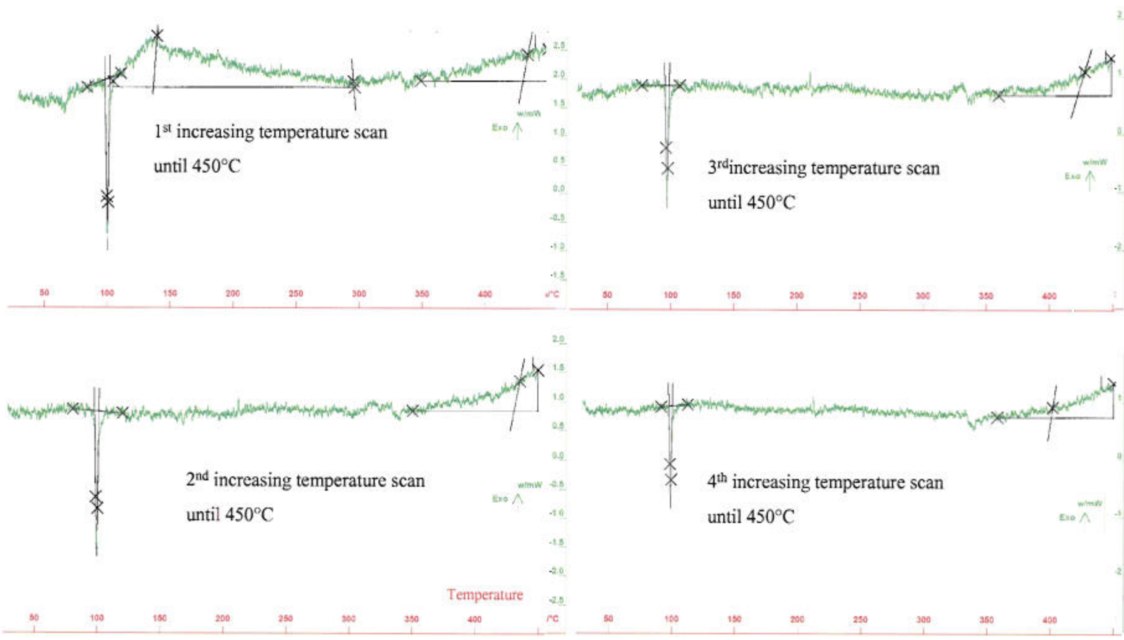

Figure 2 : Calorimetric studies of Na/CO_2 system with DSC111 calorimeter. Successive temperature scans (25°C- 400°C) Na/CO_2 ratio = 0.41

