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SODIUM FAST REACTORS ENERGY CONVERSION SYSTEMS ; NA-CO2 INTERACTION ; COMPARISON WITH NA-WATER INTERACTION OF CONVENTIONAL WATER RANKINE CYCLE.

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INTRODUCTION

The Sodium Fast Reactor is a very promising candidate for the development of Fast Neutron Reactors. It is well known owing to its wide development since the 1950's, throughout all countries involved in the development of nuclear power plants. The development of Sodium-cooled fast neutron reactors is possible due to its very attractive sodium, nuclear, physical and even some of its chemical properties. Nevertheless, the operational feedback has shown that the concept has several drawbacks: difficulties for In-Service Inspection and Repair operations due to the sodium opacity and possible detrimental effects of its reactivity with air and water when the heat conversion is performed with a conventional Rankine cycle. Moreover, the various design projects have shown some difficulties in enhancing its competitiveness with regards to existing NPPs without any new innovative options, i.e. the possibility of suppressing the intermediate circuits and/or the development of an optimized energy conversion system.

The Supercritical CO_2 Brayton Cycle option for the energy conversion has been widely suggested because of its high thermodynamic efficiency (over 40%), its potential compactness of the Balance Of Plant equipment due to the small-sized turbo machinery system, and for its applicability to both Direct or Indirect Cycle (Na, PbBi, He) assuming the hypothesis that the Supercritical CO_2-Na interaction has less serious potential consequences than sodium-water consequences in the conventional Rankine cycle. Within the framework of the SMFR (Small Modular Fast Reactor) project, developed jointly by Argonne National Laboratory (ANL-USA), the “Commissariat à l’Energie Atomique”(CEA) and Japan Atomic Energy Agency (JAEA, formerly Japan Nuclear Cycle development), this option has been selected and investigated.[14]

This paper deals with the study of the interaction between Na and CO2, based on a literature review: the result of this study will allow the definition of R&D tracks for the complementary experimental study and the appraisal of the potential consequences will contribute to weighing both the advantages and drawbacks of this innovative option, in comparison to the conventional Rankine cycle.

LITERATURE REVIEW

First of all, let us recall one of the basic principles involved in extinguishing sodium fires: when sodium is glowing, carbon dioxide is not used because it brings more oxygen than the oxygen in the air to sodium, a strong reducing agent. Moreover, in [1], it is stated that some violent reaction can occur when sodium enters in contact with carbonic snow : this effect would be due to local water vapour condensation, induced by the low local CO_2 temperature. Therefore, the sodium fire is smothered, using a safe and effective extinguishing agent, a dry mixture made of sodium and lithium carbonate powder, fluidified with graphite, referred to in France as “Marcalina”.’(Fig.1)

Figure 1 : Na fire extinction (Na school in CEA France)

These initial elements, well known by users and sodium facility operators, has led us to investigate the chemical interaction between carbon dioxide and non incandescent liquid sodium, our potential reference situation, whose main characteristics we wish to know in order to evaluate the phenomena involved and thereby determine the potential consequences. In such an event, this will enable us to suggest a means of mitigation.

Let us first point out that placing these two products in the presence of each other amounts to placing a very powerful reducing agent, sodium and an oxidizing agent such as carbon dioxide together. It is therefore not surprising to have a reaction between the two products: our whole purpose is to determine what the reaction kinetics are. As we shall see later on, some authors note that carbon monoxide can be produced by the interaction as well; therefore, it is also necessary to investigate the secondary interaction between sodium and carbon monoxide.

Let us now analyze the status of knowledge on the interaction between liquid sodium and CO_2 or CO in gas phase, and consequently the behavior of Na_2CO_3 and C in sodium, the main products of the reaction.

Interaction Na-CO_2

R. SETTON [2] has shown that all the alkaline metals (except Li, which is rather surprising) could react with CO_2 and produce some CO and corresponding metal carbonate.

F. BEGUIN et R. SETTON [3] have analyzed in greater detail the reactions involved with all the alkalines M (Li, Na, Cs, Rb,…) and observed the formation of metal oxalate, CO and carbonate. Therefore they suggest the following equation :

$M+CO_2 \rightarrow 0.5/(1+\alpha) M_2C_2O_4 + 0.5\alpha /(1+\alpha)\ CO + 0.5\alpha /(1+\alpha)\ M_2CO_3 + 0.5/(1+\alpha)\ M$ (1) (where α is not a constant but a function of temperature). They have found an increase of the kinetics when temperature increases.

