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**Disposal or recycling plan for tritium ready**

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### Summary

SCK CEN holds 5 Ti-getters and one NaK getter. The tritium content of each of the getters was unknown at the start of this project. To complicate things NaK is a very reactive liquid metal. This deliverable report presents a disposal or recycling plan for these getters.

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## Abbreviations

BP	BelgoProcess
BR2	Belgian Reactor 2
DCP	Decontamination and Clean-up Processes
DoA	Description of Action
EC DG RTD	European Commission – Directorate General for Research and Innovation
ECCP	Electronic Collaborative Content Platform
ExCom	Executive Committee
G1L	Getter 1 long
G1S	Getter 1 short (where short stands for the size of the container)
G2L	Getter 2 long
G2S	Getter 2 short
G3L	Getter 3 long
GB	Governing Board
NaK	Liquid metal mixture of sodium and potassium ( <u>N</u> atrium and <u>K</u> alium in Dutch)
PMO	Project Management Office
PQP	Project Quality Plan
PR	Periodic Report
QA	Quality Assurance
SCK CEN	Belgian Nuclear Research Centre
Simsan	SIMple SAfe Natrium destruction system
Ti	Titanium
VNS	Variable Neutron Shield
WP	Work Package
WPL	Work Package Leader

## **Summary**

SCK CEN holds 5 Ti-getters and one NaK getter. The tritium content of each of the getters was unknown at the start of this project. To complicate things NaK is a very reactive liquid metal. This deliverable report presents a disposal or recycling plan for these getters.

## **1 Introduction**

SCK CEN holds 5 Ti-getters and one NaK getter [1]. The tritium content of each of the getters was unknown at the start of this project. To complicate things NaK is a very reactive liquid metal. In the interim report [1] there was reported on: the research for disposal or possible reuse options for the getters, the investigation for possible neutralization of the NaK getter, partners used in this project and the tritium inventory measurements.

The tritium inventory measurements made it possible to look for solutions for the 5 Ti-getters and the NaK getter. After a number of paths have been investigated in the interim report [1] this final report proposes the solutions for the 5 Ti-getters and the NaK getter.

## **2 Proposed solution for the Ti-getters**

The 5 Ti-getters hold a tritium inventory of 60 TBq. In the interim report [1] 3 kinds of solutions were considered as possible: stack release options; disposal as nuclear waste and recovery of tritium from the getters. The main disadvantage of the stack release options versus the two others is the direct release of tritium to the environment, which is not an option that SCK CEN wishes to pursue. Further internal investigation has shown that disposal of the getters without recovery of the tritium has 2 setbacks compared to recovery of the tritium (and sending back the detritiated getters): first the mere fact that the tritium would not be recovered and can therefore not be used anymore for other purposes, and second the only option to dispose off the tritiated getters would be a very costly disposal as (radiation) sources.

At this point it seems that when the tritium is recovered from the getters, the total tritium inventory of the emptied getters and the containers will be in the order of magnitude of 10 GBq. This is too high for free releasing them. However if no re-use is foreseen, when passivated, they can be disposed of as standard compressible radioactive waste. We are convinced that the combination of these advantages, i.e. recovery with reuse of the tritium and less costly 'normal' disposal will be competitive compared to disposal as radiation source. Therefore a tender will be issued early 2020 for the recovery of the tritium from the Ti-getters.

### **3 Proposed solution for the NaK getter**

The NaK getter contains 500 g NaK. The tritium amount of the NaK getter was below the minimal measurable amount that could be detected with the used calorimetry set-up. Based on a reproducibility experiment it was calculated that the NaK getter would contain not more than 0.5 TBq of tritium. In the interim report [1] two options were put forward for the treatment of the NaK getter. Considering the uncertainties connected to the treatment options outside SCK CEN, we do not wish to pursue these options or elaborate further.

On the other hand the limited tritium inventory of the NaK getter makes it possible to treat it in SCK CEN's tritium laboratory. SCK CEN has some past experience on sodium treatment with its Simsan (SIMple SAfe Natrium destruction system) process on a pilot scale. A pilot-size installation was used to treat 8 kg of sodium. Afterwards the Simsan process has been reassessed in a series of lab-scale experiments for the treatment of (non-nuclear) NaK [2]. In the paragraphs below the available information from almost two decades ago [2,3,5,6] will be combined with the present information of the NaK getter to evaluate the Simsan for NaK as a solution for SCK CEN's NaK getter.

#### ***3.1 Historical sodium treatment research at SCK CEN***

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 neutron 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. When the nuclear industry started the decommissioning of nuclear facilities, research was carried out for the treatment of metallic sodium.

More than 25 years ago SCK CEN started to look for an efficient and safe technology for metallic sodium waste resulting in a waste form which is ready for further conditioning [3]. 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. In the 2000's SCK CEN 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.



### 3.2 The Simsan process

The Simsan process is a three step process. The chosen design makes use of a heated mechanically stirred reactor, where the molten sodium is firstly coated on  $\text{Na}_2\text{CO}_3$  particles prior to gaseous reagents ( $\text{O}_2$ ,  $\text{CO}_2$ ) addition at  $270^\circ\text{C}$ .

After initial testing of the process on lab scale, a semi-industrial pilot installation was constructed to demonstrate the process with non-active sodium for batches of about 1-5 kg sodium. The PID of the semi-industrial pilot installation is shown in Figure 1. In total 8 kg of metallic sodium was converted and carbonatation rates of more than 99% were achieved.

