Report on tritiation of cement and steel particles

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Summary

This report describes the tritium loading conditions and the characterisation of the particle before and after the tritium exposure. In the first part, the results deal with the surrogate stainless steel particles described in the report D.3.1. To prepare the treatment, exposures under hydrogen were studied and characterised thanks to XPS. High temperature exposure was the most efficient to reach high specific radioactivity. The results allowed to define a reproducible process and to produce tritiated particles with a specific radioactivity around 1 MBq/mg. The second part of the results concerns the cement particles collected during a cutting operation as described in the report D.3.2. The specific radioactivity in this case reached 0.4 MBq/mg after exposure to 3H gas at room temperature.

Approval

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Abbreviations

GDMS	Glow Discharge Mass Spectrometry
SSA	Surface specific area
XPS	X-ray Photo-electron Spectroscopy

Summary

This report describes the tritium loading conditions and the characterisation of the particle before and after the tritium exposure.

In the first part, the results deal with the surrogate stainless steel particles described in the report D.3.1. To prepare the treatment, exposures under hydrogen were studied and characterised thanks to XPS. High temperature exposure was the most efficient to reach high specific radioactivity. The results allowed to define a reproducible process and to produce tritiated particles with a specific radioactivity around 1 MBq/mg.

The second part of the results concerns the cement particles collected during a cutting operation as described in the report D.3.2. The specific radioactivity in this case reached 0.4 MBq/mg after exposure to ^{3}H gas at room temperature.

1 Objectives

To represent particle produced during dismantling operation, the strategy of the TRANSAT WP3 is based on the tritium loading of particles. The tritiation were performed on particles chosen and described in the report dedicated to:

- steel particle production (D3.1)
- cement particle production (D3.2)
- characterization of steel and cement suspensions (D3.2).

Consequently, this study aimed:

- to load with tritium cement and steel particles in a glove box using a volumetric gas absorption method at different temperatures and pressures;
- to characterize the tritiated particles in terms of radioactivity released from the surface and radioactivity trapped in the material bulk.

2 Methodology

2.1 Tritium loading: the set-up

The tritium bench used for the tritium labelling is contained in a dedicated glovebox. The set-up (Figure 1) permits to expose a solid sample to a controlled atmosphere of tritium gas. The tritium is stored on uranium beds as tritide (FI and FII). Vacuum on the lines is managed by a turbomolecular pump (assisted by primary pump for the highest pressure). The vacuum is measured by two pressure gauges (CI and CII). For the tritium loading, a glass tube can be connected directly to the volume V_1 or using a T pipe fitting.

The direct connection is used for the loading at room temperature without pre-treatment. In that case, the sample is exposed to the chosen pressure during a dedicated time.

The T pipe fitting (Figure 2) allows to carry out complementary treatments on the sample. Especially an additional valve permits to isolate the sample tube from the rest of the device. For instance, for metallic sample M, a reduction process could be apply. Each metallic surface exposed to the air is covered by an oxide layer, the native oxide M_xO_y (x and y depend of the oxide). Reduction process aims to reduce this layer to put directly the metal form to the expected atmosphere. H_2 gas permits the reduction of M_xO_y as follow:

$$M_xO_y + yH_2 \rightarrow xM + yH_2O$$
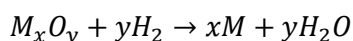
Using a cold trap at one part of the T pipe permits to separate the H_2O produced during the reduction process from the metallic sample in the tube connected to the other part of the T pipe. This process was efficient for the case of tungsten as described by El Karbachi *et al (complete reference at the end of the document)*.

The chosen process consists of 3 steps.

First, the sample is exposed to a reducing atmosphere of H_2 at 1.4×10^5 Pa and 450°C during 2 h. The water formed during the process is trapped in a cold trap (Figure 2)

Secondly, the sample is exposed to a reducing atmosphere during 2 h by increasing the pressure at 1.6×10^5 Pa (temperature remains at 450°C). After these steps, the sample is put under vacuum.

