

## **Development of a Safe Technology for the Treatment of Sodium Waste: Early Experience**

J. Braet, E. Cantrel, J. Seghers  
SCK•CEN  
Boeretang 200, 2400 Mol, Belgium

### **ABSTRACT**

In the primary circuit of fast breeder reactors and in some other nuclear facilities, elemental alkali metals are being used as coolant. SCK•CEN, the Belgian Nuclear Research Centre, has carried out several experiments involving molten sodium as coolant, 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 the campaigns the fuel bundles were provisionally stored, lacking an effective process for the safe treatment of contaminated sodium.

Some years ago SCK•CEN started to look for an efficient and safe technology for this waste resulting in a waste form which is ready for further conditioning. Direct controlled oxidation with water or with an alcohol was considered to be inadequate for our purposes mostly for safety reasons and because of possible complications during the further immobilization of the produced waste. Recently we started the development of a simple and safe batch process to meet safety requirements and which would render the sodium into a non-reactive form, compatible with the further conditioning of the waste into an acceptable form.

The proposed process is a three-step reaction in a batch reactor. The end product is sodium carbonate containing the radionuclides. At the end the sodium carbonate can be immobilized in a concrete or glass matrix. During this process no hydrogen is formed, while the turbulent conditions guarantee a complete conversion of the metal and excellent heat transfer capabilities, eliminating explosion risks.

After initial testing of the process on lab scale, a small pilot installation was constructed to demonstrate the process with non-active sodium in batches of about 1-5 kg sodium in 50 kg sodium carbonate. The paper will describe the process, technique and results of the cold tests.

### **INTRODUCTION**

The nuclear industry has widely used metallic sodium in the fields of research, development and operation of fast breeder reactors. Most of the time metallic sodium has been chosen as coolant in these projects. This choice has been based on the physical properties of the metallic sodium (no moderation, low neutronic absorption cross section, thermal conductivity, wide temperature range of use in liquid state, viscosity...). The choice was made despite the chemical properties of the metallic sodium as it reacts violently with numerous substances.

SCK•CEN, the Belgian Nuclear Research Centre, has carried out several experiments involving molten sodium as coolant, 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.

Now that the nuclear industry has started the decommissioning of nuclear facilities, research has been carried out for the treatment of metallic sodium. Several processes have been developed but none could simultaneously satisfy the safety constraints and the total conversion required for the destruction of metallic sodium. Besides processes based on a reaction with an alcohol that have been abandoned (casualty), the processes currently used are based on a reaction with water or an aqueous solution of sodium hydroxide. The release of heat associated with the production of hydrogen makes these processes rather unsafe.

In this context, new processes for the safe treatment of metallic sodium are under development. Besides the obvious criteria regarding the conversion, the constraints of the process include the intrinsic safety of the process (control of the reaction, no production of hydrogen, etc...).

Some years ago SCK•CEN started to look for an efficient and safe technology for this waste resulting in a waste form which is ready for further conditioning. The feasibility of converting the alkali metal into a stable form by oxidation and further carbonation with a mixture of O<sub>2</sub> and CO<sub>2</sub> was studied in the frame of the SANDS (SAFe Na Destruction System) project [1]. Some disadvantages of SANDS prohibited large scale demonstration. More recently at SCK•CEN the development of a new simple and safe batch process, SimSan, was started. The project had the same objectives: to meet safety requirements and to render the sodium into a non-reactive form, compatible with the further conditioning of the waste into an acceptable form. The chosen design makes use of a heated mechanically stirred reactor, where the molten sodium is firstly coated on Na<sub>2</sub>CO<sub>3</sub> particles prior to gaseous reagents addition. After initial testing of the process on lab scale, a semi-industrial pilot installation has been constructed to demonstrate the process with non-active sodium for batches of about 1-5 kg sodium.

## TOWARDS A SAFER SODIUM DESTRUCTION SYSTEM

### Description of the SimSan Process

The SimSan process is based on the controlled oxidation-carbonation reaction described by the following balance:

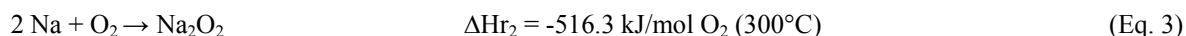
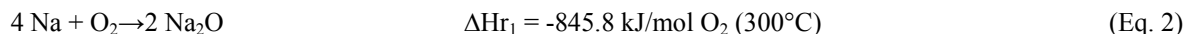


The chosen design makes use of a mechanically stirred and heated reactor, where the molten sodium is firstly coated on Na<sub>2</sub>CO<sub>3</sub> particles prior to gaseous reagents addition. In this design, a high sodium surface area is prepared targeting:

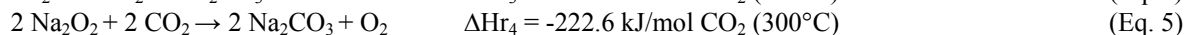
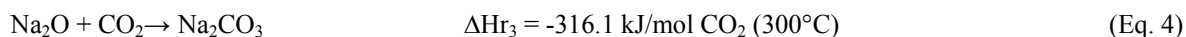
- the complete conversion of the metallic sodium;
- a large contact surface area between the gaseous reagent and the sodium;
- a high chemical yield;
- a good control of the chemical reactions and associated heat production;
- an efficient heat transfer.

The different reactions involved in the process and the related reaction heats are indicated below:

#### *Oxidation reactions:*



#### *Carbonation reactions:*



The sodium treatment process converts the metallic sodium into sodium carbonate in three consecutive stages. In a first step the sodium carbonate inert matrix is dried in the reactor while the sodium is molten separately. Under high agitation the molten sodium is then added to the matrix, forming a coating on the sodium carbonate particles, resulting in a high sodium surface contact area. Once the liquid metallic sodium has been coated on the inert matrix, it is firstly oxidized above 270°C by injection of a mixture of O<sub>2</sub> and CO<sub>2</sub> in Argon. Already in the oxidation step a smaller amount of CO<sub>2</sub> is injected in order to limit the accumulation of the unstable Na<sub>2</sub>O<sub>2</sub> produced by a side oxidation reaction (conversion into carbonate). From a thermodynamic point of view this reaction is favored when

O<sub>2</sub> concentration in the gas mixture is increased. When the oxidation of the sodium is completed, CO<sub>2</sub> is then injected to complete carbonation of the sodium oxide.

Main characteristics of the SimSan process can be summarized as follows:

- the process is operated batch wise;
- the conversion occurs in a mechanically stirred reactor;
- no hydrogen and/or water production;
- the metallic sodium is coated on calibrated particles to ensure "high active surface" prior to injection of the gaseous reagents
- exothermic but controllable reactions;
- reaction controlled by injection of gaseous reagents.

