DOI: 10.15669/pnst.8.205

Progress in Nuclear Science and Technology
Volume 8 (2025) pp. 205-208

ARTICLE

Innovative Sodium Cleaning Process using Saline Solutions

Leïla GICQUEL*, Sébastien LEFEVRE, Sacha BRUNO,
Laure MOINOT and Benjamin TARDIVEL

CEA, DES, IRESNE, DTN, Cadarache, F-13108, Saint-Paul-lez-Durance, France

During the development of NOAH process at CEA in the 1980s, the addition of sodium hydroxide to water was identified as an interesting way to moderate the kinetics of the sodium-water reaction. Based on these observations, studies were launched at CEA in 2007 with the aim of developing an innovative process for treating remaining sodium in the components of a sodium fast reactor (SFR). This process would have the following advantages: control of the sodium-water reaction and limitation of its effects by adding an appropriate salt; flexibility and increase in treatment rates by rapid immersion of the components. In order to overcome the corrosive nature of sodium hydroxide, new salts were studied. Several salts appeared promising in that, for some of them, the reaction no longer generates a shock wave despite an excess of water, the kinetics are slowed down and the release of energy occurs gradually in the reaction medium. Following these results, new experimental campaigns were launched and enabled to identify the influential parameters and to quantify the effects of two salts on the moderation of the sodium-water reaction: tetrasodium EDTA and sodium acetate.

KEYWORDS: sodium, cleaning process, sodium treatment, saline solution, sodium-water reaction

I. Introduction

During the development of NOAH process at CEA in the 1980s,[1] the addition of sodium hydroxide to water was identified as an interesting way to moderate the kinetics of the sodium-water reaction. Based on these observations and as part of the development of the IVth Generation of nuclear reactors, new studies were launched at CEA in 2007 with the aim of developing an innovative process for treating sodium from the components of a sodium fast reactor (SFR). This process would have the following advantages:

- Control of the sodium-water reaction and limitation of its effects by adding an appropriate salt;
- Flexibility and increase in treatment rates by rapid immersion of the components.

In order to overcome the corrosive nature of sodium hydroxide above 80°C, new salts were studied at CEA, in particular as part of Lacroix's PhD work in 2014.[2] Several salts appeared promising in that, for some of them, such as lithium acetate, tetrasodium EDTA or iron III chloride, the reaction no longer generates a shock wave despite an excess of water, the kinetics are slowed down and the release of energy occurs gradually in the reaction medium. These results led to the publication of a patent in 2015.[3] The research work undertaken on this subject did not make it possible to understand the phenomena involved. In order to continue these studies, other experimental campaigns were carried out from 2019, including small-scale experiments and pilot-scale experiments. Small-scale experiments enabled to quantify the impact of salt concentration on the effects of the sodium-water reaction. In particular, it has been shown that the optimal concentration of tetrasodium EDTA is around 0.1 mol/L and a threshold value of sodium acetate has been identified around 2 mol/L beyond which the reaction effects are attenuated. In addition, pilot-scale experiments seemed to indicate that there is no scale effect.

Following these results, a new experimental campaign comprising more than thirty parametric tests was launched at the end of 2023.

II. Sodium-Water Reaction

The actual industrial process used for cleaning the irradiated assemblies and components of a sodium fast reactor, during operation (maintenance, in-service inspection, repair…) but also during decommissioning and dismantling, is cleaning with water.

The sodium-water reaction (SWR) is an exothermic reaction with a reaction enthalpy of -184 kJ/mol$_{Na}$, taking into account the dissolution of sodium hydroxide in water. The reaction equation is the following:

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

In addition to the exothermic nature of the reaction, it has the following characteristics:

- Almost instantaneous, explosive and leading to overpressure due to the pressure wave released (**Fig. 1**);
- Production of sodium hydroxide, which can lead to corrosion problems;
- Production of hydrogen, which is a flammable and explosive compound depending on its concentration (between 4 and 75% in volume in air) and the presence of oxygen in the environment.