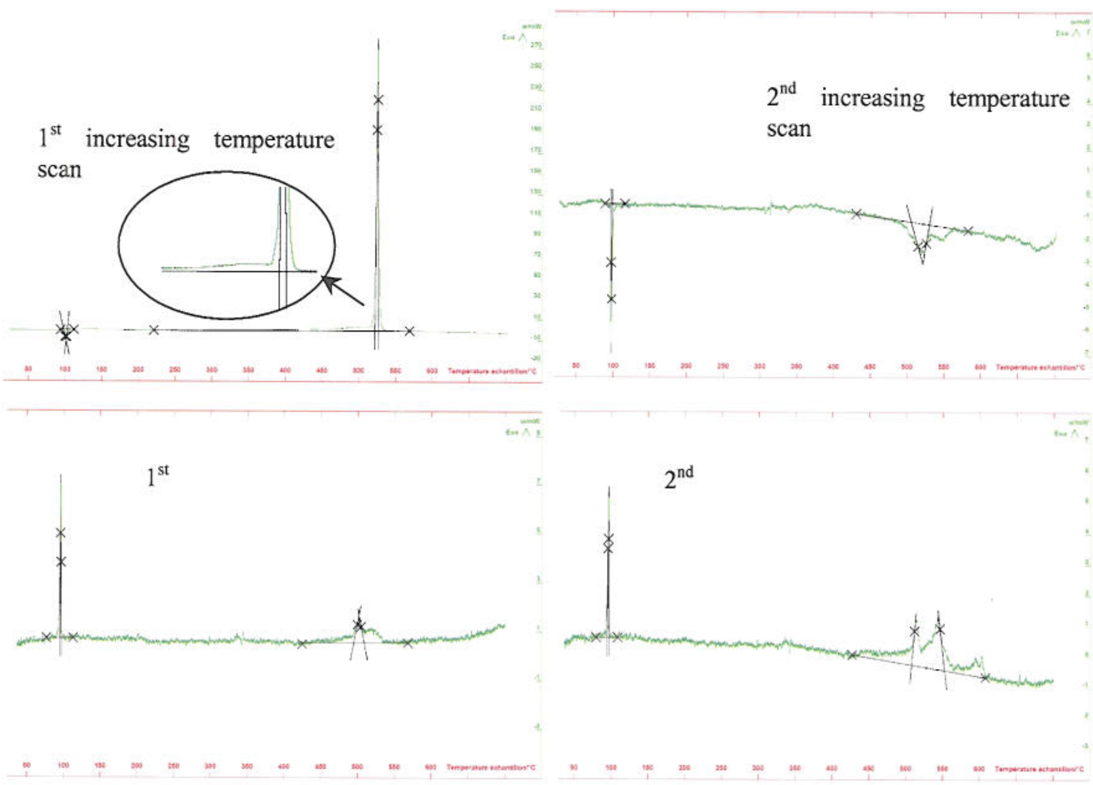

Figure 3 : Calorimetric studies of Na/CO_2 system with DSC111 calorimeter. temperature cycles (25°C- 700°C) Na/CO_2 ratio = 1.67

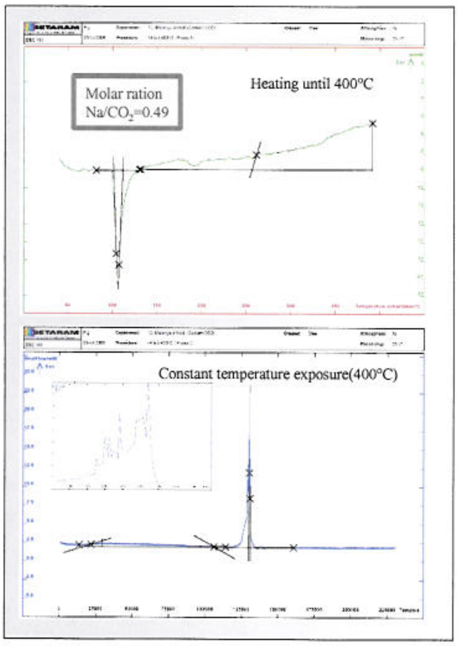

Figure 4 : Calorimetric studies of Na/CO_2 system with DSC111 calorimeter. Isotherm experiment (400°C) Na/CO_2 ratio = 0.49

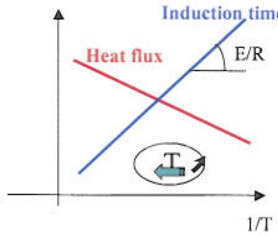

Figure 5 : autocatalytic reaction. induction time and heat flux versus temperature.

The induction time and the max isothermal heat flux variations are reported in the figure 7 and show obviously that the Na/CO_2 reaction does not in fact correspond to an autocatalytic phenomenon.

We may suggest, to explain the induction time and the complexity of the exothermal peaks, the occurring of an auto-combustion event.

II.C. $Na_2C_2O_4$ and Na_2CO_3 behaviour

From literature review, we foresee that the main expected reactions products are Na_2CO_3, $Na_2C_2O_4$, CO(g), and C. Some of these compounds are likely to react with sodium, especially Na_2CO_3, $Na_2C_2O_4$ and also CO(g).