For Na, at 260°C, they have experimentally found : $\alpha = 1.43$.(quite different from Cs, Rb, K (respectively 0.21, 0.40 and 0.42). They have observed that Na has a specific behavior : at room temperature (Na solid), le sodium doesn't react with CO_2. The reaction causing the appearance of a grey color in the sodium occurs when the temperature is raised. The reaction is at first slow up to 200C°. At about 220°C it accelerates; and at 260°C it is reported to be almost complete after several hours.

In the 1960's, E.H.P. CORDFUNKE et W. OUWELTJES [4] carried out an experimental study on the interaction between CO_2 and a free surface of liquid sodium, up to 453°C, close to atmospheric pressure, with and without stirring effect. The aim of this Na-CO_2 reaction study was to investigate the applicability of the CO_2 option for energy conversion systems of sodium-cooled fast neutron reactor.

Without sodium stirring, the authors reported that pure CO_2 circulating over liquid Na reacted beginning at 175°C. At about 450°C, a rapid reaction occurs and the liquid sodium burns at surface; Contrary to experiments performed by BEGUIN and SETTON, only the presence of carbonate and carbon was evidenced among the products. (Fig.2)

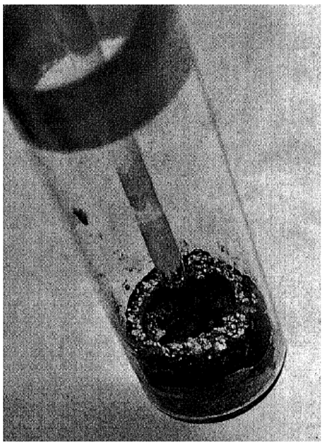

Fig. 2: Reaction tube after the experiment at 241°C [4].

The authors suggest the following equation :

$Na+0.75CO_2 \rightarrow 0.5\ Na_2CO_3 + C + 271.7$ kJ/mole (2)

The value obtained for heat of reaction is coherent with the estimation of 271.5 kJ.mole-1, established with the thermo-dynamical code, COACH (dedicated to calculations of chemical equilibria and associated heat of reactions). At a lower temperature, the reaction rate is slower (Fig.3).

The authors suggest also that the reaction described by equation 2 should, in fact, be the resulting reaction of the two following ones :

$Na+0,25CO_2 \rightarrow 0,5Na_2O+0,25\ C$ (3) and
$0,5\ Na_2O + 0,5\ CO_2 \rightarrow 0,5\ Na_2CO_3$ (4)

The reaction (3) should be rate determining: a value of 2 was determined for the order of the reaction with regard to CO_2, and the corresponding rate constants for the second-order reaction at different temperatures were established.:

The effect of stirring was also investigated: reaction rates comparable to those without stirrer were obtained at temperatures 200°C lower and this result clearly shows that there is a strong effect of stirring: it can limit the inhibition effect induced by the reduction of active contact surface due to the presence of carbonate and carbon. (Fig.4)

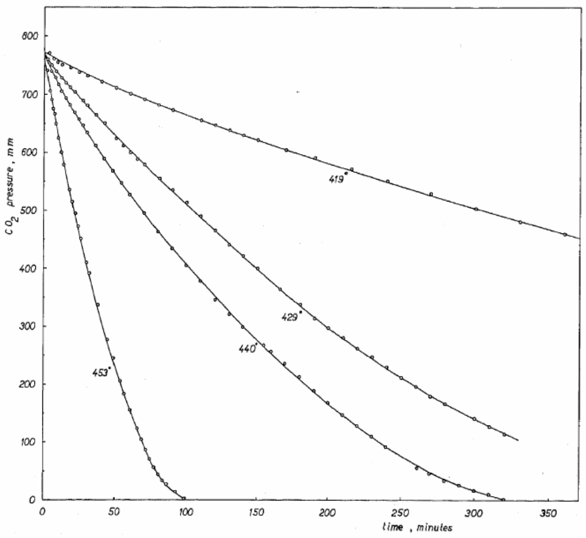

Fig. 3: Reaction rate without stirrer. [4]