*Corresponding author, E-mail: leila.gicquel@cea.fr

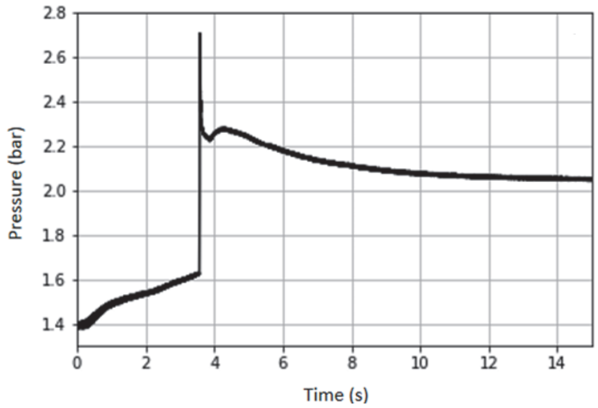

Fig. 1 Sodium-water reaction with a 4-gram pellet of sodium (ambient temperature, 700 mL of demineralized water)

III. Experimental Results with Saline Solutions

1. Experimental Grid

This new experimental campaign focused on the study of two particular salts: sodium acetate and tetrasodium EDTA. These salts were chosen based on their performance in moderation as well as their cost or environmental issues. For example, sodium acetate was preferred over lithium acetate, although the latter was recommended in Lacroix PhD thesis[2]. The following test grid (**Table 1**) corresponds to the experiments conducted during this campaign.

Table 1 Experimental test grid

Number	Salt	Salt concentration (mol/L)	Mass of sodium (g)
1	Sodium acetate	1	2
2	Sodium acetate	2.5	2
3	Sodium acetate	2	2
4	Sodium acetate	1.5	2
5	Sodium acetate	3	2
6	Sodium acetate	1	1
7	Sodium acetate	0.75	2
8	Sodium acetate	1	4
9	Tetrasodium EDTA	0.1	1
10	Tetrasodium EDTA	0.1	2
11	Tetrasodium EDTA	0.1	4
12	Tetrasodium EDTA	0.05	4
13	Sodium acetate	0.5	2
14	Sodium acetate	2	4
15	Tetrasodium EDTA	0.075	2

Each experiment was conducted twice, in order to determine the repeatability between two experiments under the same operating conditions. In addition to the experiments presented in the table, six reference tests of SWR (700 mL of demineralized water + sodium pellets of 1 to 4 grams) were also performed.

2. Experimental Facility

The experiments have been carried out in LAVINO device (Innovative Cleaning), presented in **Fig. 2**. This device comprises several parts including:

- A 3.5 L reactor. For each experiment, 700 mL of solution were introduced into the reactor, leaving a total of 2.8 L of gaseous phase volume;
- A sodium pellet introduction device. This device allows the pellet to be transported from the glove box where it has been manufactured to the reactor, while avoiding contact between the sodium and the surrounding air. Once placed on top of the reactor, it is connected to a pneumatic cylinder that allows the basket containing the sodium pellet to be immersed into the solution;
- Three thermocouples (in the solution, in the gas and on the reactor wall), a dynamic pressure sensor, and a gas analysis board (O_2 and H_2). These acquisition tools enable data collection on each experiment;

A high-speed Phantom camera (1 000 – 28 000 fps with a resolution of 1 024 x 768) as well as a GoPro camera, allowing the reaction to be filmed with varying degrees of precision through the reactor's portholes.

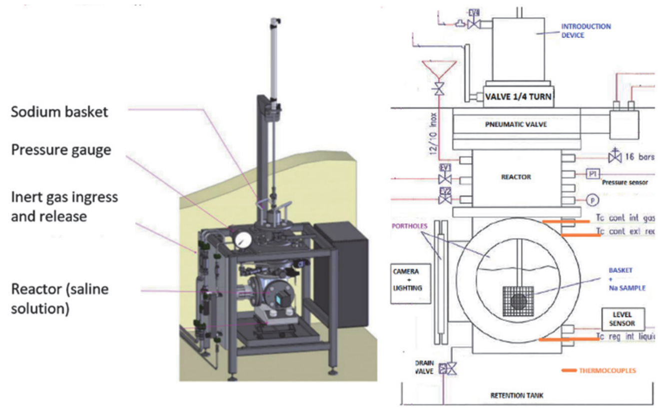

Fig. 2 Sketch and process diagram of LAVINO facility

3. Main Results

(1) Sodium Acetate

The moderation of this reaction using sodium acetate is effective. The effectiveness of this moderation increases with the concentration of the electrolyte. The tests with sodium acetate also revealed the impact of the sodium mass on the moderation of the reaction at a similar concentration. The recorded final overpressures confirm that the reaction is proceeding correctly, as there is indeed the expected production of hydrogen gas.

