IMPERMEABLE GRAPHITE: A NEW DEVELOPMENT FOR EMBEDDING RADIOACTIVE WASTE

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Abstract

Irradiated graphite has to be handled as radioactive waste after the operational period of the reactor. However, the waste management of irradiated graphite *e.g.* from the Spanish Vandellos reactor shows, that waste management of even low contaminated graphite could be expensive and requires special retrieval, treatment and disposal technologies for safe long term storage as low or medium radioactive waste.

FNAG has developed an impermeable graphite matrix (IGM) as nuclear waste embedding material. This IGM provides a long term stable enclosure of radioactive waste and can reuse irradiated graphite as feedstock material. Therefore, no additional disposal volume is required if *e.g.* concrete waste packages were replaced by IGM waste packages.

The variability of IGM as embedding has been summarized in the following paper usable for metal scraps, ion exchange resins or debris from buildings. Furthermore the main physical, chemical and structural properties are described.

1. INTRODUCTION

Irradiated graphite has to be handled as radioactive waste after the operational period of the reactor [1]. However the waste management of irradiated graphite e.g. from the Spanish Vandellos reactor shows, that waste management of even low contaminated graphite could be expensive and requires special retrieval, treatment and disposal technologies for safe long term storage as low or medium radioactive waste [2].

The most common reference waste management option of *i*-graphite is a wet or dry retrieval of the graphite blocks from the reactor core and the grouting or embedding into polymers of these blocks in a container without further conditioning [3]. This produces large waste package volumes because the encapsulation capacity of the grout is limited and large cavities in the graphite blocks could reduce the packing densities. Packing densities from 0.5 to 1 tons per cubic meter have been assumed for grouting solutions.

Graphite itself is a geological stable material proven by its natural occurrence [4]. However, its porous structure anticipates the use of graphite as long term stable waste matrix for final disposal [5]. Furthermore, a slow corrosion in aquatic phases can be induced by high irradiation doses. The porous structure is related to large surface areas and therefore the radiation induced corrosions process cannot be neglected for final disposal. Furthermore, aqueous phases will penetrate into the pore system and radionuclides adsorbed on the surface will be dissolved [6].

FNAG has developed a process for the production of a graphite-glass composite material called Impermeable Graphite Matrix (IGM) [7]. This process is also applicable to irradiated graphite which allows the manufacturing of an impermeable material without volume increase. Crushed *i*-graphite is mixed with 20 vol.% of glass and then pressed under vacuum at an elevated temperature in a hot vacuum press. The obtained product has zero or negligible porosity and a water impermeable structure. Structural analysis shows that the glass in the composite has replaced the pores in the

graphite structure. The typical pore volume of a graphite material is in the range of 20 vol.%. Therefore, no volume increase will occur in comparison with the former graphite material.

This IGM material will allow the encapsulation of *i*-graphite with package densities larger than 1.5 tonne per cubic meter (Figure 1). Therefore, a volume saving can be achieved by such an alternative encapsulation method. Disposal performance is also enhanced since little or no leaching of radionuclides is observed due to the impermeability of the material.

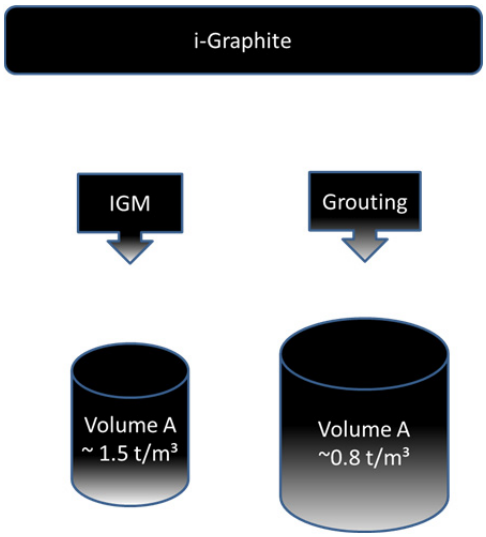

Figure 1: Volume reduction due to higher package density

However IGM will additional allow the save embedding of other radioactive wastes. Several typical radioactive wastes forms have been encapsulated into IGM as inactive simulants. These examples show that IGM is capable to form an integer and impermeable matrix around these wastes simulants. Therefore IGM is capable to substitute other embedding materials e.g. concrete. This would reduce the waste volume of the i-graphite practically to zero in an overall view (Figure 2).

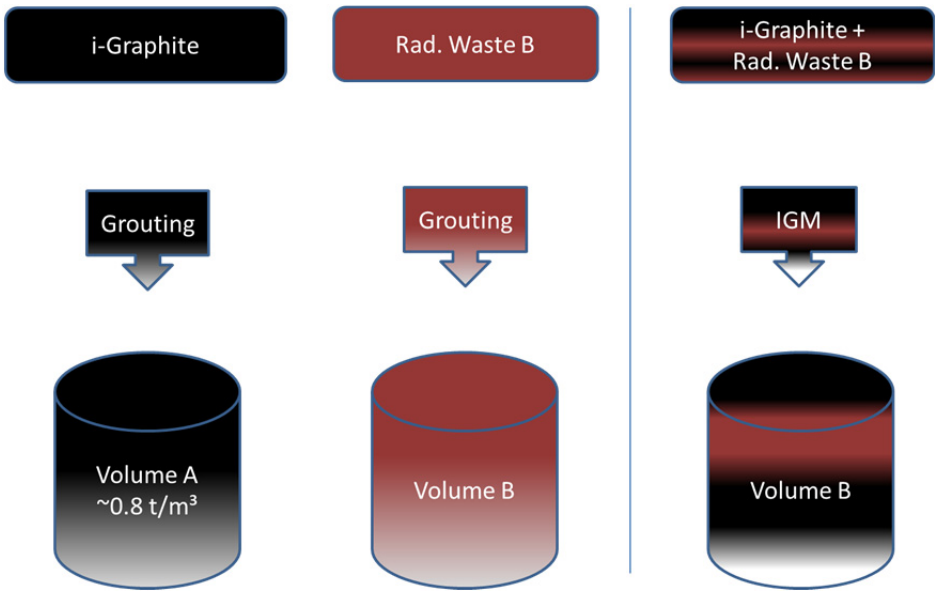

Figure 2: Volume reduction by combined waste streams

An important result has been achieved for the encapsulation of Cs which has been added as natural CsCl. Normally Cs would be released in a high temperature process because it becomes volatile at

temperatures above 800°C. However, the CsCl remained completely in the IGM matrix although the sample was manufactured at temperatures above 1100°C.