Finally, the third step is the tritium loading at the required pressure. The sample is annealed in a closed ampule of 1 cm³ during 2 h (the tritium diffusion is activated due to high temperature). . At the

end, the sample is quenched in liquid nitrogen to freeze the diffusion process and the material structure.
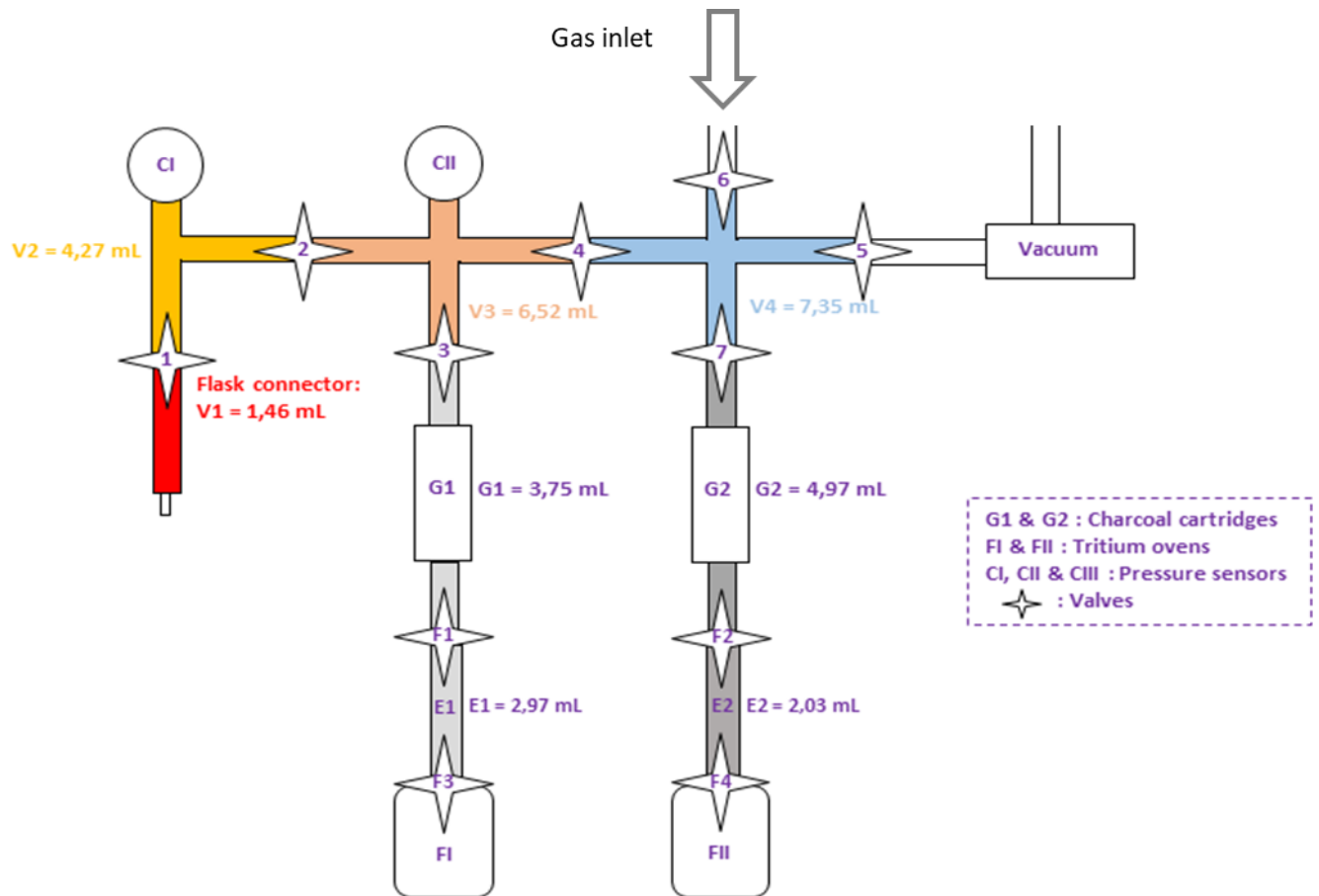
Figure 1: Scheme of the tritiation set-up
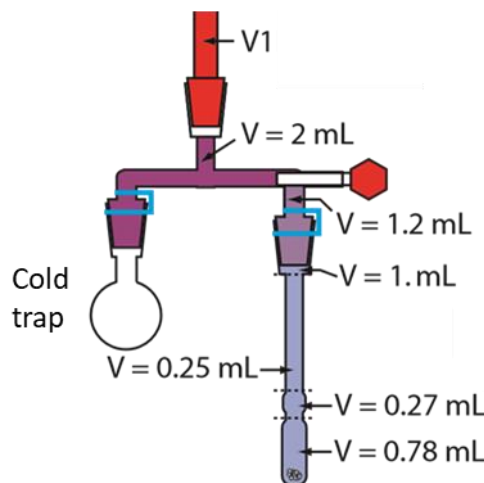
Figure 2: Scheme of the T pipe fitting during reduction process

For the steel, two kind of treatment were studied: the room temperature exposure and the thermally assisted exposure (at 450°C) with or without reduction steps. This temperature was decided to reach radioactivity around 1 MBq/mg in the particles (see part 3.3)

For the cement, the samples were exposed at room temperature. No temperature study was planned because of the transformations that could occur in the cement.

