Unsteady aspects of sodium-water reaction

Water cleaning of sodium containing equipments

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Context and objectives

Fast Sodium Reactor (FSR) is one of the most promising nuclear reactor concept ("Generation IV systems") to be issued in the next decades [1]. This technology is intended to be much safer, to have a significantly better yield and to produce less wastes with a lower nocivity. Liquid sodium is used as the thermal fluid in direct contact with the nuclear core. Ideally, the heat extracted should be transferred between sodium and water in steam generators. BUT when sodium is brought in contact with liquid water, a highly exothermal chemical reaction ensues which is believed to be explosive in certain situations [2]. Such a contact may happen in a number of instances (repairs, decommissioning,..) and not only during major accidents. This is thus a significant safety issue which may significantly handicap the development of this technology.

Unfortunately the reasons for which the mixing of sodium with water may lead to an explosion, generating blast waves like an explosive material, do not seem to have been clarified so far not even deeply studied. The primary objective of this PhD work is thus to identify the details of the phenomenology, to isolate the leading mechanisms and to propose a modelling approach.

State of the art

Very few papers are available. The global sodium-water reaction reads [3] :

$$Na_{(s)} + H_2O_{(l)} \rightarrow NaOH_{(s)} + \frac{1}{2} H_{2(g)} + Q \tag{1}$$

In terms of mass fraction, the stoichiometric mixtures contain about 50% of sodium and 50% of water. The standard amount of heat release, Q is about 141 kJ/mole. Note that if NaOH is allowed to dissolve in (excess) water, the heat of dissolution (47 kJ/mole) needs to be added. Because of the presence of hydrogen in the gaseous products, the explosive potential of the reaction is traditionally associated to a hydrogen explosion hazard.

However, some authors [4] pointed out that fast energy releases leading to significant pressure waves were possible even without any possibility for a hydrogen hazard to appear (no oxygen in the experiment).

There is thus a need to identify by which mechanism the energy released by reaction (1) can lead to a sudden expansion of gases so that a blast wave might be emitted.

Main findings

To do this, the energy transfer mechanism was systematically investigated starting from the chemical mechanism towards the blast wave production. To this end, a large body of yet unreleased experimental data extracted from the files of the French Commissariat à l'Energie Atomique (CEA) was collated. During this PhD work those data were analysed using the "tool box" of explosion experts. Additional experiments were nevertheless performed during this PhD work to fill gaps (thermochemistry) and to verify some past measurements (blast waves). These new experiments are called "SOCRATE" and presented in the following paragraphs.

The chemistry of the reaction needs to be clarified first to check whether any unstable by-products might be formed in certain situations and second to estimate the ratio Q_{exp}/Q_{chem} (Q_{chem} initial chemical energy; Q_{exp} the expansion of gaseous products). A rather classical thermodynamic equilibrium code[1] was used [5]. A large number of species like NaH, Na and Na_2O, NO,... were introduced into the database. The calculations (Figure 1) suggests that mostly water, sodium, soda, sodium oxide can be formed. Only very minor quantities of other compounds can appear. Especially at stoichiometric condition equation (1) is pretty well verified. The maximum temperature is about 1100 °C (close to stoichiometric conditions) and the maximum amount of gases is produced at about 40% in mass which is significantly below the stoichiometry, suggesting that the most severe explosions phenomena may not be observed at stoichiometric conditions but with an slight excess of water (2 mole of water for one mole of Na). Note that Q_{exp}/Q_{chem} is about 20% in this situation so that 1 kg of completely hydrolysed sodium would not be able to release more than 1600 kJ of gas expansion energy which would correspond to a maximum TNT equivalent of 35% in case all this "pressure" energy were to produce a shock wave.