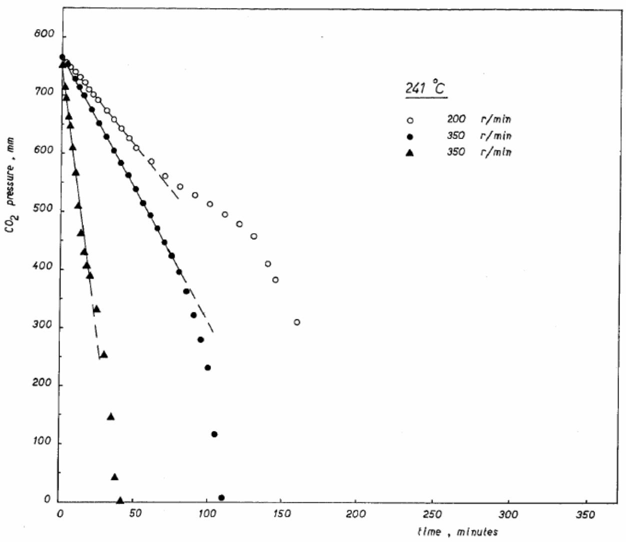

Fig 4: Reaction rate with stirrer. [4]

More recently, H. ISHIKAWA, S. MIYAHARA and Y YOSHIZAWA [5] have studied this reaction, with a constant flow-rate of CO_2 (0.01 m^3/min) for 5minutes at atmospheric pressure, over a Na sample (1.2g); the following parameters were investigated : temperature (from 473 to 923 K), pre-heating of CO_2 (573K or room temperature) and moisture concentration (up to 6000 Vppm). They observed the following main results : below 873K, CO_2 reacted in the first few seconds then the reaction was stopped. When the initial temperature was higher than 888K, the reaction occurred continuously with an orange-colored flame, as it can be seen observed in Fig 5. A maximum temperature of 1123 K was obtained, sodium carbonate and to a lesser extent, amorphous carbon were the main reaction products and CO increased significantly. They also suggested equation (2) with D_fH^0298 = - 270.2 (kJ/mol), but they suggest that the presence of CO should be due to the following reaction between C(s) and CO_2 in excess:

$C(s) + CO_2 (g)=2 CO(g)$ (5),

thermodynamically possible over 974K, but already observed beyond 673K. This observation would suggest that another reaction producing CO should occur at a much lower temperature than 974K, confirming the study of F. BEGUIN et R. SETTON.

Figure 5 : $Na\text{-}CO_2$ reaction T_{Na} =888 K from [5]

In representative conditions of interaction of CO_2 with Na, in a heat exchanger, where sodium is supposed to be surplus, because CO_2 is injected in the sodium bulk, the authors suggest, based on calculations (MALT), that the reaction (3) with D_fH^0298 = - 108.9 (kJ/mol) could occur at a temperature lower than 873K and could explain the threshold of continuous reaction:

But this explanation was not evidenced by the experiments due to the presence of sodium carbonate at temperatures as low as 823K.

Other authors indicate the possibility of obtaining not only C and Na_2CO_3 but also Na_2C_2 (sodium acetylide), $Na_2C_2O_4$ (sodium oxalate) which could be intermediate products, with Na_2CO_3 being the most stable product [6].

In conclusion, it seems that the reaction rates are slow and faster at higher temperatures, without being of the same order of those of the sodium-water, which is considered as almost instantaneous. Nevertheless, the kinetics depend heavily on the contact mode between the Na and the carbon dioxide

3. The Na-CO Interaction

Concerning the Na-CO interaction (possible due to the fact that $Na\text{-}CO_2$ could produce CO as an intermediate reactant), SINCLAIR, DAVIS et DRUMMOND [7] have carried out experimental studies to establish reaction rates, ranging from 200°C up to 500°C, with operating pressures of up to 1 atm.. They indicate that the reaction proceeds in three different stages:

- a small initial but fairly rapid reaction attributed to absorption,
- a slow reaction stage (fig.6): in fact, it is an induction period with a slow rate; the duration of this induction period being a function of the temperature of the reaction (from 15 hours to several days for a temperature below 200°C, ranging from 1 to 12 hours at 300°C and almost no induction period at 500°C.
- a final stage very fast and exothermal.

