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ARTICLE

Carbonation Process Efficiency: Effect of Cutting Procedures on Sodium-Filled Containers

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In the context of the decommissioning of the three French sodium-fast reactors, France has chosen a common dismantling strategy in which the design of the processes is focused on eliminating the chemical risks associated with the high reactivity of sodium with air and water. These include the carbonation process which converts sodium into chemically inert compounds such as sodium carbonate and hydrogencarbonate. This is a gentle, controlled and slow process making it very attractive. The gaseous reagents are water and carbon dioxide diluted in nitrogen gas as carrier gas: the water vapour first reacts with sodium to form sodium hydroxide that is instantaneously consumed by carbon dioxide to produce sodium carbonate, in chemical equilibrium with sodium hydrogencarbonate. However, the reactional surface available and the geometric constraints of the steel containers in which sodium is confined can strongly influence the carbonation efficiency. The aim of this work is to understand the influence of the steel container geometries containing sodium (e.g. rectangular tubes or squares having different cutting directions). It is shown that the efficiency of the carbonation process is significantly enhanced when cutting direction offer a higher reactional surface despite structures geometric constraints. X-ray diffraction reveals that the carbonation process lead to the formation of sodium hydrogencarbonate phase which can be explained by a higher carbon dioxide concentration used ($20\%_{vol}$).

KEYWORDS: decommissioning, sodium, carbonation process, cutting direction

I. Introduction

In the decommissioning context of the three French sodium-fast reactors (SFR), i.e Rapsodie, Phénix and Superphénix, France has chosen to use the same three-step procedure[1)] that consists in:

- Conversion of most of the sodium (primary and secondary loops) in soda solution by NOAH process;
- Conversion of the remaining sodium – that can be either in the state of micrometric films, bulk or partially oxidized - into sodium carbonate and/or hydrogencarbonate by carbonation process[2)];
- Dissolution of the obtained products in water.

The main goals of carbonation process are (i) to remove the chemical risks related to sodium as it belongs to the family of alkali metals, highly reactive in contact with air and water and (ii) to facilitate the operators handling if the immersion step has to be skipped as sodium carbonate and hydrogencarbonate are inert compounds. The carbonation process is a key step in the decommissioning context because it allows to reduce the amount of sodium, and this to limit the generated overpressures by the sodium-water reaction (SWR) during the immersion step.

In the past, several studies were done to optimize the experimental conditions of carbonation process.[1)] They were based on reactor elements having a cylindrical geometry. However, the SFR decommissioning shows there is a large variety of elements containing sodium with various geometries. The studies that have been conducted in this context highlight the morphology of the steel structures cutting direction on the sodium carbonation efficiency[1,2)]. This leads to the development of specific tools to drill, to empty or to cut the elements containing sodium.

This study investigates the influence of the geometry and of cutting axes of these elements containing sodium on sodium carbonation efficiency. Two geometries are tested, rectangular tubes and squares. At the same time, the carbon dioxide concentration of gas mixture was changed to $20\%_{vol}$ against usually $10\%_{vol}$ to probe if sodium hydrogencarbonate are formed in a major part as expected. This has been assessed by means of X-ray diffraction (XRD).

II. Cutting Procedure

Two cutting procedures, called (a) and (b) have been tested on rectangular tubes and squares (**Fig. 1** and **Fig. 2**).

In the case of procedure (a), this consisted of cutting sections of various lengths of 2; 2.5; 3 and 4 cm for rectangular pieces whereas squares pieces cut in two sections following the diagonal of the square (Fig. 1).

For procedure (b), the lengths of sections of rectangular pieces were fixed to 2 cm except at the extremity of the tubes (close to sodium filling plug) where it was fixed to 1cm (Fig. 2). In the case of square pieces, procedure (b) consisted of

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*Corresponding author, E-mail: virginie.benoit@cea.fr cutting in two sections following the diagonal as described above and then each section was cut again in two parts. This led to four sections, two of 2 cm wide and two of 1 cm wide (Fig. 2).

