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EVALUATION OF ALTERNATIVE FLUIDS FOR SFR INTERMEDIATE LOOPS

L. Brissonneau, N. Simon, F. Baqué, G. Rodriguez, M. Saez,
CEA DEN Cadarache
F-13108 Saint Paul lez Durance, France
Tel 00 33 442 254 258, fax : 00 33 442 257 287, laurent.brissonneau@cea.fr
F. Balbaud,
CEA DEN Saclay
F-91191 Gif sur Yvette, France
D. Rochwerger,
CEA DEN Marcoule
F-30207 Bagnols sur Cèze, France
A. Gerber,
AREVA NP
10 rue J. Récamier 69456 Lyon cedex
G. Prèle, A. Capitaine,
EdF SEPTEN
12-14 Avenue Dutriévoz, 69628 Villeurbanne, cedex

Abstract - *Among the Generation IV systems, Sodium Fast Reactors (SFR) are promising and benefit of considerable technological experience, but improvements are researched on safety approach and capital cost reduction. One of the main drawback to be solved by the standard SFR design is the proper management of the risk of leakage between the intermediate circuit filled with sodium and the energy conversion system using a water Rankine cycle.*

The limitation of this risk requires notably an early detection of water leakage to prevent a water-sodium reaction. One innovative solution consists in the replacement of the sodium in the secondary loops by an alternative liquid fluid, not or less reactive with water. This alternative fluid might also allow innovative designs, e.g. intermediate heat exchanger and steam generator grouped in the same component. CEA, Areva NP and EdF have joined in a working group in order to evaluate different "alternative fluids" that might replace sodium. A first selection retained seven fluids on the basis of "required properties" as large operating range (low melting point, high boiling point ...), fluid cost and availability, acceptable corrosion at SFR working temperature. These are three bismuth alloys, two nitrate salts, one hydroxide melt and sodium with nanoparticles of nickel. Then, it was decided to evaluate these fluids through a multi-criteria analysis in order to quantify advantages and drawbacks of each fluid and to compare them with sodium. Lack of knowledge, impact on materials, design, working conditions and reactor availability should be emphasized by this analysis, in order to provide sound arguments for a research program on one or two promising fluids. A global note is given to each fluid by evaluating them with respect to "grand criteria", weighted differently according to their importance. The grand criteria are : thermal properties, reactivity with structures, reactivity with other fluids (air, water, sodium), chemistry control, safety and waste management, inspection maintenance and repair (ISIR), impact on components and circuits, availability and cost, experience. The impact on reactor availability and manageability and the level of knowledge on each fluid were estimated through the former "grand criteria" and introduced in the final comparison as grand criteria. The aim of this paper is to present the methodology of evaluation, the results obtained and the choices made.

I. INTRODUCTION

Among the Generation IV systems, Sodium Fast Reactors (SFR) are promising and benefit of considerable

technological experience, but improvements are researched on safety approach and capital cost reduction. One of the main drawback to be solved by the standard SFR design is the proper management of the risk of leakage between the intermediate circuit filled with sodium and the energy

conversion system using a water Rankine cycle. The limitation of the risk requires notably an early detection of water leakage to prevent a water-sodium reaction. One innovative solution to this problem consists in the replacement of the sodium in the secondary loops by an alternative liquid fluid, not or less reactive with water. This alternative fluid (AF) might also allow innovative designs, e.g. intermediate heat exchanger (IHX) and steam generator (SG) grouped in the same component (see Figure 1). For economical reasons, this fluid must be a liquid if a Rankine cycle is chosen. Many coolants have been tried or proposed in the past for Fast Breeder Reactors¹⁻⁶, but mostly for the primary circuit, excepted notably in⁷. It was decided to evaluate the most interesting ones through a multi-criteria analysis in order to select the one or two most promising candidates which could be more thoroughly studied in a future research program.

First, the selection was restricted to fluids that respect "required" criteria. Then, CEA, Areva NP and EdF have joined in a working group of experts for the evaluation of the selected fluids. The evaluation was performed through criteria, and the working group was separated in sub-groups of experts in charge of a particular criterion.

The method of evaluation and the main results are described in this paper.

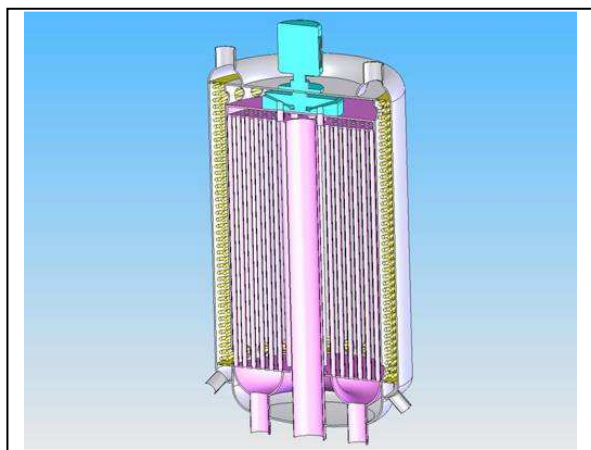


Figure 1: SFR IHX/SGU with AF coupling

II. FLUID SELECTION

The fluid must be compatible with a classical sodium reactor with a Rankine cycle. The temperature in the hot branch of the primary system is about 550°C and the one of the cold branch about 400°C. No fluid was selected or rejected *a priori*, but according to the following criteria.