2.2 Non radioactive characterisation

In order to prepare tritium experiment, complementary analyses are useful to assess the reactivity of the powder with the tritium gas. In this report, these concern especially the steel particles because of the doubt on the carbon content.

The glow-discharge mass spectrometry (GDMS) were used to study the minor elements and specially the carbon. The X-ray Photoelectron Spectroscopy (XPS) determined the surface composition in terms of chemical bond (molecular or elementary).

Before the tritium loading of the samples, control experiments were realised under dihydrogen. Indeed, an equivalent set-up is available to perform similar experiment. This permits to verify some characteristics of the material using high performance analysis devices without radioactivity contamination risk. For instance, the XPS was used to determine the efficiency of treatments to limit the carbon contamination (see hereafter 3.1 and 3.2).

2.3 Tritium measurement

After the exposure to tritium gas, different part of tritium can be distinguished considering the interaction of the studied material. A part of tritium is trapped in the bulk material at the room temperature; a part is adsorbed at the surface; a part is labile and is released rapidly in the ambient air.

To handle safely the tritiated sample, an appropriate degassing time should be observed until the degassing radioactivity becomes very low or negligible. Usually, the main release occurred in the coupled days following the exposure to the ambient air. Consequently, the release of tritium is measured during 10 to 15 days putting the sample in an airtight tank except a controlled air flow. The flow drags the degassing tritium to a bubbler MARK 7000 from SDEC, which traps the tritium in water HTO form (Figure 3). When the cumulative radioactivity reach a plateau, the main degassing part is finished.
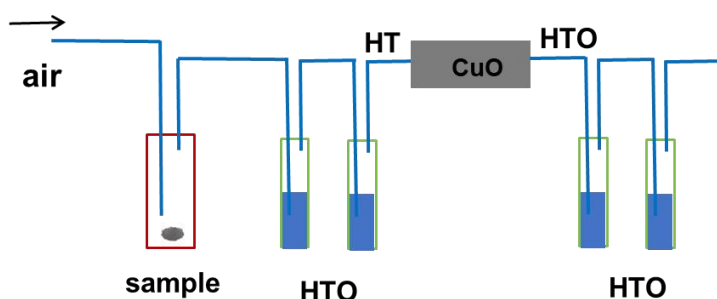
a.
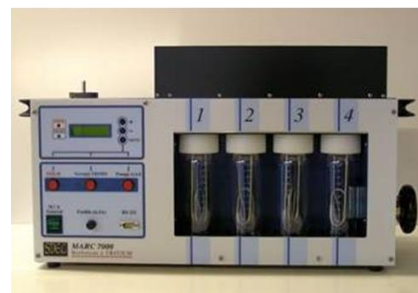
b.

Figure 3: Tritium degassing set-up (a) and tritium bubbler (b)

The degassing time is counted since the sample is placed into the airtight tank. But this operation induces an income of ^3H-contaminated air in the tank due to the atmosphere of ^3H contained in the sample vial. To assess this part of contaminated air, the first measurement after 1 or 2 hours is subtracted from the radioactivity measured in the bubbler.

To measure the tritium trapped in the material after room temperature degassing, a full dissolution is carried out. The appropriate digestive solution is first tested with non-tritiated samples.

Finally, the radioactivity is measured using liquid scintillation analyser, Tri-Carb 2910 TR from PerkinElmer. The liquid scintillation counting is the most efficient techniques to measure wide range of tritium activity but implies to solubilise the sample.

3   Results

3.1   *Characterisation of the steel particles before tritium loading*

If the composition of the steel powder corresponds to the standard (Table 1), glow discharge mass spectrometry provides precise measurement on the low concentration or trace elements (Table 2). This measurement was carried out on a pellet of the commercial powder obtained without linker. We noted that the carbon content was a bit higher than the standard content. The GDMS analyses the element by sputtering the matter layer by layer. In that way, the first measurement correspond to the sample surface. On the 316L pellet, the carbon content decreased significantly from the surface to the bulk of the pellet (Table 3). We have to take into account this surface content of carbon considering the high tritium affinity with carbon.