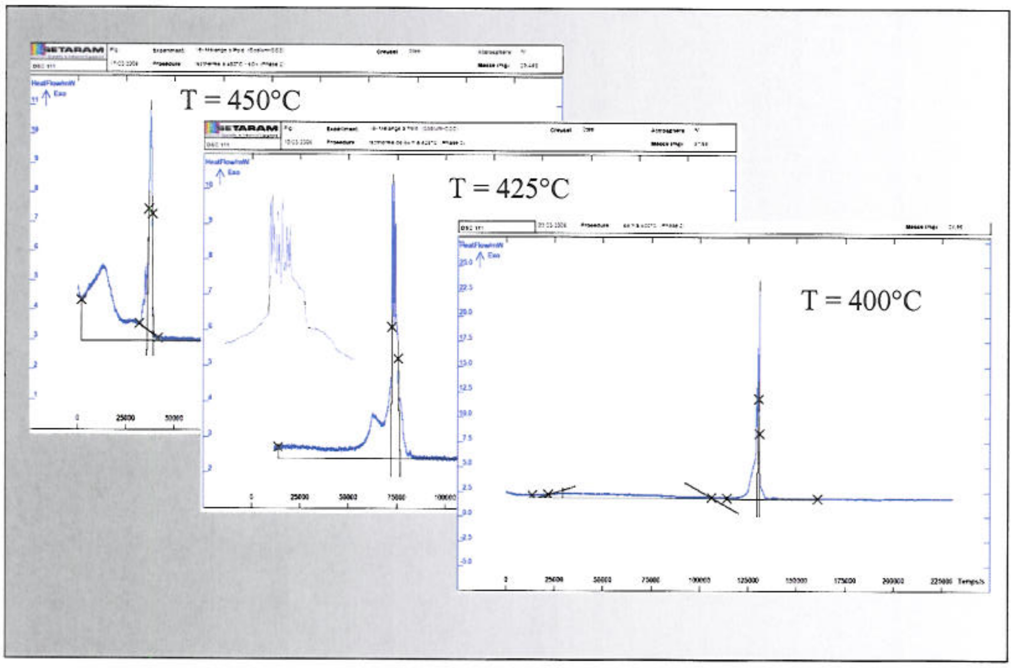

Figure 6 : Calorimetric studies of Na/CO_2 system with DSC111 calorimeter. Isotherm experiments.

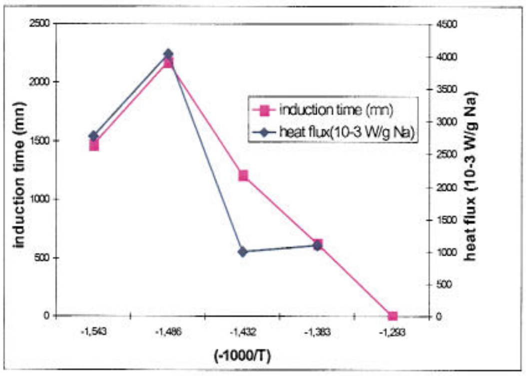

Figure 7 : system Na/CO_2 : induction time and heat flux versus temperature.

That is why calorimetric studies, involving systems as $Na/Na_2C_2O_4$ and Na/Na_2CO_3, were performed (see figures 8 and 9).

Reference experiments studying Na_2CO_3, $Na_2C_2O_4$ behaviour versus temperature in an inert medium have also been realized.