- Melting point lower than 250°C (for easy cold stop operations).
- Boiling or complete decomposition point above 650°C.
- Corrosion rate allowing long term use of the components.
- Simple mixture (limited to ternary compounds) with consistent composition of each compound (more than 5 molar %) for chemistry control sake,

- Compounds of reasonable cost and availability.
- Reactivity with water and air significantly lower than sodium.

The fluids were researched among simple elements and their mixtures, molten salts, hydroxides and organic fluids. The reactivity with water criterion eliminates the use of K, Cs, Li and most of their mixtures, as alkali metal behaves globally like sodium with water (large exothermic reaction forming corrosive products).

The corrosion criterion eliminates Ga⁸, Hg¹, Sn alloys⁶, Pb-Li^{9,10}, Bi-Li and Pb-Mg. For example for Pb-Li at a reasonable velocity of 0.8 m/s, a typical 316 IHX tube of 16 mm diameter corrodes at 520°C at a rate of about 350 μm/y¹¹. It leads that unreasonable tube thickness would be needed to assure the mechanical integrity of the component. Similar corrosion rates are expected for Pb-Mg or Bi-Li, as the corrosion process consists in the dissolution of major species of the steel (Fe, Cr...) in the fluids with no efficient oxide layer protection (as it can exist with Pb-Bi, see below...).

The criteria on melting point and simplicity of mixture eliminate pure elements other than indium, gallium and mercury and most of the molten salt compounds, especially halides.

The criterion on boiling point eliminates many chlorides, the hitec nitrate-nitrite salt (decomposition), as well as sulphur, selenium and most of cadmium compounds and high temperature organic fluids (ionic liquids).

Some indium compounds present very interesting characteristics, in particular low melting point (Bi_{22%}-In_{78%} 73°C or Cd_{26%}-In_{74%} 123°C, composition in at.%), but the high demand for indium in the recent year makes its cost being unreasonably high for this application (about 1000 \$/kg) even in a near future. However it is probable that corrosion problems would have arose as the formation of a protective iron oxide would have been impossible. Other compounds based on Au, Ag, La, Tl, Rh have also been eliminated by applying this cost criterion. This evaluation on cost and availability was mainly based on the Mineral Commodity Summary 2007 of the US Geological Survey¹².

At the end, only six fluids fulfilled these preliminary required criteria. They are binary or ternary mixtures at eutectic composition. Their composition and melting point are given in Table 1.

Pb-Bi is well known as a fluid worldwide studied for the Accelerator Driven Systems (ADS) and it has been experienced as a primary coolant in the Russian alpha class submarines^{13, 14}. Two other bismuth alloys containing cadmium could be of interest due to their low melting point. Nitrate salts are of particular interest in solar application. The NaNO₃-KNO₃ mixture selected was used as coolant in the Solar2 Project¹⁵. The hydroxides received most attention in the 1950', when they were tested as primary coolants for aeronautics applications¹⁶.

Fluid	Pb-Bi	Bi-Cd	Pb-Bi-Cd	NaNO ₃ -KNO ₃	NaNO ₃ - LiNO ₃ -KNO ₃	NaOH-KOH
Composition (mol. %)	Pb 45% Bi 55%	Cd 55% Bi 45%	Pb 38% Bi 48% Cd 14%	NaNO ₃ 64% KNO ₃ 36%	NaNO ₃ - 17% LiNO ₃ -37% KNO ₃ 46%	NaOH 49% KOH 51%
Melting point	124°C	144°C	92°C	235°C	120°C	170°C

Table 1: Selected fluids for evaluation at SFR intermediate loops, molar composition and melting point.

Three other fluids could also be considered of interest: sodium with additions of nickel nanoparticles¹⁷⁻¹⁹, Na-Pb mixture⁵ and the eutectic CuCl-KCl but very few is known about them. The chloride mixture has a low melting point and quite high boiling point but strong corrosion is attended and it was thus not retained in the first selection. The mixture Na with about 9% at. Pb (50 % weight) was suggested as being able to impeach inflammation of sodium (low vapour pressure of lead preventing vapour feeding with Na). However the mixture is not an eutectic, the liquidus (320°C) would be much higher than the desired melting point and below the liquidus a biphasic range could induce plugging problems. For these reasons, this mixture has not been retained in this first selection. The sodium with nickel nanoparticles seems much more promising, as the authors of the patents claim that the sodium water reaction can be lowered¹⁷. It was decided to evaluate also this fluid but, as little is known, the results will be presented apart.