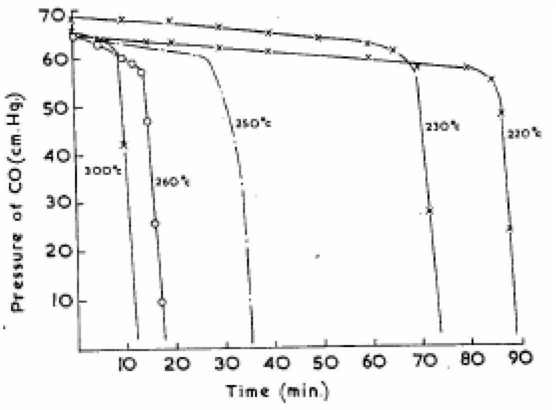

Figure 6:CO + Na Reaction; Induction period. [7]

The length in time of the two first phases decreases if the temperature is increased. The final product of the reaction is a complex mixture composed of sodium carbonate, sodium acetylide, sodium rhodizonate$C_6O_6Na_2$…..

J. BESSON and M. RENAUD [8] also studied the reaction of carbon monoxide on alcaline metals and especially on sodium and confirm that between 100°C and 300°C and with pressures ranging between 0.1 and 10 Torr a rather fast reaction with a particularly notable production of sodium salt of hexahydroxybenzol. The speed constant was established and is expressed differently according to the field of pressure concerned: $k=K_1\ P\ (CO)$ for weak pressures, $K= K_2\ [P(CO)]^2$. The limit pressure between these two fields increases slightly with the temperature (2 Torr to 122°C versus 3.6 Torr for 285°C).

According to WING and WARLEY [9] cited by JP MAUPRE [10] the reaction kinetics would be linear between 290°C and 430°C but the speed of the reaction would be proportional to the square of the pressure.

4. Interaction Na - Na_2CO_3

Taking into account the fact that the sodium carbonate is the preponderant formed compound in liquid sodium, and that it is present in the form of particules, knowledge of its behaviour in a sodium medium is necessary: A study, carried out in the USA [11] and published in the FOUST encyclopedia [1] proposes two possible reactions to reduce the concentration in sodium carbonate:

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \qquad (6)\ \text{and}$$

$$4\ Na + Na_2CO_3 \rightarrow 3\ Na_2O + C \qquad (7)$$

From the thermodynamic standpoint, the decomposition reaction (6) is impossible but the reaction (7) is possible: this would explain why, according to FOUST [1], there would be no reliable value of solubility of the carbonate Na_2CO_3 in liquid sodium. According to other authors, the carbonate would be hardly soluble in sodium. Furthermore, we have not identified in the study literature pertaining to this subject, the decomposition kinetics of the carbonate in a liquid sodium medium, yielding carbon, according to the reaction (7).

5. Carbon solubility in sodium

The carbon solubility in sodium is low as indicated in Fig.7; temperature has a strong influence on it; therefore, carbon transfer will occur throughout the non-isothermal sodium circuits of the reactor.

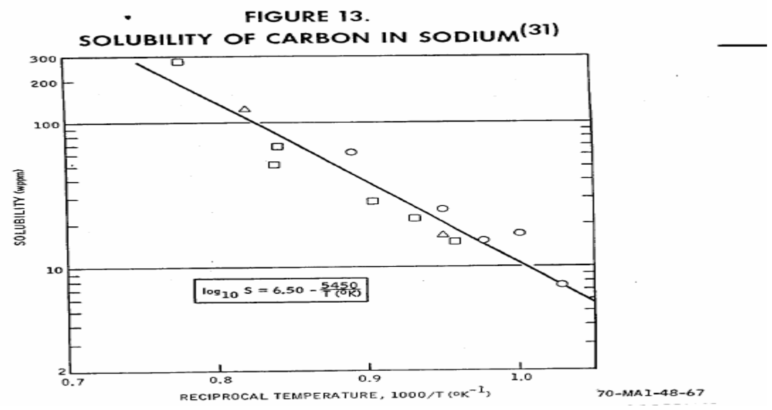

Figure 7 : Solubility of carbon in liquid sodium [13]

At high temperatures, the diffusion rate of carbon in steel is fast enough to cause changes of carbon concentrations in cladding materials. Generally speaking, unstabilized steels are decarburized at 600-700°C, while stabilized steels pick up carbon from sodium for environmental sodium purity typical of sodium-cooled reactors. The carburization affects not only the surface but the entire thickness of cladding materials as shown in Fig. 8 [12]. The uptake of carbon influences the microstructure since carbides precipitate in areas of the highest concentrations; this lead to evolutions in mechanical properties of cladding materials: carburization increases the strength and reduces the ductility of steels. Carbon exchanges seem to be of less importance at lower temperatures (450-550°C). The diffusion being much slower affects thin zones of material surfaces. Carburization and decarburization are then dependant on material composition and sodium purity. Therefore, due to the low carbon content in sodium (low solubility) and relatively low temperature if there is an intermediate circuit (indirect energy conversion system), the consequences of carbon ingress should be very limited. Nevertheless, if a direct energy conversion system is foreseen, with a possible higher primary temperature, the possible impact of carburization at carbon content should be investigated., particularly for cladding materials.

