SAFE AND COMPLETE DISMANTLING OF NUCLEAR INSTALLATIONS CONTAINING ALKALI METALS

A. Rahier, B. Petitfour, J. Seghers, R. Vandevoorde
SCK•CEN, Belgian Nuclear Research Center, Boeretang 200, B-2400 Mol, Belgium
Telephone : +32 14 33 22 79; Fax : + 32 14 32 15 29; Email : arahier@sckcen.be

ABSTRACT

In the nuclear sector, elemental sodium is being used as coolant in the primary circuit of fast breeder reactors. Other alkali metals or eutectics are also encountered (e.g. NaK is used for trapping hydrogen isotopes). Next to nuclear safety, classical safety is a very critical issue for the recovery, treatment and conditioning of these metals, due to their chemical reactivity. The acceptance criteria of the final waste are also quite severe. Therefore, the total costs associated to all related dismantling and treatment operations are high. The SCK•CEN (Studie Centrum voor Kernenergie / Centre d'étude de l'Energie Nucléaire) faces these questions as a result of tests carried out in the past, mainly for qualifying fast breeder fuel elements. An R&D program has been launched, focussing on all required operations from the extraction of the metal to the safe conditioning of the final waste. Five main steps were identified : (a) recovery of the metal, (b) dismantling of the process vessels and piping, (c) cleaning of the dismantled pieces, (d) treatment of the recovered alkali metals and (e) final conditioning of the waste. For the first three steps, adequate technical solutions are being developed. However, these techniques depend heavily on the initial concept and particularly on the geometry of the installation to be dismantled. Therefore, they may not be applicable in other practical cases. For the treatment of the recovered metal, the SCK•CEN has conceived and patented a new and safe process that is fully compatible with the further conditioning of the waste into an acceptable form. In this process, molten alkali metal is injected into a fluidized bed reactor containing calibrated sand particles. The fluidizing gas is argon but nitrogen can also be used. A preheated mixture of oxygen and carbon dioxide is introduced into the reaction vessel, allowing the metallic droplets to be oxidized and carbonated. The reactions involved generate no hydrogen while the turbulent conditions prevailing into the reactor guarantee a complete conversion of the metal. The presence of carbon dioxide not only supports formation of the carbonate(s), the formation of peroxides is also avoided. Depending on the level of radioactive contamination, the mixture of sand and carbonates may be considered as the final waste, or may be further conditioned as glass. This paper defines general guidelines to be observed for the safe recovery of the alkali metals and discusses the results obtained for the treatment of the main mass (the bulk) in the case of sodium.

INTRODUCTION

From 1970 to around 1990, the SCK•CEN has carried out several experiments involving molten sodium as coolant. The aims of these efforts were mainly to qualify fuel elements for fast breeder reactors, to assess the thermal and post-irradiation behavior of the fuel in the presence of sodium, and to assess the post-accidental heat removal from damaged fuel pins. At the end of these experimental campaigns, because there existed no effective process for the safe treatment of contaminated sodium, the SCK•CEN decided to provisionally store the fuel bundles, still containing metallic sodium. However, for safety reasons, we looked for acceptable techniques to dispose of this waste. In the early 1990's, still no safe process was known for the treatment of the bulk. Therefore, we decided to launch an R&D program focussing on this essential step while defining also adequate routes to recover the metal and to dismantle the experimental loops. Very rapidly, we found that all the necessary operations were complicated because of the chemical reactivity of the sodium. The apparently evident solution, which consists in allowing water to react with the metal, appeared to be quite unsafe. The simultaneous generation of hydrogen and heat does not fit into the ALARA principle. Even when using an alcohol instead of water, thereby allowing easier control of the reaction, the safety principles are not fulfilled; hydrogen is still being generated together with heat, while the organic reactant and product (an alkoxide) bring even additional fire risks into the process. Moreover, the final waste arising from these schemes is not acceptable. Using water, a corrosive aqueous solution of sodium hydroxide is obtained. In the case of alcohol, the situation is even worse because the waste is organic and flammable. The intermediate alkoxide has to undergo further reaction with water, regenerating the alcohol and still leading to an aqueous solution of sodium hydroxide. All these processes require additional treatment of the waste to cope with the acceptance criteria for long term storage.