An additional benefit of IGM is the remaining graphite structure with a high thermal conductivity. Calculations showed that an IGM waste package has only a small temperature increase if heat generating wastes are enclosed.

The following paper describes the manufacturing of IGM and embedding of waste simulants as well as the properties of the manufactured IGM.

2. MANUFACTURING OF IGM

The base material for the manufacturing of IGM is a mixture of graphite and glass with a volume ratio of 4 to 1. A prefer graphite is natural graphite like FP 99,5™ form GK Kropfmühl. However this graphite can be replaced by irradiated graphite as feedstock material. Therefore the irradiated graphite has to be crashed during or after retrieval from the reactor core. The manufacturing is divvied into the following main steps:

1. Mixing of crushed graphite with glass binder
2. Filling of the mixture into a pressing tool
3. Pressing of the mixture under vacuum at elevated temperatures

Additional steps like granulation could be helpful to improve the pressing procedure but they might not be necessary. The following scheme (Figure 3) shows a principal outline for the process.

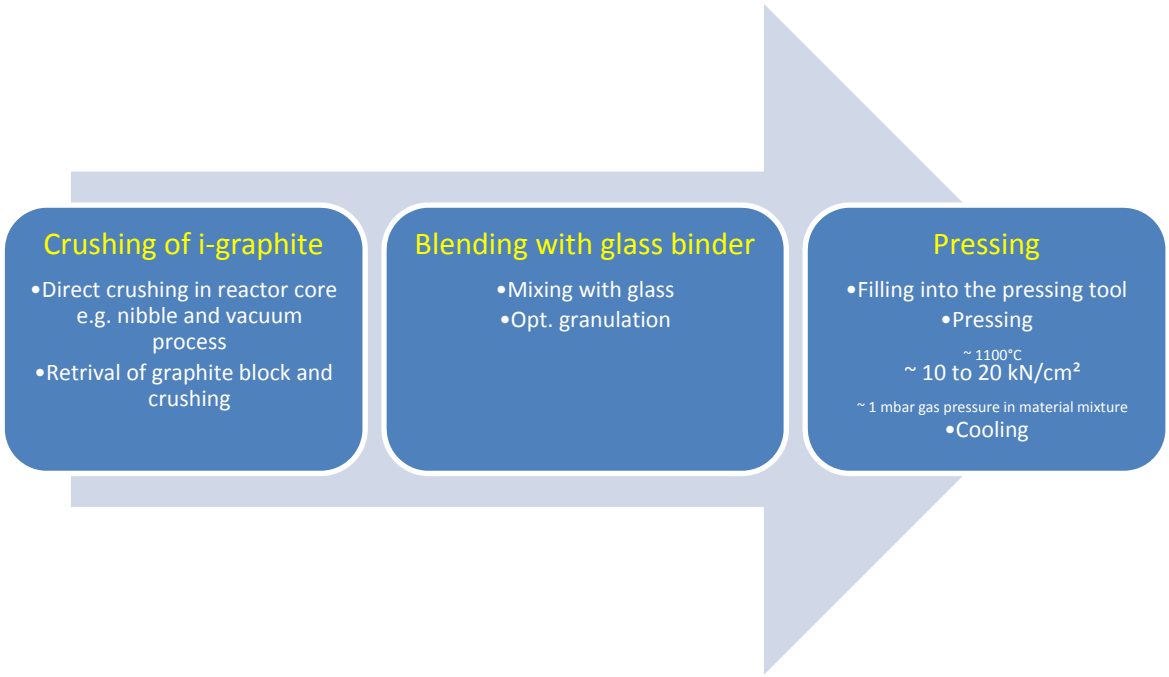

Figure 3: Principal manufacturing scheme

The first step is a general step for all treatment methods for *i*-graphite if the graphite blocks should not be grouted directly. Therefore this step has not been considered in detail.

Mixing as well as granulation are well standard procedures in chemical and metallurgical processes as well as in ceramic manufacturing. Therefore a special development of equipment is not required. However the process must be performed in a dust tight housing to avoid contaminations. For example such technology has been utilized for the mixing and pressing of MOX fuel powder.

The pressing can be performed by three different methods.

- Hot vacuum pressing in an axial die (HVP)
- Spark plasma sintering in an axial die (SPS)
- Hot isostatic pressing in a can (HIP)

It has been shown that all methods will lead to a good IGM matrix material with comparable properties and all systems are available in industrial scale.

The HVP is an axial press enclosed in a vacuum chamber. A graphite pressing die is mounted between the press strokes after it has been filled with the IGM mixture outside of the press. The die will be heated up after evacuation of the vacuum chamber by graphite heaters, which are placed around the die. The pressing is performed after the die has reached the required temperature, which depends on the glass type. This is in the range of 900°C to 1200°C. This process time is in the range of 2 to 4 hours. However following cooling down of the system required about 8 hours. Therefore a transfer system of the pressing die is proposed for an industrial solution which is capable to remove the die at a temperature of 600°C. Than the final cooling can be made in a separate cooling area and the press is ready for next pressing. A press for testing is available at the press manufacturer FCT with a maximum diameter of 150 mm and a maximum pressing height of 130 mm. Presses can build by FCT with a maximum diameter of 600 mm and pressing heights of 900 mm.

The processing time could be reduced by approximately half by using SPS. The SPS system is similar to HVP but the heating is performed by an electric current which passes the material to be pressed. Furthermore this method allows active cooling after pressing through the punches of the press. However SPS generates a different temperature profile during the pressing process. HVP heat the IGM from outside and therefore the temperature gradient leads to higher temperatures at the outside of the IGM than in the middle. SPS heats the IGM by an electric current without heating the die, which creates an opposite temperature gradient. Such temperature gradients are important for transport processes of volatile components and there distribution in the IGM afterwards. Furthermore HVP and SPS would produce IGM blocks where active material is directly on the surface.