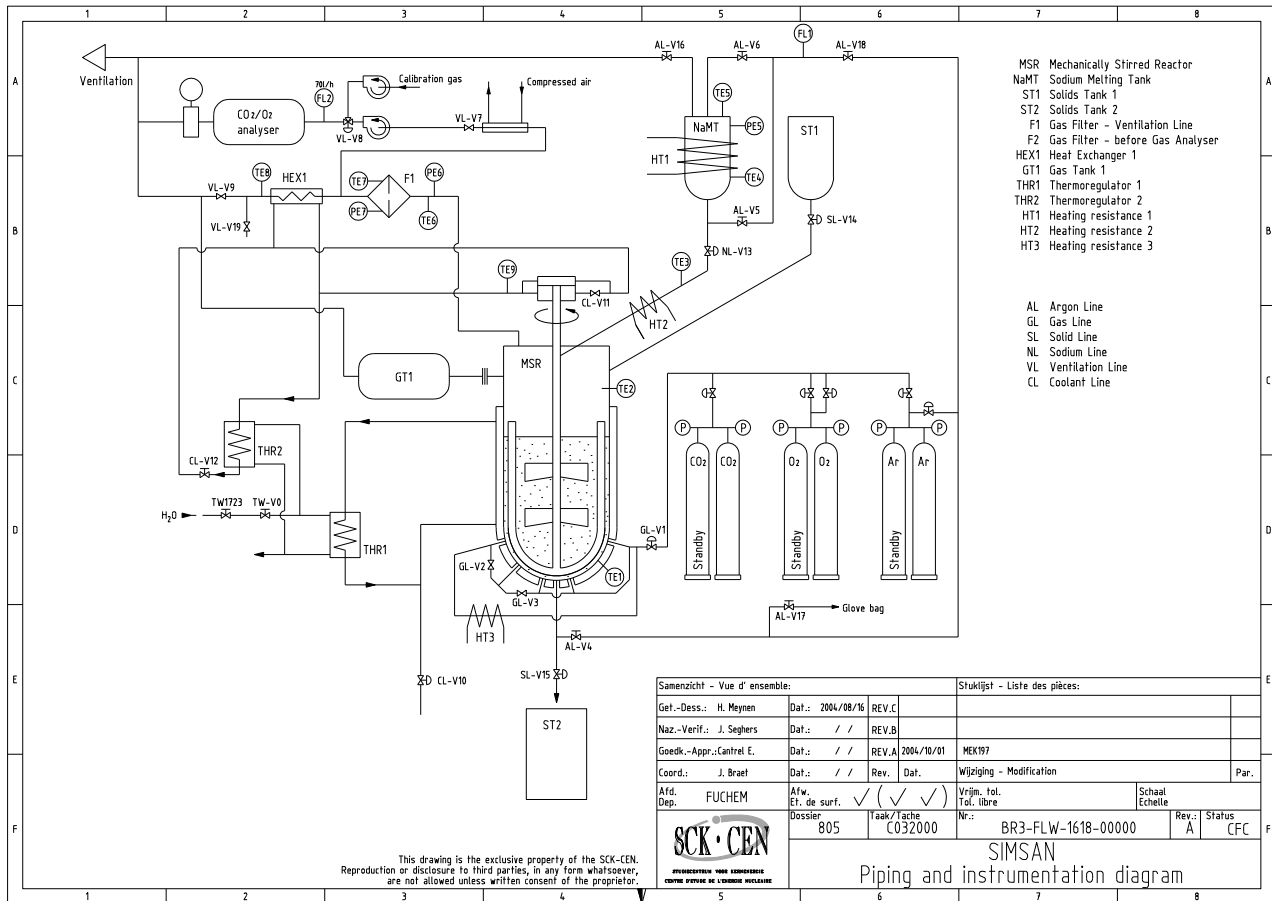


Figure 1: General PID

### 3.3 The Simsan process for NaK

The Na Simsan proces can be converted to a NaK Simsan proces. The core of the Simsan process for NaK consists of 5 similar steps as that of treating Na with Simsan:

1. drying of sodium carbonate granules under inert atmosphere

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2. coat dry sodium carbonate granules with NaK under inert atmosphere
3. oxidise the NaK completely to Na<sub>2</sub>O and K<sub>2</sub>O
4. carbonatise these oxides to Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>
5. reuse of the carrier

The steps are explained below.

##### *Drying*

As NaK can react violently with water in further steps, all water needs to be removed from the sodium carbonate carrier as a first step. This step is not different than with the treatment of Na and will be done at a temperature of at least 260°C and under inert atmosphere. This is necessary to remove all water (also water of crystallisation) from the carbonate.

##### *Coating*

Also, under an inert atmosphere during the coating step the NaK gets distributed in a uniform layer over sodium carbonate granules. In its original use (to treat sodium) heating was necessary to liquefy the sodium.

##### *Oxidation*

The oxidation reaction is executed in a stirring reactor by adding oxygen to the inert (Ar) gas flow. This should be done at a temperature that allows for an immediate reaction between NaK and oxygen to form sodium oxide and potassium oxide (1)(2). The formation of peroxides (3)(4) is limited by only introducing the minimal amount of oxygen necessary. From the moment oxygen is detected at the exit gas stream of the reactor the oxygen feed is cut off in order to give reaction (5) and (6) the chance to take place.

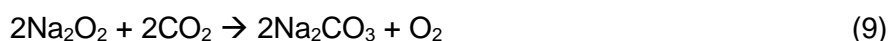
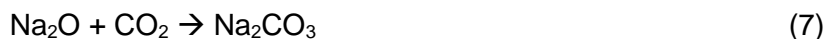


##### *Carbonatation*

After all NaK is oxidised carbon dioxide is sent through the reactor. Again this should be done at a temperature that allows for a complete transformation of all sodium- and potassium oxides to sodium- and potassium carbonates. These reactions are shown in (7) and (8). The end of the

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reaction is detected by the appearance of carbon dioxide in the exit gas stream from the reactor. If peroxides were present this will be detected by the presence of oxygen from the moment carbon dioxide is added to the feed gas stream by reactions (9) and (10).



*Reuse of the carrier*

Since potassium carbonate and sodium carbonate have similar properties the carrier material with the newly formed carbonates might be reused as carrier for following batches.

### **3.4 Evaluation of work done on NaK-Simsan**

In the frame of an internship for a master's student a series of experiments were executed to look for the possibility to treat (non-nuclear) NaK with the Simsan process [2]. An overview of these experiments is given in Table 1.

In the paragraphs below an evaluation of these experiments is made in perspective of stirrer and reactor orientation, granulation of the end product and working temperatures

#### *3.4.1 Stirrer and reactor orientation*

The used stirrer and orientation of the reactor can have an impact on the process. Several stirrers and orientations have been evaluated to find an optimal combination for Simsan on NaK.

When processing Na using the Simsan process the end product would have an increase in smaller particles, which could limit the reuse of the end product. Therefore a small test program was set to evaluate 3 different combinations of stirrers and reactor orientations to process NaK with the Simsan process on a lab-scale. An overview of the performed tests is given in Table 1. Table 2 is an overview of the used stirrer and reactor orientations.

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**Table 1: Overview of lab-scale evaluation tests for Simsan process applied on NaK**

	Unit	Test 1	Test 2	Test 3
Temperature	[°C]	20	20	270
NaK load	[g]	5	5	5
Na <sub>2</sub> CO <sub>3</sub> load	[g]	214	Not reported	Not reported
Mixer type		Spiral	Propeller	Propeller
Ar gas flow	[L/min]	1.0	1.01	1.01
O <sub>2</sub> gas flow	[L/min]	0.11	0.12	0.12
CO <sub>2</sub> gas flow	[L/min]	0.11	0.12	0.12
Reactor orientation		Vertical	Vertical	Vertical
Na oxidation		None	None	Complete
K oxidation		None	None	Complete
Na(per)oxide carbonatation		None	None	Complete
K(per)oxide carbonatation		None	None	Complete
Other observations		Sticky NaK/carrier around axes	Problem with axes seal Blocking of stirrer	Problems with axes seal

	Unit	Test 4	Test 5	Test 6
Temperature	[°C]	150	200	270
NaK load	[g]	10	5	20
Na <sub>2</sub> CO <sub>3</sub> load	[g]	300	300	200
Mixer type		Plough share	Plough share	Plough share
Ar gas flow	[L/min]	1.00	1.50	1.50
O <sub>2</sub> gas flow	[L/min]	0.20	0.20	0.20
CO <sub>2</sub> gas flow	[L/min]	0.20	0.20	0.20
Reactor orientation		Horizontal	Horizontal	Horizontal
Na oxidation		Incomplete	Incomplete	Complete
K oxidation		Complete	Complete	Complete
Na(per)oxide carbonatation		None	None	Complete
K(per)oxide carbonatation		None	None	Complete
Other observations				






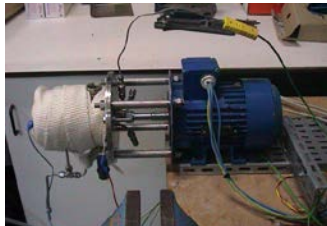
Dry Na<sub>2</sub>CO<sub>3</sub> is can easily be stirred during drying. However this changes during the coating with NaK. However, the mixture with the carbonate is very sticky due to the high surface tension of the NaK. To cope with this duality a powerful enough stirrer with a variable rotation speed is necessary.