Table 1: Mass composition (wt %) of the 316L stainless steels

Type	Fe	Cr	Ni	Mo	Mn	C
316L	Bal.	16-18	10-14	2-3	< 2	< 0.03

Table 2: Mass composition (wt ppm) of the low concentration element in the commercial 316L stainless steel powder (GDMS analysis)

B	C	N	Na	Mg	Si	P	S	Ti	V	Co	Cu	W	Zr
11	420	60	8.2	3.5	3500	300	250	8.5	385	1050	3210	98	9.5

Table 3: Carbon mass concentration (ppm) of the commercial 316L stainless steel powder from the surface (measure 1) to the bulk (measure 6).

Measure	1	2	3	4	5	6
ppm	1850	610	425	410	435	415

Specific surface area was determined for the commercial powder at 0.424±0.012 m^2/g.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface composition of the commercial powder. The XPS overview spectrum (Figure 4) showed different peaks corresponding to binding energies of Fe-2p, Mn-2p, Cr-2p, O-1s and C-1s. The relatively high peak of carbon revealed a high content of organic carbon at the surface. The analyses of the other elements suggested that the surface is covered by mixed oxide of iron and manganese. This oxide layer is approximately 5 to 10 nm of thickness.
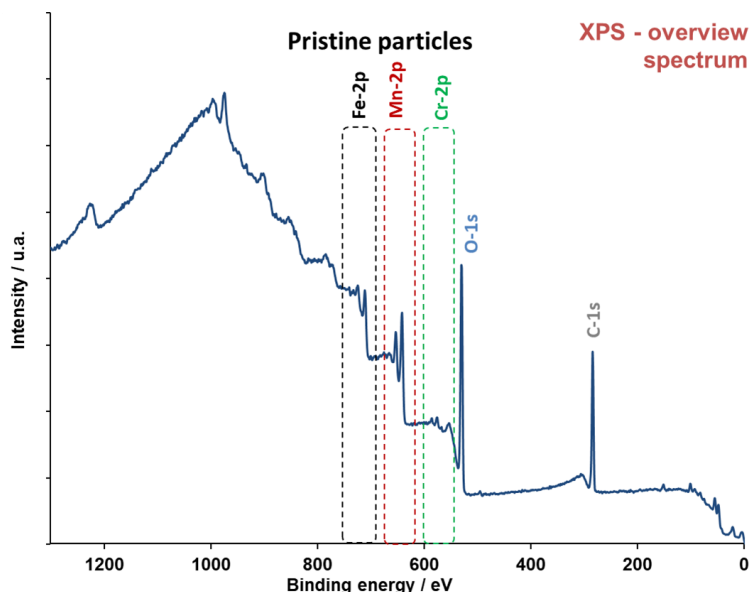
Figure 4: XPS overview spectrum of the commercial particles as received from the supplier

The commercial powder presented a high content of carbon at the surface detected by a GDMS and XPS. The XPS was a suitable technique to control the efficiency of treatments to clean the steel particles.

3.2 Treatment of steel particles: cleaning, evolution of oxide layer under hydrogen atmosphere

- Cleaning process

Concerning the content of carbon at the surface of the particle, cleaning process were assessed from XPS analyses (Figure 5). For each process, particles were cleaned in the selected solution. Different organic solvent were used as ethanol or dichloromethane. Hydrochloric acid solutions at 1 mol/L and 0.1 mol/L were also considered. The cleaning consisted in a stirring with an ultrasonic bath during 5 min. Then the samples were filtered on a membrane. The powder was finally dried 2 hours at 100°C.