These drawbacks must be taken into account for all operations involving elemental alkali metals. However, the treatment of the bulk is the critical step in which radically different ways must be defined because of the large amount of metal to be treated. For the cleaning of the metallic pieces arising from the dismantling operations, the reaction with water may be considered, provided all possible measures are taken during the extraction phase in order to minimize the amount of residual alkali metal in contact with the structural material. For the recovery of the alkali metal, and for the dismantling operations themselves, one has also to take reasonable precautions to avoid the contact of the metal with water and, if possible, with oxygen.

In 1995, keeping in mind the above-mentioned safety aspects, we started to look for alternative routes for all necessary operations, from the recovery of the metal to the conditioning of the final waste. Our basic points of reference were the physico-chemical properties of sodium, the radiological characterization of the metal to be recovered and treated (table 1) and the physical characteristics of the equipment containing the alkali metal. This is because at that point, we also considered all the operations, including cutting. We used these data to progressively define a new approach that would be acceptable from a safety point of view.

Table 1 : Radiological characterization of the sodium present in the equipment at SCK•CEN[a]

Radioisotope	Specific activity $(Bq.kg^{-1})$[b]	Date of validation
^{137}Cs (γ)	4.8×10^{10}	1994-01
^{134}Cs (γ)	1.8×10^{8}	1994-01
^{22}Na (γ)	4.9×10^{5}	1994-01
^{60}Co (γ)	2.9×10^{5}	1994-01
^{125}Sb (γ)	9.3×10^{4}	1994-01
Total U (α)	2.7×10^{3}	1994-01
Total Pu (α)	4.0×10^{4}	1977-11
Total Am + Cm (α)	2.0×10^{5}	1977-11

Notes :　(a) : Contact equivalent dose rates were also measured at different locations and dates. The upper value was 0.08 $mSv.s^{-1}$ in December 1983
(b) : Several measurements were carried out at different places and on different rigs. The presented data correspond to the upper values resulting from all measurements

Table 2 : Physical characteristics of the equipment

Description	Data	Units
General shape	Cylinders	Not applicable
Maximum length	7	m
External outer diameter	From 0.2 to 0.45	m
Estimated mass	200 - 250	kg
Sodium inventory (per rig)	20	L
Construction materials	SS 304, SS 316, tungsten	Not applicable

CUTTING THE VESSELS AND RECOVERING THE ALKALI METAL

Two options are possible : either the vessels are cut apart before recovering the metal, or the recovery precedes the cutting of the pieces. The choice between those two possibilities depends on the external geometry of the vessels, on the total inventory of sodium and on the availability of adequate hot cells to carry out the real operations. Since our vessels consist of cylinders whose length is around 7 m while the diameters never exceed 0.5 m, we choose to cut the vessels before recovering the metal. Another important reason for doing so is that our vessels contain complicated internals like heat exchangers, pipes, fuel pins and other inner volumes. In such circumstances, trying to extract the metal before cutting the vessels could result in very poor extraction efficiency. This would impair the safety of the cleaning operation as discussed in the next paragraph. The drawback of this approach is that the cutting operations must be carried out with more caution since the sodium is still present in the loop. For safety reasons, an inert atmosphere is recommended to avoid any contact between the metal and oxygen.

Based on previous experience, we decided to plan the cutting operations in the hot cell of the BR2 reactor. We will use a saw that moves slowly and alternatively in a horizontal plane. Earlier experience proved that this device is reliable. The cutting will be carried out under a continuous argon flux. Each cut piece will be 0.6 m long and will be

installed vertically into a vessel containing an inert atmosphere wherein the recovery will take place. To assess the efficiency of the metal recovery, cold experiments were carried out using a mock-up device whose geometry corresponds exactly to the in-pile section containing the fuel pins. The unit was heated up to a temperature slightly above the melting point of sodium and the mock-up piece was drained. Still due to the particular geometry of our vessels, we opted for gravity as the only driving force to extract the metal. This simplifies considerably the recovery installation. But we were ready to adapt the system by providing well located overpressures or underpressures to help in draining the molten metal if necessary. Our cold experiments demonstrated that more than 95 % of the sodium could be recovered by this technique.