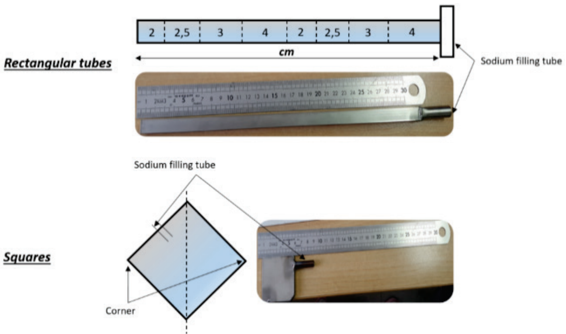

Fig. 1 Scheme of cutting procedure (a) of rectangular tubes and squares filled with sodium. The dotted lines represent the cutting axes

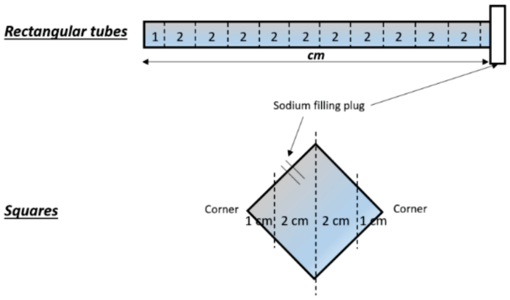

Fig. 2 Scheme of cutting procedure (b) of rectangular tubes and squares filled with sodium. The dotted lines represent the cutting axes

Let note that a specific tool had to be used to cut the rectangular tubes and squares steel elements. A shear was chosen in order to avoid a local increase of the temperature that could ignite sodium leading to a fire.

III. Carbonation Process

1. Background

Carbonation process transforms sodium into sodium carbonate and hydrogencarbonate phases (*i.e*, Na_2CO_3 and $NaHCO_3$) that are chemically inert compounds, more easily handled. It is based on a slow and controlled chemical reaction between sodium, at the solid state, and reagents that are water vapour and carbon dioxide transported by nitrogen as carrier gas.[3)]

Firstly, sodium reacts with water vapour to generate sodium hydroxide and dihydrogen gas, following the equation of reaction (1):

$$Na_{(s)} + H_2O_{(g)} \rightarrow NaOH_{(s)} + 1/2\, H_{2(g)} \qquad (1)$$

During carbonation tests, dihydrogen gas concentration is monitored to assess sodium consumption as a function of time that is linked to sodium carbonation kinetic. This is based on stoichiometry of equation of reaction (1).

Concentration of carbon dioxide in the carrier gas is in large excess against water vapour. Therefore, sodium hydroxide produced is instantly transformed into a sodium carbonate phase which is in chemical equilibrium with sodium hydrogencarbonate phase according to the reaction Eqs. (2) and (3):

$$2\, NaOH_{(s)} + CO_{2(g)} \longrightarrow Na_2CO_{3_{(s)}} + H_2O_{(g)} \qquad (2)$$

$$Na_2CO_{3_{(s)}} + CO_{2(g)} + H_2O_{(g)} \leftrightarrow 2NaHCO_{3_{(s)}} \qquad (3)$$

This is important to highlight that when carbon dioxide concentration is close to $20\%_{\mathrm{vol}}$, the chemical equilibrium is shifted in favour of sodium hydrogencarbonate phase.

Carbonation experiments lead to the growth of a layer of sodium carbonate and hydrogencarbonate above sodium. The ability of this layer to expand depends strongly on steel structures constraints related to the vessel geometry, and then the available volume above sodium. When the vessel geometry is favourable, this layer of sodium carbonate and hydrogencarbonate may achieve 5 or 6 times the initial volume of sodium (**Fig. 3**).