### Layout of the experimental pilot plant

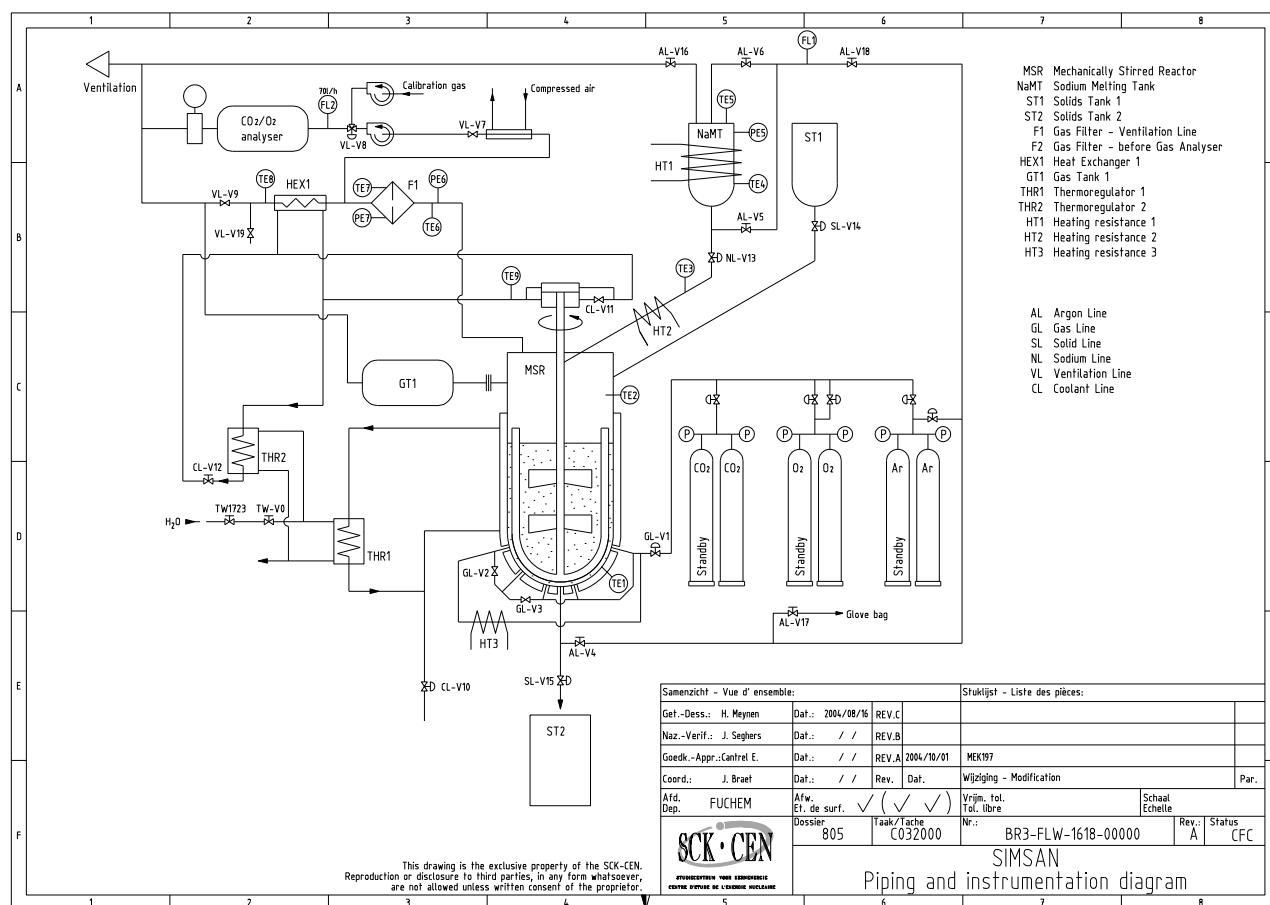


Figure 1: General piping and instrumentation diagram

The installation is settled in a dedicated confinement built in the "Turbine Hall" of the BR3 building (Figure 1). The process control system, the secondary heat exchangers, the gas bottles and the special device dedicated to prepare and to feed continuously the process with the adequate gas mixture are located outside the confinement. The confinement is highly ventilated: 1500 m<sup>3</sup>/h which equals to about 30 renewals/h. The necessary safety devices are in place, as there are fire extinguishers, fire blankets and fire detection in the confinement.

Since the required argon flow rates for the reactor loop and the melting tank for a single experiment are rather limited, it has been decided not to recycle process gases in this pilot facility. The process operates at atmospheric pressure under an argon flow rate of less than 1 m<sup>3</sup>/h.

The gas circulation line includes an argon feeding unit, one heat exchanger, a surge tank with a capacity of 150 l at a maximum pressure of 10 bars, a porous metal filter and a vent line. The gas buffer tank, which is equipped with a rupture disk (3 bars), protects the whole vent line (filter, heat exchanger) and the reactor from overpressures and avoids gas backflows. The so-called "Porol-inox"® filter is provided by Filtermat and made of 4 cartridges of 200 cm<sup>2</sup> filtering area each allowing retention of particles larger than 1.5 µm (gas stream).

The heat exchanger is a once-through multi-tubular type with 19 tubes. It is dedicated to cool down the process gases prior to exhaust in the atmosphere. The coolant fluid is synthetic organic (dibenzyl toluene) heat-transfer medium which is thermally stable up to 300°C. Chemical inertia of the oil towards metallic sodium has been demonstrated at 300°C [2]. The oil also flows through the reactor double wall, to bring the particle bed to working temperature and to evacuate the heat produced during the processing of the metallic sodium. The oil is cooled down or heated up using two secondary heat exchangers (TOOL-TEMP thermoregulators) located outside the confinement. The two identical thermoregulators have a heating and cooling capacity of respectively 16 kW and 46 kW (at 200°C). In the present configuration, one is used to cool down the off-gases, the axis of the stirrer and the supporting flange (THR2), while the other one allows warming up the mechanically stirred reactor (MSR) and evacuating the heat produced during the processing (THR1).

The gas injection system is composed of:

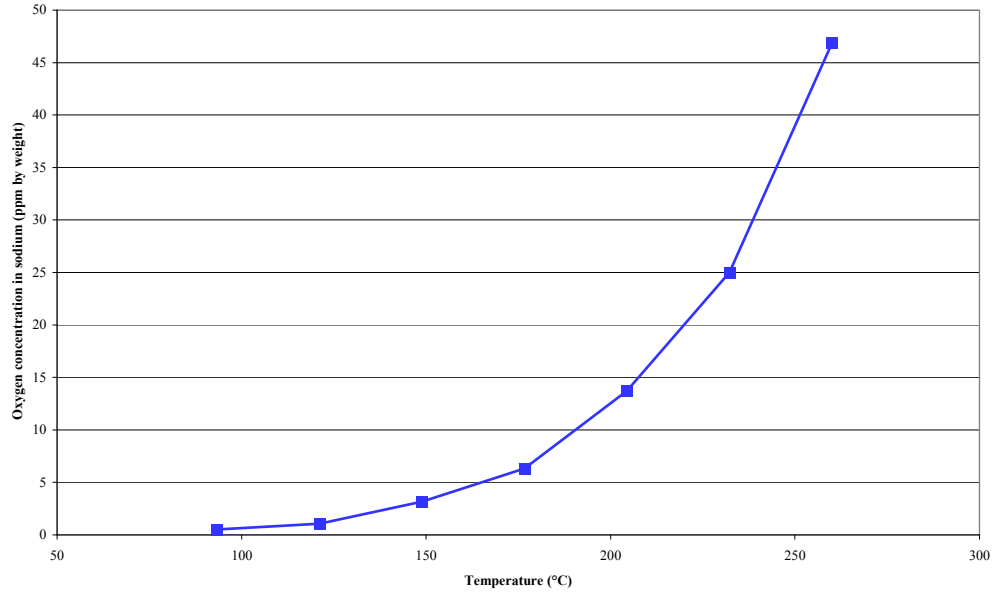
- Two bottles of each gas (oxygen, carbon dioxide and argon) which are connected to the installation through a so-called "central CLSA" that continuously feeds the installation with gas.
- An O<sub>2</sub>/CO<sub>2</sub> analyzer from ABB analyses the amounts of oxygen and carbon dioxide circulating in the system. The oxygen concentration measurement is based on the paramagnetic properties of oxygen. An infrared analyzer determines the carbon dioxide content in the gas. The O<sub>2</sub>/CO<sub>2</sub> measuring unit is a very important part of the process since its output is part of the diagnosis to determine the end of the different treatment steps.