The HIP procedure is a completely different process. The IGM material will be filled in an evacuated metal can. Such a process has already been developed at ALD in industrial scale to transfer reactive metal powder into an evacuated storage can. The can is automatically sealed by welding after filling. The filled can is transferred into a pressure vessel, heated to the required temperature and pressed by an inert gas with a pressure between 1000 and 3000 bar. Such systems have been test for nuclear application by ANSTO and USA by Idaho National. Another advantage is the availability of large HIP systems (Figure 4) with sizes of 2 metres diameter and 3 metres height as working space. Figure 5 shows the principal process scheme to transfer i-graphite into IGM for save final disposal.

Test samples in lab scale have been prepared with all three methods.

Figure 4: Large HIP from Avure
(http://www.france metallurgie.com/index.php/search/hot%20isostatic%20pressing)

The embedding of additional radioactive wastes can be performed in three different ways. Smaller waste particles like inorganic ion exchange resin, metal scrap, concrete granules, salts or other smaller waste particles can be directly mixed into the IGM powder mixture and filled as one mixture into the pressing tool. Larger parts can be placed in prepressed green bodies with cavities. Such a method would be applicable for small fuel elements from CANDU reactors. Another method is proposed for embedding HTR fuel pebbles. First a layer of IGM powder is placed on the bottom of the pressing tool. The fuel pebbles are placed on this layer and then the empty spaces between the pebbles are filled with the IGM powder. This can be supported by a smooth vibration of the pressing tool.

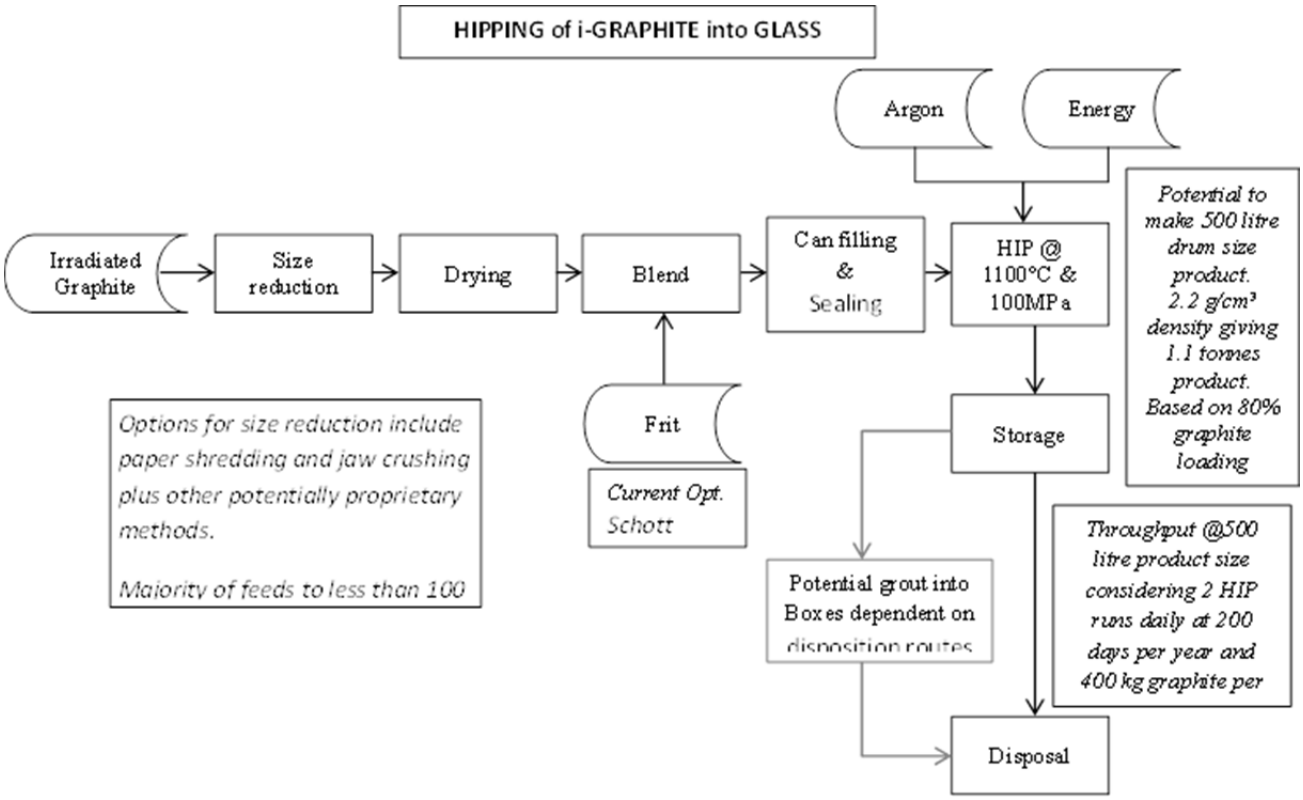

Figure 5: Schematic process for transferring *i*-graphite into IGM by HIP

Furthermore, the IGM block can be produced with an additional IGM cover out of contamination free IGM mixture prepared from natural graphite. This can be done by two different methods. The ready pressed IGM block including the radioactive material will be placed in a prepressed IGM green body with a corresponding cavity. Then the whole block will be pressed again. A simpler method is the filling of the pressing tool with a waste bearing and a non-waste bearing area. Therefore a thin tin cylinder is placed into the pressing tool. The inner part of the cylinder is filled with the IGM containing the radioactive waste and the outer part with an uncontaminated IGM mixture. The pressing process is the same as for pure IGM mixtures.