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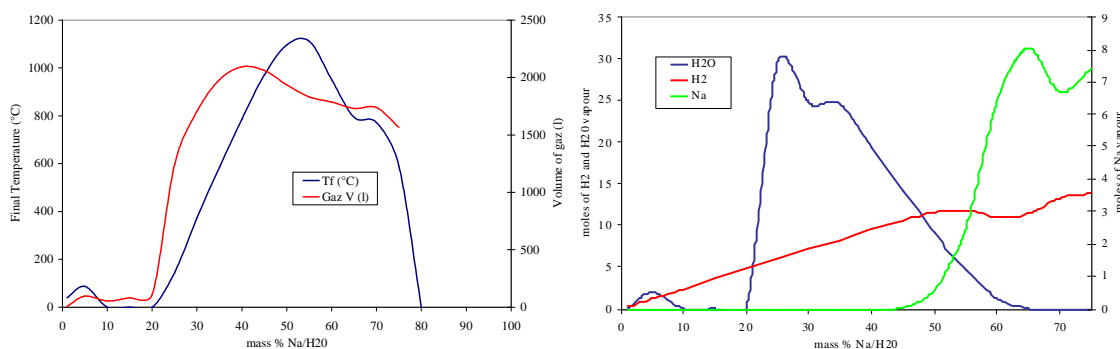
[1] The principles of the software are classical. Given a list of possible compounds, the thermodynamic equilibrium of the reaction is calculated by minimising the free enthalpy whereas the standard conservation laws (species and energy) are obeyed.
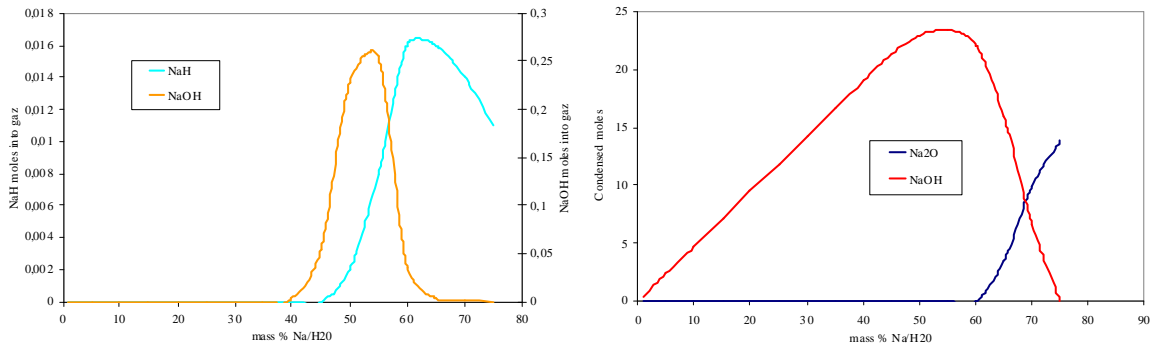
Figure 1: Final reaction temperatures, volume of gases and composition as function of the mass fraction of Na in 1 kg of (Na + H$_2$O) mixture (at 1 bar)

Available experimental evidence tends to confirm a number of points. In particular, the maximum temperature is about 1000°C whereas systematic calorimetric measurements[2] confirms that the reaction between sodium and water is not equimolar but corresponds to 1.5 mole of water reacting with 1 mole of sodium (Figure 2). The final products are NaOH, water steam and H$_2$. But Q_{exp}/Q_{chem} is only 10%. The rest of the energy is transferred to the condensed products (NaOH and liquid water) and used to vaporise the excess water (0.5 mole of water for one mole of Na). Apparently the reaction is more dissipative than suggested by the thermodynamic calculations.
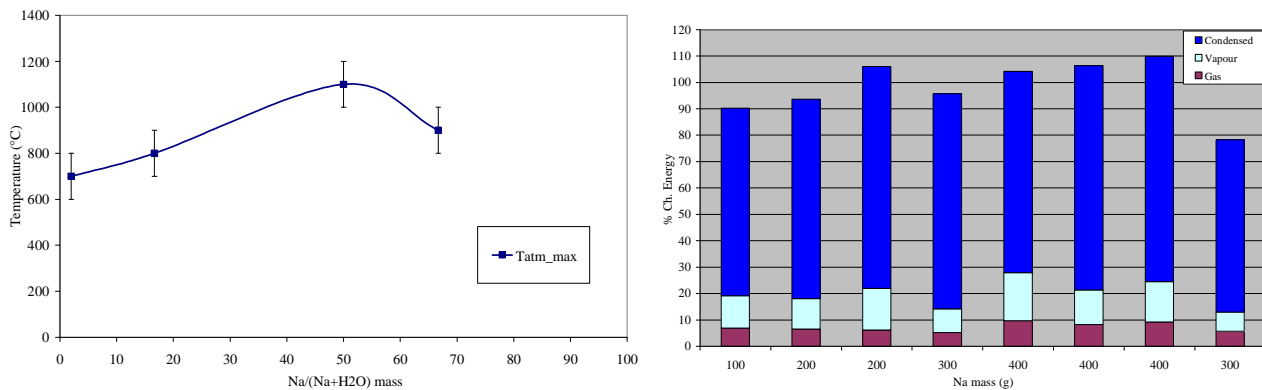