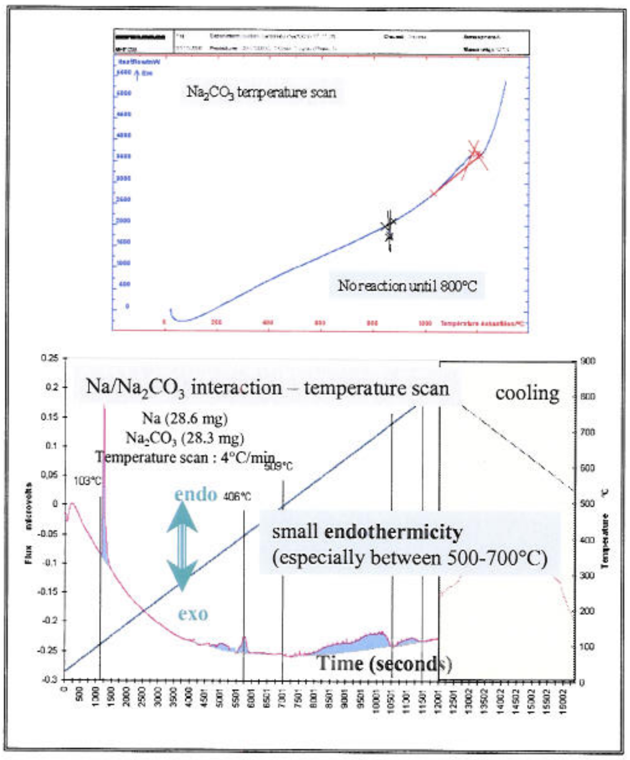

Figure 8 : Na_2CO_3 behaviour as a function of temperature alone or in presence of sodium.

Both compounds may partially react with sodium.
Na_2CO_3 may form Na_2O and carbon via the reaction :
$4\ Na + Na_2CO_3 \rightarrow 3\ Na_2O + C$
Such a reaction is thermodynamically possible (HSC calculations [8] are consistent with a negative value of ΔG in the studied temperature range) and the formation of

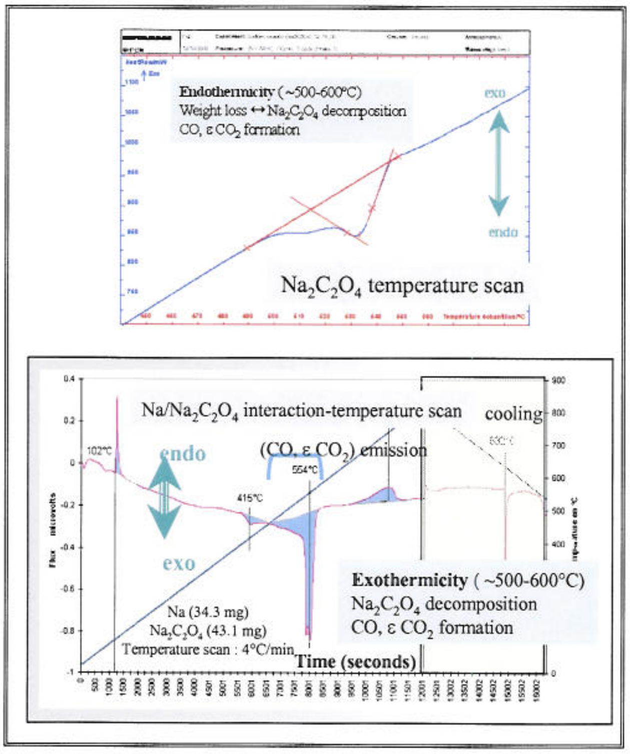

Figure 9 : $Na_2C_2O_4$ behaviour as a function of temperature alone or in presence of sodium.

Na_2O is corroborated by the small endothermic event arising between 509°C and 794°C, which is also observed in a DSC111 thermogram of a system Na/Na_2O. Nevertheless, this interaction between Na and Na_2CO_3 which seems very limited has to be checked by more detailed experiments.
The reaction between Na and $Na_2C_2O_4$ is more obvious and may be written as
$4\ Na + Na_2C_2O_4 \rightarrow 3\ Na_2O + CO(g) + C$
Na_2O formation is once again consistent with the endothermicity between 613°C and 785°C. We also observe CO(g) formation during a similar experiment conducted in a furnace connected to a microchromatograph apparatus. HSC calculations show that this reaction is thermodynamically possible ($\Delta G<0$ in the studied temperature range).
Let us notice that sodium oxalate reaction with Na leads to the formation of CO (g) which is also a sodium reactant according to literature data (see below for discussion).