III. EVALUATION METHOD

A. Principles of the method

It was decided to evaluate each of the selected fluids through a multi-criteria analysis. Eleven grand criteria were defined and weighted according to their importance for the intermediary circuits (see Table 2 and below) by a group of experts from CEA, Areva NP and EdF. The weights range from 10 (less important) to 50 (most important).

For each of the nine first grand criteria, sub-criteria with relative weights were also defined by sub-groups of experts. Then a list of technical questions was established for each sub-criterion in order to rationalize the evaluation of the fluids through a consensual notation ranging from 0 (very bad) to 40 (very good).

The two other grand criteria, "confidence" and "availability and manageability of the reactor" are

evaluated through the other nine grand criteria, by giving also a notation for these criteria when the sub-criteria are assessed. For example a sub-criterion can be evaluated as being "good" but the confidence on the answer as "very good" and the consequence on the availability and manageability of the reactor as "very bad". This would be for example the case when considering the consequence of sodium leakage if sodium is considered as the secondary fluid (well-known problem, no related safety concerns but to the prize of an heavy investment and a lower availability of the reactor).

The analysis was applied to the six selected fluids of Table 1. The sodium was also evaluated for sake of comparison. It was also decided to evaluate the fluid "sodium with nickel nano-particles", but as very few is known about it, the results will be presented separately.

Two meetings between experts of each group were at least necessary. The first in order to define the sub-criteria, their respective weights and the list of technical questions. The second for the final evaluation. Between the two meetings, a web site was created for promoting and facilitating the communication between experts and the exchange of documents.

When all notations are completed, a weighted summation of the different criteria yields the final evaluation of the fluid (given as % of the maximum note). It was also thought that the best fluids should present a well-balanced notation for each criterion: hard weak points should not be hindered by a good global note. It was decided to evaluate this quantitatively by calculating the average of the notation of grand criteria dividing by the standard deviation between the notations. Practically, it leads to an "equilibrium note" between 1 (bad unbalanced fluid) and about 10 (very good and balanced fluid).

Comments were given for each notation in order to evidence possible impact of the fluid on the design and the operation of the reactor as well as research program that could be necessary to comfort or not the use of the fluid.

Grand criteria	Thermal properties	Interactions with structure	Interactions with fluids	Chemistry control	Safety, Security Environment	
weight	30	50	50	30	50	
Grand criteria	ISIR	Components & circuits	Cost	Level of use	Level of confidence	Availability and manageability
weight	30	20	20	10	30	30

Table 2 : grand criteria and their relative weight (10 less important, 50 most important).

B. Grand criteria

A brief description of the nine grand criteria is given below.

Thermal properties:

The ability of the fluid to transport and transfer the heat will directly impact the cost of investment by determining the size of the circuits and the areas of the exchangers (as the temperatures of the fluid in the intermediary circuit are assumed fixed, the lower are the transport and transfert properties, the larger are the component). The power of the pump will impact the in-service cost. This can be assessed through characteristic groups of properties of the fluid (heat capacity, thermal conductivity...). The method has been described in a previous paper²⁰, few adaptations were proposed. Except for Pb-Bi, which for an extended and recent review is available²¹, the properties (heat capacity, thermal conductivity...) of the mixtures were calculated by using classical interpolations from the properties of pure compounds.

Interaction with structures

The interactions between the fluid and the material of the circuits and components lead to particular choices for the material. This item includes general corrosion (oxidation or dissolution), localized corrosion (grain boundary corrosion, liquid metal embrittlement...), mass transfer (plugging, fouling), mechanical properties and long term modelling. The general corrosion must not induce an unacceptable loss of the mechanical or heat transfer properties of the material. For example, if an oxide is formed on the surface of the material, the increase in its thickness during the lifespan of the reactor should not induce a decrease in the thermal transfer more than about 20%. In case of mass transfer, the quantity of corrosion products should not reasonably exceed dozens of kilograms per year (equivalent of the maximum expected in the primary circuits of the SFR). The best known corrosion resistant "industrial" material for each fluid has been selected for the evaluation. As they vary from one fluid to another, the mechanical properties of the materials were also compared, as well as their resistance to water or sodium corrosion (respectively in the steam generator SG or in the intermediate heat exchanger IHX). The availability of the reactor can be affected by the corrosion, the mass transfer or the loss of mechanical properties.

Interaction with other fluids

The intermediate fluids can react with sodium, water, air or other materials or fluids like concrete or oil. The thermodynamics, the kinetics and the by-products of these

reactions and their effects (corrosion, erosion, plugging, toxicity...) must be considered.

Chemistry control, operating range

The coolant can be operated in domains of temperature, pressure and chemistry (of the fluid or the gas phase) that have to be specified. The wider the ranges, the easier the operation of the reactor. The consequences of out-of-range operations (temperature sudden rise, impurity ingress...) must be evaluated. Instrumentation is required to assure that the fluid is being operated in the specified range and a dedicated chemistry control system may be necessary to maintain the fluid in that domain. For example, it is generally specified that hydrogen level in a sodium secondary circuit should be less than 0.1 ppm, for a sufficiently early sodium water reaction detection. This can be done by precipitating the hydrides in a cold trap and by controlling the resulting dissolved H concentration with a hydrogen-meter (by membrane diffusion and spectroscopy or by an electrochemical probe).