Figure 2: Reaction temperature and chemical energy repartition as function of sodium mass for some experimental tests

This might come from the **kinetics** of the reaction especially if the latter is rather slow. SOCRATE were performed to estimate the speed of the reaction and especially the rate of heat release. Within the frame of explosions, it is usually sufficient to estimate the evolution of the rate of heat release with the temperature according to the simplified Arrhenius law[3] :

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[2] Performed in a closed vessel wuth a nitrogen gaseous blancketing with measurement of the pressure and of the temperatures (sodium, gases, water).

[3] The dependency with reactants concentration is neglected since, as supposed in explosions problems, expected temperatures are generally high and exponential term becomes predominant.

$$\Phi_{rea} = \Delta H_{rea} A e^{\left(-\frac{E}{RT}\right)} \tag{2}$$

where Φ_{rea} (J/mole of Na/m^2 of sodium sample) is the reaction heat flux density, T the mixture temperature , A and E are respectively the activation energy and pre-exponential factor, ΔH_{rea} is the total heat produced by the reaction [J/mol of Na]. Note however that equation 2 may be representative of a number of additional processes related to the chemical phenomena s for instance local diffusive processes. To obtain A and E. it is necessary to measure simultaneously Φ_{rea} and T. To do this a totally new experimental concept was devised. A sodium sample is deposited on the surface of a large heat absorbing body (copper having the same heat transfer properties) as presented in Figure 3-a. When water comes in contact with the sodium sample, the reaction starts and heats up the heat sink. By measuring the temperature at several points inside the holder, it is in principle possible to calculate at each time step the power transferred to the holder (Φ_{con}) and to estimate the reaction temperature using an inverse method (see below).
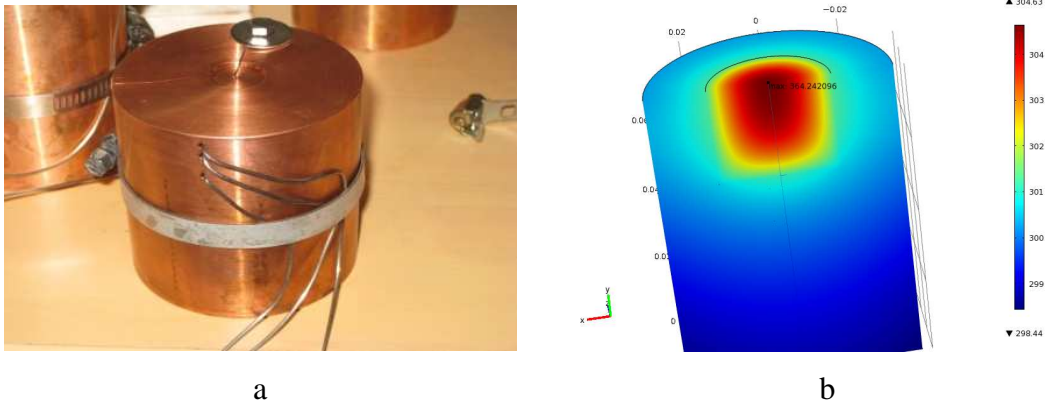

a   b

Figure 3: Copper holder with embedded thermocouples. On the top, the small cavity where sodium is casted (a) and calculated inner temperature field using an inverse method via COMSOL (b)

Obviously, only a part of the reaction heat is conducted inside the holder, the remaining part being transferred to the water. But since the total quantity of heat released is accurately known a heat transfer coefficient h (average) between the reaction zone and the water can be calculated to close the thermal balance (equation 3 where m_{Na} is the amount of sodium per surface of sample) so that, at each time step Φ_{rea} can be estimated according to equation 4 :

$$h \cdot \int \left(T_{rea} - T_{water}\right) \cdot dt + \int \Phi_{con} \cdot dt = \int \Phi_{rea} \cdot dt = m_{Na} \cdot \Delta H_{rea} \tag{3}$$