3. EMBEDDING OF DIFFERENT WASTE MATERIALS

IGM has the potential to enclose radioactive wastes for geological time scales. In principal following applications or similar waste streams could be considered:

- Embedding of spent HTR fuel elements
- Embedding of spent CANDU fuel elements or other fuel elements of similar size
- Inorganic ion exchange resins
- Metal scrap
- Gravel
- Volatile radionuclides

Several samples have been prepared in lab scale to demonstrate the feasibility of the embedding process. Figure 6 shows an example for embedded metal scrap and gravel from demolition work. Additionally the picture shows an outer zone free from waste as protective cover. This sample has been prepared by separation the outer and inner area by a tin cylinder.

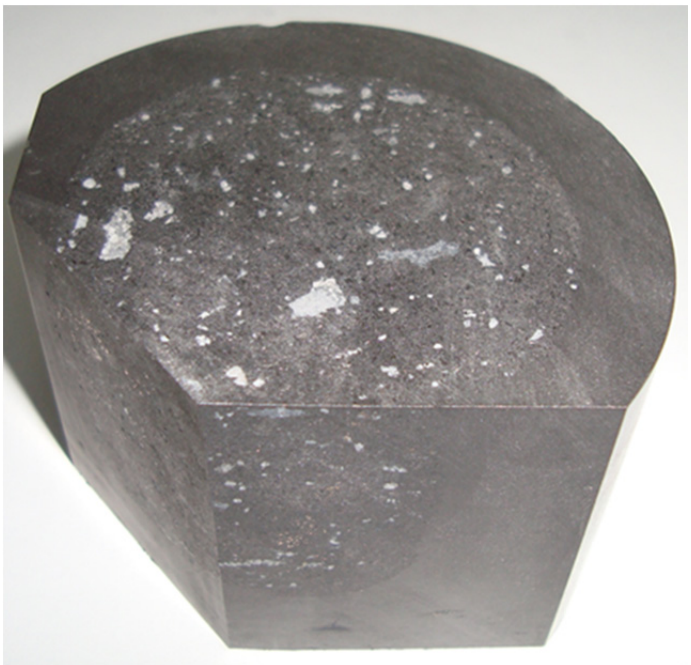

Figure 6: IGM with outer shell and embedded metal scrap and gravel

The next example shows embedded graphite pebbles as simulant for HTR fuel elements. The pebbles have been placed layer by layer into the pressing tool (Figure 7) and filling the cavities each the placements of each layer with IGM powder. Figure 8 shows a cut of the manufactured sample which proves the successful embedding of the pebbles.

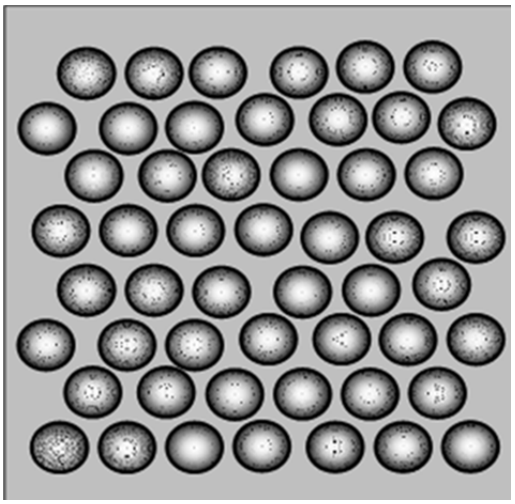

Figure 7: Model of the filled pressing tool with HTR pebbles and IGM base material

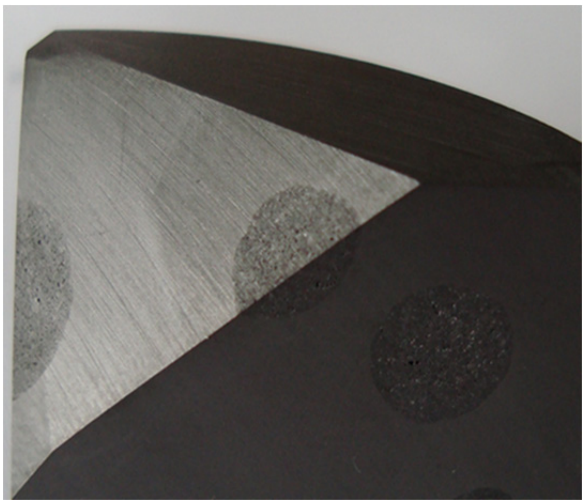

Figure 8: Section of sample with graphite pebbles.

Figure **9** shows a typical example for a placement into a cavity. A welled metal capsule filled with Iodine was placed in a cavity of an IGM green body. The empty space of the capsule was compressed together during the pressing process. The cutting showed that the capsule walls were still intact after pressing. However the iodine was lost during the cutting procedure.

Figure 9: Embedded metal capsule filled with iodine

The following Figure 10 shows an example for an embedded ion exchange resin. The inner part of the sample contained 50 vol.% of a Zeolite.

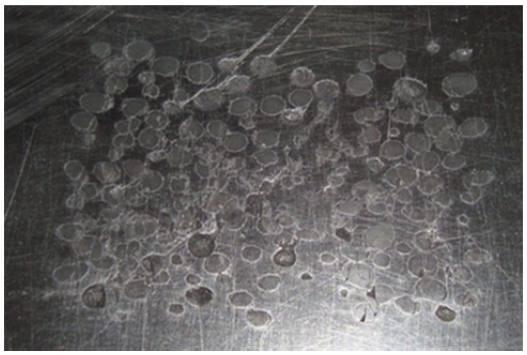

Figure 10: IGM with embedded Zeolite (50 vol.%)

Sea salt has also been embedded into IGM up to a content of 60 vol.%. The salt is homogenously distributed in the IGM after pressing and could not be detected by optical methods. The determination of the salt distribution by chemical analysis is in process.

Furthermore CsCl has been added to the IGM powder as simulant for Cs-137. Caesium is one of the critical nuclides for treatment processes at elevated temperatures because of volatility of caesium above 800°C. Therefore the caesium distribution in IGM has been investigated. Natural CsCl has been added as simulant because the use of radioactive tracers is not allowed in FNAG labs.

Two samples spiked with CsCl were cut into slices for analysis. Figure 11 shows an EDX map of chlorine from an area near the edge of a slice and from an area in the center of the slice. The intensity of the chlorine distribution shows no significant difference and indicates a homogenous distribution.