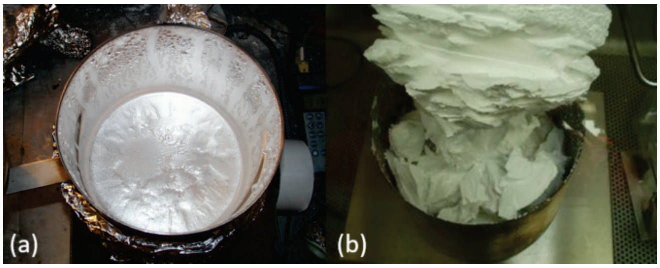

Fig. 3 Vessel containing sodium before carbonation experiment (a) and growth of sodium carbonate and hydrogencarbonate layer during carbonation experiment for a reference geometry having small constraints (b) © CEA

2. Materials

(1) Carbonation Set-up

The carbonation set-up is constituted of the elements illustrated on **Fig. 4** and described below:

- a first module permits to prepare the gas mixture in the requested volumetric concentrations. The range of carbon dioxide concentration varies between 10% and $20\%_{\mathrm{vol}}$. The chosen value depends on the experiment target, in particular if the chemical equilibrium must be displaced in favour of the sodium carbonate phase or the hydrogencarbonate one. The concentration of water vapour is fixed to $3.5\%_{\mathrm{vol}}$. Nitrogen completes gas mixture and its range varies between 76.5% and $86.5\%_{\mathrm{vol}}$;
- a carbonation chamber in which the vessel containing sodium is placed. This is equipped of thermocouples to monitor inside the temperature of carbonation gas mixture;
- a micro-chromatograph that provides the concentration of the formed dihydrogen gas in the carbonation gas mixture as function of time. This apparatus also monitor the concentrations of nitrogen, carbon dioxide and oxygen in the carbonation device during experiment;

- two cameras are positioned inside the set-up ensuring a visual recording of the volume expansion of sodium carbonate and hydrogencarbonate layer during carbonation;
- oxygen and hydrogen detectors are installed after the carbonation chamber. This is essential to monitor oxygen concentration inside the carbonation device during the experiment to detect quickly an air inlet that can induce a strong reaction with sodium. After the carbonation chamber, carbonation gas mixture containing dihydrogen is released to atmosphere. Therefore, dihydrogen detector is essential to track dihydrogen concentration and to remain under the Lower Flammability Limit (LFL). Moreover, carbonation devices are not usually ATEX (explosive atmosphere) certified. Beyond oxygen and dihydrogen safety thresholds fixed, the reagents flow (i.e. water vapour and carbon dioxide) is stopped. However, nitrogen gas flow is maintained to release the dihydrogen gas from the carbonation chamber and to avoid a local dihydrogen concentration inside carbonation device.

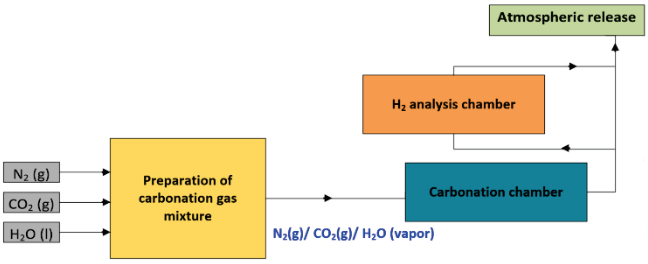

Fig. 4 Basic diagram of the carbonation device

To perform a carbonation experiment, several safety rules must be respected. The temperature of the carbonation device should be higher than the dew point temperature of the carbonation gas mixture of few degrees. The temperature should be between room temperature and 60°C maximum. Under nominal conditions, the amount of water vapour has to be controlled to limit the dihydrogen gas production. A slight overpressure is applied to avoid an air ingress inside the carbonation device. A re-circulation of the carbonation gas mixture is realized to avoid areas where dihydrogen gas could be accumulated inside carbonation chamber.

At last, it is important to highlight that the whole carbonation set-up, i.e. pipes and carbonation chamber, is thermally insulated to avoid a cold spot that could induce the condensation of water vapour leading to sodium-water reaction locally.

(2) X-ray Diffraction

X-ray diffraction measurement were performed using a D-5000 diffractometer from Bruker (Germany). Data collection was carried out in the 2θ range 10–90° using Cu Ka radiation (l=1.5418A). Phase identification was performed by using the ICDD powder diffraction file database.