$$\Phi_{rea} = \Phi_{con} + h \cdot \left(T_{rea} - T_{water}\right) \tag{4}$$

To extract Φ_{con} and T_{rea}, an "inverse" method was devised using COMSOL software. COMSOL is a finite element numerical solver traditionally used in mechanics and heat transfer [6]. A PID solver was used. PID means "Proportional-Integral-Derivative" and is a concept issued from process regulation technologies. The principle is to minimize the difference between an observed response of a system (here the temperature calculated at one location inside the holder) from a predefined target (the experimental temperature signal at the same point) by changing the input (Φ_{con}). The consistency of the method can be checked by comparing independently the calculated/measured temperature at the others points. The method proved consistent and offers an accuracy of about 1 % for the temperatures, resulting in a predictive capability of about 4% for heat fluxes. Figure 3-b shows a simulated temperature distribution inside the holder and a typical evolution of Φ_{rea} and T_{rea} as function of time for a typical SOCRATE test is shown on Figure 4.
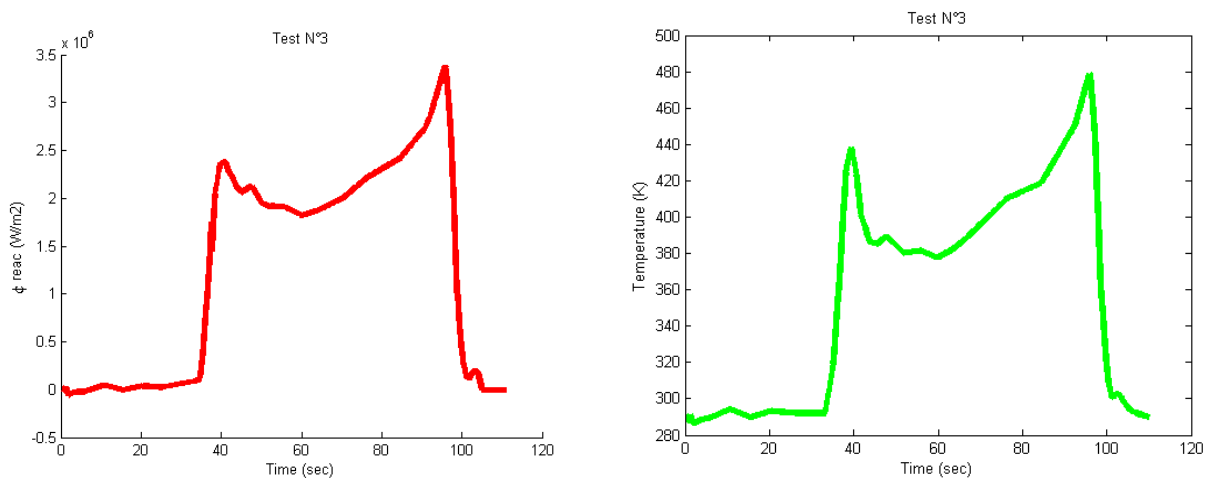

Figure 4: Evolution of Φ_{rea} and T_{rea} as function of time for a typical SOCRATE test

The quantity of sodium deposited on the holder was varied and a reasonably consistent estimation of the parameters of equation 2 was obtained (Figure 5).
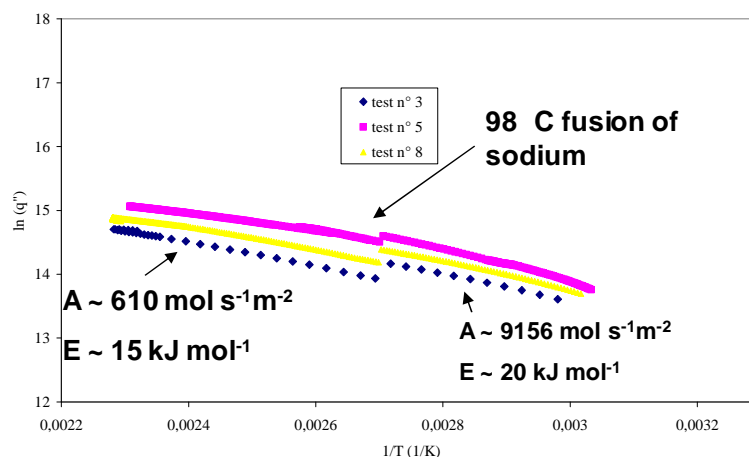
Figure 5: Logarithmic heat flux vs the inverse of temperature SOCRATE tests

A change in the slope is observed at about 98°C corresponding to the fusion of Na. Globally the relatively low value of the activation energy (E in Figure 5) suggests a diffusion limited process which is confirmed by the order of magnitude of Φ_{water} (h (T_{rea}-T_{water})) (1 MW/m^2 : "film boiling regime"). This finding suggests that the details of the chemical process might be ignored. Only the total quantity of heat matters, the latter being large enough to justify explosion effects. Unfortunately, it was also shown in the PhD work, using the "explosion expert toolbox" that the rate of heat release as deduced from these measurements is also much too small to explain any explosive like phenomena as reported in the literature.