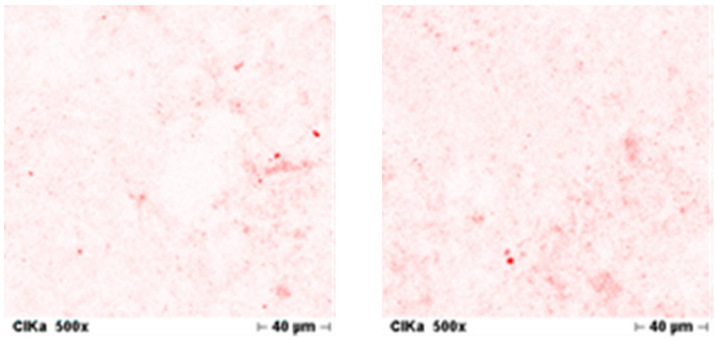

Figure 11: EDX Cl map of sample NS 327
a) outer region b) central region of the sample

Figure 12 shows the distribution of the two elements versus the diameter of the IGM block. This sample was prepared by HIP without Cs-Cl free cover area. It can be seen, that the distribution is more or homogenous in the whole IGM block.

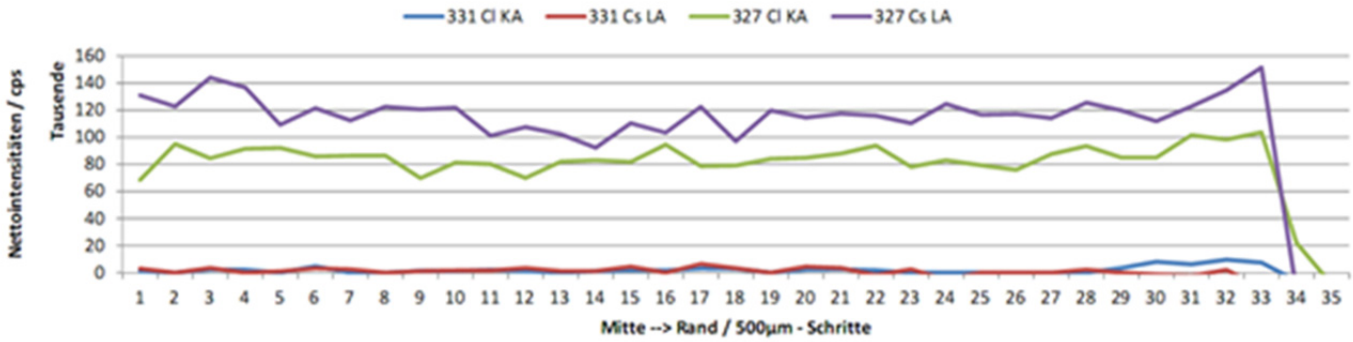

Figure 12: Cs and Cl distribution of IGM sample 327 manufactured by HIP

A different distribution has been revealed in IGN sample with an outer cover without CsCl prepared by HVP. 3 % CsCl has been added into the center part. The corresponding Cs and Cl distribution is indicated by the dotted lines in Figure 10. After pressing the Cl is concentrated in the center of the IGM block whereas the Cs shows a cylindrical distribution shown by the solid lines in Figure 10. An explanation for such a distribution could be the transport of CsCl during the heat up phase to the center of the block. The coldest zone of the sample is the center during the heating process from outside. Therefore, the mobile CsCl will be transported in this direction. Then the IGM is compacted by the pressing. The temperature gradient has an opposite direction in the following cooling phase. However the mobility is reduced in the high dense material. Only the more mobile Cs will be transport a small way to the outside. When the sample has been cooled below 800°C the transport is stopped and the distribution remains as shown in Figure 13. This explanation must be proofed by more detailed investigations which are outside the capabilities of FNAG. But anyhow it has been proven, that the manufacturing of IGM can be performed without losses of volatile Cs.

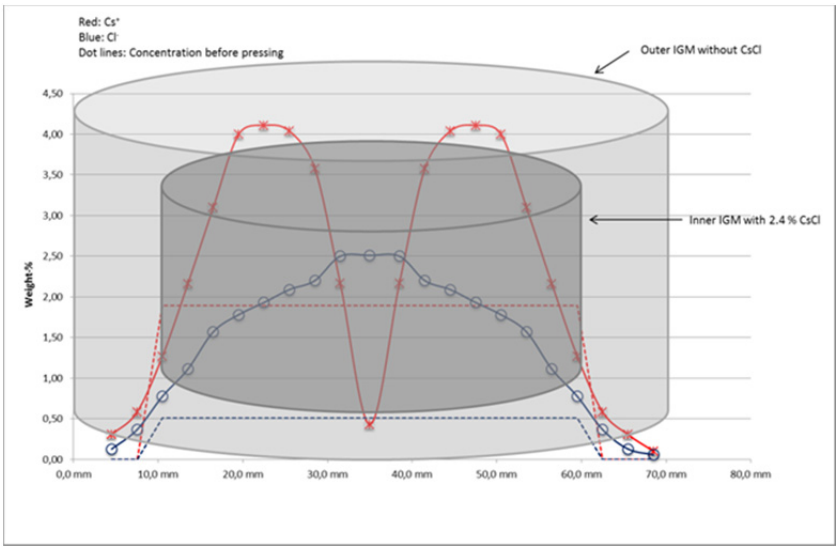

Figure 13: IGM with 3 % of CsCl in the center part and pressed by HVP

4. PROPERTIES OF IGM

4.1. Density

The impermeability of IGM is related to negligible porosity of the material. Densities near to theoretical density can be used as indicator negligible pore volumes. Therefore the density has been measured as selection criteria for further detailed measurements.