IV. Experimental Results

The carbonation of rectangular tubes and squares were carried out simultaneously in the carbonation chamber (Fig. 4). They were done using (a) and (b) cutting procedures described in Fig. 1 and Fig. 2. For the carbonation test based on the (a) cutting direction, the carbon dioxide concentration in the gas mixture was set to $10\%_{vol}$ against $20\%_{vol}$ for the cutting procedure (b). The goal was to form in a major part the sodium hydrogencarbonate phase. The water vapour concentration and temperature were maintained to $3.5\%_{vol}$ and 42°C for the two tests.

Figure 5 represents the volumetric percent of the produced H_2 gas as function of time for sodium carbonation of rectangular tubes and squares based on the (a) and (b) cutting procedures.

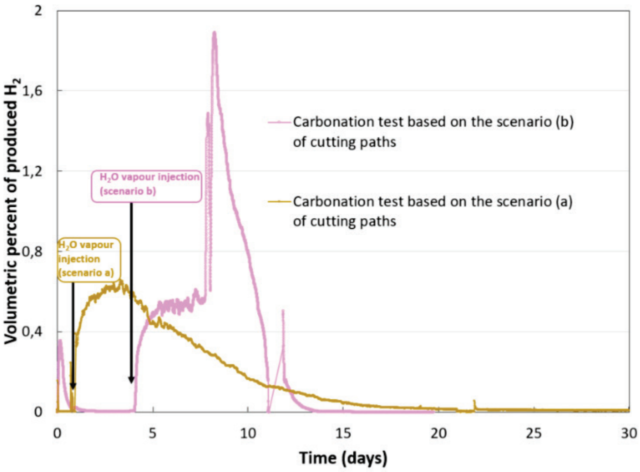

Fig. 5 Volumetric percent of the produced H_2 as a function of time based on the (a) (brown curve) and (b) (pink curve) cutting directions

At the beginning of carbonation tests, carbonation gas mixture was only constituted of nitrogen and carbon dioxide. During the first few hours, a release of H_2 gas is observed of $0.15\%_{vol}$ and $0.35\%_{vol}$ respectively for the (a) and (b) cutting procedures. This can be attributed to the transformation of a small amount of sodium in contact with the humidity traces of the introduced gases (carbon dioxide and nitrogen as carrier gas), following the reaction Eq. (1). Then, water vapour was added to the carbonation gas mixture until reaching the carbonation nominal conditions. In both cases, the addition of water vapour lead to a strong increase of the released of H_2 gas during the first few days. For the carbonation test involving (a) cutting procedure, the volumetric percent of produced H_2 reaches $0.6\%_{vol}$ on the third day (brown curve, Fig. 5). For the one based on the (b) cutting procedure, the produced H_2 reaches $0.5\%_{vol}$ the fifth day and then it is followed by a strong rise up to $1.9\%_{vol}$ the eighth day (pink curve, Fig. 5). This strong H_2 volumetric percent was explained by a temporary dysfunction of the water injection line that led to the addition of a concentration of water vapour higher than carbonation nominal conditions. In both cases, the production of H_2 can be related to a strong increase of sodium consumption. **Figure 6** represents the sodium carbonation kinetics of sodium contained in rectangular tubes and squares based on (a) and (b) cutting procedures.

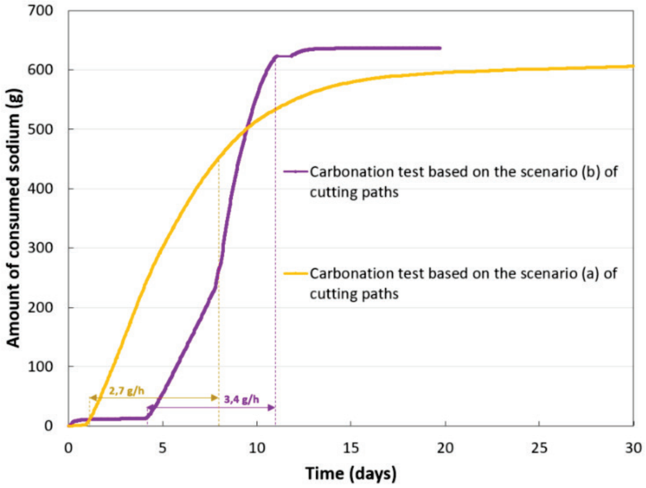

Fig. 6 Evolution of the sodium amount as a function of time based on the (a) (yellow curve) and (b) (purple curve) cutting procedures