Measurement and control systems are evaluated through their reliability, sensibility, accuracy, toughness, efficiency...

The manageability and availability of the reactor can be affected by the operating range and the operation to be conducted in case of out of range operation, and also affected by the methods of measurement and control. For example, if numerous maintenance operations are necessary on the purification units.

The tritium behaviour (diffusion, trapping...) was also evaluated in this criterion.

Safety, security and environment

The consequences of different kinds of leaks and reaction between fluids on the safety were evaluated, by taking into account the risks of core plugging, gas bubbles in the core, exothermicity of reactions, risks of fire, explosion... The capacity of the fluid to absorb transient regime was also roughly estimated as well as the possibility of using the intermediate loop for Decay Heat Removal DHR, as an assistant of the classical DHR systems.

The manageability and availability of the reactor are of course affected by a proper management of the consequences of the leaks.

The management of effluents and wastes during maintenance or dismantling operations was evaluated. This takes in consideration recycling of the fluids and the toxicity of the fluid or of the by-products.

*In Service, Inspection and Repair*²²: In operation, the following physical properties of the fluid must be measured: temperature, flow rate, pressure. The leaks of one fluid in another must also be detected, the faster the higher the damages they might induce. The most critical for the safety is the leak of the alternative fluid in the sodium of the primary circuit. Some aspects of leak detection were treated in the group dealing with the chemistry control, for example air ingress in the AF, as it is generally detected by instruments connected with the fluid purity control system. The inspections of the components are conducted periodically during shutdown of the reactor. They must guarantee that any defect is likely to induce latter malfunctioning in service.

Maintenance of the components and circuits is periodical operations, when repair operations are not. But the related problems are globally the same: components must be cleaned (and decontaminated for the IHX), re-qualified and strict procedures of start-up of the reactor must be followed. It is well known that with sodium coolant, problems arose mainly during the start-up of the reactor after maintenance operations, due to fast caustic corrosion effect. The availability and manageability of the reactor are affected by all these aspects.

Components & circuits

The process (including weldability) and approximate costs of the following components and circuits were assessed: IHX, SG, pumps, valves, main circuit, auxiliary circuit, chemistry control circuit, instrumentation. The nature of the component, their size and their material can greatly differ from one fluid to another. Input data were given by all the other groups (thermal properties for the size of the component, interaction with the structures for the material, chemistry control for the purification unit...).

Experience

A fluid can be most confidently chosen if it has been already experienced as a coolant, especially in a nuclear context. Moreover, the R&D cost can be decreased if test infrastructures already exist.

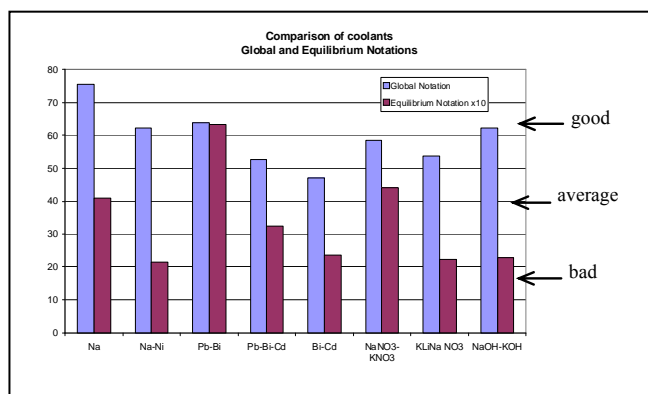


Figure 2 : Global (first bars) and equilibrium (2nd bars) notes of AF for SFR intermediate circuits.

Cost

The cost of a fluid (with purity specification) was estimated, as well as the availability of the component and the cost in operation.

It can be seen that criteria related to Thermal properties, Components & circuits, Experience and Cost are rather related to investment costs, when Interaction with structures, Interaction with fluids, Chemistry control, Safety, ISIR and Availability are rather related to operation costs and protection of the investment. Globally, 1/4 of the notation was on the first group of criteria and 3/4 on the second group.

IV. RESULTS

A. Final results

The final results of the evaluation are given in Figure 2. The final notation of the fluid is given as a percentage of the maximum note, first (blue) bars. The “equilibrium notes” are the second (red) bars (x10 for easier comparison in the graph). The note given to Na-Ni is also reported and the note of sodium is given for sake of comparison. The best note is obtained by Pb-Bi, 64%. It corresponds to a note between “average” and “good”. Pb-Bi is also the fluid with the best “equilibrium note”, 6.6. Two other fluids have also good notes but their equilibrium notes are much lower NaOH-KOH and Na-Ni, 2.2. Most important features to understand the notations are given below. It is worth noting that a sensitivity analysis relative to the weights for the grand criteria (in particular by giving less weight to the interaction with fluids and a higher one to components & circuits) has pointed out that the results keep globally unchanged in a reasonable extent.