Figure 14 shows the obtained density of the HIP samples. The samples 255 to 258 have been pressed at 1000°C. The temperature was increased to 1100°C for the samples 321 and 323 The results reveal already high densities obtained by HIP better than 98% of theoretical density. However, densities of VHP samples are > 99% of theoretical density prepared at 1100 °C with a pressing force of 20 kN/cm². This is explained by the lower viscosity of the glass at the lower temperatures. Therefore, the temperature was increased to 1100°C for the samples 321 and 323. The average density was increased by this measure up to 99 % for the Glass 8250. The sample 321 with glass 8330 requires even a temperature above 1100°C to obtain densities > 99 % of theoretical density. IGM_HIP samples with glass 8800 had densities in the range of 2.25 which is about 99.8 % of theoretical density. This indicates that the pressing parameters for this IGM mixture are sufficient to obtain a nearly pore free material.

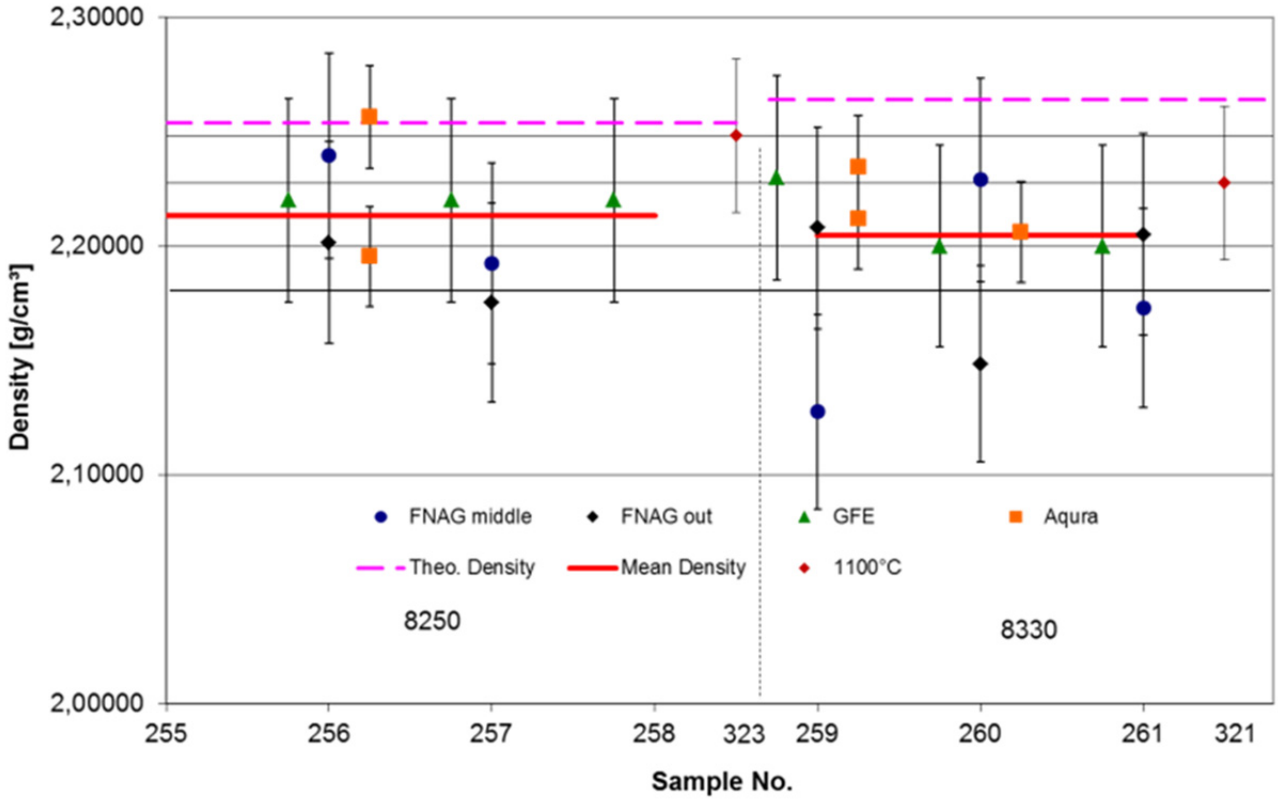

Figure 14: Density of IGM samples

4.2. Porosity

Computer Tomography (CT) scans were carried out with the XRadia MicroXCT machine by the University of Manchester to detect porosity within the material. One scan of a central region of interest was carried out per specimen. The voxel size achieved for all scans was 0.6 µm, corresponding to a reconstructed volume of 1.22 × 1.22 × 1.22 mm. Figure 15 shows the reconstructed orthogonal slices from a CT scan of samples NS321. Under the limits of the spatial and contrast resolution, porosity could not be detected in any of the samples. All samples showed a two-phase mixture of a higher (lighter pixel) and a lower density (darker pixel) material which is related to the distribution of the graphite and the glass.