These graphs (**Fig. 3**), representing pressure as a function of time, demonstrate whether the reaction is well moderated or not. At a concentration of 1 mol/L, the explosion phenomenon disappears when a 2-gram pellet reacts (up in the figure), but this phenomenon is still present during the same reaction with a pellet twice as heavy, and therefore thicker (bottom left). In terms of concentration, it is clear that a 3 mol/L solution is more effective than a 1 mol/L solution (bottom right). The comparison is first made based on the pressure rise, which appears smoother and more regular at higher concentrations. It is also made in terms of reaction time, which is much longer when using a 3 mol/L sodium acetate solution.

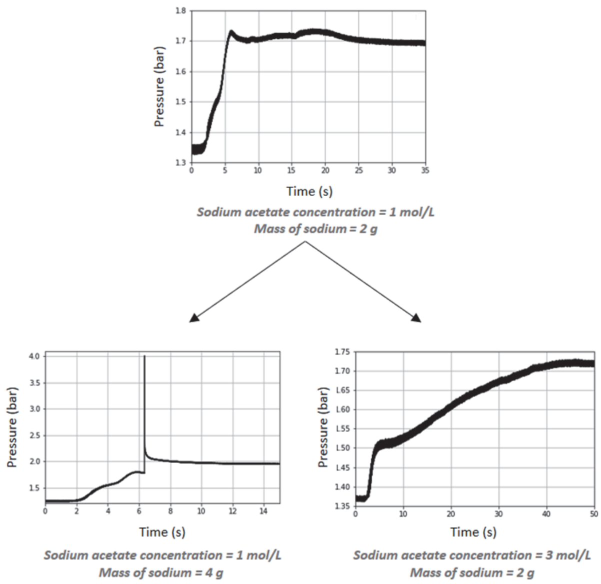

Fig. 3 Reaction of a pellet of sodium with a solution of sodium acetate

Moreover, it can be noticed that with a 4-gram pellet and a 1 mol/L concentration, the pressure peak appears after 6 seconds, whereas it appeared after 4 seconds for a sodium-water reaction. This delay can be attributed to the difference of the layers of oxides, but it is highly possible that it is due to an ionic layer in solution. This hypothesis will be studied during a future PhD in the laboratory.

It is possible to determine the average consumption rate of the sodium pellet by dividing the mass of sodium used by the total reaction time. By doing this for tests with the same mass of sodium (see **Fig. 4**, with a 2-gram pellet), a clear trend in the consumption rate of the sodium pellet can be observed. This phenomenon has to be investigated in future experiments in order to be validated.

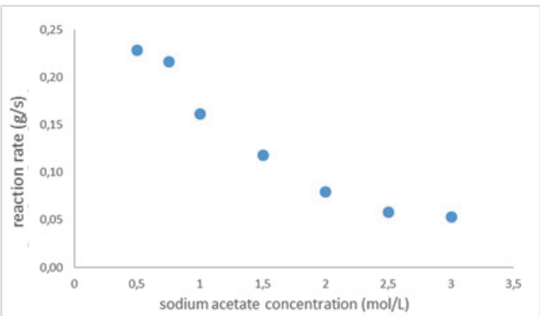

Fig. 4 Reaction rate as a function of sodium acetate concentration for a 2-gram pellet of sodium