The Figure 5 shows that the carbon content was significant in any case especially in the cut and the as received particles. The cut particles correspond to the particle obtained during a cutting operation as described in the Report D3-1. These particles are collected from the sediment (i.e. particle size range is broad from 1 to 100 µm). Each cleaning treatment decreased the carbon content at the surface: the most efficient seems to be the dichloromethane.
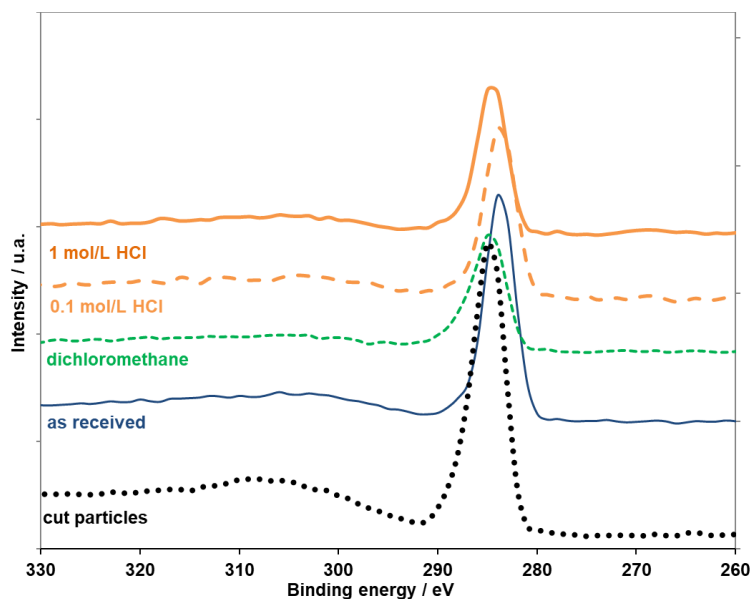
Figure 5: XPS spectra of the commercial powder as received and from different treatments (cleaning in 1 mol/L of hydrochloric acid, cleaning in 0.1 mol/L of hydrochloric acid, cleaning in dichloromethane) compared to the spectrum of cut particles (sediments collected during a cutting operation).

- Hydrogen treatment (action on oxide layer)

Exposure to tritium gas at 450°C is expected to induce a significant level of tritium specific activity. So, the influence of temperature on the oxidation stage of the powder surface was also investigated. Samples of the commercial powder were exposed to pure hydrogen atmosphere during 2 h at 250°C and 450°C. The comparison of the annealed sample to the as received particles is presented in the Figure 6. On the surface of the as received and the 250°C-annealed particles, the oxide was similarly composed of iron and manganese. However, the annealing at 450°C changed the oxide composition to chromium and manganese.

Although both oxides are different from the oxide present at the surface of the "cut" particles which were collected from a cutting operation. For those ones, the oxide was mainly composed of iron. In any case, no trace of metallic bond was detected by the XPS. Even after the annealing in a reducing atmosphere of hydrogen, an oxide remained at the surface. The change in the oxide with temperature corresponded to the formation of the most stable oxide rich in chromium.
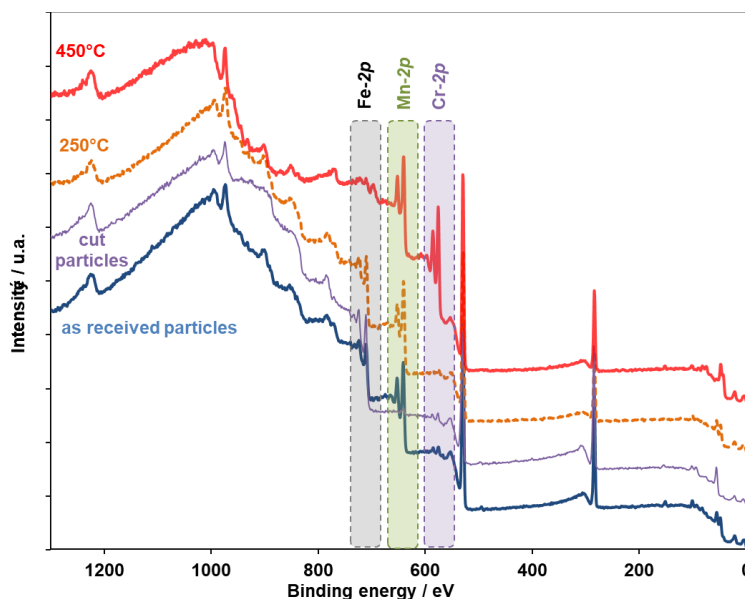
Figure 6: XPS spectra from samples exposed to hydrogen gas at 250°C and 450°C compared to the as received and the cut particles

3.3 Tritium loading on the steel particles

Steel particles were exposed under several conditions to test the specific radioactivity and its stability. The parameters were at stake:

- the cleaning process using organic solvent or acidic solution;
- the annealing under reducing conditions at 450°C with hydrogen and a cold trap;
- the temperature of exposure to tritium gas, either room temperature or 450°C.

The cleaning process aimed at reducing the carbon contamination at the particle surface (see above).

The annealing process under hydrogen aimed to remove the oxide layer from the particle in order to expose metallic surface to tritium. However, the XPS study revealed that the conditions did not permit to avoid an oxide layer at the stainless steel powder. Consequently, this step was performed to stabilise the oxide layer to a chromium rich oxide before the tritium loading at the same temperature (see above).