The chosen method is certainly not universal and may not be applicable to all practical cases. If we ever had to face bigger installations involving tanks and more compact geometries, or if complicated internals were absent, we would extract the liquid before cutting the vessels. This increases the safety of the cutting operations while still allowing extracting most of the metal. Moreover, additional experimental work is needed to assess the efficiency of the recovery when the internals are more complicated.

In an attempt to further reduce the residual amount of sodium in the cut pieces before cleaning them, we carried out an in situ oxidation and carbonation by circulating nitrogen, oxygen and carbon dioxide (in proportion 3:2:1) under atmospheric pressure through the system. Two experiments were carried out. The duration and treatment temperature of the first experiment were 56 hours and 288 K respectively. The second experiment was carried out at 393 K during 47 hours. The post-experimental speciation of the residual products was carried out by progressively and carefully immersing the treated piece into water while monitoring hydrogen and oxygen in the gas phase by gas chromatography. Measuring the ratio of carbonates on hydroxides after dissolution made a further assessment of the product composition. Our results indicate that not all the metal reacts with oxygen and carbon dioxide, even at $393^{\circ}K$. A passivation layer grows rapidly at the surface of the metal and prevents against further oxidation and carbonation of the metal. Also, sodium peroxide was detected in the reaction products. For these reasons, we decided to abandon the idea of reducing the inventory in situ after drainage, preferring to rely on a more efficient cleaning operation to completely eliminate the alkali metal residues.

Still in the framework of the metal recovery, we investigated another technique based on distillation. This operation is better carried out under reduced pressure to avoid coping with high temperatures. It relies on the thermal pumping of the sodium vapor from a hot point (i.e. the vessel to be emptied) and a cold point located beneath the hot point. A mock-up installation was also constructed and allowed us to observe that the transfer of the metallic sodium is very efficient. However, the operation is very slow and although we worked around 100 Pa, the required temperature was still as high as 870 K to ensure that the distillation proceeds at a reasonable speed. We noted that the partial pressure has to be continuously maintained by regularly pumping out any gas that appears in the distillation unit otherwise the distillation process slows down and can even stop. This observation is of particular importance when dealing with alkali metal containing hydrides: as the metal distills, hydrogen is also released in the distillation vessel and the thermal pumping effect becomes much less efficient. Nevertheless, our experiment demonstrated that more than 99 % of the metal could be transferred by this method. An attractive advantage of distillation is that the alkali metal is purified at the same time it is extracted. When using drainage by gravity, no purification is carried out and one may even expect that relatively big pieces of the internal structure accompanies the drained metal. This is especially true when the vessels are cut before drainage, because internal pieces (e.g. tubings) may be detached from the vessel by the cutting operation. They remain in place as long as the sodium is frozen, but they may escape from the vessel during the drainage. This requires particular attention for the later treatment of the bulk. Another advantage of the distillation is that it can empty all internal dead zones that reach the boiling temperature of sodium corresponding to the chosen pressure. Drawbacks result from the need to maintain high temperatures for long periods of time. Not all structural materials can withstand these conditions. Our tests demonstrated that using 4.6 kW for the heating power, about 0.38 kg of sodium could be distilled within 16 hours.
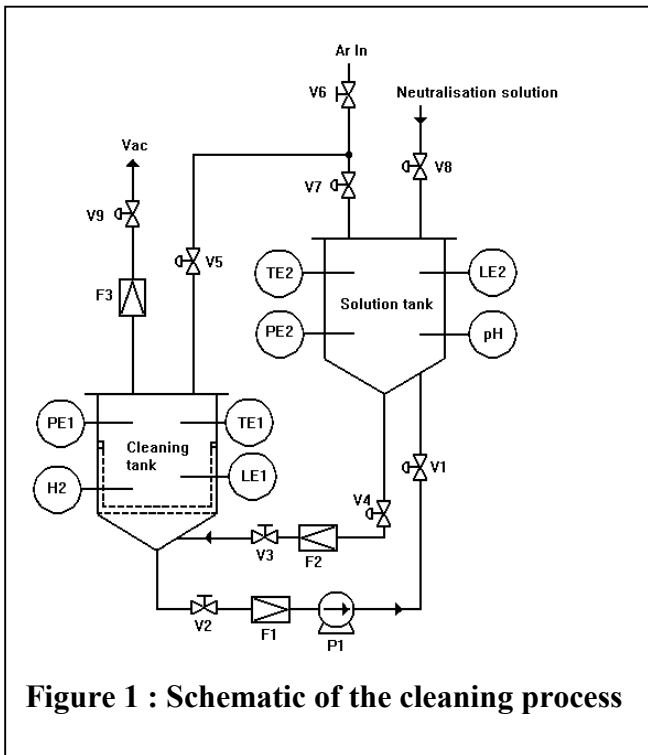
CLEANING THE CUT PIECES