II.D. VSP experiments

Two adiabatic experiments were conducted with a Vent Sizing Package apparatus.
The first one consisted in a temperature heating scan until 400°C, the second one carried out an isothermal experiment. Results are respectively presented in the figures 10 and 11.

Temperature scan

Na was contacted with CO_2 gas at room temperature. CO_2 is the minor component during the experiment. Then temperature was increased until 400°C at a heating rate of 0.2°C/min.

On the figure 10 are reported the experimental data of the temperature and the pressure inside the cell during this experiment. At 100°C, we observed sodium fusion. From 200°C to 300°C, we noted a first exothermicity, followed by a second one which was slower (300-320°C), then a series of several small and diffuse exothermicities as the temperature increased from 320°C to 400°C.

The corresponding molar reaction heat may be evaluated : ΔH_R = -61.4 kJ/ (mol CO_2).

Gas analysis (figure 12) exhibited CO formation and confirmed the part played by this intermediate product.

Scanning Electron Microscopy of the solid residue emphasized that it contains C, Na, O. This is consistent with the formation of products as $Na_2C_2O_4$, Na_2CO_3. (figure 13).

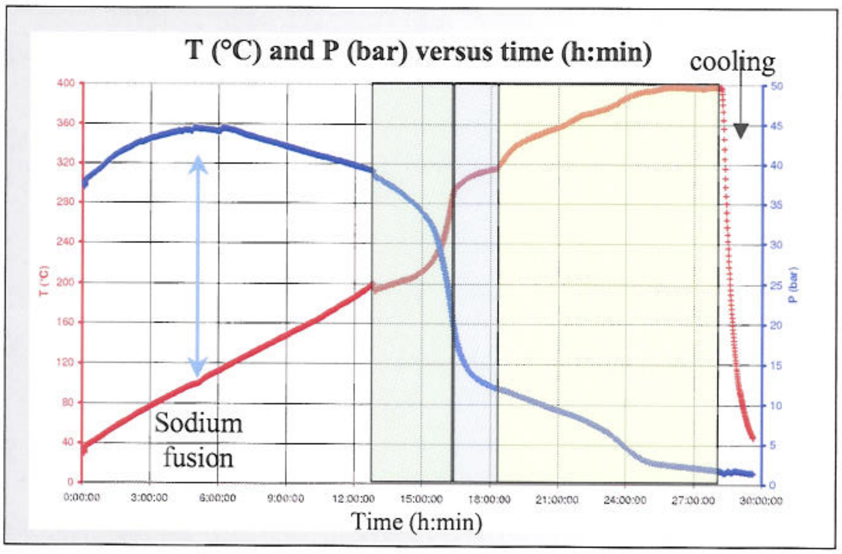

Figure 10 : VSP experiment : 0,3 mole Na contacted with CO_2 gas (0.16 mole – pressure 37.6 bars) at room temperature. Temperature exposure scan until 400°C.