The sodium melting tank NaMT has been designed and constructed at SCK•CEN. This tank is made of 316L SS and is qualified and certified to handle pressure as high as 7 bars. Its maximal capacity is 20 l. At the outlet of the melting tank there is a perforated plate with holes smaller than the diameter of the injection line to prevent bigger oxide particles from blocking the line. The tank and the injection line are heated by means of a heating wire. The tank is heated up to 150°C, the line up to 200°C. Doing so, prevents the precipitation of oxides in the injection line since the solubility of the oxide increases with temperature (Figure 2).

In the SimSan pilot-installation, the melted metallic sodium is simply introduced by gravity into the reactor MSR. The injection line is as short as 70 cm between NaMT and MSR and includes only one valve. Literature indicates that a 50 µm thick layer of metallic sodium can be expected to remain on the inside walls after the injection. This means that only a few grams (about 5 g) of metallic sodium will remain trapped inside the injection line under inert atmosphere. The injection line is held at a constant temperature above the melting point of sodium (98°C at 1 atm) thanks to a resistance heater (HT2) welded all around the tubing.

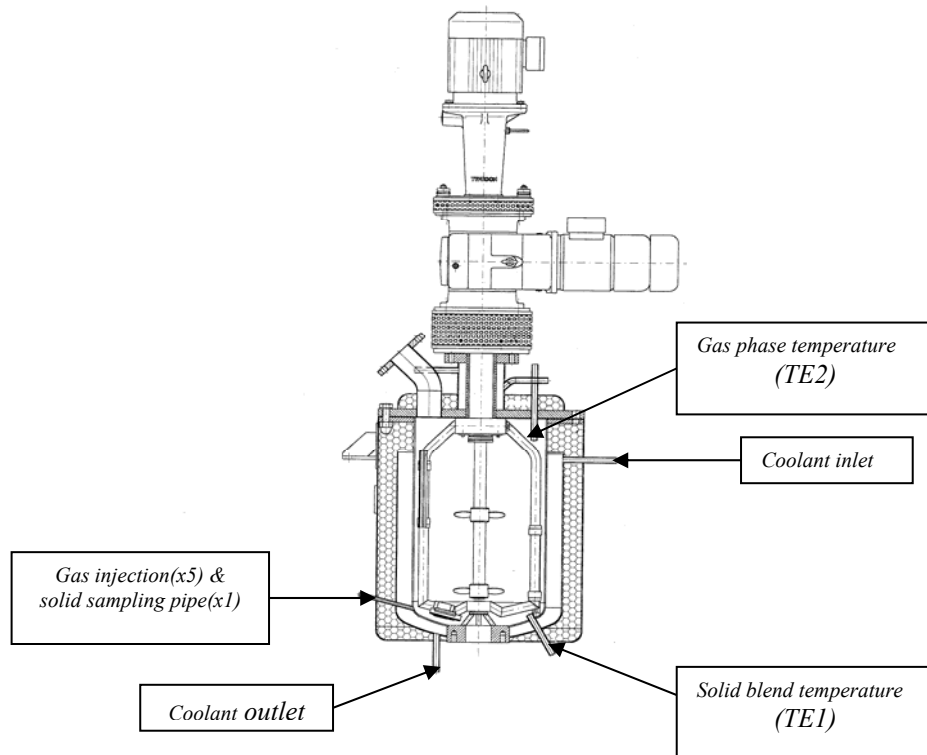
The reactor MSR is the heart of the process where the metallic sodium coating, the oxidation and the carbonation reactions are carried out. This reactor has a double mantle, wherein the coolant circulates at about 70 l/min, warming up the solids, evacuating the reaction heat and cooling down the solids when the processing is completed. The double mantle and the cover of the reactor are thermally insulated. The tank body and the tank jacket have been designed and qualified to stand, respectively, 3 and 1 bar pressure. The maximal content of the reactor is 75 l.

Thorough mixing of the particle bed is ensured by a coaxial stirring system composed of a conventional stirrer with 2 propellers and a rotating frame equipped with stainless steel scrapers. The scrapers and the stirrer are driven by two independent engines of, respectively, 1.5 and 2.2 kW power. The stirrer's critical rotating speeds are between 360 and 760 rpm. Therefore, the minimal working speed during the processing has been set at 800 rpm.

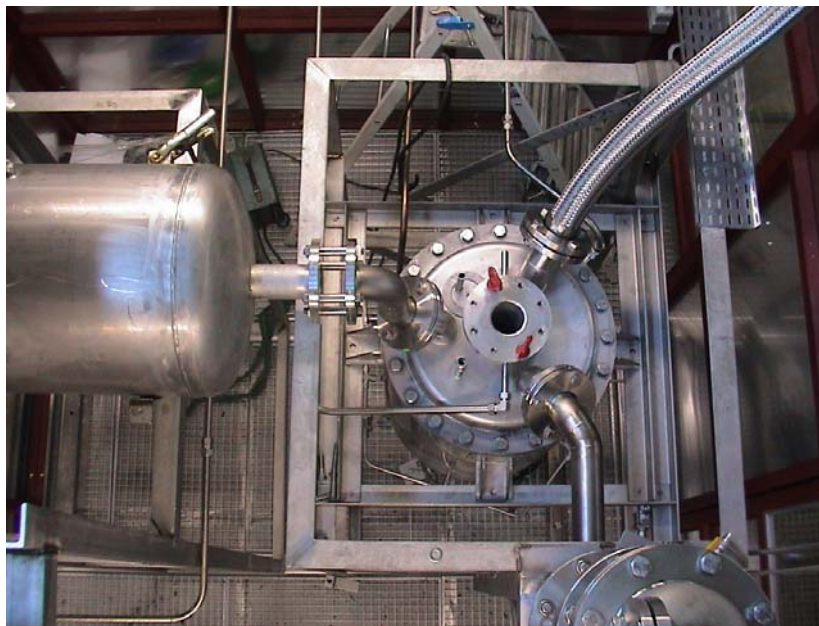


**Figure 2: The solubility of oxygen in sodium**

Figure 3 and Figure 4 show a detailed view of the reactor.