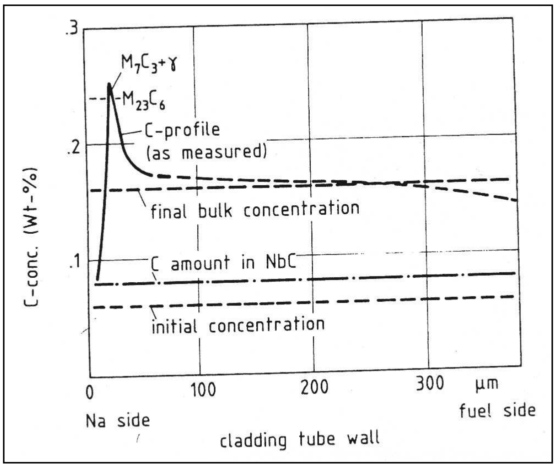

Figure 8: Carburization of a cladding material
in Na at 700°C, 5000 hours of exposure [12]

6. Discussion

In conclusion, it seems therefore that the interaction reactions Na-CO_2 et Na-CO are slow and become faster at high temperature, without being of the same order as the Na-H2O° reaction, almost instantaneous; they can be total. The kinetics would depend heavily on the contact more between the Na and the carbon dioxide. The carbonate formed would react very little with the liquid sodium and therefore would be relatively stable.

Thus, the three main consequences of a potential interaction between Na and carbon dioxide to be investigated are the following:

- potential particle formation: this brings about the necessity of planning adapted purification systems, allowing us to obtain a satisfactory quality; these systems probably function with filters, spillways to eliminate particles on the free levels…the quantity of Na_2CO_3 introduced can be controlled thanks to an early detection in sodium.
- Possible interactions between the carbon saturated sodium and the structure materials: carburization phenomena which act on the mechanical properties of the structures.

  Given the short periods of contact, providing, of course, that we are able to lower quickly and durably the carbon concentration, the consequences should be extremely limited, on an intermediate circuit structural material. If a direct energy conversion system is foreseen, the impact should be estimated.
- The occurrence of possible "westage" effects in the tube bundle. (if this type of exchanger is chosen). The elements in the current literature seem to indicate that such risks of occurrence would be limited.

At this stage in the analysis, comparison between the water vapor and CO_2 options shows that the potential use of the CO2 necessitates a quite comprehensive physico-chemical study (Table 1)

In order to consolidate this vision of the behavior of carbonated products in sodium, we have undertaken the following actions :

- the study of the interaction between sodium and CO_2 and, if necessary, with the CO, in representative interaction conditions (i.e high pressure, gas injection in the dynamic Na medium…) Knowledge of the both kinetics and the confirmation of the heat reaction would enable us to verify the occurrence possibility of a "wastage" scenario: following the piercing of a first tube, creating a "blow pipe" effect which would damage the neighboring tubes through thermal, mechanical and chemical effects, scenario which is possible and has been extensively studied for a Steam Generator Unit.

In order to study the interaction of Na with CO_2, we have decided to use the existing technology, used for characterization of thermal runaway phenomena, used in the conventional chemistry for thermal hazard assessment : the so-called VSP (“Vent Sizing Package”), developed by DIERS (Design Institute for Emergency Relief Systems), in order to obtain data for the calculation of the relief systems for the venting lines. This device has two main characteristics : a very low adiabaticity factor ($\Phi = 1 + (Cp_C.m_C) /$

($Cp_{sample}.m_{sample}$), and the possibility to perform tests with a very high pressure (up to 200 bar). At the end, it is foreseen to characterize the residues.(Fig. 9)