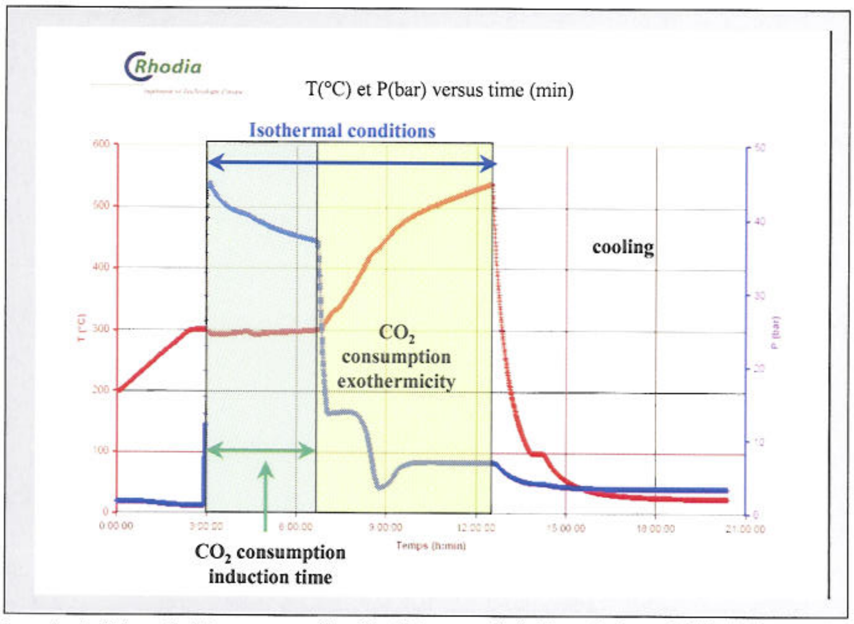

Figure 11 : VSP experiment : 1.97 mole Na contacted with CO_2 gas (0.066 moles) at 300°C after sodium fusion. Isotherm conditions : 400°C.

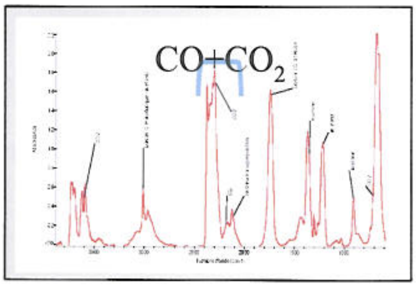

Figure 12 : gaz analysis after VSP experiment

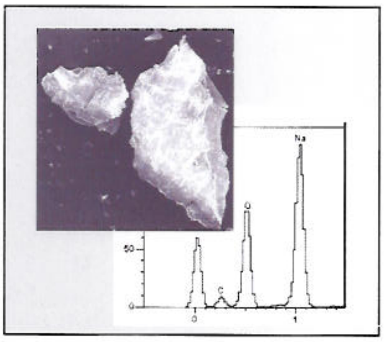

Figure 13 : scanning electron microscopy on VSP residue

Isothermal studies

As soon as CO_2 was introduced in the cell at the beginning of the isothermal conditions, CO_2 pressure (P_{CO2}) decreased as shown in the figure 11. Nevertheless, no increase of temperature was observed during four hours. At this time, P_{CO2} suddenly decreased and an exothermic event began, leading the temperature of the sample from 300°C to 540°C in 5 hours.
That is obviously consistent with our calorimetric results and the arising of an induction time when working temperatures are below 500°C.

III. DISCUSSION

According to our experimental results, the main features of the sodium/CO_2 interaction seem to claim for a reaction the nature of which depends highly on temperature :

- at low temperature (below 500°C), CO_2 and sodium react and exhibit an induction time which decreases when temperature increases.
- Above 500°C, we observe a global phenomenon with a fast and instantaneous chemical reaction which may be understood as an auto-combustion of CO_2 in sodium.

We clearly demonstrated that (Na/CO_2) interaction doest not proceed as an auto-catalytic process and is more satisfactorily explained by the occurring of an auto-combustion phenomenon.

In the first case (low temperature), we forecast that the existence of the induction period is due to the formation of CO(g) as an intermediate product. This gas has been put into evidence during VSP experiments and is also a product of the reaction of oxalate (cited in literature as an intermediate product of Na/CO_2 reaction) and sodium. A glance on the literature published on the possibilities of Na/CO(g) interaction [6] emphasizes the fact that such a reaction proceeds in three stages, the first one fast and corresponding to gas adsorption, the second one slow with an induction period which decreases when temperature increases, the third one very fast and exothermal.

In the figure 14, Sinclair et al. put into evidence the induction time of Na/CO reaction [9].