Figure 1 : Schematic of the cleaning process

The cut pieces must be completely cleaned to circumvent the question of the acceptance criteria related to the metallic sodium. Due to the internal complexity of the pieces, dead zones containing sodium are expected to be present inside the pieces. This must be taken into account in the design phase of the cleaning process. Since the use of gaseous reactants was not convincing at all, we decided to clean the pieces very carefully with liquid water. From a safety point of view, this is acceptable if and only if the amount of residual sodium has been minimized. As a general guideline, we decided to limit the maximum allowed amount of sodium in one piece to 1 kg. Should this amount be higher than the defined limit, then additional efforts are needed to further extract the metal before cleaning. For this purpose, the distillation technique is preferred because of its high transfer efficiency, even when complex internal structures are present.

To allow the water to reach the internal dead zones, a special design involving several cycles is presently being considered. The cleaning process consists of two tanks. The first one is the cleaning tank. It contains the cut piece to be cleaned. The second one is referred to as the solution tank. It contains the cleaning solution (see figure 1). During the cleaning step, the liquid is transferred from the solution tank into the cleaning tank, using vacuum. This allows the liquid to reach the dead zones. The cleaning tank is flushed through a pipe, thanks to a pump. The sodium reacts with water, yielding hydrogen bubbles, which prevent further reaction in the dead zones. Therefore, the cleaning process has to be repeated several times, involving cycles of successive filling and flushing operations of the cleaning tank. During the whole operation, the pressure prevailing in the cleaning tank, and more specifically, the partial pressure of hydrogen, are being continuously monitored. When the partial pressure of hydrogen increases too fast, the water is rapidly transferred back to the solution tank through the pump and avacuum condition is re-established in the cleaning tank. Combining the maximum allowable amount of metallic sodium in the cleaning tank, the described procedure results in enough flexibility to control the rate of the reaction of sodium with water. The cleaning is considered to be complete when at least two successive cycles are performed, ensuring that the liquid fully covers the piece in the cleaning tank while no hydrogen generation is being detected anymore. When the cleaning is finished, the piece is dried under vacuum and taken out of the cleaning tank for later conditioning. Next, the solution is neutralised and another piece may be treated. After cleaning several pieces, the number of which depends on the amount of residual sodium, the cleaning solution is drained and replaced by fresh water. The liquid effluent, consisting of an aqueous solution of sodium hydroxide, is evacuated as waste.