In Figure 3, a radar graph represents the notes of the grand criteria for the three most promising fluids: Pb-Bi, NaOH-KOH and Na-Ni. It can be seen that Pb-Bi does not suffer any weak point but does not present either very good notations. On the contrary, NaOH-KOH and Na-Ni have very good and bad notes. It must be kept in mind that as very few is known about the Na-Ni fluid, the relative notations are only rough estimates.

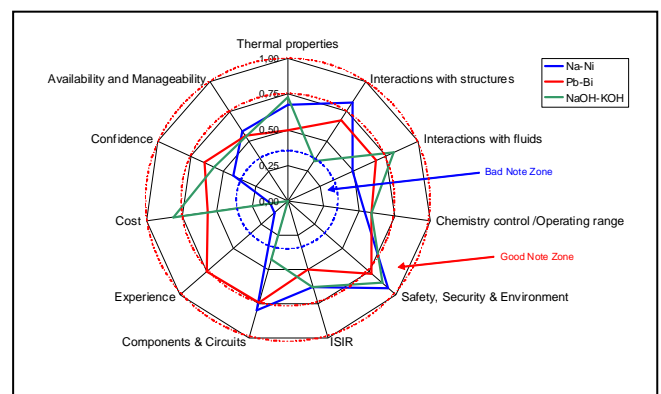


Figure 3: Radar graph of the notations of grand criteria for Pb-Bi, Na-Ni and NaOH-KOH.

B. Key features

Thermal properties.

Molten salts are the best for heat transport (high $\rho \cdot C_p$, where ρ is the fluid density and C_p its heat capacity), when Heavy Liquid Metals (HLM) are more efficient for heat transfer (linked with thermal conductivity λ). But sodium is much better concerning energy performance (extracted power on pumping power) due to his high λ and C_p and low ρ . First calculations showed that exchanger areas would be almost twice larger for molten salt than for sodium (heavy metals are intermediate). For Pb-Bi and Na, details of the results can be found in ²⁰. Globally all fluids have good final notes for this criterion.

Interactions with structure

Heavy liquid metals ²³⁻³⁵ and nitrate salts ³⁶⁻³⁹ allow, in specific operating conditions, the formation of protective oxide layer on the classically used T91 ferritic martensitic and 316 austenitic steels (see Figure 4). For HLM, the concentration of oxygen has to be approximately above the concentration needed for the formation of magnetite Fe_3O_4 ⁴⁰. It was calculated for T91 immersed in stagnant Pb-Bi by using an oxidation model established for oxygen saturated conditions and developed in ³⁰⁻³², that the steel would, at 520°C and for an intermediate level of oxygen (about 10^{-2} ppm, see § Chemistry control), develop an oxide layer of about 40 μm in 20 years. Strong attention must be paid to the fact that this model was developed for oxygen saturated conditions, and that its application to intermediate levels of oxygen concentrations has not been validated. It should be emphasized that lower corrosion rates and less constraint on oxygen control could be obtained by lowering the maximum fluid temperature (lower than 500°C by example) or by using innovating high resistant corrosion materials (protected by alumina-forming layer). Mass transfer due to the possible spallation of the magnetite layer (half of the oxide layer) could be observed. It was postulated that similar rates could be obtained with the other HLM, provided the oxygen concentration could be maintained in the targeted range. For nitrate salts, the oxidation rates appear to be somewhat lower, and 316 steel can be used (in HLM, nickel is preferentially leached leading to important corrosion rates for temperatures above 500°C even for controlled oxygen conditions). However, long term tests are missing (max 7000 h)³⁷. For both HLM and nitrates, clear gain could be obtained by operating at lower temperature or by using corrosion resistant steels (forming alumina or silica protective layers ^{28, 41, 42}). Embrittlement by lead-bismuth is mostly observed in non-oxidizing conditions ensuring wetting of the specimens and for temperatures below 400 °C, this point has to be considered carefully especially for Fe-9Cr steels ⁴³. Cadmium is known as an effective embrittler of ferritic steels ⁴⁴.

The NaOH-KOH mixture induces high corrosion rates and nickel base materials show the best resistance ^{16, 45, 46}. Many

phenomena occur during corrosion : nickel oxidation, dissolution and reaction with Na to form a mixed oxide ⁴⁵. Very few data are available in the temperature range considered here (around 500°C) and the data available are very scattered, corrosion rates are usually high (more than 50 μm /year for iniconel at 500°C) and so is the associated mass transfer of nickel (at 500°C about 0.5 $kg \cdot m^{-2}$) in the cold zone. Moreover, caustic cracking might occur in some particular conditions.

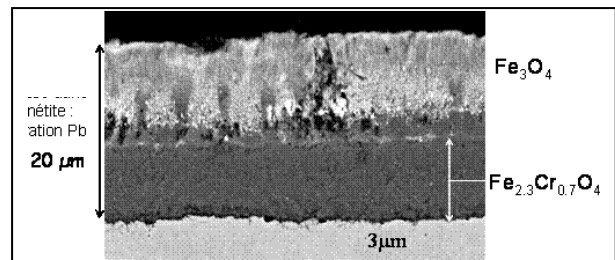


Figure 4 : oxidation layers on a T91 steel, 3700h at 470°C in oxygen saturated Pb-Bi (by courtesy of L.Martinelli, CEA Saclay).