Figure 5 shows the theoretical ($\Delta T_{sol.th}$) and experimental ($\Delta T_{sol.exp}$) temperature variations of the solution and the maximum temperature variation in the gas phase ($\Delta T_{gas\ max}$) during double tests for three different sodium masses. The higher the temperature variation of the gas phase the lower the temperature variation of the solution, which corresponds to the expected one, with the exception of tests with a 1 g pellet. $\Delta T_{sol.th}$ is calculated by considering that the entire reaction enthalpy is transferred to the liquid phase, i.e. $\Delta T_{sol.th} = \Delta Hr/m_{sol}C_p = 187 \cdot n_{Na}/m_{sol}C_p$ with n_{Na} the number of initial moles of sodium, m_{sol} the mass of saline solution and C_p the heat capacity of water (4.18 kJ/Kg/K). The uncertainty of the thermocouples is ± 1.5°C. Since the results are presented in temperature variation, the uncertainty varies quadratically: $U(\Delta T) = \sqrt{U(-T)^2 + U(+T)^2}$ which gives a final uncertainty of ± 2.1°C. Taking this uncertainty into account, the results are consistent.

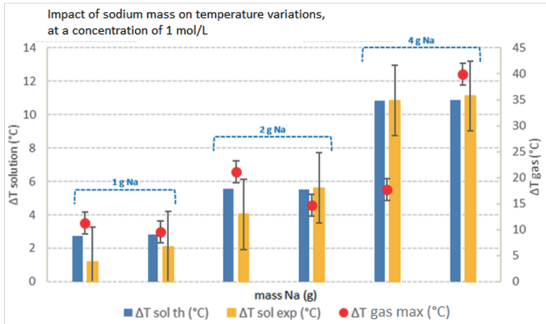

Fig. 5 Temperature variations for 1 mol/L sodium acetate solutions as a function of the mass of sodium

It can also be observed in **Fig. 6** that the salt concentration influences this temperature variation in the gas phase, the reaction being less violent at high concentrations. The temperature variation of the solution is closest to the expected value for the highest concentrations of sodium acetate.

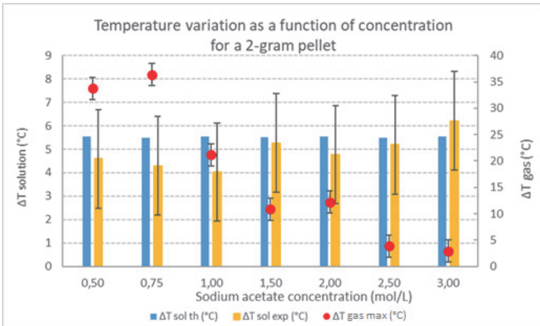

Fig. 6 Temperature variations for 2-gram pellets as a function of sodium acetate concentration

(2) Tetrasodium EDTA

All these trends can be observed in tests with tetrasodium EDTA solutions. Indeed, for a concentration of 0.1 mol/L, the reaction is moderated whether it is for a pellet of 1, 2, or 4 grams; however, it is not for a concentration of 0.075 mol/L with a 2-gram pellet or a concentration of 0.05 mol/L with a 4-gram pellet. These two graphs (**Fig. 7**) highlight a concentration threshold between 0.05 mol/L and 0.1 mol/L for moderating the reaction with 4-gram pellets. Similarly, a threshold between 0.075 mol/L and 0.1 mol/L is valid for 2-

gram pellets. As with the sodium acetate tests, it is possible to determine experimental consumption rates.

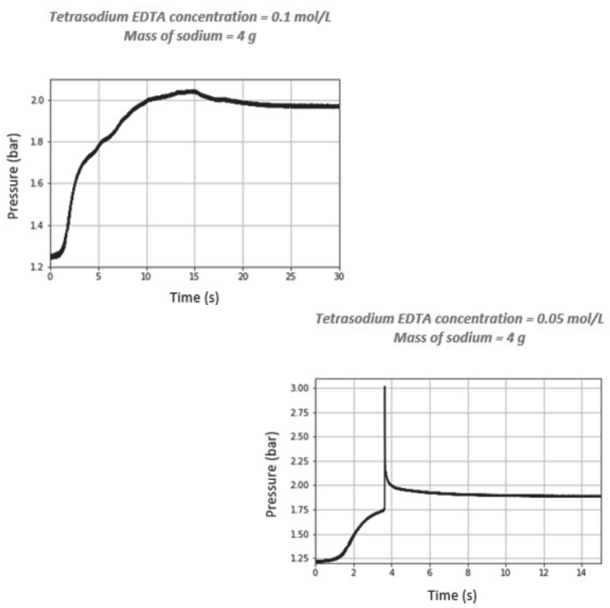

Fig. 7 Reaction of a pellet of sodium with a solution of tetrasodium EDTA.