The carbonation kinetics show a strong sodium consumption during the first ten days of the tests. For the carbonation test based on the (a) cutting procedure, the rate of sodium consumption was 2.7 g/h in six days against 3.4 g/h for (b) cutting procedure. This can be explained by a surface-based chemical reaction between sodium and water vapour following the chemical reaction (1). Moreover, this chemical reaction is promoted by the (b) cutting procedure that provides a larger sodium reactional surface against the (a) procedure. Indeed, each side of the cut pieces of rectangular tubes and squares are accessible to the carbonation gas mixture, except the corners. The sodium carbonate and/or hydrogencarbonate layer is being formed and then does not limit the diffusion of carbonation gas mixture until the sodium.

The recording of cameras shows, at the beginning of carbonation, small agregates of sodium carbonate and/or hydrogencarbonate are formed and cover the sodium surface. These agregates grow over time until they become friable filaments and then a layer of sodium carbonate and hydrogencarbonate which covers the rectangular tubes and squares at the end of carbonation tests as illustrated in **Fig. 7**.

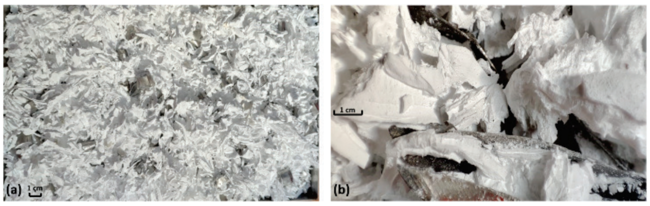

Fig. 7 Visual appearance of layer of sodium carbonate and hydrogencarbonate (a) and a zoom of this layer formed at the corners of squares (b)

A strong decrease of the produced H_2 is observed until reaching $0.05\%_{vol}$ the fifteenth (brown curve, Fig. 5) and the eleventh (pink curve, Fig. 5) day. Then, the production of H_2 gas is almost zero until the end of carbonation in both cases. Nevertheless, it does not mean that the whole amount of sodium is carbonated as demonstrated by the carbonation efficiencies. At the same time, Fig. 6 shows the appearance of a threshold of sodium consumption from the fifteenth and the eleventh days until the end of carbonation tests. The rates of sodium consumption are a few milligrams per hours.

The efficiency of sodium carbonation is of 86% in 25 days for the (a) cutting procedure against 97.5% in 14 days for the (b) cutting procedure. This suggests that sodium carbonation kinetics are firstly governed by a surface-based chemical reaction between sodium and water vapour. Secondly, the decrease of H_2 production can be related to the gas diffusion phenomenon through the sodium carbonate and hydrogencarbonate layer. Moreover, the carbonation gas diffusion is certainly limited by the geometric constraints of steel structures of rectangular tubes and squares that involve probably a densification of sodium carbonate and hydrogencarbonate layer. In the specific case of the (b) cutting procedure, the carbonated layer is probably denser due to the carbon dioxide concentration that may promote the formation of sodium hydrogencarbonate phase preferentially.

The cameras recording shown that the pressure of sodium carbonate and hydrogencarbonate layer on the steel structures of rectangular tubes and squares did not allow to open them to provide a larger surface to sodium access for the carbonation gas mixture. Therefore, this contributes to a decrease of the efficiencies of sodium carbonation kinetics.

After carbonation tests, sodium carbonate and/or hydrogencarbonate phases formed in rectangular tubes and squares were scraped for further analyses and also to evidence any residual amount of sodium (**Fig. 8**).