The old report [2] mentions that after test 1 the spiral stirrer was abandoned because of the creation of a sticky NaK / Na<sub>2</sub>CO<sub>3</sub> agglomerate in the center of the stirrer. It also mentions that test 2 with the propeller mixer resulted in a better mixing of NaK and Na<sub>2</sub>CO<sub>3</sub>; but that the stirrer blocked several times leading to problems with the closure sealing of the axes. Sealing problems were also reported for a second experiment with the propeller stirrer (test 3) although without mentioning of blocking of the stirrer.

For the experiments with the horizontal set-up with a plough share mixer no mechanical problems with stirrer, sealing or NaK/ Na<sub>2</sub>CO<sub>3</sub> mixing were reported. This was then assigned to shorter axes and better mixing properties.

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**Table 2: Stirrers and reactors used in evaluation for NaK processing with Simsan on lab scale**

Stirrer type	Spiral stirrer	Power stirrer	Plough share stirrer
Picture of the stirrer			
Stirrer engine	IKA 28 stirrer 220W	IKA 28 stirrer 220W	Pump motor 480W
Rotation speed	Variable 60- 1400 rpm	Variable 60 – 1400 rpm	Variable via frequency steering
Reactor orientation	Vertical	Vertical	Horizontal
Reactor picture			
Tests (ref Table 1)	Test 1	Test 2, Test 3	Test 4, Test 5, Test 6

**Limitations**

The old report [2] does not take the temperature into account for tests 1 and 2. These tests were executed at room temperature, all other experiments were done at at least 150 °C. The viscosity of NaK is very temperature dependent. This is shown in Figure 2 [4].

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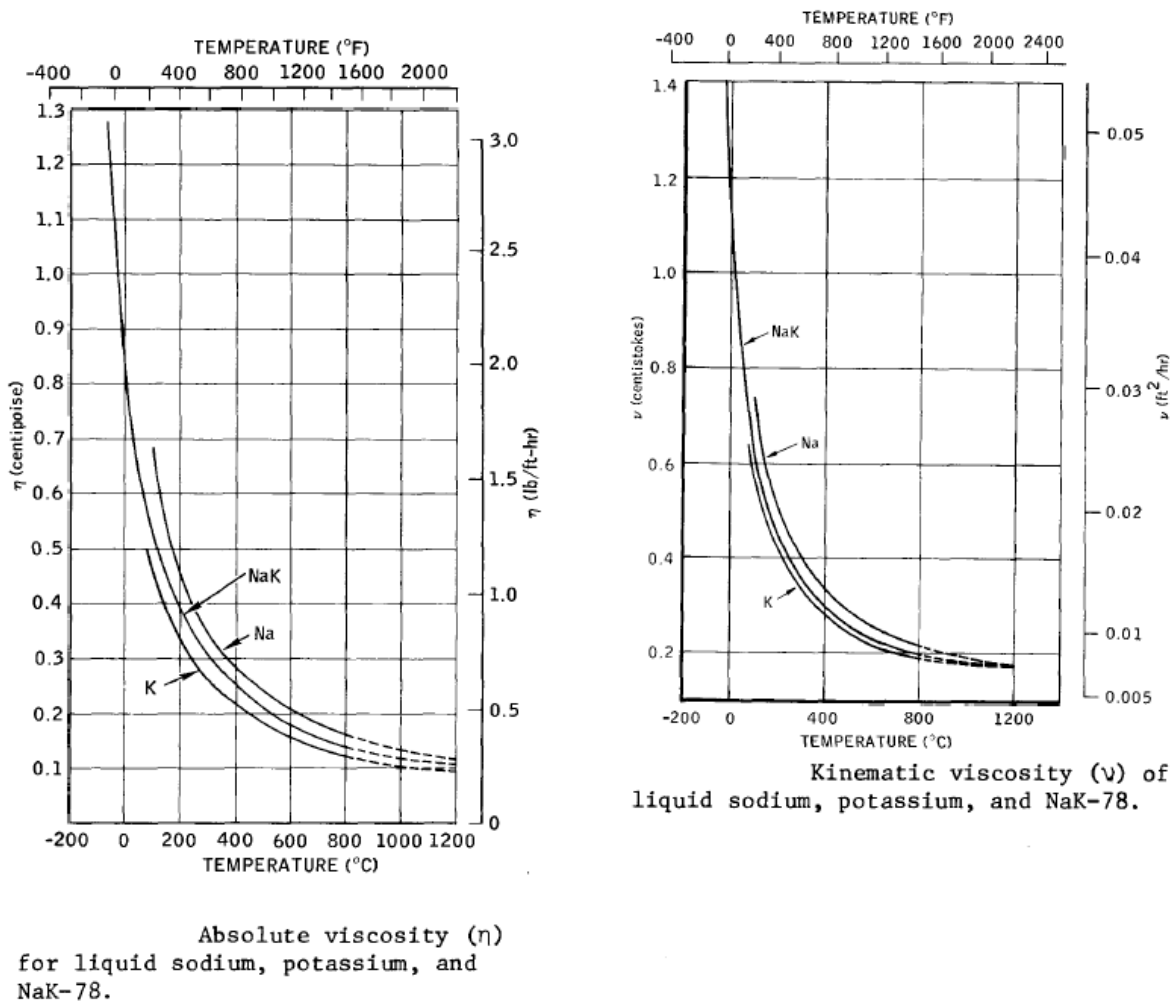


Figure 2: Absolute and Kinematic viscosity of liquid sodium, potassium and eutectic NaK

At 270°C the viscosity of NaK is merely half of that at 20°C. The unmixed agglomerate reported for test 1 and the blocking of the stirrer reported for test 2 might find their origin in the too high viscosity of NaK at 20°C. These blockings may have been the cause of the sealing problems reported for the second experiment with the propeller stirrer (test 3).

These limitations, however, do not lesser the lack of mechanical / stirring problems with the horizontal plough share mixer.

**Conclusions**

At elevated temperatures a horizontal reactor with a plough share mixer worked fine for processing NaK with the Simsan process. The mechanical and mixing problems that occurred with a vertical reactor and a spiral stirrer or a propeller stirrer might find its origin in the (too high) viscosity of NaK at room temperature.

### *3.4.2 Working temperatures*

The initial step in the Simsan process is the drying of the  $\text{Na}_2\text{CO}_3$  carrier. This process is identical for NaK Simsan as for Na Simsan. As for Na Simsan, already a drying temperature of  $260^\circ\text{C}$  was evaluated as optimal, this remains unchanged.

While eutectic NaK is liquid at room temperature, the  $\text{Na}_2\text{CO}_3$  carrier and NaK were observed not to mix well at room temperature which resulted in a poor quality of coating. This can be related to the higher viscosity of NaK at lower temperatures. From Figure 2 can be seen that the viscosity of NaK is – independent of the temperature – always a bit lower than of Na. Since  $130^\circ$  [5] was established as a good working temperature to obtain good coating of the carrier we will keep this unchanged.

In Table 1 can be seen that NaK Simsan experiments have been executed at  $150^\circ\text{C}$ ,  $200^\circ\text{C}$  and  $270^\circ\text{C}$ . Full carbonatation of sodium and potassium was only obtained during operation at  $270^\circ\text{C}$ . This was also the working temperature for the pilot installation for Na Simsan. .