**Figure 3: Technical drawing of the reactor and mixers**



**Figure 4: View from the confinement roof of the SimSan pilot installation with the 50-l gas buffer tank (on the left hand side) and the inert matrix loading pipe (on top right corner)**

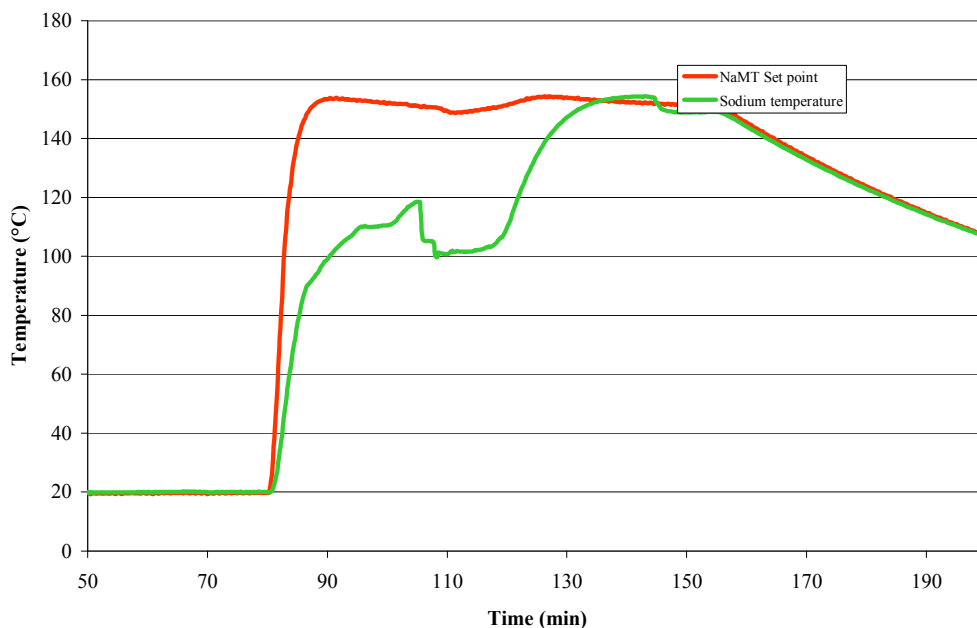
## EXPERIMENTS

Each sodium treatment experiment is carried out according to the following sequence:

- Drying of the fresh matrix (depending on packaging, transport and storage conditions);
- Warming up of the reactor up to an optimal temperature for coating sodium on  $\text{Na}_2\text{CO}_3$  (around  $130^\circ\text{C}$ );
- Introducing the sodium in the melting tank under Ar atmosphere;
- Melting of the sodium;
- Injection of sodium & preparation of "High Surface Sodium" coating;
- Heating the reactor up to conversion temperature ( $300^\circ\text{C}$ );
- Oxidation & carbonation (between  $270$  and  $300^\circ\text{C}$ );
- Drain or reuse of the sodium carbonate.

Non hydrated  $\text{Na}_2\text{CO}_3$  is highly hygroscopic. To prevent metallic sodium from reacting with water absorbed by the matrix, the latter is dried above  $260^\circ\text{C}$  inside the reactor under Ar atmosphere. During this first campaign of experiments, simultaneous process parameter changes have been limited to the minimum for investigation purposes. For instance, the inert matrix was replaced after each run to prevent any significant change in size distribution or chemical composition between the different experiments.

Once air has been flushed out of the melting tank (NaMT), the sodium rods are introduced, the tank is tightly closed and the melting can be initiated. The tank is heated up above the sodium melting temperature ( $98^\circ\text{C}$ ). The beginning and the end of the melting process are easily detected by monitoring the tank content temperature as illustrated in Figure 5.



**Figure 5: Melting of a batch of 5 kg of sodium**

Once the sodium is completely melted its temperature increases again until the set-point temperature of the melting tank is reached. At this point, sodium can be injected inside the reactor and the coating stage is initiated. To ensure that the molten sodium is effectively discharged inside the reactor a slight argon overpressure (a few hundred mbars) is set inside NaMT before opening the injection valve.

The coating is achieved by stirring the mixture of Na and  $\text{Na}_2\text{CO}_3$  at a temperature between 120 and 140°C, usually during 15 min. In the actual design, the seemingly instantaneous discharge of melted sodium inside the reactor induces a sudden increase of the power required by the central stirrer engine. The power required to mix the blend smoothly decreases as the sodium is gradually dispersed on the matrix. The central stirrer power uptake is monitored and when necessary the bed is aerated by adding, manually, supplementary argon via the discharge line (AL-V4) at the bottom of the reactor.

Once the reactor blend has reached the reaction temperature (between 270°C and 300°C), the oxidation is initiated. Oxygen injection flow-rate is gradually increased until the desired treatment throughput is reached. A smaller quantity of  $\text{CO}_2$  is injected simultaneously to limit  $\text{Na}_2\text{O}_2$  accumulation. When adjusting  $\text{O}_2$  and  $\text{CO}_2$  injection flow rates, the coolant temperature set-point is also regularly adjusted (manually) until temperature of the solid blend stabilizes and steady state conditions are reached.

End of oxidation and carbonation stages are detected by monitoring the matrix temperature,  $\text{O}_2$  and  $\text{CO}_2$  concentrations in the exhaust gases. When the nominal injection  $\text{CO}_2$  concentration is obtained at the exhaust, the experiment is stopped. The reactor is cooled down while maintaining heavy stirring conditions under constant Ar flow.

## EXPERIMENTAL RESULTS

Two preliminary experiments (experiments n° 1 & 2) were carried out without metallic sodium. They led us to select the dense dry carbonate (free flowing density of  $1\text{t/m}^3$ ) as the most suitable carbonate matrix amongst the different granulometry grades available on the market. Indeed significant particle carry over was observed when drying the light matrix thereby reducing the total gas flow rate operating range. These experiments also allowed us to train the operators, rehearse and validate the working and emergency procedures and evaluate important process parameters

such as gas detection dead time at exhaust (~15 min), reactor warming up and cooling down profiles, matrix drying time, etc. .

Up to now, 4 treatment experiments have been carried out with amount of metallic sodium increased up to 5 kg per batch. The objectives, the operating condition, the duration of the different process stages and the main results obtained are summarized in Table I. Three of these 4 experiments were carried to completion, i.e., complete conversion of metallic sodium into oxides and high yield carbonation of the oxides.

**Table I: Summary of the conducted experiments**

N°	Objective(s)	Inert Matrix	Na (kg)	Gaseous reagent flow rate (L/min)	Duration (min)	Conversion rate (weight %)	Remarks
1	Evaluation of inert matrix & validation of procedures	25 kg Light Na <sub>2</sub> CO <sub>3</sub> (0.5 t/m <sup>3</sup> )	0	Ar = 10-15		-	-
2	Evaluation of matrix & validation of procedure	50 kg Dense Na <sub>2</sub> CO <sub>3</sub> (1 t/m <sup>3</sup> )	0	Ar = 10-15		-	-
3	Feasibility demonstration	50 kg Dense Na <sub>2</sub> CO <sub>3</sub>	1	Ar = 2-2.5 O <sub>2</sub> = 1-3.5 CO <sub>2</sub> = 0.5-5	Coating = 35	> 95 %	Central stirrer jamming resulting in axis and engine overheating
					Warming up = 70		
					<b>Conversion = 275</b>		
4	Conversion of 2kg batch	50 kg Dense Na <sub>2</sub> CO <sub>3</sub>	2	Ar = 2-2.5 O <sub>2</sub> = 1-3.5 CO <sub>2</sub> =0.5-5		-	Oil leakage into the reactor due to wrong orientation of axis lips sealing
5	Conversion of 2kg batch & measuring heat exchange coefficient	50 kg Dense Na <sub>2</sub> CO <sub>3</sub>	2	Ar = 5-6 O <sub>2</sub> = 1-3 CO <sub>2</sub> = 1-5	Coating : 15	> 97 %	-
					Warming up : 100		
					<b>Conversion : 500</b>		
6	Conversion of 5kg batch & measuring heat exchange coefficient	50 kg Dense Na <sub>2</sub> CO <sub>3</sub>	5	Ar = 6-8 O <sub>2</sub> = 2-5 CO <sub>2</sub> = 2-8	Coating : 15	> 99 %	-
					Warming up : 70		
					<b>Conversion : 480</b>		

As an example, experiment 6 is discussed in more detail. After the successful conversion of 1 and 2 kg batches, the sodium amount is increased to 5 kg. The main objectives of this experiment are:

- investigate matrix maximum loading capacity;
- increase conversion rate;
- assess the heat transfer capacity of the reactor.