The particles were loaded with tritium, as decribed in the methods section, then, the specific radioactivity was determined. The total radioactivity degassed at room temperature from the sample and normalised to the sample mass is plotted against the time (Figure 7). The HTO part from the degassing is also presented (Figure 8). In any case, a plateau was reached after 4 or 5 days in a range between 0.2 to 0.5 MBq/mg. The main part of the tritium released was as HTO form. The temperature of exposure had a low impact on the degassing curves. Although the activity of the ^{3}H trapped in the particles was significantly higher for the high temperature sample compared to the room temperature exposure (Table 4).

The annealing process at 450°C (2 reductions under hydrogen) before an exposure to tritium gas at 450°C led to similar results with or without dichloromethane. In the same way, results were reproducible using around 68 mg or 366 mg of powder.

Consequently, the particles will be used treated by 2 steps of annealing process at 450°C and a step of ^{3}H exposure at 450°C which leads to controlled conditions and the highest specific radioactivity.
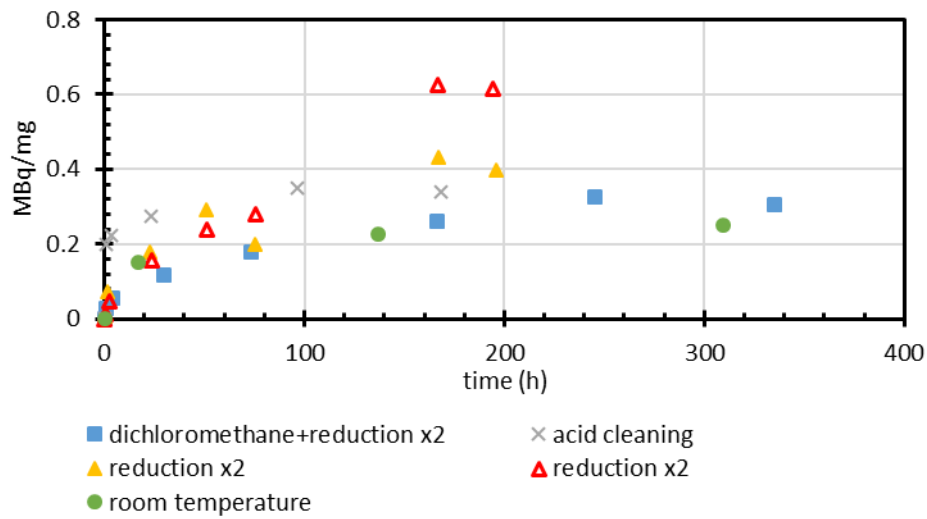
Figure 7: Cumulative (HTO+HT) radioactivity release from stainless steel particles for different treatments.
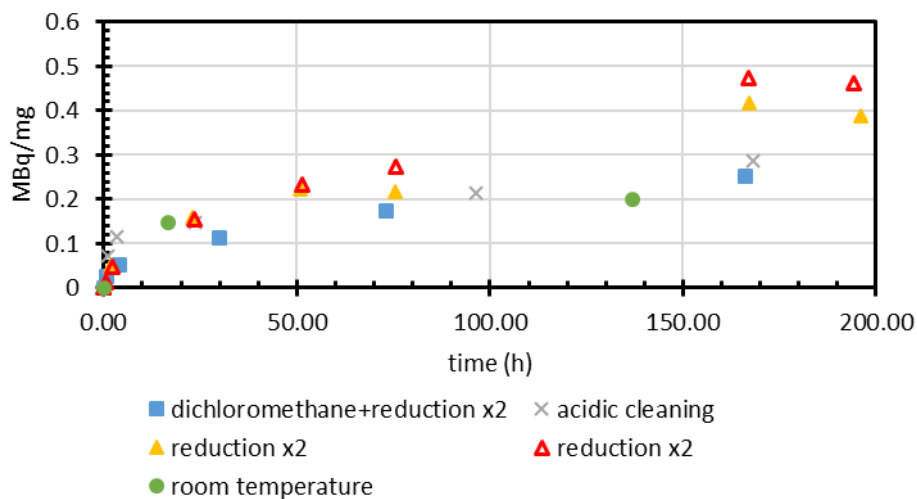
Figure 8: Cumulative HTO radioactivity release from stainless steel particles for different treatments.