### **Conclusion**

Despite NaK is liquid at room temperature (and Na only at  $98^\circ\text{C}$ ) a good operation of NaK Simsan requires the same operation temperatures as with Na Simsan. This means  $260^\circ\text{C}$  for drying of the carrier;  $130^\circ\text{C}$  for coating and  $270^\circ\text{C}$  for oxidation and carbonatation.

### *3.4.3 Granulation*

The impact of these aspects on the granulation distribution is evaluated based on measurements done over time and over different projects in the past. A drawback is that throughout these different tests not the same set of granulation test sieves were used and direct comparison is only possible on grouped results. These results are summarized in Table 3.

During pilot operation of the Simsan with Na installation was already noticed that the propeller mixer caused a shift to a smaller particle size. This will lead on one hand to an increase of the total available surface area when this product would be reused for a next batch. On the other hand this increase in smaller particles should be prevented to prevent agglomeration phenomena, filter clogging or dust production.

Although the gentle mixer does not seem to suffer from this phenomena not much conclusions should be drawn from this test as it was only done on carrier product. An experiment using a spiral mixer to coat  $\text{Na}_2\text{CO}_3$  with NaK was unsuccessful, although as mentioned in paragraph 3.4.1. this might be related to the too low working temperature during that experiment.

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Ultimately in a lab-scale experiment where NaK was treated with the Simsan using a plough share mixer in a horizontal layout the shift in particle size of the end product was only limited compared to the used carrier, so that reuse of this matrix in further stages could be an option.

**Table 3: Grain distribution of different tests**

	<b>Carrier</b>	<b>Na Simsan</b>	<b>Gentle mix carrier</b>	<b>Plough share NaK</b>
<b>Stirrer</b>	-	Propeller	Spiral	Plough share
<b>Reactor orientation</b>	-	Vertical	Vertical	Horizontal
<b>Installation scale</b>	-	Pilot scale	Lab	Lab
<b>Amount treated product / carrier</b>	-	5 kg / 50 kg	0 / 200g (assumption)	20 g / 200 g
<b>Grain distribution</b>	[%]	[%]	[%]	[%]
<b>&gt;250 µm</b>	48	25	69	58
<b>125-250 µm</b>	42	39	29	33
<b>0-125 µm</b>	8	36	2	9

**Explanations of labels:**

**Carrier :**

Granulation of a sample of bought Na<sub>2</sub>CO<sub>3</sub> carrier. Na<sub>2</sub>CO<sub>3</sub> with a density of 1t/m<sup>3</sup> (also known as 'dense Na<sub>2</sub>CO<sub>3</sub>') was qualified carrier product for treating sodium with the Simsan Process [5].

**Na Simsan:**

Granulation of a sample of 5 kg Na + 50 kg Na<sub>2</sub>CO<sub>3</sub> carrier after treatment with the Simsan process [5,6]. The treatment was done in a pilot installation that made use of a propeller mixer in a pilot scale vertical reactor.

**Gentle mix Carrier:**

Granulation of a sample of Na<sub>2</sub>CO<sub>3</sub> carrier after 307 min mixing in a small scale lab installation with a spiral mixer in a lab scale vertical reactor [2].

**Plough share-NaK:**

Granulation of a sample of 20 g NaK +200 g Na<sub>2</sub>CO<sub>3</sub> carrier after treatment with the Simsan process using a plough share mixer in a lab scale horizontal reactor (test 6) [2]

**Conclusion**

Using a horizontal reactor with a plough share reactor seemed to have the least impact on the granulation of the carrier and end product.



## 4 Simsan for the SCK CEN tritiated NaK-getter

### 4.1 Dimensioning of the installation

In the above paragraphs the pilot scale Simsan process for sodium and the lab scale Simsan process for NaK have been discussed. Neither of these 2 installations are still present at SCK CEN. The dimensions of neither of these two installations would fit the treatment of the NaK getter. But a comparison of both could help with the dimensioning of a Simsan installation to treat the NaK getter.

**Table 4: Proposed dimensioning for NaK Simsan process based on Pilot Simsan and Lab-scale Simsan**

	Pilot Simsan	Lab-scale Simsan (Test 6)	Proposed Simsan
<b>Processed Material</b>	Na	NaK	Tritiated NaK
<b>Na(K) Batch size to be processed</b>	5 kg	0.02 kg	0.2 kg
<b>Stirrer</b>	Propeller	Plough share	Plough share
<b>Reactor Orientation</b>	Vertical	Horizontal	Horizontal
<b>Reactor Volume</b>	75 L	1.2 L	3 – 5 L
<b>Na<sub>2</sub>CO<sub>3</sub> –carrier weight</b>	50 kg	0.2 kg	2 kg
<b>Na<sub>2</sub>CO<sub>3</sub> + K<sub>2</sub>CO<sub>3</sub> produced</b>	16 kg	0.04 kg	0.4 kg
<b>Drying temperature Na<sub>2</sub>CO<sub>3</sub></b>	260 °C	260 °C	260 °C
<b>Oxidation + Carbonation temperature</b>	270 °C	270 °C	270 °C
<b>Gas speed O<sub>2</sub> + CO<sub>2</sub></b>	7.5 L/min (10% Reactor Volume /min)	0.4 L/min (33% Reactor Volume /min)	0.3 – 1 L/min (10 – 20 % Reactor Volume /min)
<b>Gas speed Ar</b>	15 L/min (20% Reactor Volume / min)	1.5 L/min (133 % Reactor Volume /min)	0.3 – 2 L/min (20 – 40 % Reactor Volume /min)

Since there is only one tritium NaK-getter containing 500 g of NaK we will propose to build a small scale installation for NaK. If the batch treatment size is kept to 200 g a reactor volume between 3 and 5 L should suffice. That way the NaK needs to be treated in 3 batches.

There are also other NaK samples present at SCK CEN. These are samples from nuclear research but not related to any tritium project. The total volume of these samples is about 4 L. A different destination path has been established for these samples. In theory these samples could be treated in 15 – 20 batches with a 3-5 L sized reactor. Would it be necessary to establish a Simsan treatment route for this additional NaK a 10-15 L sized reactor would be more practical.

## **4.2 Location for the installation**

SCK CEN's tritium laboratory is licensed for exploitation with 25 TBq of tritium. This laboratory is equipped with a walk-in process cell in which the installation can be set up.



**Figure 3: The process cell in SCK CEN's tritium laboratory.**

The process cell is ventilated at a rate of 4500 m<sup>3</sup>/h and has an internal volume of 50 m<sup>3</sup>, this means that the air in cell will be refreshed at a rate of 90 cycles per hour. About 350 MBq / h HTO could be released into the cell without causing overexposure to HTO to a present worker in the cell.

## **4.3 Tritium release prior to oxidation and carbonatation**

We need to assume that the NaK getter will contain 0.5 TBq. In the Pilot Simsan the sodium was heated to 130°C when it was injected to the reactor. For the lab-testing there was no injection temperature reported. As seen in 3.4.1 above, the viscosity of NaK will be lower than that of sodium.

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Therefore we can assume that the NaK needs to be heated to 130 °C prior to injection in the reactor. When the coating has finished the reactor will be increased to 270 °C.