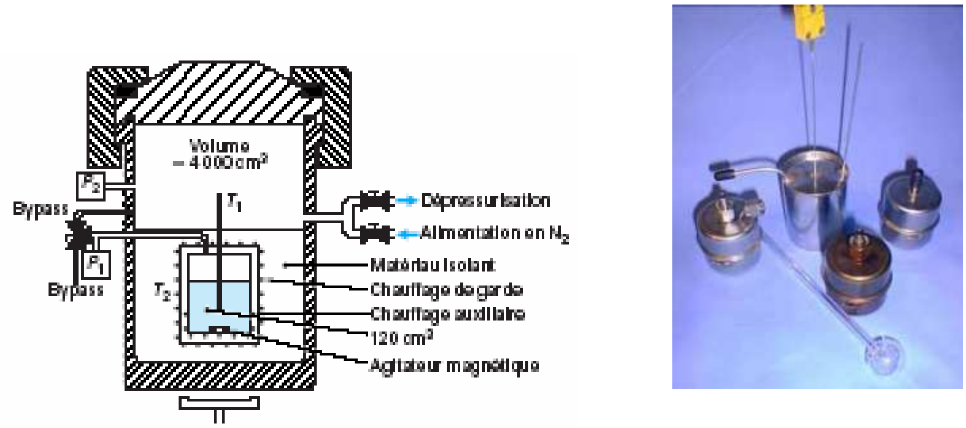

Figure 9 : VSP technology for Na- CO_2 investigation

- study of the behavior of Na_2CO_3 in liquid sodium to determine both its stability in sodium and to confirm its low reactivity which would result in maintaining particles in sodium, the presence of which would be likely to bring about consequences on the functioning safety of the reactor.
- investigate in more details the detection of such an event : Several detection means could be investigated : there is a necessity to first define specifications (sensitivity, time for detection, implementation constraints,…) for a reliable detection system, then to evaluate the existing measurement devices, already developed (Diffusion carbon-meter, electrochemical carbon-meter, gas chromatography,…)
- assessment of analytical carbon measurement in sodium,
- evaluation of purification means (filters,…) and procedure.

7- Conclusion

The Supercritical CO_2 Brayton Cycle could be a promising option to enhance the competitiveness of future Sodium Fast Reactors. A literature review has been carried out in order to evaluate the potential interaction of sodium with supercritical-carbon dioxide. If the reaction kinetics seem much slower than those corresponding to a sodium-water interaction, this interaction exists and its consequences have to be investigated in order to determine if it is better to avoid this interaction through design options (double wall heat exchanger, intermediate fluid,…) or to mitigate the possible consequences of such an event by early detection, fast CO_2 circuit depressurization, purification by adapted means to eliminate potential particles, cover gas purification, …etc. Due to the high solubility of carbon in sodium, the issue of carbon activity rise-up has also been addressed. Finally, a comparison of the Water steam Rankine cycle and the Supercritical -CO_2 Brayton cycle with regards to interaction, potential consequences and mitigation has been performed and provides arguments to contribute to the selection of a safe and efficient conversion system.

Event	**Water ingress**	**CO_2 ingress**	**Comments**
Pressure (H_2O or CO_2)	168 bars	200 bars	Impact of pressure on Hex design
ΔH (kJ/mol)	162	271.5	
Kinetics of reaction	Almost instantaneous	Order 2 / CO_2	For CO_2 to be investigated in realistic conditions
Products of reaction	NaOH, $O^{=}$, H^{-}	Na_2CO_3, C, and Na_2C_2, $Na_2C_2O_4$ as intermediate products	Necessity to investigate carbonate dissolution in sodium
Particulates?	Not	Yes (Na_2CO_3)	Necessity to foresee filters
Soluble products trapping	Cold trap, hot trap	To be defined	Necessity to foresee a carbon trap?
Non-soluble products trapping	Not necessary	Filters,	Implementation has to deal with thermal-hydraulics
General corrosion	Yes but very limited due to NaOH conversion with Na	Not	
Carburization	No	Yes at high temperature and high C content	Probably very limited consequences
Possibility of Leak detection	Yes (hydrogen-meter, acoustic detection system,...)	Yes (diffusion or electrochemical carbon meter, sampling then analysis,..)	Must assess the response time for CO_2
Wastage	Yes	Probably not	To be investigated
Risk of Explosion	Yes, if contact with oxygen	Not	Probability of loss of tightness of gas plenum to be investigated
Risk of combustion	Not	Yes	Operating conditions to be investigated

Table 1 : Comparison between water steam and SC CO_2 options.

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