Having conducted fewer tests with this salt due to the narrower concentration range, the conclusion is that a 2-gram pellet and a 4-gram pellet are consumed at the same rate at a concentration of 0.1 mol/L. Indeed, these two experiments led to a consumption rate of around 0.27 g/s. Conversely, a 1-gram pellet has a slower consumption rate, around 0.06 g/s.

The graphs presented **Fig. 8** and **Fig. 9** show that during the experiments with 1-gram pellets, the temperature variation is lower than expected. In addition, it seems that when the explosion phenomenon occurs, the temperature variation is closer to the theory. However, the temperature in the gas phase does not seem to depend on the mass of sodium involved, nor on the tetrasodium EDTA concentration of the solution (**Fig. 9**). This means that the high temperature rise in the gas phase is not only related to the quantity of dihydrogen produced but also to the phenomenon of sodium combustion.

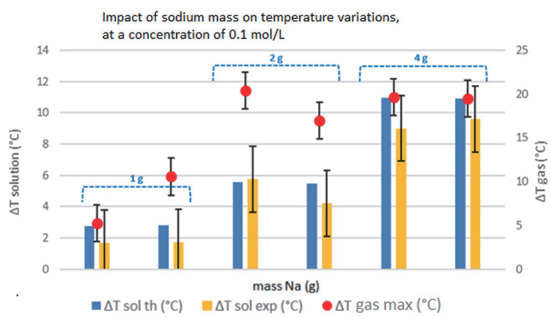

Fig. 8 Temperature variations for 0.1 mol/L tetrasodium EDTA solutions as a function of sodium mass

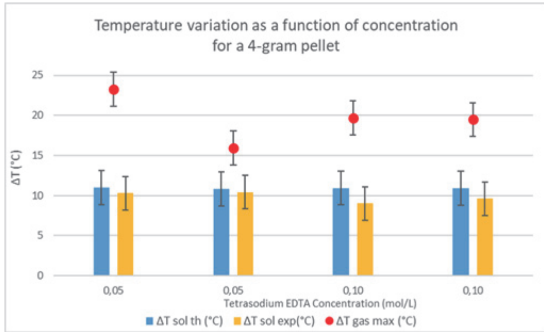

Fig. 9 Temperature variations for 4-gram pellets as a function of tetrasodium EDTA concentration

III. Conclusion

These experimental results provide initial trends in the moderation of the sodium-water reaction. In order to improve the results, in the aim of establishing the reaction kinetics, the future experiments will be realized with some modifications. Molds with specific weights will be used to manufacture the sodium pellets in a pure argon environment. This modification will enable to confirm the concentration thresholds (perfect spherical pellets, no oxide crust on the surface). In addition, some evolutions of LAVINO device will be done in order to be able to collect samples of the liquid solution and gas during the reaction. This modification will enable the determination of the reaction kinetics in a near future.

Acknowledgment

The authors acknowledge the former research team who worked on this subject in CEA Cadarache and the project managers and team managers for their financial and material support.

References

1) G. Rodriguez, “Le caloporteur sodium,” Tech Ingénieur, BN 3680v2, (2021). [in French]
2) M. Lacroix, “Étude de l’effet modérateur de sels sur la réaction sodium-eau, pour le lavage d’assemblages de combustible irradiés issus de réacteurs à caloporteur sodium,” *PhD thesis,* Pierre and Marie Curie University, (2014).
3) M. Lacroix, H. Lorcet, C. Perrais, “Procédé de traitement du sodium par une solution de sel aqueux et procédé de lavage d’assemblages combustibles de réacteur nucléaire utilisant ledit procédé de traitement,” WO2015/110480 A1, (2015).