THE TREATMENT OF THE BULK : SAFETY CONSIDERATIONS, EXISTING PROCESSES AND SCK ALTERNATE PROPOSAL

Among the known existing sodium treatment processes, none may be considered as being sufficiently safe. For instance, the NOAH (anagram for NaOH, sodium hydroxide) process, which has been applied in the framework of the DESORA programme ("DEstruction du SOdium contaminé du circuit primaire du réacteur expérimental RAPSODIE") (1-3), consists in allowing sodium to react with liquid water. Since we are dealing with the treatment of the bulk, several tons of alkali metal are involved and a considerable amount of hydrogen is being released together with heat (Eq. 1).

$$2 \, Na + 2 \, H_2O \longrightarrow 2 \, NaOH + H_2 \quad (Eq. \ 1)$$

The reaction is violent and tends often to become explosive. Next, the reaction product is a solution of sodium hydroxide, which requires further treatment due to its corrosive properties. In an attempt to lower the risks of incidents, CEA has proposed to replace water by alcohol because the reaction of the latter with sodium is less violent (4). But hydrogen is still being produced together with heat. Moreover, the reaction product is an alkoxide that has to be hydrolysed to turn back to a solution of sodium hydroxide. Finally, both the alcohol and the alkoxide are flammable. This process has been abandoned for safety reasons.

The calcination process, studied in ANL in the USA (5), is by far less dangerous, but it does not allow converting easily the totality of the metal while sodium peroxide (a relatively unstable product) is present in the reaction products.

For all these reasons, the SCK-CEN has developed and patented a new sodium treatment process (6), with the financial support of Electricité de France (EDF). This process is based on the sodium oxidation-carbonation reaction (Eq. 2).

$$2\ Na + CO_2 + 1/2\ O_2 \longrightarrow Na_2CO_3 \qquad (Eq.\ 2)$$
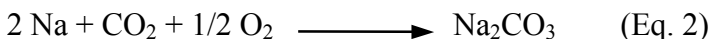
This reaction does not yield hydrogen, thereby reducing explosion and fire risks. The reaction occurs in a fluidised bed reactor, which allows a good control of heat exchange, and a total conversion of metallic sodium, thanks to a turbulent flow. The inert matrix of the fluidised bed is sand, allowing linking the sodium oxidation step with a future vitrification step : the process is integrated, and the ultimate waste is ready for long term storage.