Table 4: Specific radioactivity of stainless steel particles depending on the preparation conditions

Sample conditions		specific radioactivity MBq/mg (mean±SD)	
dichloromethane + reduction x2	Exposure at 450°C	1.0	± 0.08
acidic cleaning	Exposure at 450°C	0.5	± 0.05
As received + reduction x2-0 (68 mg)	Exposure at 450°C	1.1	± 0.1
As received + reduction x2-1 (366 mg)	Exposure at 450°C	1.0	± 0.1
As received + reduction x2-2	Exposure at 450°C	0.94	± 0.1
As received	Exposure at 20°C	0.037	± 0.004

The particles are expected to be used in water suspension in the following tasks of the project. Consequently, the stability of the radioactivity was measured in ultrapure water. Few milligrams of

powder were dispersed in 2 mL of water. The Figure 9 reveals that a significant release of tritium occured after 4 days in solution. The radioactivity release tended to a plateau around 0.4 to 0.5 MBq/mg in 10 days.

Particles will be stored at air in closed vial. Measurements of the trapped radioactivity of particles (prepared after the 2 reduction process) confirmed that this storage does not induce significant changes (1.1±0.1 mg).

■ dichloromethane+reduction x2 - 7.2 mg ✖ control - 6.2 mg

▲ reduction x2 - 9.4 mg △ reduction x2 - 4.0 mg
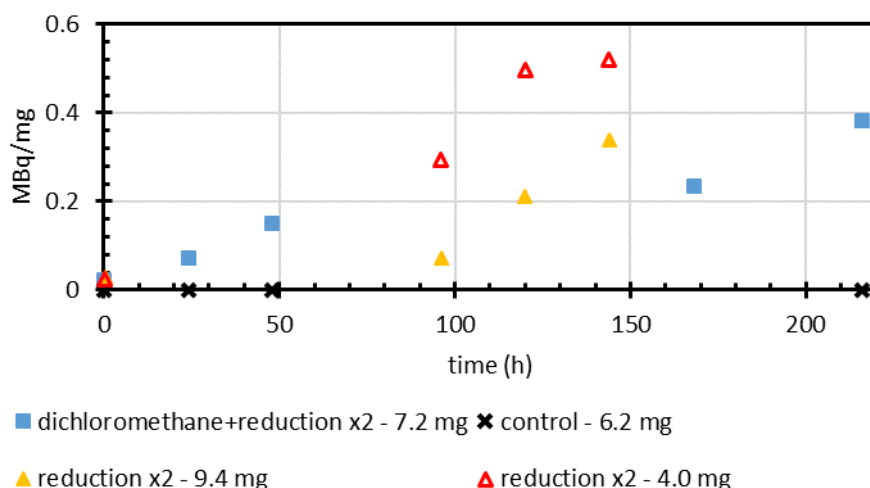
Figure 9: Cumulative tritium release from stainless steel particle in ultrapure water

To summarize, the use of commercial particles implies more analyses to control the suspected carbon contamination. The dichloromethane cleaning is the most efficient to decrease the carbon contamination at the surface of the particles. However, the treatment in 3 steps at 450°C leads to reproducible specific radioactivity at 1 GBq/g with or without cleaning.

3.4 Tritium loading on the cement particles

For cement, the high content of ^1H in the material (due to the high humidity content) would lead to a significant amount of ^3H absorbed. For that reason, the first ^3H exposure tests were carried out at the room temperature.

The particles used for this study were prepared as described in the Report D3.2 in the IRSN lab. These particles were not sorted by size but were collected on a membrane during a cutting operation of a cement plate produced at the CEREGE. The measurements presented here permit to assess the order of magnitude of the expected radioactivity.

A sample (4.9 mg) was exposed 2 hours at 0.4 bar of tritium at room temperature (the same pressure of tritium than steel particle).

The degassing phase at room temperature showed a huge release of tritium from the sample, (Figure 10) reaching 170 MBq/mg.

Considering the high level of released radioactivity in that condition, another sample was exposed to diluted tritium with hydrogen gas at 10% for the same time. The dilution induced a significant decrease of the tritium release until 0.15 MBq/mg.