In an old theoretical design document [7], it is argued that for partial pressure of tritiated hydrogen above the NaK-getter can be related to a NaK – KH system. In this system the partial pressure of hydrogen gas in equilibrium (with hydrogen saturated NaK) can be expressed according to following equation :

$$\ln P_{H_2/NaK}^S = 21.3216 - \frac{14460}{T+273} \quad (T \text{ in } ^\circ\text{C}, P \text{ in atm}) \quad (11)$$

In the same document is also assumed that the same equation be valid for tritium in gas. Below are the calculations of the partial pressure of HT done for 130°C. Calculations for 20°C and 270°C can be done in a similar fashion. The results are summarized in the table below.

From (11) follows that:

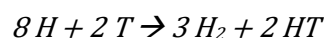
$$P_{HT/NaK}^S = e^{21.3216 - \frac{14460}{130+273}} = 0.475 \times 10^{-8} \text{ atm} = 0.0475 \text{ Pa} \quad (T \text{ in } ^\circ\text{C}, P \text{ in atm}) \quad (12)$$

From the ideal Gas Law With  $V = 1\text{m}^3$  ;  $P = 0.0475 \text{ Pa}$ ;  $R = 8.31 \text{ J/molK}$  and  $T = 403\text{K}$  can be calculated that=

$$n = \frac{P.V}{R.T} = \frac{0.0475 \text{ Pa} \times 1 \text{ m}^3}{8.31 \text{ J/mol.K} \times 403 \text{ K}} = 14.2 \times 10^{-6} \text{ mol}$$

The concentration of (HT+ H<sub>2</sub>) above the NaK getter at 130°C is thus  $14 \times 10^{-6} \text{ mol/m}^3$ .

If we take in to consideration that at time of gettering on the NaK getter the maximum H/T ratio was 1/1 and that the NaK gettering has happened 2 tritium half lives ago (25 years) we can conclude that at current date the H/T ratio is 4 /1. This means that, after release from the getter, the recombination of hydrogen and tritium will occur in following ratios:



Per 5 moles of gas composed of 3 moles H<sub>2</sub> and 2 moles HT only 2 mol of tritium will occur in the atmosphere above the NaK getter or 2.5 times less than shown above. With Avogadro's number ( $6.02 \times 10^{23} \text{ atoms/mol}$ ) and the decay constant of tritium  $1.7828 \text{ E-9 / s}$ , the tritium concentration in the atmosphere above the NaK getter is can be calculated by:

$$[T] = \frac{14.2 \times 10^{-6} \text{ mol/m}^3 \times 6.02 \times 10^{23} \text{ atoms/mol} \times 1.7828 \times 10^{-9} \text{ Bq}}{2.5} = 6.1 \text{ GBq/m}^3$$

Similar calculations can be done for the different temperatures at the different steps before oxidation / carbonatation, the results are summarized in the table below.

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**Table 5: Calculated partial pressures and tritium concentrations above NaK getter**

Step		Preparation	Coating	Heating before oxidation
Temperature	[°C]	20	130	270
Partial pressure H <sub>2</sub> /NaK	[atm]	6,7E-13	4.8E-7	5.0E-3
Tritium concentration	[Bq/m <sup>3</sup> ]	12 k	6.1 G	47 T

Since in this step the internals of the whole system are in inert atmosphere, the tritium will all be under the form of tritiated gas (HT+H<sub>2</sub>). The proposed max argon flush flow is 2 L/min (see Table 4). This would mean that before during the coating at 130 °C the release from the system can be as big as:

$$7.3 \text{ GBq/h } (= 2 \text{ L/min} \times 61 \text{ GBq/m}^3 \times 60 \text{ min/h} \times 1 \text{ m}^3/1000\text{L})$$

Even though the NaK getter will contain at maximum 0.5 TBq of tritium at 270°C, i.e. during heating before oxidation the release rate could reach 5.7 TBq/h and thereby for a short time the laboratory release limits.

The total ventilation flow of the tritium lab is 9500 m<sup>3</sup>/h. The tritiated gas stack limit of the tritium laboratory is 69400 kBq/m<sup>3</sup>. This means that the stack release for HT is 659 GBq/h. The stack limit for HTO is 20 kBq/m<sup>3</sup> and thus a release of 0.19 GBq/h could be allowed for.

An assumption that must be made for safety precautions is that 1% of all HT that will be released from the NaK getter will be converted to HTO [8] before its detection in the tritium stack release measurement system. Taking into account the 1% HT to HTO conversion, this would mean that, at maximum 19 GBq/h can be released from the getter in the tritium lab. This release rate can be reached quickly. Measures should be taken to prevent too high release rates. This might be done by oxidation of tritiated gas to tritiated water and capture it on a molecular sieve.

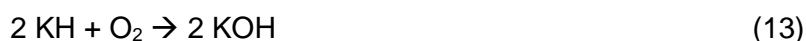
#### **4.4 Tritium releases during carbonation and oxidation**

From the previous reported experiences [5] it is known that it takes up to 4 hours before the carbonation starts. In the same document the oxidation / carbonation step is reported to take up to 9.5 hours.

If we assume, in contrary to the previous chapter, that no tritium will removed from the NaK getter due to heating before oxidation and carbonation, the vast majority of the tritium, i.e. 100 GBq/100 g of the to be treated NaK will be released during the oxidation and carbonation step.

When the oxidation and carbonation reactions occur it can be assumed that all remaining tritium/hydrogen in the NaK will be converted to sodium- and potassium carbonates following similar reactions with hydrogen.

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Reactions (13) and (15) occur as of respectively 200 °C and 230 °C. They should be occurring during the oxidation and carbonation steps of the Simsan process. The problem is thus that nearly all remaining tritium in the NaK getter will be converted to HTO.

The design is made to treat about 200 g NaK per batch. This would mean than nearly 0.2 TBq of HTO will be released in 9.5 hours of time or 21 GBq/h, which is more than 100 times higher than the maximum allowable amount that can be released per unit of time via the stack of SCK CEN's tritium laboratory (0.19 GBq/h). Capturing the generated HTO on a molecular sieve during Simsan processing might deliver a solution for this.

#### ***4.5 Molecular sieve filtering after Simsan***

In theory molecular sieves can dry out an atmosphere down to a dewpoint of -100 °C. After regeneration the JET molecular sieves could, in optimal real working conditions, achieve a dewpoint of -90 °C [9]. In Table 6, a couple of scenarios are calculated / summarized regarding making use of a molecular sieve to capture the HTO that is released during the carbonatiation / oxidation step. For these calculations a number of plausible assumptions have been made:

1. At time of gettering on the NaK getter the maximum H/T ratio was 1/1.
2. The NaK gettering has happened 2 tritium half lives ago (25 years)

As a result at current date the H/T ratio is now 4/1. Per 2 moles HTO generated in reactions similar to reactions (13 - 16), 3 moles of H<sub>2</sub>O are generated. Per 5 moles of generated tritiated water vapour only 2 moles contain tritium. Taken this into account, it can be calculated how effective molecular sieves should be to keep the tritium release below stack limits. This is done in the Table 6.

From this table can be concluded that, despite that a molecular sieve only will need to capture a small amount of tritiated water (0.46 mmol or 8.3 mg) it must be very effective. A dew point of at least -80 °C must be achieved.