The composition of the reactor solid blend is 10% in weight metallic Na in Na<sub>2</sub>CO<sub>3</sub>. This experiment was successfully completed without any incident to be reported. During the experiment, O<sub>2</sub> and CO<sub>2</sub> flow rates were regularly and simultaneously increased up to, respectively, 5 and 3.5 L/min corresponding to a maximum heat flux of about 4 kW.

As can be seen on Figure 6, an oil temperature as low as 266°C was required to maintain the solid mixture at 300°C for O<sub>2</sub> and CO<sub>2</sub> flow rates of, respectively, 4 and 3 L/min (3.3kW). In this experiment gas flow rates were not further significantly increased since we did not want to decrease the oil temperature below the temperature required to initiate the oxidation reaction (experimentally measured at 270°C). Indeed cold spots could appear at the interface



with "dead volume" or where particles are not sufficiently renewed and would lead to accumulation of "cold" coated particles. This could slow down the conversion process and reduce the metallic sodium oxidation rate. The possibility to work with larger temperature differences depends mainly on the mixing pattern and efficiency and must be further investigated. O<sub>2</sub> and CO<sub>2</sub> injection patterns and concentration profiles in exhaust gases are shown on Figure 7. Sampling and analysis of the final solid blend showed complete oxidation of metallic sodium and overall carbonation yield higher than 99%.

This experiment demonstrates that:

- the dense Na<sub>2</sub>CO<sub>3</sub> inert matrix can be loaded with a Na amount as high as 10% without impairing process efficiency nor safety of the process;
- the heat transfer capacity of the actual reactor (taking into account the stirring device) allows a minimum conversion rate of 625 g/h.