Figure 2 illustrates the piping and instrumentation diagram of the process. The fluidized bed reactor is installed into a leaktight vessel, together with a gas circulator, a heat exchanger and a temporary storage tank. The primary feed tank and the mass flow controllers installed on the gaseous reactant feedlines are located outside the main vessel. To start up the unit, the reactor is first filled with 50 kg of sand particles whose mean diameter is around 75 μm. This operation is carried out through a funnel located above the reactor vessel (not represented on figure 2). It takes about 4 minutes to install the full load. After having checked that the coolant circuits are functioning properly, the reactor is heated up to around 393 K by circulating the pre-heated fluidization gases through the bed. The reactor body is equipped with a double wall, allowing circulating oil for the purpose of ensuring heat exchange. During the heat up phase, hot oil is circulated between both walls of the reactor body to help in achieving the required initial temperature. Already during this phase, fluidization occurs inside the reactor, in a non-bubbling regime. The nominal gas flow rate is around 2.5 $Nm^3.h^{-1}$. At the same time, the sodium injection line located beneath the reactor is also being heated up to at least 393 K. This line has been carefully designed to avoid any leak and to ensure that sodium cannot freeze anywhere on its way to the reactor. When the required temperature is reached, sodium is introduced into the external storage tank and an inert cover gas is installed above the metal. Next, the temperature of the external tank is increased until sodium is fully molten. At that point, a check of the gaseous reactants injection lines (oxygen and carbon dioxide) is made to ensure proper operation. The sodium is then forced to the reactor using a pre-heated pump located on the sodium injection line. The flow rate is carefully adjusted to the nominal value of 0.36 $kg.h^{-1}$. The sodium injection line terminates inside the reactor, at the base of the bed. At this end of the line, there is a bi-fluid nozzle, which ensures the correct dispersion of metallic droplets into the fluidized bed. When the sodium begins to enter the reactor, the mass flow controllers for the gaseous reactants are turned on and adjusted to their nominal set points. A careful follow up of the temperature inside of the reactor is made. Indeed, at this stage, the oxidation-carbonation reaction occurs and heat begins now to be released inside the reactor. The coolant temperature is rapidly adjusted to switch from the heating mode to the cooling mode. The reactor is kept running in this regime for the desired duration. The nominal temperature inside the reactor should not exceed 673 K in steady state. Theoretically, a load of 50 kg of sand allows to work continuously during 21 hours after which the ideal ratio of sodium on silicium is reached to allow an easy later vitrification of the waste. After that period, the reactor may be switched off according to a safe procedure. A cool down period is foreseen before the reactor may be discharged downwards and the waste can be transferred to a temporary storage.
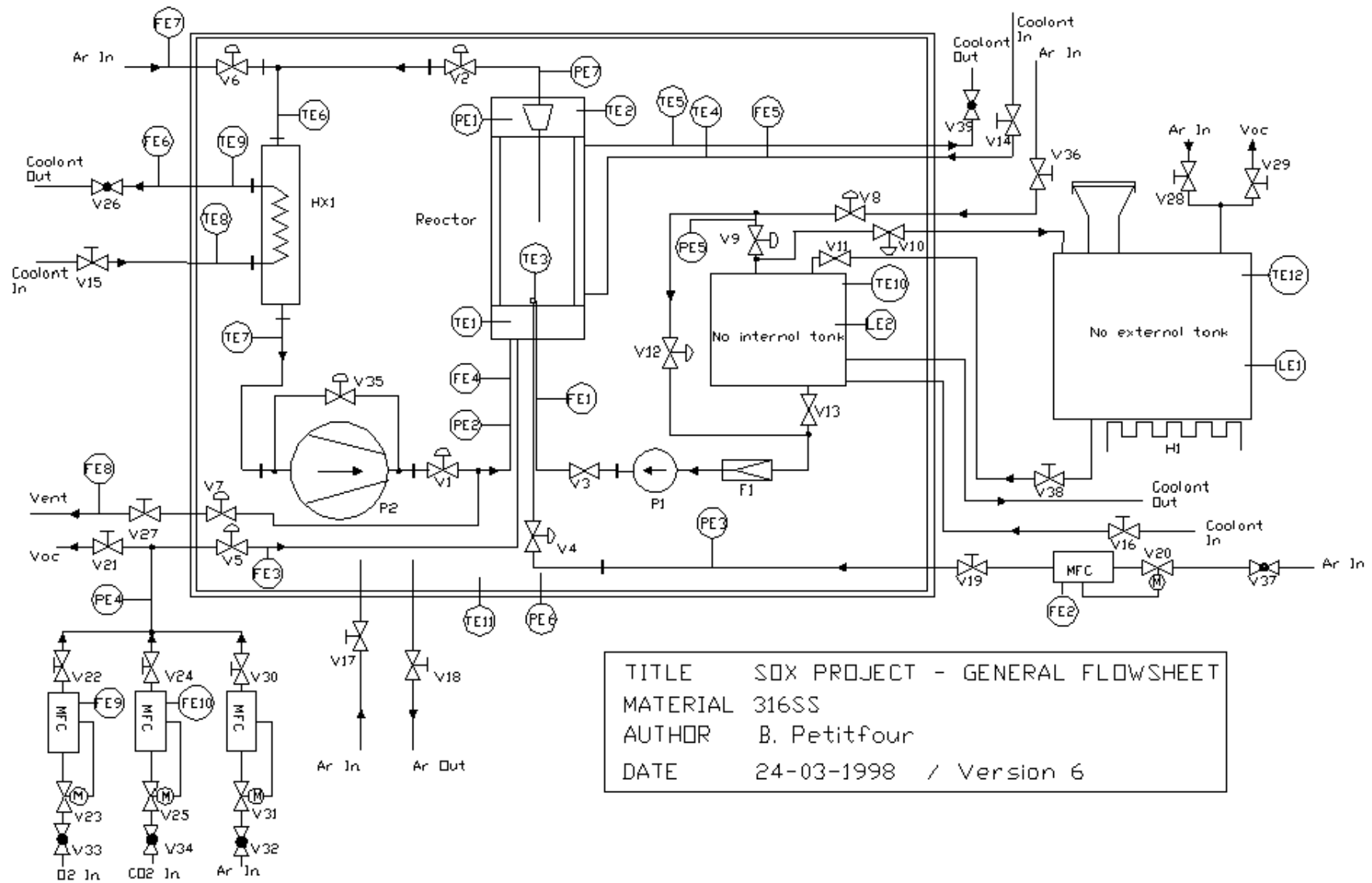
Figure 2 : Piping and instrumentation diagram for the treatment of the bulk