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**Table 6: Necessity of molecular Sieving with Simsan processing of tritiated NaK**

Item	Unit	Value
<b>Simsan Proces properties equal for all 3 scenarios</b>		
NaK weight to be processed in one Simsan Batch	[g]	200
Tritium content of the NaK batch	[Bq]	2.0E+11
Decay constant of tritium	[1/s]	1.8E-09
Process time oxidation / carbonatation step	[h]	9.5
Process time oxidation / carbonatation step	[min]	570
Number of tritium atoms	[#]	1.1E+20
Max amount of HTO generated in oxidation/carbonatation step	[mol]	1.9E-04
Max amount of 3H <sub>2</sub> O+2HTO generated in oxidation/carbonatation	[mol]	4.6E-04
Minimal gasflow through installation	[L/min]	0.3
Average 3H <sub>2</sub> O+2HTO gas flow rate	[mol/L]	2.7E-06
Average HTO gas flow rate	[Bq/L]	1.2E-09
<b>Scenario 1: No molecular Sieve</b>		
Mole fraction 3H <sub>2</sub> O+2HTO in gasflow	[mol/L]	6.2E-05
Corresponding dewpoint	[°C]	<b>-47</b>
Average HTO release from Tritium lab stack during Simsan	[Bq/h]	2,1E+10
Max allowed HTO release from tritium lab	[Bq/h]	1.9E+08
<b>Scenario 2: Ideal Molecular Sieve (MS)</b>		
Mole fraction of 3H <sub>2</sub> O+2HTO in gasflow		2.0E-08
Corresponding dewpoint	[°C]	<b>-100</b>
Average HTO release after molecular sieve	[Bq/h]	6.7E+06
Max allowed HTO release from tritium lab	[Bq/h]	1.9E+08
<b>Scenario 3: Minimal Required Molecular Sieve (MS)</b>		
Mole fraction of HTO+H <sub>2</sub> O in gasflow		5.6E-07
Corresponding dewpoint	[°C]	<b>-80</b>
Average HTO release from Tritium lab stack during Simsan	[Bq/h]	1.9E+08
Max allowed T2O release from tritium lab	[Bq/h]	1.9E+08

#### **4.6 Controlled release, oxidation to HTO and molecular sieve filtering**

As shown in the paragraphs above, the processing of the NaK with the Simsan process can lead to too high tritium releases to the stack of the tritium lab. There is a strong relation between the temperature of the NaK getter and the partial pressure of the hydrogen (or tritium) released from it. Thus by controlling the temperature of the NaK getter the tritium release from the NaK can be controlled. A process to ensure controlled tritium release below the SCK CEN's tritium laboratory release limits is shown in Figure 4. This process can be executed first to detritiate the NaK. Then the NaK can be processed with Simsan without the risk for too high tritium releases.



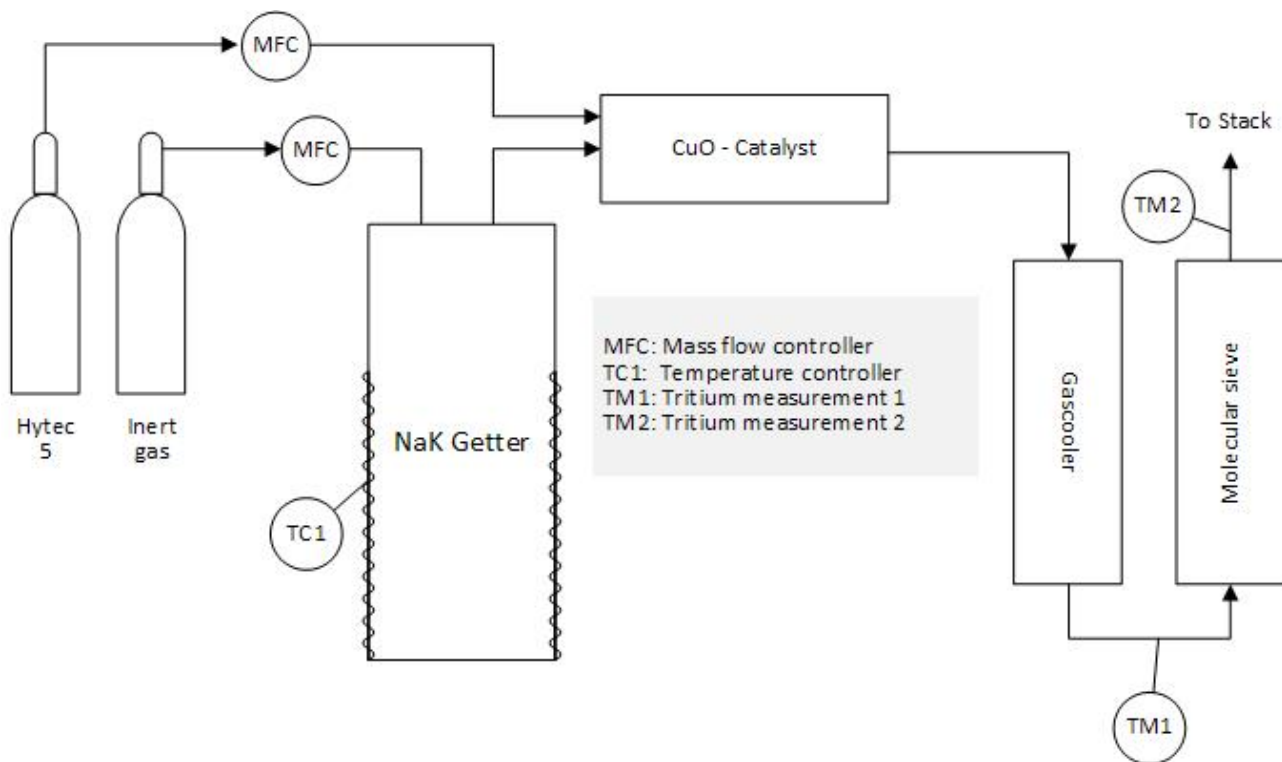


Figure 4: Proposed system for controlled tritium release of the NaK getter.

The system works as follows:

1. The temperature of the NaK getter is controlled by TC1. The higher the temperature of the NaK the more tritium will be released from it due to the relation between temperature and partial hydrogen (tritium) gas pressure (see equation 12)
2. An inert gas flow is sent through the NaK. This gas flow is controlled by a mass flow controller and will transport the released tritiated hydrogen gas. The higher the flow the more tritiated hydrogen gas can be transported.
3. The inert gas loaded with tritiated hydrogen gas is sent over a CuO-catalyst. The CuO catalyst is heated sufficiently to ensure the oxidation of the tritiated hydrogen gas.
4. An additional gas flow of hytec 5 gas (5% hydrogen – 95 % Argon) is sent over the heated CuO catalyst as well. This gasflow is also controlled by a mass flow controller. The purpose of this gas is to dilute the tritium concentration in the gas flow.
5. In the CuO catalyst all (tritiated) hydrogen will be converted to tritiated water vapour.
6. In the latter two stages before release to the stack the gas flow will be cooled down. Most of the tritiated water vapour will be kept on the molecular sieve.

*Calculation example*

In this paragraph the operation of the system in Figure 4 is illustrated by calculations. The results of the calculation are summarized in the highlighted line of Table 7.