To solve this paradox, the results of yet unreleased experiments (PROSE test series) were analysed. In these experiments, the behaviour of small sodium balls immersed into a water pool was filmed using high speed video. The explosion is not immediate but, rather, a gaseous layer is formed around the ball containing apparently liquid NaOH. After some time the film collapses and a strong explosion ensues. Our assumption is that the gaseous layer is formed from the very beginning of the contact between Na and water as a result of the reaction (equation 1), proceeding at a low temperature, so very gently. This layer would contain only H_2 and NaOH. The reaction will then continue slowly, being limited by the rate of diffusion of water vapour through this film. During this period of time the heat released would be at least partly accumulate inside the sodium increasing its temperature. A first tentative modelling of this process was initiated: a sodium ball is surrounded by a thickness of gaseous layer at a given time corresponding to the amount of Na hydrolysed according to equation 1. Water vapour is produced at the saturation pressure at the border between the gas layer and the liquid water and diffuses through the gaseous layer according to Fick's law. The heat released diffuses inside the sodium, increasing its temperature, but also outwards although to a limited extent (a few %). Surprising results were found (Figure 6-a). Its turns out that the rate of heat release is large enough to increase the temperature of the sodium sample, especially because the gaseous layer acts as a good insulator. The sodium reaches its boiling point with at least one possible major consequence : since sodium vapours moves outwards it will tend to initiate some diffusion flame closer to the border of the liquid water, heating it very strongly and disrupting it. This might be the reason for the sudden collapse of the gaseous layer. After, a direct mixing between the boiling sodium and the liquid water seems unavoidable. As the boiling of liquid water above the superheat limit (approx 300°C), is nearly instantaneous, it appears that 0.5 mole of water can be vaporised instantaneously if the initial amount of sodium was 1 mole (Figure 6-b). The rate of the remaining sodium (about 60% of the initial amount) is unclear but the

droplets of liquid sodium immersed into a large quantity of water vapour might continue to "burn" but in a rather gentle manner.

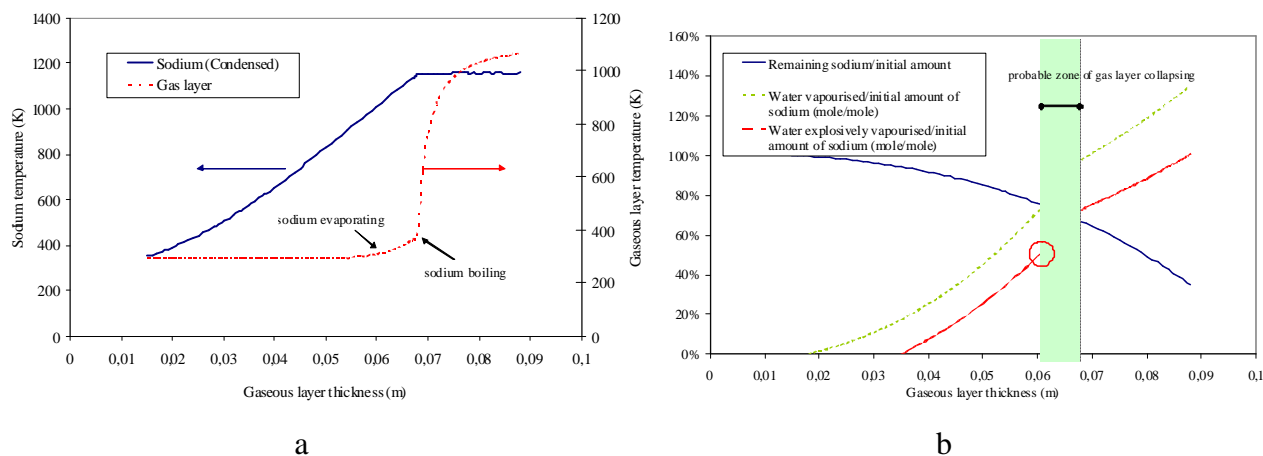a   b

Figure 6: evolutions of the temperature of the sodium sample and of the gaseous layer as function of the gaseous thickness (on the left) and fraction (mole/initial number of moles of sodium) of water being vaporised after the disruption of the gaseous initial thickness (on the right) (for 13 g of cold sodium in cold water)