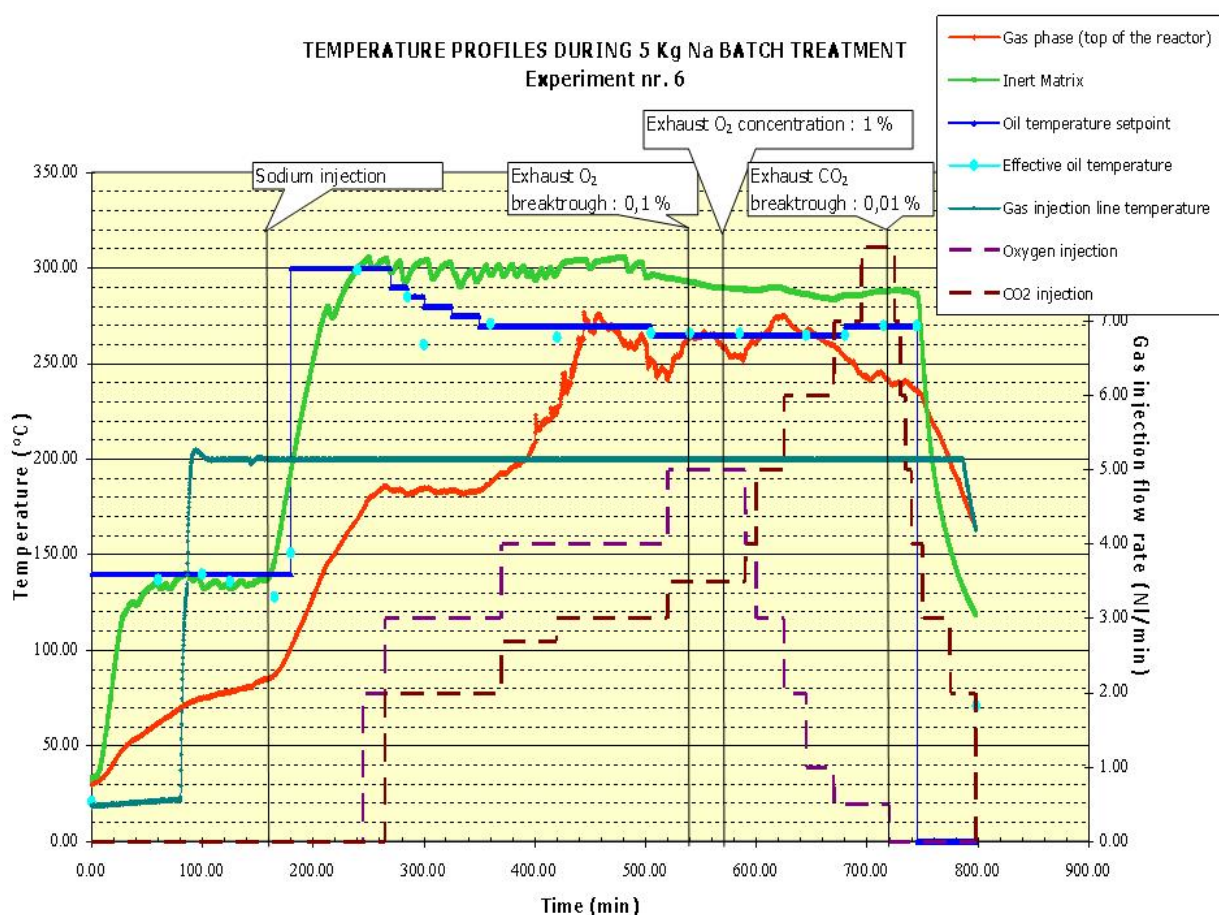


Figure 6: Temperature profiles during the treatment of 5 kg Na batch

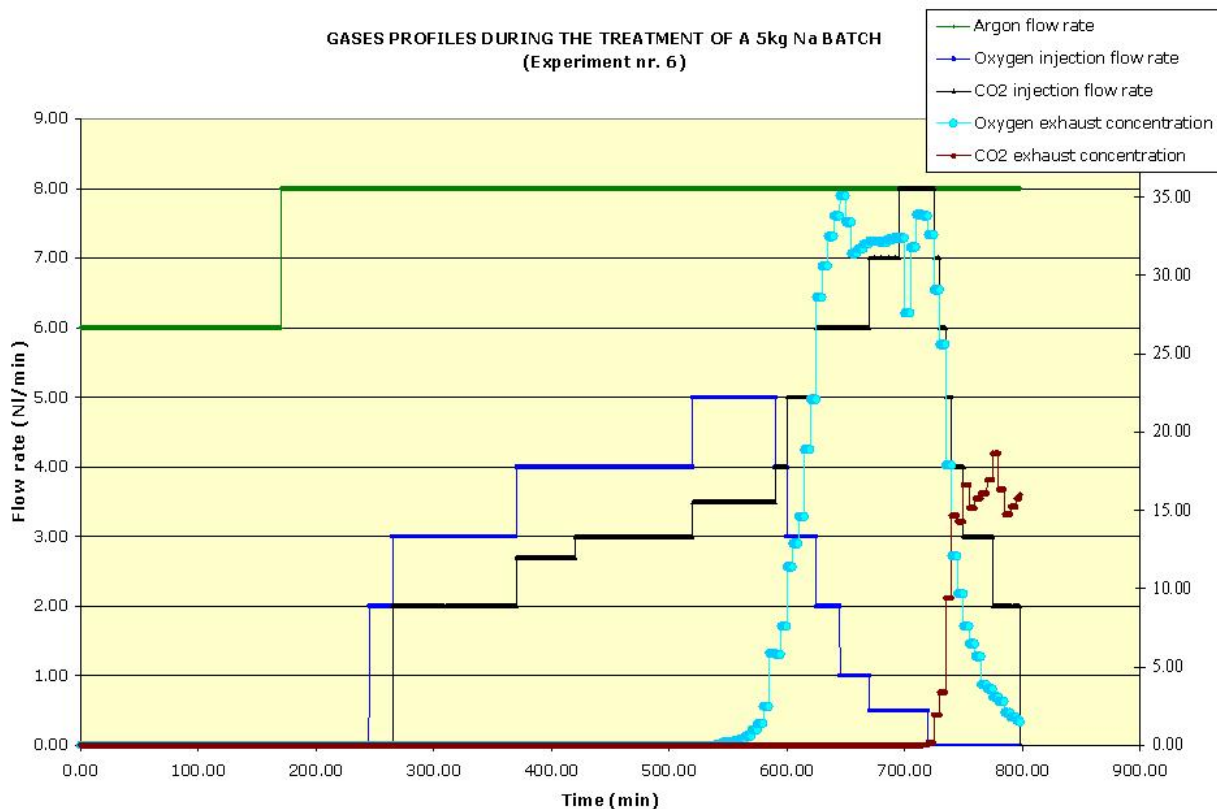


Figure 7 : Gaseous reagent injection pattern and concentration profiles

### HEAT EXCHANGE COEFFICIENTS

The global heat exchange coefficient exists of 5 components:

- Forced convection in the coolant fluid circulating inside the double mantle;
- Conduction through the inner stainless steel wall of the reactor;
- Conductive heat exchange between the reacting particles and the wall of the reactor;
- Contactive heat transfer between the carrier gas and the matrix;
- Radiative heat transfer inside the reactor.

The radiative component is usually neglected when the temperature of the particles involved in the heat transfer is rather low. The heat exchange coefficient for conduction through the stainless steel wall is: 4750 W/m<sup>2</sup>K. The supplier of the reactor gives a forced convection heat exchange coefficient of about 2500 W/m<sup>2</sup>K for the oil circulating inside the vessel jacket at a flow rate of 70 l/min at 300°C. The effective heat exchange surface area between the bed and the wall is 0.6 m<sup>2</sup>. Predictive correlation for the particle bed in a gas flow at the fluidization limit (Zadbrowski) led to heat exchange coefficient between the reactor content and the inside wall in the order of magnitude of 500 W/m<sup>2</sup>K, which strongly limits the heat transfer.

In a mechanically stirred reactor where no fluidization occurs, the conductive heat exchange coefficient is expected to be smaller. Experiments 3, 5 & 6 confirmed that the temperature differences predicted with this correlation were not sufficient to evacuate the heat produced with the chosen working conditions.

### Global heat exchange coefficient

Experiment 5 and 6 allowed us to calculate a global heat exchange coefficient for steady state operation at different heat fluxes (different gas flow-rates) according to Newton's law:

$$Q = U \times A \times \Delta T$$

With :

$Q$  = heat flux (W)

$U$  = global heat exchange coefficient (W/m<sup>2</sup>K)

$\Delta T$  = temperature difference between the oil and the reactor (usually calculated taking the logarithmic mean between inlet and outlet)

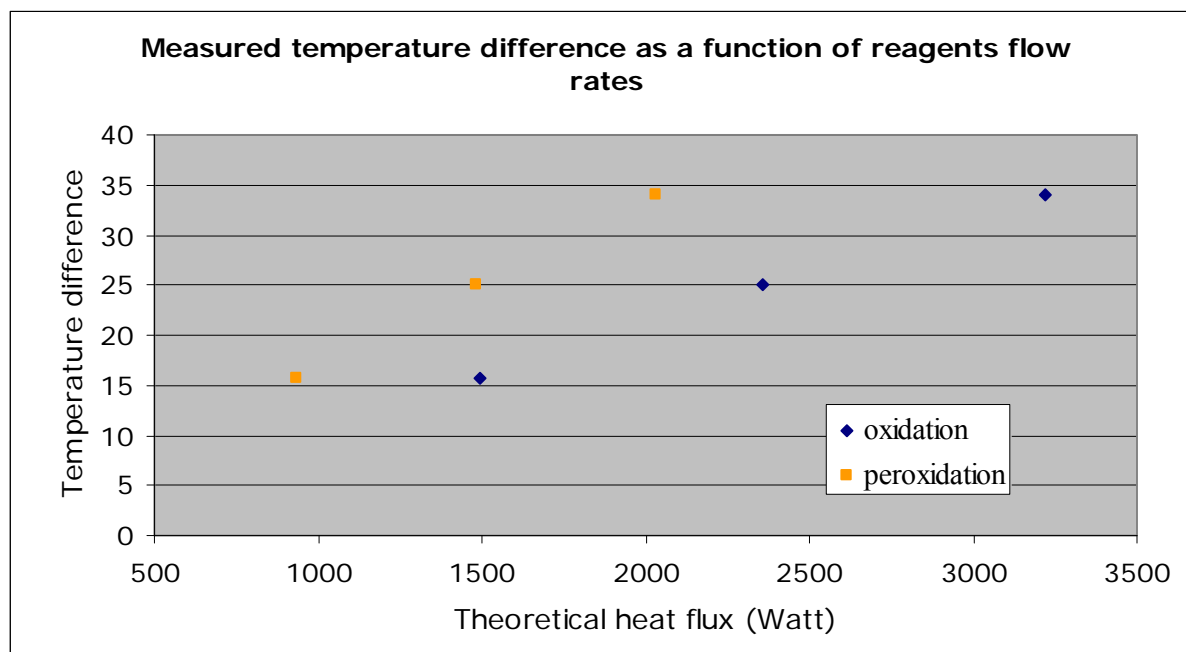
$A$  = available heat exchange surface area (inner wall of the reactor is considered as surface of reference)

Since the exact ratio between peroxidation and oxidation is unknown, heat fluxes have been calculated theoretically by assuming either 100% oxidation or 100% peroxidation in order to obtain a minimum and a maximum value of the heat exchange coefficient. As the experimental conditions have been chosen to minimize peroxidation (significant addition of CO<sub>2</sub> during oxidation stage), we can reasonably assume that the real heat exchange coefficient is in the upper range. As can be seen in Table II a good agreement is obtained between the global heat exchange coefficients measured with different heat fluxes during experiments 5 and 6.