The calculation is made for following conditions:

- The hourly HTO release limit to SCK CEN's tritium laboratory stack is limited to 0.19 GBq/h (see paragraph 4.3). For certainty the installation will be designed to a maximum release of 0.10 GBq/h.
- Maximum 2 out of the 5 moles of hydrogen gas in the atmosphere released from the NaK getter will be HT (see paragraph 4.3).
- The mixing of the Hytec gas and the gas flow coming from the NaK getter will be perfect.
- Complete oxidation of all HT and H<sub>2</sub> will be achieved by sending the gas mix over the CuO catalyst.
- The molecular sieve will achieve a dewpoint of -70 °C or less. According to [10] this corresponds to a partial pressure of water vapour in air of 0.00194 mmHG or 0.259 Pa.
- The gas cooler brings down the temperature to 20 °C.
- The HTO/H<sub>2</sub>O ratio in the gas mix before and after the molecular sieve will be the same.
- The inert gas flow rate through the NaK getter is 1 L/min
- The NaK getter is heated to 160°C

With formula (12) the partial pressure of the tritiated hydrogen gas above the NaK can be calculated at any given temperature. Inserting this in the ideal gas law with V = 1 L and T = 160°C the concentration of hydrogen gas can be calculated by the following formula:

$$c_{(HT+H_2,160^\circ C)} = \frac{101325 [Pa/atm] \times e^{\frac{21,3216 - \frac{14460}{(160+273)[K]}}{8.31 [J/mol.K]}} [atm]}{8.31 [J/mol.K] \times (160+273)[K]} \times \frac{1 [m^3]}{1000[L]} = 1.6 \times 10^{-7} [mol/L] \quad (17)$$

Suppose this gas gets undiluted through the oxidiser and the cooler then the mole fraction of all HTO and H<sub>2</sub>O in the gas can be calculated by:

$$c_{(HTO+H_2O,20^\circ C)} = c_{(HT+H_2,160^\circ C)} \times \frac{(160+273)}{(20+273)} = 2.4 \cdot 10^{-7} [mol/L] \quad (18)$$

At room temperature and at atmospheric pressure 1 L gas consists out of 0.0416 mol:

$$\frac{101325 [Pa] \times 1[L]}{8.31 [J/mol.K] \times 293 K \times 1000 [L/mol]} = 0.0416 [mol] \quad (19)$$

Substitution of (19) in (18) gives that the mole fraction of the tritiated water to stack without molecular sieve nor dilution with Hytec would be

$$\chi_{undiluted\_no\_MS} = 5.7 \cdot 10^{-6} \quad (20)$$



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Remember that the Gasflow  $F = 1 \text{ L/min}$  and that maximum 2 out of 5 moles tritiated water are actually HTO. The tritium release to the stack without Hytec dilution nor molecular sieve can be calculated by:

$$R_{HTO} = c_{HTO+H_2O} \times F_{gas} \times DF_{getter} \times \lambda_T \times N_A \quad (21)$$

With

- $c_{HTO+H_2O}$  = molar concentration tritiated water in gasflow =  $2.4 \cdot 10^{-7} \text{ mol/L}$
- $F$  = gasflow =  $1 \text{ L/min}$
- $DF_{getter}$  = Dilution factor due to getter =  $1 \text{ mol HTO} / 2.5 \text{ mol (HTO} + \text{H}_2\text{O)}$
- $\lambda_T$  = decay constant of tritium =  $1.7828 \cdot 10^{-9} \text{ s}^{-1}$
- $N_A$  = Avogadro's constant

Substitution gives:

$$R_{HTO\_no\_MS\_undiluted} = 6.1 \text{ GBq/h} \quad (22)$$

Without molecular sieve filtering or Hytec dilution the release to the stack would be 61 times higher than our target.

When the molecular sieve is operational at  $-70^\circ\text{C}$ , the partial pressure of water in this gas will be  $0.00194 \text{ mmHg}$  according to [10]. This corresponds to a molar fraction of tritiated water in gas of  $2.6 \cdot 10^{-6}$ .

$$\chi_{undiluted\_with\_MS} = 2.6 \cdot 10^{-6} \quad (23)$$

In this case the molecular sieve would result in a reduction factor of 2.2 in the tritium release to the stack.

$$\frac{\chi_{undiluted\_no\_MS}}{\chi_{undiluted\_with\_MS}} = 2.2 \quad (24)$$

As a result of adding the molecular sieve the Release to the stack is:

$$R_{HTO\_with\_MS\_undiluted} = 2.8 \text{ GBq/h} \quad (25)$$

The tritium concentration in the gas that enters the CuO catalyst needs to be brought down by a factor 28. This can be achieved by adding Hytec gas to the stream. Figure 5 shows how this can be done.

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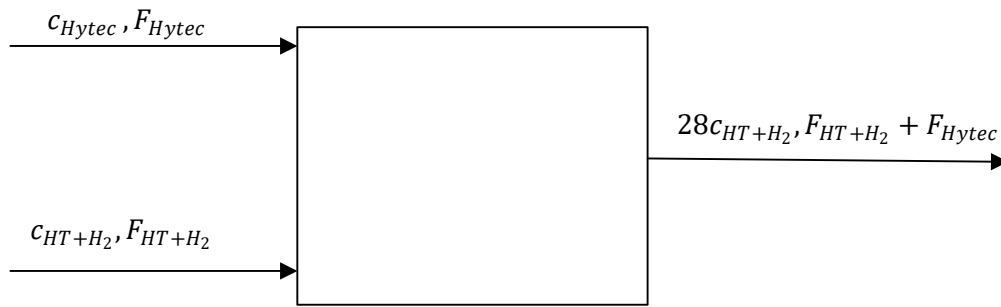


Figure 5: Calculation model for dilution by Hytec

The hydrogen concentration in the exit flow is 28 higher than the hydrogen concentration in the flow coming from the NaK getter. The resulting flow rate is the sum of the flowrate from the Hytec gas and the gas stream coming from the NaK getter. Putting everything together gives

$$c_{HT+H_2}, F_{HT+H_2} + c_{Hytec} \times F_{Hytec} = 28c_{HT+H_2} \times (F_{HT+H_2} + F_{Hytec}) \quad (26)$$

From this follows:

$$F_{Hytec} = F_{HT+H_2} \times \frac{c_{HT+H_2} \times (29-1)}{c_{Hytec} - 29 \times c_{HT+H_2}} \quad (27)$$

As Hytec 5 consists out of 5% its molar hydrogen fraction is 0.05. The hydrogen concentration at room temperature and atmospheric pressure can be calculated:

$$c_{Hytec} = 0.05 \frac{\text{mol } H_2}{\text{mol}_{Hytec}} = 0.0221 \frac{\text{mol } H_2}{L_{Hytec}} \quad (28)$$

Substituting all known data gives that:

$$F_{Hytec} = 2.9 \cdot 10^{-3} L/min \quad (29)$$

Since the NaK getter contains at maximum 0.5 TBq tot start of and the release from the NaK getter is 6.1 GBq/h it will take approximately 82 hours to detritiate the getter.

$$\frac{0.5 \text{ TBq}}{R_{HTO\_no\_MS\_undiluted}} = 82 \text{ h}$$

As the release to the stack is only 0.1 GBq/h or 8.2 GBq in total the majority of the tritium will be captured on the molecular sieve.

Similar calculations are summarized for different temperatures and for different flow rates of the inert gas through the NaK in Table 7 on the following page.