This mechanism, although still hypothetical, would be in full accordance with the experimental observations : maximum temperature close to the sodium boiling point, 0.5 moles of steam and 0.5 moles of hydrogen in the products of the reaction for 1 mole of Na hydrolysed. A first very direct implication is that the part of the chemical energy released after the collapse of the gaseous film might be mostly dissipated inside the bulk water. This is again in line with the observed difference between the theory and the experiments (Figure 2). The second one is that only the part of the water vaporised explosively could take part to the production of a blast wave leading potentially to a TNT equivalent on the order of 15% (rather that 35%).

To check this very important practical conclusion, the **explosion yield** was determined experimentally using both existing (yet unreleased data : RENAGE test series) and additional data obtained during SOCRATE experiments specifically performed during this PhD work. During RENAGE test campaign molten sodium (1 kg) was dropped into a water pool in the open air as presented in Figure 7. During SOCRATE, smaller quantities where used (a few tens of g) but under a nitrogen atmosphere. The results are presented under the TNT diagram familiar to explosion experts (figure 10). First both sets of data are fully coherent suggesting the incidence of the nature of the atmosphere is insignificant and that the explosive potential is not linked to a hydrogen hazard. Second the TNT yield is about 15% as suggested by the model.
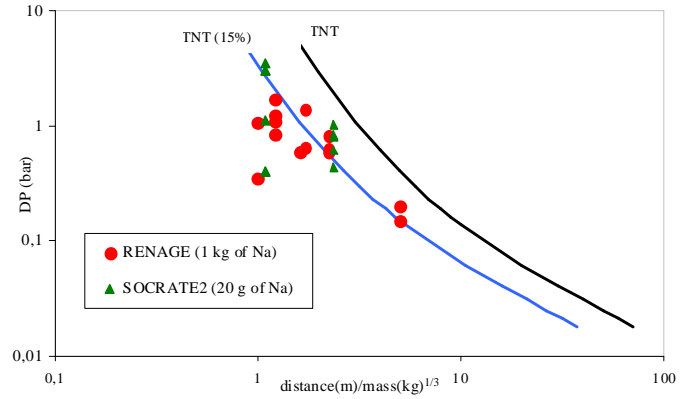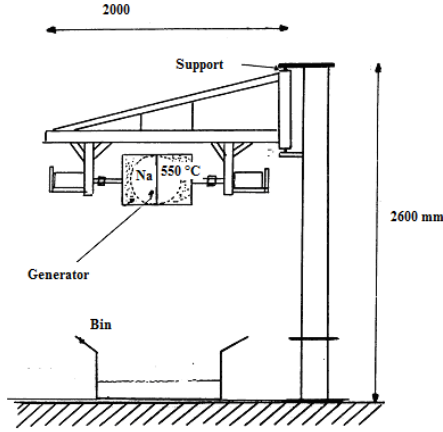
Figure 7: RENAGE installation system (on the left) and TNT equivalent for RENAGE and SOCRATE tests (on the right): shock waves overpressures vs distance from reaction zone

Implementation

There is a strong need to be able to account for these potential explosion effects early in the design phase of the nuclear power generator. A rather simple tool is desired and the above mentioned results were used. To this end, SOVEXP model was prepared during the course of this PhD work. It resembles an energy conservation model usually easy to understand by non specialized engineer.

V_1 is supposed to be the initial volume occupied by the mixture sodium + water in excess (at T_1) so that equation 1 is valid. The gaseous compounds should be water vapour and hydrogen whereas the condensed products should be liquid water and liquid NaOH. If the reaction is assumed infinitely rapid, then, after completion of the reaction, the same volume (than originally occupied by the reactants) is occupied by NaOH, hydrogen and excess water (so $V_2=V_1$). The final pressure in this volume is p_2 (temperature T_2). The conservation of energy reads:

$$Q = \left[n \cdot Cp \cdot (T_2 - T_1) \right]_{H_2} + \left[n \cdot Cp \cdot (T_2 - T_1) \right]_{H_2Ovap} + \left[n \cdot Cp \cdot (T_2 - T_1) \right]_{NaOH} + \\ + \left[n \cdot Cp \cdot (T_2 - T_1) \right]_{H_2Oliq} + \left[n \cdot L_{vap} \right]_{H_2Ovap} \tag{5}$$