**Table II: Experimental global heat exchange coefficient**

Experiment	Na batch (kg)	O2 flow rate (L/min)	CO2 flow rate (L/min)	Measured temperature difference (DT)	Theoretical heat flux by oxidation (W)	Heat exchange coefficient considering oxidation (W/m <sup>2</sup> .K)	Theoretical heat flux by peroxidation (W)	Heat exchange coefficient considering peroxidation (W/m <sup>2</sup> .K)
5	2	2	1	15.7	1494	155	934	97
6	5	3	2	25	2358	154	1484	97
6	5	4	3	34	3223	154	2033	97

Figure 8 shows the temperature differences required for different treatment throughput (i.e. different gas injection flow rates).

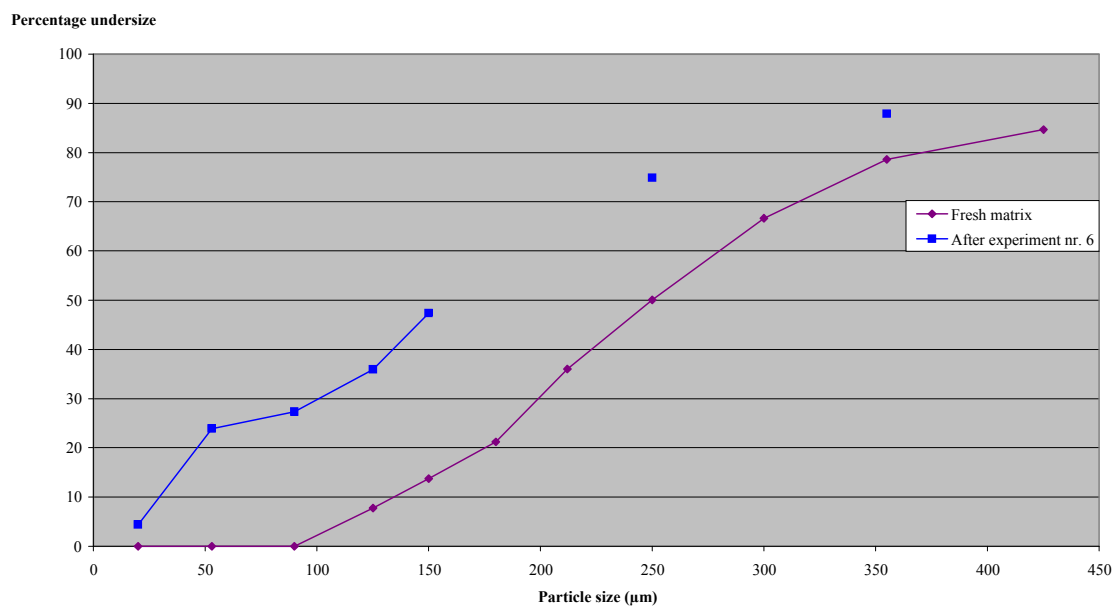


**Figure 8: The temperature differences required for different treatment throughput**

It can be concluded that the pilot treatment throughput is strongly limited by the rather low heat transfer coefficient between the solid and the inner wall. A minimum value for the global heat exchange coefficient of the actual design is 130 W/m<sup>2</sup>K. Considering a forced convection heat exchange coefficient in the oil of about 2500 W/m<sup>2</sup>K (reactor supplier calculation) and a global heat exchange coefficient of 130 W/m<sup>2</sup>K (experimentally measured) leads to a heat exchange coefficient between the solid blend and the wall of about 200 W/m<sup>2</sup>K. This confirms our first assumption that the heat exchange between the stirred bed and the wall is the limiting component in the heat transfer in the actual design. Consequently, to ensure a minimum inner wall temperature of 270°C and avoid "cold" spots, the oil temperature must be maintained above 265°C. Heat transfer capacity (and process throughput) can be optimized by improving the solid mixing pattern (stirring device design) and the gas distribution system in the reactor (porous plate). The influence of the carrier gas properties (specific heat and viscosity) should also be checked. Other possible candidates are N<sub>2</sub> and He.

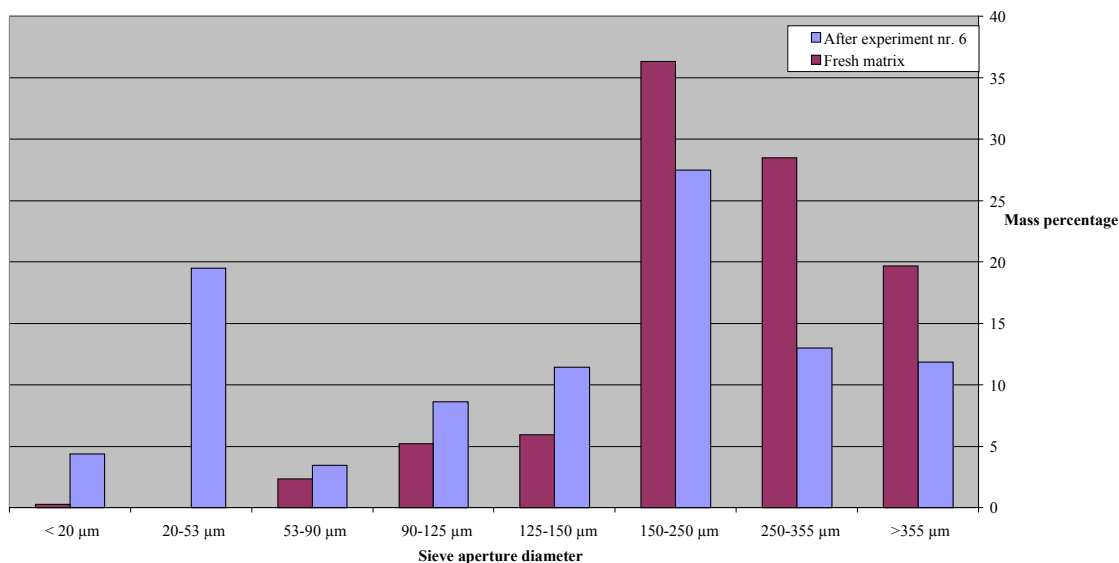
## INERT MATRIX BEHAVIOR

Amongst the different available types of inert material recommended to prepare the "high surface sodium" [3], Na<sub>2</sub>CO<sub>3</sub> presents the advantage of being also the final product of the chemical treatment. Logically this matrix has been selected considering the chemical homogeneity of the final solid blend as an advantage for process stability and minimization of secondary waste generated. Indeed the SimSan process principle and design should allow re-use of the final blend as a matrix until reactor maximum volume or maximum accumulated activity (depending on local regulations and practices) is reached. According to the literature [3], up to 10% in weight of metallic sodium could be incorporated (coated) on this matrix without impairing efficiency or yield of further chemical processing of the alkaline metal (clustering, thickness of the coating layer). Attrition caused by the mixing device and production of very fine particles through the chemical reactions could impair the recycling of the matrix. Granulometric analyses have been carried out on the raw material as well as on the processed blend (Figure 9 and Figure 10).