**Table 7: Calculation table for necessary time and hytec flow rate to ensure tritium release below 0.1 GBq/h to the stack of SCK CEN's tritium laboratory.**

$T_{\text{Nak}}$ [°C]	$F_{\text{HT+H2}}$ [L/min]	$C_{(\text{HTO}+\text{H}_2\text{O}, 20^\circ\text{C})}$ [mol/L]	$\chi_{\text{undiluted\_no\_MS}}$ [mol/mol]	$R_{\text{HTO\_no\_MS\_undiluted}}$ [Bq/h]	$\chi_{\text{undiluted\_with\_MS}}$ [mol/mol]	$R_{\text{HTO\_with\_MS\_undiluted}}$ [Bq/h]	$RF$	$DF$	$F_{\text{hytec}}$ [L/min]	$t$ [h]
100	1	1,1E-09	2,7E-08	2,8E+07	2,7E-08	2,8E+07	1,0			
120	0,5	7,9E-09	1,9E-07	1,0E+08	1,9E-07	1,0E+08	1,0	1	4,0E-08	4891
120	1	7,9E-09	1,9E-07	2,0E+08	1,9E-07	2,0E+08	1,0	2	3,8E-06	2445
140	0,5	4,7E-08	1,1E-06	6,1E+08	1,1E-06	6,1E+08	1,0	6	5,4E-05	823
140	1	4,7E-08	1,1E-06	1,2E+09	1,1E-06	1,2E+09	1,0	12	2,4E-04	412
160	0,5	2,4E-07	5,7E-06	3,1E+09	2,6E-06	1,4E+09	2,2	14	7,0E-04	163
160	1	2,4E-07	5,7E-06	6,1E+09	2,6E-06	2,8E+09	2,2	28	2,9E-03	82
180	0,5	1,0E-06	2,5E-05	1,3E+10	2,6E-06	1,4E+09	9,6	14	3,1E-03	37
180	1	1,0E-06	2,5E-05	2,7E+10	2,6E-06	2,8E+09	9,6	28	1,3E-02	19
200	0,5	4,0E-06	9,6E-05	5,2E+10	2,6E-06	1,4E+09	37,0	14	1,2E-02	10
200	1	4,0E-06	9,6E-05	1,0E+11	2,6E-06	2,8E+09	37,0	28	5,1E-02	5

From Table 7 following observation can be made:

- Up to NaK temperatures of 100°C no molecular sieve, nor Hytec dilution are necessary at the given gas flow rates (to prevent a release above 0.1 Gbq/h to the stack).
- To come to workable detritiation times the NaK getter should be heated up to at least 160°C.
- An increase in NaK temperature of 20°C can result in an increase of tritium release from the getter by nearly an order of magnitude.
- Increase in gas flow rate through the NaK getter will result in a linear increase of the tritium release from the NaK.

From the above it can be concluded that the proposed solution can be used. In a first run an eye should be kept on tritium monitors TM1 and TM2 (see Figure 4) whilst gradually increasing the NaK temperature above 120°C, in order to prevent too fast increases in tritium release. The readouts of TM1 and TM2 can also be used to determine when no more tritium will be released from the NaK.

After the detritiation of the NaK Getter the same gas handling system can also be used at the exit of the Simsan system as shown in Figure 6.

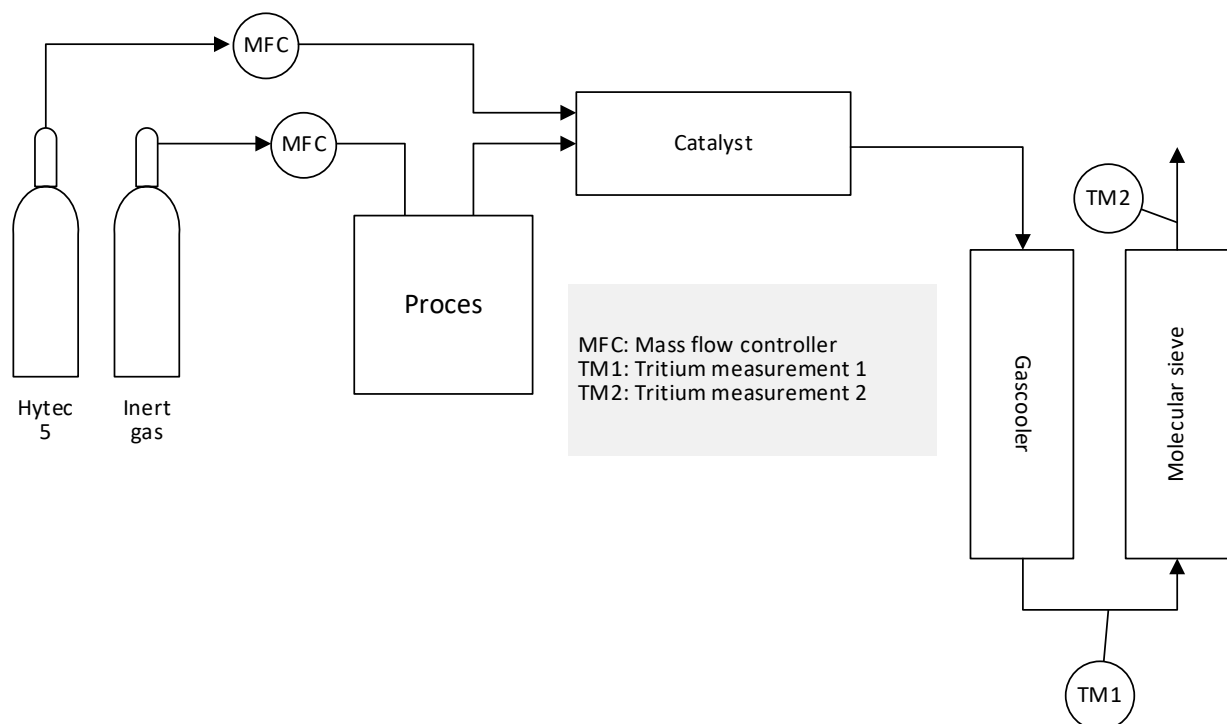


Figure 6: Controlled HTO release in the Simsan process

## 4.7 Conclusions for using Simsan for the tritiated NaK getter

It seems possible to process the NaK of the SCK CEN getter to less reactive  $\text{Na}_2\text{CO}_3$  using an adapted Simsan process provided that the NaK getter is detritiated before the Simsan processing. The NaK detritiation consists out of heating and gas inert flushing through the NaK and treating the off gasses by catalytic oxidation and molecular sieving.

These processes can be executed without surpassing the tritium stack limits of SCK CEN's tritium laboratory. The resulting end products (possibly tritiated  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and molecular sieves) are non reactive and can be disposed off as nuclear waste.

## 5 General conclusions

SCK CEN holds 5 Ti-getters and one NaK getter. The tritium content of each of the getters was unknown at the start of this project. To complicate things NaK is a very reactive liquid metal. This deliverable report presents a treatment and recycling plan for these getters. The tritium of the 5 Ti-getters will be recovered for reuse by an external partner, the emptied and passivated getters can be disposed of as standard compressible waste. The NaK getter will first be detritiated and then converted to practically unreactive mix of sodium carbonate and potassium carbonate. Most of the NaK's tritium will be captured on a molecular sieve. In contrary to the reactive tritiated NaK, the unreactive molecular sieve, sodium carbonate and potassium carbonate will most probably allow for nuclear disposal in a standard waste category.

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