Interactions with other fluids

The three considered HLM will react with Na above 400°C and form solid phases as $BiNa_3$ and $BiNa$ ^{7, 47, 48}. The $BiNa_3$ formation is very exothermic, 190 $kJ \cdot mol^{-1}$ from pure components ⁴⁸, which can be compared with the 180 $kJ \cdot mol^{-1}$ for the reaction between vapour and sodium. In EBR-II, Sn and Bi spilled in the sodium after failure of the liquid seal of the rotating plug, but no ²¹⁰Po generated from Bi activation was detected in the sodium, contrary to Sn isotopes ⁴⁹. It was concluded that Bi is removed from the sodium in the cold trap, where it precipitated. Lead in solution in sodium should also be precipitated in the cold trap, but cadmium rather not (according to phase diagrams ⁴⁷). According to Miyahara et al. ⁷, heavy $BiNa_3$ particles might settle and only those which diameter is smaller than one micron are transported by the sodium. Nitrates react exothermically with sodium to form $NaXO$ ($X = Na, K, Li$) and N_2 . The heat of reaction of $NaNO_3$ with Na is about 800 $kJ \cdot mol^{-1}$. NaOH-KOH should form Na_2O and NaH in sodium that should finally dissolve as O and H in sodium. Pb-Bi slightly reacts with air, the reaction being exothermic. It is certainly related to its low vapor pressure and its effectively very protective oxide layer. By contrast, Bi-Cd should be able to inflame at low temperature, by analogy with cadmium. CdO vapors are toxic. Because of the low Cd content in Pb-Bi-Cd, inflammation should be much more difficult than for Bi-Cd. Pb-Bi slightly reacts with water, though attention must be paid to the problem of steam explosion ⁵⁰. Reaction between Cd and liquid water is possible (the free enthalpy for CdO formation is negative for $T > 150^\circ C$) and is slightly endothermic but produces toxic CdO. Nitrate salts and hydroxides are inert with air and water.

Chemistry control, operating range.

Pb-Bi has a large liquid range (125°C - 1670°C), a low vapor pressure ($\approx 10^{-5}$ times lower than sodium at 520°C)²¹ but suffers from oxygen contamination. The oxygen content must be kept between two extreme values on the operating range⁴⁰: the upper limit corresponds to PbO formation (risk of plugging) and the lower value to the formation of protective oxide layers (Fe₃O₄) necessary for the protection against corrosion. Practically, the oxygen content should be fixed between $5 \cdot 10^{-4}$ and 10^{-2} ppm⁴⁰. As the oxygen activity is lower for CdO than for PbO formation, it could be expected that the operating oxygen contents for Bi-Cd and Pb-Bi-Cd are narrower or may not exist. However, preliminary calculations show that it should be close to the one of Pb-Bi. The oxygen content is measured by electrochemical sensors⁵¹⁻⁵³. Their most important drawbacks are stability and little durability⁴⁰. In normal operating conditions, the oxygen should be consumed by oxidation of the structures. The oxygen content can be controlled by gaseous systems (e.g. H₂O/H₂ mixtures^{54,55}) which might be complex and inefficient in large systems or by solid/liquid exchange systems, first developed in Russia, where PbO pellets dissolve in Pb-Bi^{40, 56}. In start-up operation or in case of large contamination (air ingress), a purification system should be used (by filtration...) ⁴⁰. It is postulated that the same considerations hold for cadmium alloys, if replacing PbO by CdO. The volume change at fusion for HLM is very low – almost 0 for Pb-Bi²¹. The tritium behavior in the reactor is not clear. The hydrogen solubility in Pb-Bi is very low⁵⁷ and thus most of the tritium should be found in the primary system (cover gas and cold trap), in the cover gas of the intermediate circuit and in the SG. It should be noticed that chemistry control constraints and tritium behavior might be easier to manage if an alumina-former steel is used (less oxygen consumption, tritium blocked at walls).

Nitrate salts operating range and chemistry control is ruled by their decomposition in nitrites $\text{NO}_3^- = \text{NO}_2^- + 1/2\text{O}_2$ ³⁷. At equilibrium at 520°C about 1% of the nitrates decomposes, and the exchanger would operate in biphasic mode if nitrite concentration is not well controlled. Moreover, temperature excursions could lead to higher decomposition (e.g. about 3% at 550°C). The methods for in-line measurement and control of nitrite content are not well defined. It must also be stressed that volume change at fusion is quite important for the ternary salt ($\approx 15\%$). The tritium will probably be retained as tritiated water in the salt.