**Figure 9: Evolution of size distribution of the inert matrix during processing (cumulative undersize plot)**

The cumulated plot shows a significant shift of the size distribution of the solid mixture to the left (lower particle diameter). Attrition caused by the stirring device could explain a global shift of the distribution to smaller size. However starting from a normal distribution of sizes, one would expect that the attrition phenomenon produces a normal distribution.



**Figure 10: Evolution of size distribution of the inert matrix during processing (histogram)**

The histogram shows even more clearly that the size distribution of the processed solid blend is not normal anymore. The resulting distribution is likely to be a superposition of two distributions: the first one resulting from the attrition of the fresh matrix and the second one corresponding to the size of particles produced by the chemical reactions. Agglomeration of fine particles produced by attrition might also explain the peak observed between 20 and 53 μm.

Possibility to recycle the solid blend for successive batch treatment still has to be assessed. Complementary experiments are required. Even if production of fines could increase the total specific surface area available for the coating, their accumulation in the process is to be limited to prevent agglomeration phenomena, filter clogging or dust production.

## TREATMENT OF NaK

Sodium-potassium alloys (NaK) have different application possibilities like use as catalyst or as heat-transfer liquid because of their great heat-transfer properties and their low vapor pressure at high temperatures.

For these reasons NaK is also used as a heat-transfer agent in fast breeder reactors. As a consequence there is contaminated and activated NaK stored as radioactive waste in several places in the world. NaK is very reactive and will in contact with air or water flare up spontaneously with an exothermic reaction. Also the formation of a superoxide layer on top of the product when stored for long term can cause problems when processing. Care will have to be taken regarding the handling of NaK in order to avoid any hazardous move of the container before the loading of the NaK. A freezing device could be necessary for the handling of NaK waste.

The chemical reactions of the SimSan process are suitable to treat NaK. Nevertheless, the handling and treatment of NaK is more complex as very unstable compounds such as superoxides can be present in the to be treated substance or produced during the treatment. The method has been successfully tested on laboratory scale using small amounts of NaK (20g on 200g of sodium carbonate). Reactions with potassium occur at lower temperatures compared to sodium. The conversion is quantitative around 270°C [4].

## IMMOBILIZATION OF SODIUM WASTE

As a final step the treated sodium waste needs to be immobilized. Waste form immobilization converts raw waste, usually containing mobile contaminants, into a solid and stable form. The properties of the waste-form enable it to be handled, stored and disposed of safely and conveniently, significantly reducing potential release of radionuclides into the environment. Waste immobilization should avoid release of contaminants from the matrix during storage and retard release during disposal. Estimating the chemical durability during disposal of a waste matrix is a key consideration in assessing an immobilization method.

In the frame of the latter, SCK•CEN elaborated an experimental program in cooperation with ANSTO to enhance the amount of sodium bearing waste ( SBW) that can be introduced in a given matrix while maintaining excellent leaching performances. This is done by comparing the sodium bearing waste immobilization potential of different ANSTO matrices (full and glass ceramic matrices by Hot Isostatic Pressing (HIP)) with an adapted formulation to the traditional borosilicate glass. This program comprised MCC-1 & PCT-B leaching experiments on simulated waste and optical microscopy, SEM and XRD to look for and verify gross effects, phase development, microstructure and microscopic homogeneity. The objective is to make a first evaluation of the leach resistance of the various waste forms in standard conditions.

In an initial evaluation, samples were assessed based on their sodium immobilization potential only and consequently the simulated waste stream consisted only of  $\text{Na}_2\text{CO}_3$ . All samples contained a waste loading of at least 20% sodium on a  $\text{Na}_2\text{CO}_3$  basis, which corresponds with the maximum amount of sodium that can be retained by the reference glass.

Following waste form options were proposed and produced for evaluation.

- A standard boro-silicate (reference) glass. (made by SCK)
- Refractory glass prepared by HIP. (made by ANSTO)
- Sodium-zirconium phosphate (NZP) full-ceramic option. (made by ANSTO)

After analysis it was concluded that all elements present are better retained in the refractory glass made by HIP and that the SCK•CEN reference glass sample had reasonable durability but performed less well, +/- an order of magnitude lower over all time periods. The NZP full ceramic option made by HIP would not be a satisfactory waste form for the immobilization of such high amounts (42%) of  $\text{Na}_2\text{CO}_3$  according to the MCC-1 tests. Electron microscopy also indicated leaching of unincorporated sodium [5].

A more detailed characterization of the  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  sample was done by ANSTO after the unexpected negative behavior of the NZP. The sample was examined using NMR MAS. The result indicated that the sample was hydrating and decomposing at room temperature and thus the crystallinity would be low. This result was not anticipated from earlier work on NZP. The unstable nature of the  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  makes it very unsuitable for a waste form.

However, the experiments have clearly demonstrated the ability to prepare high-quality waste forms via hot-isostatic pressing, which also provides the additional benefit of eliminating any high-temperature off-gas emissions. Further promising research is underway (for example with iron phosphate glass) to continue the evaluation and to optimize the full ceramic and glass ceramic formulation for sodium waste.

## GENERAL CONCLUSIONS

Some years ago SCK•CEN started to look for an efficient and safe technology for this waste resulting in a waste form which is ready for further conditioning. The proposed SimSan-process is a three-step reaction in a batch reactor. The end product is sodium carbonate containing the radionuclides. At the end the sodium carbonate can be immobilized in a concrete or glass matrix. During this process no hydrogen is formed, while the turbulent conditions guarantee a complete conversion of the metal and excellent heat transfer capabilities, eliminating explosion risks.

After initial testing of the process on lab scale, a small pilot installation was constructed. We were able to demonstrate the technical feasibility of the SimSan process on a pilot scale. 8 kg of metallic sodium have been successfully converted. Carbonation rates higher than 99% have been achieved with the chosen experimental conditions. High surface sodium can be prepared on dry  $\text{Na}_2\text{CO}_3$  with Na load as high as 10% in weight. Possibility to further increase the sodium load must be investigated. The SimSan pilot has a metallic sodium conversion throughput in the range of 0.6 – 1 kg/h. Formation of particle clusters resulting in an heterogeneous blend should be considered as the most likely risk when increasing further the matrix loading. The minimum global heat exchange coefficient of the SimSan pilot is 150 W/m<sup>2</sup>K. This value can be safely used for industrialization and up-scaling design studies.

Further experiments are required to optimize process working conditions, treatment throughput and to demonstrate the applicability of the SimSan concept to other alkali metal and alloys (NaK). The know how and the knowledge available at SCK•CEN are sufficient to initiate up-scaling design studies related to the safe treatment of industrial amount of metallic sodium with the SimSan process.

Processing contaminated and/or activated metallic sodium requires treating the off gasses from the reactor. To design an adequate gas treatment system, the origin of the sodium must be clearly identified. When dealing with activated sodium, the main activation products to take into account are Na-22 (2,6 years) and H-3 (significant concentrations of Li can be found in industrial grade metallic sodium). Na-24 and Na-25 are very short lived radioisotopes (respectively 15h and 1 min) and do not represent any significant activity at the time of the treatment.

Possible carry over of radioactive particles (Cs-137, Na-22 ...) is handled by using a double barrier filtration system made of a pre-filter and an HEPA filter. When H-3 activity justifies it, a scrubber is added on the gas treatment system.

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