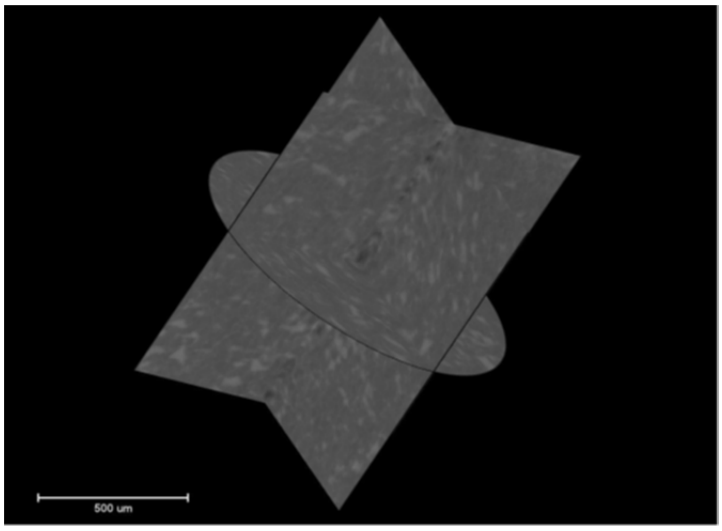

Figure 15: Central orthoslices of sample NS321

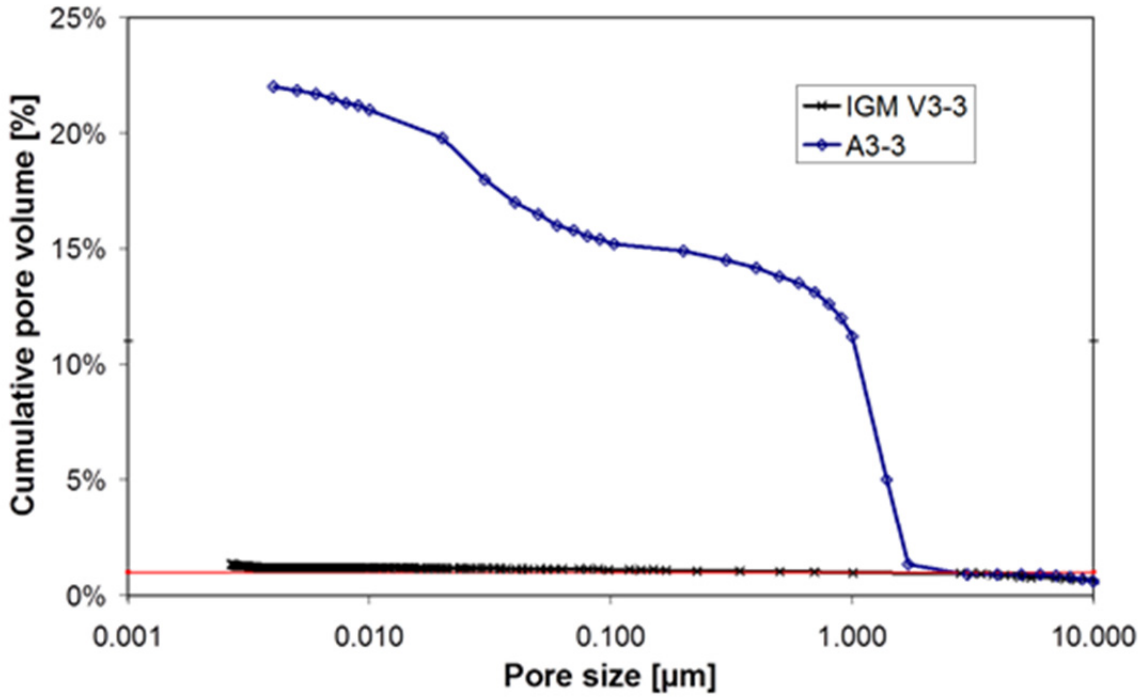

Figure 16: Mercury porosity measure of IGM sample and HTR fuel matrix material A3-3

This is in accordance with mercury porosity measurement performed with IGM samples prepared by VHP show in Figure 14. This IGM sample had density of 99.1 % of theoretical density. No pores were detected larger than 0.1 µm. Figure 16 shows additionally the pore size distribution of graphite like material A3-3 used as matrix material for HTR fuel pebbles. The majority of the pores have a pore size in the range of 1 up to 3 µm. This pore distribution is typical for most of the graphite material. Investigations of the water ingress into A3-3 revealed that the water uptake volume of A3-3 is related to the pore volume of pores > 0.8 µm. This could be explained by the hydrophobic character of graphite. The capillary repulsion forces become higher than the water pressure. The pore volume is also an indicator for the required amount of glass. Typically 20 % of glass is sufficient to obtain a pore-free structure.

4.3. Structure

Optical microscopy investigations have been performed to study the bulk distribution of the glass in the graphite. Figure 17 andFigure 18 show pictures of sample NS 260 prepared with virgin MAGNOX graphite. The graphite grain size was less than 0.5 mm. Figure 17 shows a picture taken at an outer edge of the sample. Figure 18 shows the middle of the samples. The comparison of the glass areas shows a nearly equal distribution of the glass in the graphite. Figure 19 shows also a larger graphite particle which remained as an intact particle. The occurrence of such grains was not observed often but raster electron microscopy (REM) of such grains revealed that the glass has also partially penetrated the graphite structure and fills the void space between the lamella. An EDX mapping (Figure 20) reveals this effect.