Using this system as well as previous versions of it, we carried out an orientation test, injecting a total amount of 100 g of sodium into the reactor. We could demonstrate that more than 99.99 % of the metallic sodium is converted into sodium oxide (82 %) and sodium carbonate (18 %). Neither elemental sodium nor sodium peroxide could be found back in the reaction products. The repartition of sodium between oxide and carbonate after the reaction can be explained by the fact that the duration of the reaction was not long enough to allow the oxide to be converted into carbonate. The reaction products are all solid while the reactants are in the liquid and the gaseous state. Therefore, the temperature of the products is quite high and it takes some time to the oxide to be converted into the carbonate. Also, at present, we still do not know which practical CO_2/O_2 ratio would be optimal to favor the carbonate rather than the oxide. Further experiments are needed to investigate the optimum values of the process variables.

In the next experimental step, we develop a theoretical support, focussing on the heat exchange at the early stage of the work.

Concerning the acceptability of the reaction products as waste, it appears that carbonates diluted in sand can be easily conditioned. This is true not only in Belgium but also in other countries. Indeed, the carbonate is much less corrosive than an aqueous solution of sodium hydroxide. One additional argument in favor of this is that one of the proposed next treatments for a solution of hydroxide is precisely to proceed to a carbonation. Our process reaches this state in one step. When the specific activity of the sodium is low, there is no need to vitrify the mixture. In this case, the reaction may be continued in such a way that the proportion of carbonate in sand is much higher, thereby reducing the volume of the final waste. However, there are two cases where the vitrification may be considered :

- The specific activity of the sodium is high: vitrification may be carried out to end up with an accepted and adequate conditioning of HLW
- The specific activity of the sodium is not high, but the sodium is to be treated as a result of the dismantling of a fast breeder reactor : in this case, HLW will be produced by other dismantling activities and the mixture of sand with sodium carbonate produced by the sodium treatment may be economically used to condition these HLW. This allows to combine two waste fluxes, thereby reducing the total cost of waste

Finally, when vitrification is not carried out, and assuming that the mixture of carbonate and sand would not be desirable, the product may undergo a further reaction to yield any other chemical compound containing sodium. An example of this would be the treatment of non-radioactive metallic sodium. In this case, neutralization of the mixture with hydrochloric acid is followed by discharge of the effluents into the sea, provided no other chemical contaminant prevents doing so. Even in the case of non-radioactive alkali metals, the process proposed by SCK remains attractive, because of its intrinsic safety.

CONCLUSIONS

Contaminated alkali metals are unacceptable waste because of their chemical reactivity. Facing this question, the SCK•CEN proposes a complete solution for the dismantling and the clean up of installations containing alkali metals. A particular accent is put on the safety aspects of the treatment of the recovered metal. However, the proposed solution is also integrated for the following reasons :

- The proposed process for the treatment of the bulk is fully compatible with the further conditioning of the waste under the form of a glass. If necessary, alternate conditioning may be foreseen which makes the proposed solution quite flexible. In all cases, the question of the waste is being solved.
- Particular attention has been paid to the safe recovery of the alkali metals out of existing installation. Also, the safe dismantling of installations chemically contaminated with alkali metals has been considered. Further work is going on to demonstrate the full proposal, from the extraction of the metal to the final conditioning of the waste

ACKNOWLEDGMENTS

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