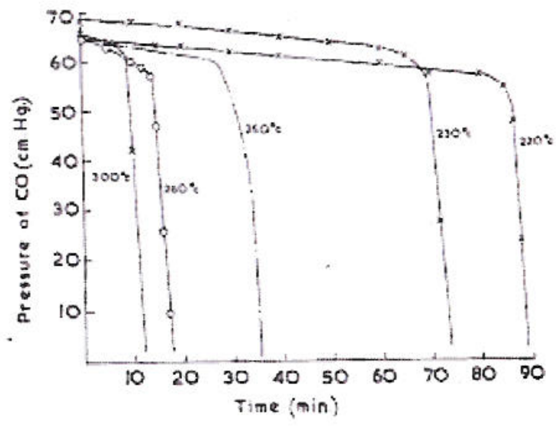

Figure 14 : CO/Na reaction. Induction time as a function of reaction temperature [9].

As a matter of fact, it seems to us that we should suggest the following reaction :

$$4\ Na + 4\ CO_2\ (g) \rightarrow Na_2C_2O_4 + CO\ (g) + Na_2CO_3$$

$Na_2C_2O_4$ reacts with sodium as seen previously to form Na_2O , C and CO(g). CO(g) formed with these two reactions reacts itself with sodium according to chemical processes suggested in literature leading to products as sodium carbonate, sodium acetylide [9].

In the range of temperature above 500°C, the results obtained are in a good agreement with Ishikawa et al. [4] experimental tests. They observed, for temperature higher than 615°C, a continuous reaction with an orange–coloured flame.

In order to consolidate our understanding of Na/CO_2 reaction, we have to determine with a great accuracy all the products formed and especially the intermediate ones, by performing calorimetric studies on more important quantities of materials and stopping the experiment just after each exo/endothermic event to analyse what the intermediate product is, just after the event. This should allow us to write the different chemical reactions arising during the processes. Studies are in progress, related to this point. Furthermore, the consequences of the potential formation of particles in sodium medium (as for example Na_2CO_3 particles) have to be considered within a short time.

Knowledge of kinetics is of great importance to check the occurrence possibility of a wastage scenario, leading to damage of several tubes of the exchanger with thermal, mechanical and chemical effects. One of our challenges is to determine the main kinetic parameters of the reaction.

Let us consider now the development of such a system in a Sodium cooled Fast neutron Reactor and more especially for a Brayton cycle. The temperature of the circuit will change along the heat exchanger and as a consequence the behaviour of the potential Na/CO_2 reaction will depend on the place of the leak. We have to investigate in details the consequences and to adapt reliable detection means to the temperature features of the reaction : instantaneous at high temperature, with an induction time at low temperature.

ACKNOWLEDGMENTS

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REFERENCES

1. R. Setton Bull. Soc. Chim.1958, P.1400.
2. Beguin and Setton. Action des métaux alcalins sur l'anhydride carbonique (Bull. So . Chim . Fr.11, 1970, 3814-3816.,
3. E.H.P. Corfunke et W. Ouweltjes, The reaction between CO_2 and liquid temperature, Journal of Nuclear Materials 33 (1969) 328-332.
4. H. Ishikawa, S. Miyahara and Y. Yoshizawa, Experimental study of sodium- carbon dioxide reaction. Proceedings of ICCAP'O5, Seoul, KOREA, May 15-19, 2005.
5. J.H. Choi, S.D. Suk, D.Cho, J.M.Kim, D. Hahn and J.H. Cahalan Capsule test for Investigating the Sodium-Carbon Dioxide Interaction. Proceedings of ICCAP'O6, Reno, NV USA, June 4-8, 2006.
6. C. Latgé, G. Rodriguez, N. Simon. Supercritical CO2 Brayton Cycle for SFR : Na-CO_2 interaction and consequences on design and operation. Proceedings of GLOBAL 2005, Tsukuba, Japan, October 9-13, 2005.
7. J.-L. Gustin, Risque d'explosion en phase condensée, Techniques de l'Ingénieur, SE 5 040.
8. HSC Chemistry, Chemical Reaction and Equilibrium Software with Extensive Thermodynamical Database. Version 3.0, Outokumpu Research Oy, Pori, Finland, 1997.
9. V.M. Sinclair, R.A. Davis and J.L. Drummond Reaction of carbon monoxide with sodium. The Alkali Metals Proc.Symp. , Nottingham England July 19-22 1966.