NaOH-KOH has a large temperature operating range (170- >1000°C) and intermediate vapour pressure at 550°C. But it should be operated in reducing atmosphere to lower the corrosion rate, this being proved to be difficult to control in large systems⁵⁸. The volume change at melting is large ($\approx 15\%$)⁵⁹. The tritium will be trapped in the fluid itself (by isotopic exchange and formation of NaOT-KOT).

Safety, security and environment.

For HLM, the leaks in primary sodium could lead to safety problems if the reaction products (BiNa₃...) might plug the assemblies or, to a lesser extent, wear the primary pumps.

For alloys with Cd, risks of fire, CdO toxicity and SG plugging by CdO are serious drawbacks compared to Pb-Bi. The risks of steam explosion have to be dealt with.

For nitrate salts, the major safety concern is the production of N₂ (with a highly exothermic reaction) in the primary sodium in case of sodium/nitrate reaction, as gas bubbles could enter the core. For nitrates containing lithium, lithium enrichment in ⁷Li could be necessary to prevent the risk of large tritium build-up. Moreover because of their important decomposition above 520°C, these fluids are less capable to remove residual heat or accommodate temperature sudden increase. For NaOH-KOH, it was estimated that the risks of plugging by Na₂O or the risks of NaOH-Na corrosion were limited. In case of temperature sudden rise, the corrosion could be dramatically increased.

The effluents of the fluid will not be easy to manage. Pb and especially Cd are very toxic and there is an actual trend to try to decrease their content in all effluents. As the nitrates and the hydroxides will contain tritium, adequate treatment would be necessary before release.

ISIR

The detection of HLM and nitrates reactions with sodium could be performed by using two complementary methods : ultrasonic (US) measurement for BiNa₃ particles⁷ or N₂ gas bubbles, and Laser Induced Breakdown Spectroscopy (LIBS) for elements dissolved in sodium (as Bi, Pb or Li, with a detection limit postulated to be around 1 ppm, but not K, which content in sodium is generally high, >150 ppm). For NaOH-KOH leaks in primary sodium, an optimized plugging indicator should detect O and H build-up in the sodium. In HLM, small water leaks could be detected by electrochemical sensors and large one by acoustic sensors. For nitrates and hydroxides, it is believed that periodical sampling could be sufficient for small leaks detection.

The external leaks could be detected in each case by using shifted insulations and instrumented collecting pots.

Due to the safety risks induced by the leaks of the intermediate fluid in the primary sodium, the IHX has to be carefully and periodically controlled, which might induce delays by comparison with a SFR with Na as an intermediate fluid where only the SG is periodically controlled.

On the contrary, maintenance operations should be easier as the cleaning of the fluid might be easier compared to sodium, for which particular care has to be taken to prevent caustic corrosion. For Pb-Bi, a cleaning solution⁶⁰ could consist in the ternary H₂O₂/ethanol/acetic acid mixture used to remove residual HLM for the preparation of metallographic samples^{26, 61}. It should be checked that a related process might be efficient at the industrial scale. For nitrates and hydroxides, water cleaning should be sufficient.

Components & circuits.

It was estimated that use of coatings were an unrealistic solution for large components and circuits as their deposition would be difficult and the complete tightness

impossible or very difficult to control in each point. For HLM, the hot branch materials should be T91 type (9 Cr) steels, when austenitic steels (316) could possibly be used in the cold branch (lower than 400°C). Due to the high density of the liquids, short circuits are preferred (for seismic resistance purposes...). Auxiliary circuits are necessary for the purification and the oxygen content control. For nitrates salts, components are made of 316 steel but they have to be larger or more numerous by comparison to a sodium circuit. Also, degassing systems have to be implemented to avoid the risk of bubbles passing into the core. Particular care has to be drawn to the valves because of the large volume change at melting point. NaOH-KOH would require expensive circuits because of the large components and the costs of the nickel based materials. Except for 316 steel, the demonstration of the feasibility of large and thick components with long time reliable mechanical properties is still an open question (in particular their weldability).

Experience

Lead Bismuth is the only fluid that benefits from some experience as a coolant in nuclear facilities (Russian submarines) and international experimental facilities, in the framework of the ADS programs. NaNO₃-KNO₃ has been tested as a coolant in solar applications at an industrial scale and some experimental facilities exist, in particular in the USA (Sandia National Lab) and Europe (ENEA). No other fluids benefit from facilities though possibly HLM with Cd could be tested in Pb-Bi facilities and the ternary nitrate with no problem on those dedicated to the binary salt. But it should be underlined that the facilities do not address all problems arising when using these fluids in a SFR (in particular, reaction with sodium).

Cost

Lead, bismuth and cadmium are rather low cost elements (max 10\$/kg for Bi), but the cost of the pure mixture could be one order of magnitude higher. This has to be compared to the estimated price of nuclear sodium, about 5 \$/kg. The availability of bismuth is an opened question : according to reference ¹², the estimated bismuth reserves are of 680000 metric tons. It could then be estimated that a maximum of 250 large power SFR reactors could be run at the same time, if no other bismuth resources are discovered. Nitrates and hydroxides are rather low cost compounds and the specifications on purity (low chloride or magnesium content in nitrates for example) should not change drastically their cost. On the other hand, it was considered that lithium enrichment should be necessary for the ternary nitrate. In that case, this compound would become very expensive and its availability very low.