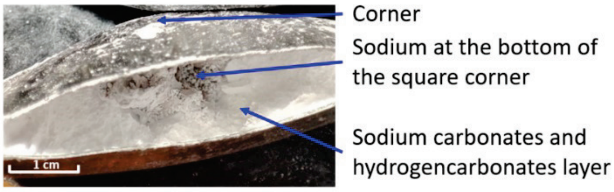

Fig. 8 Example of remaining sodium in the corner of square

For the (a) cutting procedure, sodium was observed mainly inside the pieces of rectangular tubes having a length higher than 2 cm but also in the corners of squares and rectangular tubes. For the (b) cutting procedure, the sodium was observed inside the corners of squares as illustrated in Fig. 8 but also in some corners of rectangular squares. Let note that in the case of (b) cutting procedure, metallic sodium was not observed for all pieces having a length of 2 cm.

In order to corroborate the formation of a major part of sodium hydrogencarbonate phase for the (b) cutting procedure, samples obtained after carbonation were analysed using XRD. The obtained diffractograms are given in **Fig. 9**. They demonstrate that hydrogencarbonate is the only phase formed upon carbonation processes, whatever the cutting direction.

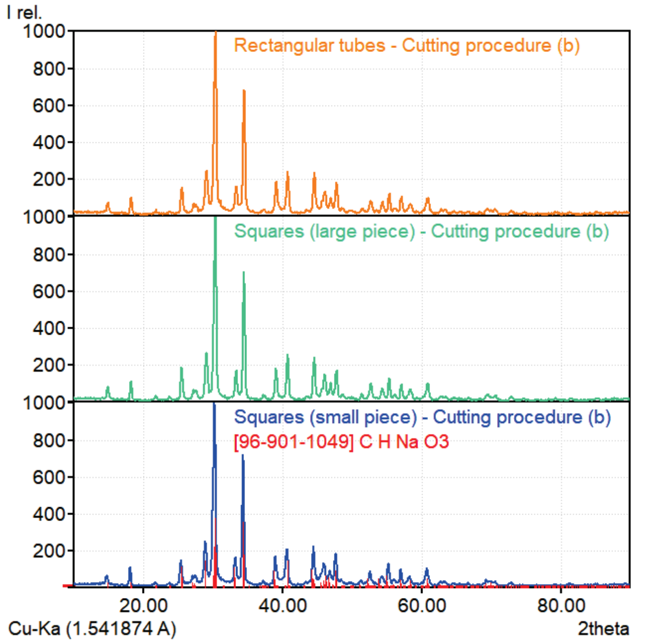

Fig. 9 X-ray diffractograms obtained in the case of cutting procedure (b) for different cutting directions

V. Conclusion

In the context of SFR dismantling, the shape of the container but also the cutting procedure are crucial parameters that can strongly influence the sodium carbonation efficiencies and therefore the water immersion step.

In the specific case of the rectangular tubes and squares, the (b) cutting procedure provides a larger sodium surface accessible to carbonation gas mixture, unlike the (a) procedure. Despite geometric constraints related to the steel structures of rectangular tubes and squares, this second experiment allowed to enhance significantly the efficiency of the sodium carbonation. Indeed, 97.5% of sodium was transformed against 86% for the (a) cutting procedure. The unconsumed sodium is mainly localized in the corners of squares and a part in the corners of rectangular tubes. Unlike the (a) cutting procedure, the unconsumed metallic sodium was not found inside pieces of rectangular tubes of length of 2 cm. Therefore, this means that a length less than 2 cm is favourable to treat entirely the sodium inside rectangular pieces.

For the (b) cutting procedure, the XRD analysis performed after the carbonation reveals that only hydrogencarbonate phase was formed which is consistent with the carbon dioxide concentration. Further investigation will be done in order to carry out a new carbonation experiment using (b) cutting procedure and $10\%_{\text{vol}}$ carbon dioxide to assess the effect of sodium carbonation efficiency.

Acknowledgment

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