Note first that NaOH is not dissolved if all the available water is effectively vaporised. Note also that the number of mole of NaOH equals that of the initial amount of sodium and the number of moles of H_2 half the initial quantity of sodium. The Clapeyron law is added to close the system (quantity of water in the products) and an iterated calculation is proposed to obtain T_2 and the number of final vapour moles formed during reaction. The part of the initial energy available for the pressure generation and stored into the gas bubble is calculated :

$$Q_{exp} = \left[n \cdot Cp \cdot (T_1 - T_2) \right]_{H_2} + \left[n \cdot Cp \cdot (T_1 - T_2) \right]_{H_2Ovap} \tag{6}$$

The evolution of Q_{exp} as function of the mass fraction of sodium in the sodium water mixture is shown on Figure 8.
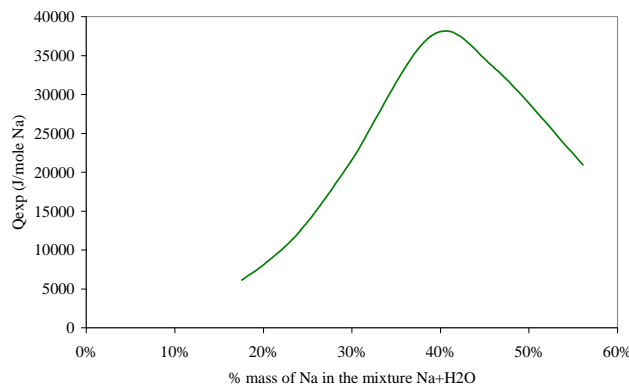

Figure 8: Estimated value of Q_{exp} as function of the mixture ratio (excess water only)

This information can be directly used to calculate the pressure effects of a sodium water reaction. Note that the ratio 1.5 mole of water for one mole of sodium corresponds to sodium mass fraction of 46%. Q_{exp} is then 30 kJ/mole. If the reaction is produced in a closed space, the resulting "explosion" overpressure applied on the walls after the attenuation of the initial blast wave[4] could be calculated from Q_{exp} using for instance the first principle of the thermodynamics. A very good agreement with the experimental results is observed (Figure 9). In this case both steam and hydrogen production participates to the expansion and pressurisation. In situations where a blast wave is expected the amplitude of the propagating pressure wave might be estimated taking into account of the steam production only meaning only half of Q_{exp} i.e. 15 kJ/mole of Na. For 1 kg of Na Q_{exp} would then amount 0.65 MJ to be compared to a value of Q_{exp} of about 4.5 MJ for 1 kg of TNT. The TNT equivalent is then 15% in very good agreement with the RENAGE/SOCRATE tests. The TNT curves may then be used to calculate the pressure field.
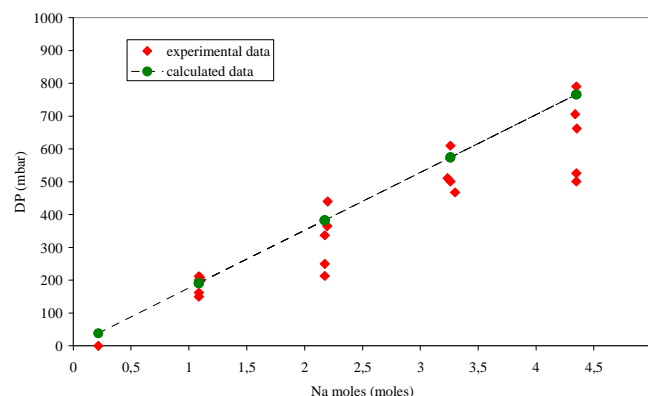

Figure 9: Comparison between calculated and experimental results (CREON)

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[4] If any...if the reaction is produced for instance deep under the surface of the water, the inertia of the liquid refrains the expansion of the gas bubble containing the products of the reaction and no blast appears

This modelling activity was used in parallel to the course of this PhD work to help designing/reinforcing washing cells devoted to the decommissioning of sodium reactors (Figure 10) and to promote specific washing procedures. On this latter point, since the exact quantity of Na remaining may be difficult to estimate, the aspersion conditions were refined to limit the total quantity of water spilling on each object.

Figure 10: Washing cell picture with portholes and water injection systems

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