Availability and manageability

The notes of the fluids for this criterion are rather low, in particular in comparison with sodium, when it was expected that the elimination of the reactions with air and water would greatly improve this point. This is mostly due to the

corrosion impact and the risks of the reaction with the sodium and the sensors which have to be implemented to detect it. Moreover, fluids with cadmium suffer from the high toxicities of this element and of its oxide.

Sodium with nanoparticles of nickel.

This fluid was estimated as being equivalent to sodium in many points. Its claimed advantages are linked to its lower reactivity with air and water (but it does not lower the risk due to caustic corrosion after maintenance), but they are still to be proved in real situations (reduction of wastage occurrence in case of a water sodium reaction...). According to our estimations, its drawbacks are its experience, its cost/availability and the risk of instability of the solution (growth, sedimentation of the particles) and thus the management of the fluid: in-operation control that the nanoparticles respect the required specifications. Moreover, the use of electro-magnetic devices, in particular pumps seems not to be possible. Finally, it was considered that no best compound than nickel could be used as nanoparticles (oxides would react with sodium, carbides are too much abrasive, metallic elements are too much soluble or can form oxides with sodium and oxygen in solution).

V. SELECTION OF FLUIDS

A. Fluid selection

Three fluids seem to require attention considering their global notes: Pb-Bi, NaOH-KOH and sodium with nanoparticles. Pb-Bi is a fluid with no major drawbacks (good equilibration note) and it benefits from an international research. It was thus considered that a complementary research program should be conducted on the most salient points for its use in SFR. Sodium with nanoparticles is less equilibrated but its major drawbacks (experience, cost) are due to its too recent merging. Further attention should be paid to it if it could be confirmed that it notably reduces the sodium water reaction risk.

On the contrary, the major drawbacks of NaOH-KOH, corrosion and costs of materials, seem large enough to not retain that fluid as a consistent solution (though it presents the best evaluation concerning thermal and safety aspects for example).

B. R&D program.

For Pb-Bi, it was found that the following points should be investigated for having this fluid used in a SFR, in a preference order: 1) reaction with sodium, safety impact ; 2) long term corrosion and prediction at intermediate oxygen content (between dissolution of the material and precipitation of lead oxide); 3) Purification and oxygen management ; 4) sodium/ Pb-Bi reaction detection : LIBS and US sensors ; 5) steam water explosion ; 6) design of compact components, mechanical properties of the selected materials (creep, cyclic softening, liquid metal

embrittlement) 7) tritium management ; 8) bismuth availability ; 9) large scale cleaning ; 10) procedures of use (melting/freezing management...).

If sodium with nanoparticles is found to require further studies, they should be by order of preference : 1) sodium/water reaction ; 2) production of fluids; 3) fires ; 4) stability of the fluid : growth, sedimentation of the particles ; 5) in-operation size measurements ; 6) fluid management ; 7) physical properties determination ; 8) effects on corrosion/erosion 9) methods of cleaning 10) efficiency of US sensors ; 11) possible effects in the primary circuits (neutronic impact, plugging ?).

C. Impacts on operation and design

The use of Pb-Bi as an intermediate fluid would have the following impacts on design. The circuits have to be short and integrated components are preferred. The zones with fast velocity should be avoided to limit the erosion problems. The activation of the fluid must be avoided (to prevent ^{210}Po formation). The IHX must enable periodical controls. A purification circuit and an oxygen control circuit are necessary. No fast drain circuit should be needed.

The use of Pb-Bi as an intermediate fluid would have the following impacts on operation. The oxygen content must be carefully controlled and possibly the operating temperature lowered. The non-occurrence of leak into sodium must be constantly checked. Frequent maintenance operations will be necessary on the purification circuits (filters, oxygen sensors, oxygen control systems). The tritium release and effluents with Pb will have to be carefully managed. Moreover, the operators will have to manage two fluids with very different behaviors; sodium and Pb-Bi, which means that a higher level of formation will be required.

VI. CONCLUSION

We present a method for estimating the best fluid that could replace the sodium in the intermediate circuit of an SFR. First, a selection was systematically applied to point out best promising coolants among a large number of fluids. Six fluids were selected, and also a recently proposed fluid, sodium with nanoparticles of nickel. A multi-criteria analysis was developed to evaluate the fluids, through grand criteria related to the qualities required for an intermediate coolant. The evaluation was performed by groups of experts for each criterion who decided of the sub-criteria and of the relative technical questions for the evaluation and notation.

From this evaluation, it was concluded that the eutectic alloy Pb-Bi was the most promising fluid. Also, the sodium with nickel nanoparticles could be of interest if a clear gain is put in evidence for the sodium water reaction.

R&D programs for a thoroughly evaluation of these two fluids have been proposed. The impacts on the design and on the operation of the reactor have also been highlighted.

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