After full dissolution (in aqua regia), the radioactivity trapped in the sample was measured, and found almost 10 times lower for the sample exposed at 10% (Table 5). Moreover the total release of tritium occured also in ultrapure water after several days.
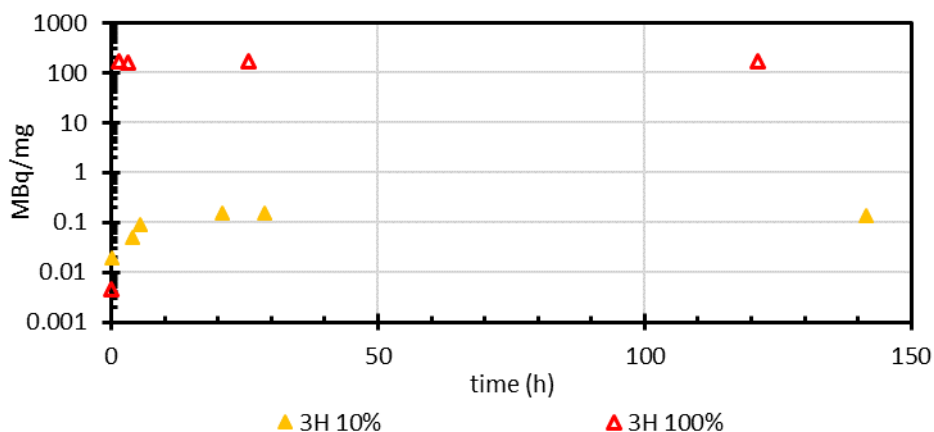
Figure 10: Cumulative release radioactivity of tritium from cement particles exposed 2 h in tritium gas.

Table 5: Specific radioactivity of cement particles depending on the tritium content

Sample	specific radioactivity MBq/mg (mean ± SD)	
pure 3H	0.40	± 0.01
dilute 3H (10%)	0.003	-

4 Conclusions

This work aimed to develop the method for producing tritiated particles in a reproducible manner in terms of tritium content for the *in vivo* and *in vitro* studies of TRANSAT WP3.

For the stainless steel particles, the recommended protocol is divided in 4 parts:

- The sample has to be cleaned with an organic solvent (dichloromethane was the most efficient in the tested conditions) to limit the carbon content at the industrial surrogate particle surface;
- 2 steps of reduction at 450°C under hydrogen gas permitted to control the oxide layer formed at the particle surface (this avoids to induce oxide layer transformation during the tritium exposure at high temperature as expected);
- Exposure to tritium gas at 450°C during 2 hours permitted to reach a specific radioactivity around 1 MBq/mg (1GBq/g).

Due to similar results with or without the solvent cleaning, the simplified protocol is finally deciced during the WP3 meetings:

- 2 steps of reduction at 450°C under H_2 during 2 h;
- Exposure to tritium gas at 450°C during 2 h.

For the cement particles, the room temperature exposure was sufficient to obtain a specific radioactivity of approximately 0.4 MBq/mg (400 MBq/g). However, cautions must be taken for the handling of tritiated particles regarding the high amount of tritium that could be released during the degassing phase just after the ^{3}H-exposure. Moreover, the tritium could also release in water. Further investigations will be performed before the use of these particles for the *in vivo* and *in vitro* studies.

5   References

A. El-Kharbachi et al., INT J HYDROGEN ENERGY, 39 (2014) 10525-10536

6   Acknowledgments

7 Appendix

Other tests were performed in order to minimise the oxide layer. The metallic bond of the stainless steel particles was detected by XPS only after a cleaning process with acidic solution at 1 mol/L.
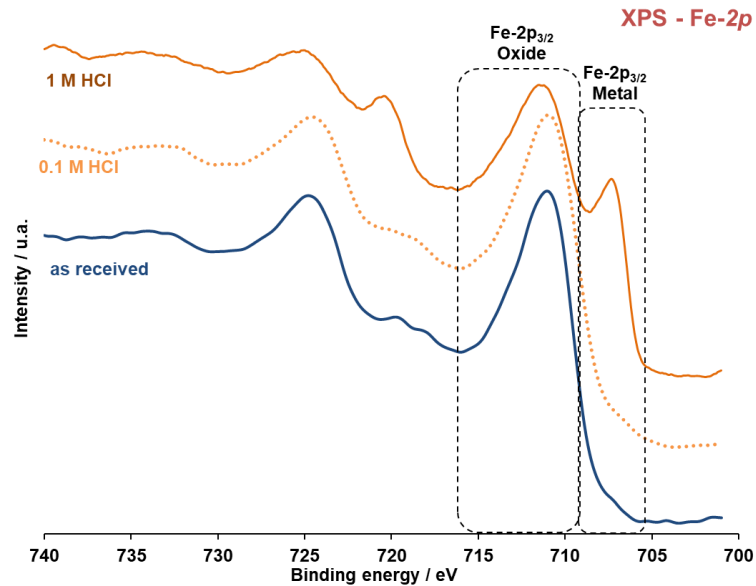

Figure 11: Comparison of the XPS spectra focused on the Fe-2p binding energy concerning as received samples and cleaned samples in hydrochloric acid (1 mol/L and 0.1 mol/L)