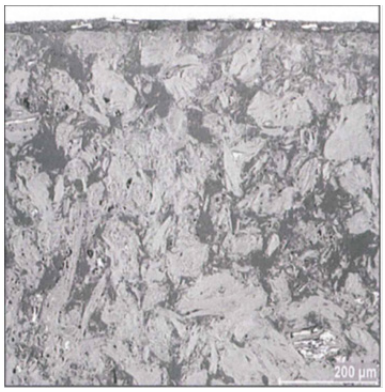

Figure 17: Sample NS 260 outer sample area

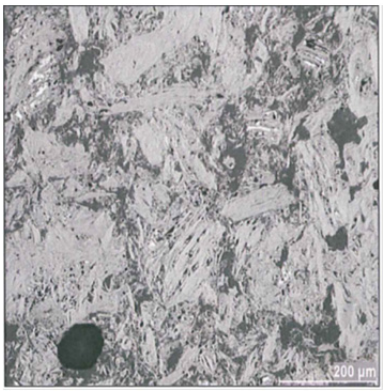

Figure 18 Sample NS 260 central sample area

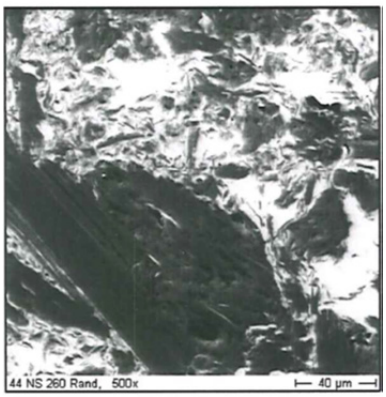

Figure 19: REM picture of a MAGNOX graphite grain in IGM

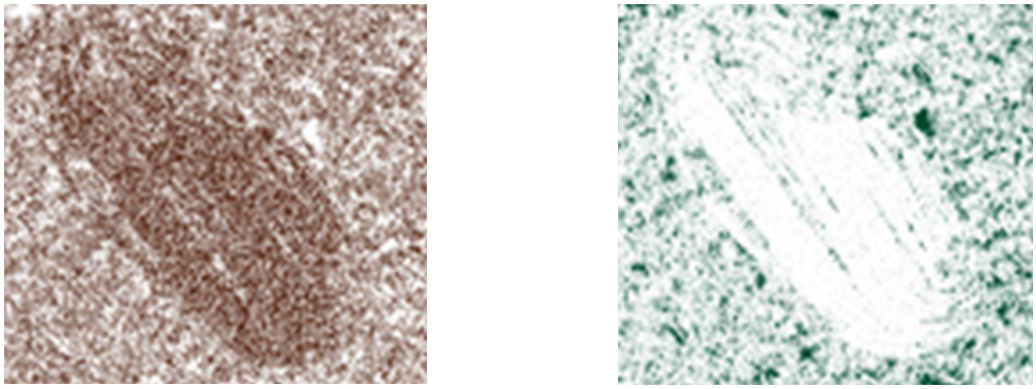

Figure 20: EDX map of graphite grain in IGM

a) Carbon b) Silicon

5. TEMPERATURE OF IGM MATRIX

High active waste will generate a temperature increase of the waste package depending on the load on the thermal properties of the package material. The temperature development of the IGM waste package has been calculated with the following assumptions:

- 200 l waste
- Waste load of 65 kg and 130 kg zeolites.
- Heat loading 0.3 W/kg zeolite
- Thermal conductivity of Zeolith 0.11 W/(m*K) /100 °C
- Thermal conductivity of IMG 97 W/(m*K) /100 °C
- Distance between waste packages 4 m (Center to Center)
- Temperature of surrounding air 25 °C
- Temperature of basement 25 °C
- Worst case (Heat transport in centre only by Zeolith):
- Load 65 kg 130 kg

- Temperature at can surface 27°C 28 °C
- Temperature in centre 61°C 97 °C
- Temperature taking in account heat conductivity of IGM:
- Load 65 kg 130 kg
- Temperature can surface 27°C 28 °C
- Temperature in centre 31°C 35 °C

IGM can withstand temperatures below the transition point of the glass which is about 500°C in case of glass 8800. Therefore temperature of 97°C with load of 130 kg of zeolite is acceptable even if the heat conductivity of the IGM matrix is neglected. However this is a worst case scenario which assumes that the zeolite is separated of the IGM in the center of the waste package. This is only theoretical possible. The normal temperature evolution of the waste package will 35°C maximum in the given geometrical arrangement.

6.0. CORROSION STABILITY

One important function of the IGM is the save enclosure of the radionuclides in case of a water ingress into the disposal side. Therefore, the corrosion behaviour of IGM with 13 different glass types has been studied by FNAG by long time leaching experiments in de-ionsed water as reference solution.

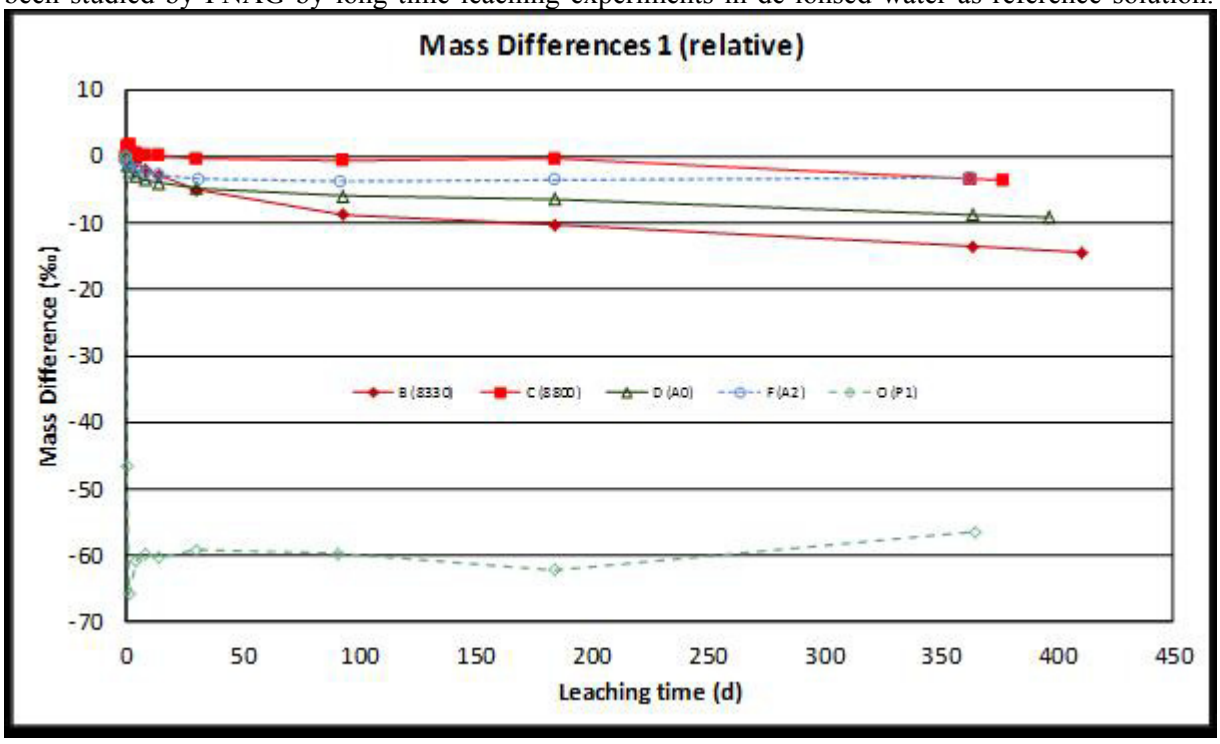

Figure 21 and Figure 22 reveal the weight loss of IGM samples in de-ionsed water as reference solution. All samples show a slide weight increase in the start phase. This is related to the hydrolysis of glass surfaces. This is followed by a mass loss phase which has a duration of up to 100 days followed by a more or less weight constant phase. The weight loss of sample C after 350 days is related to mechanical damage with a high probability. The glasses B, C, D and F showed the best corrosion stability and therefore they are selected for future investigations.

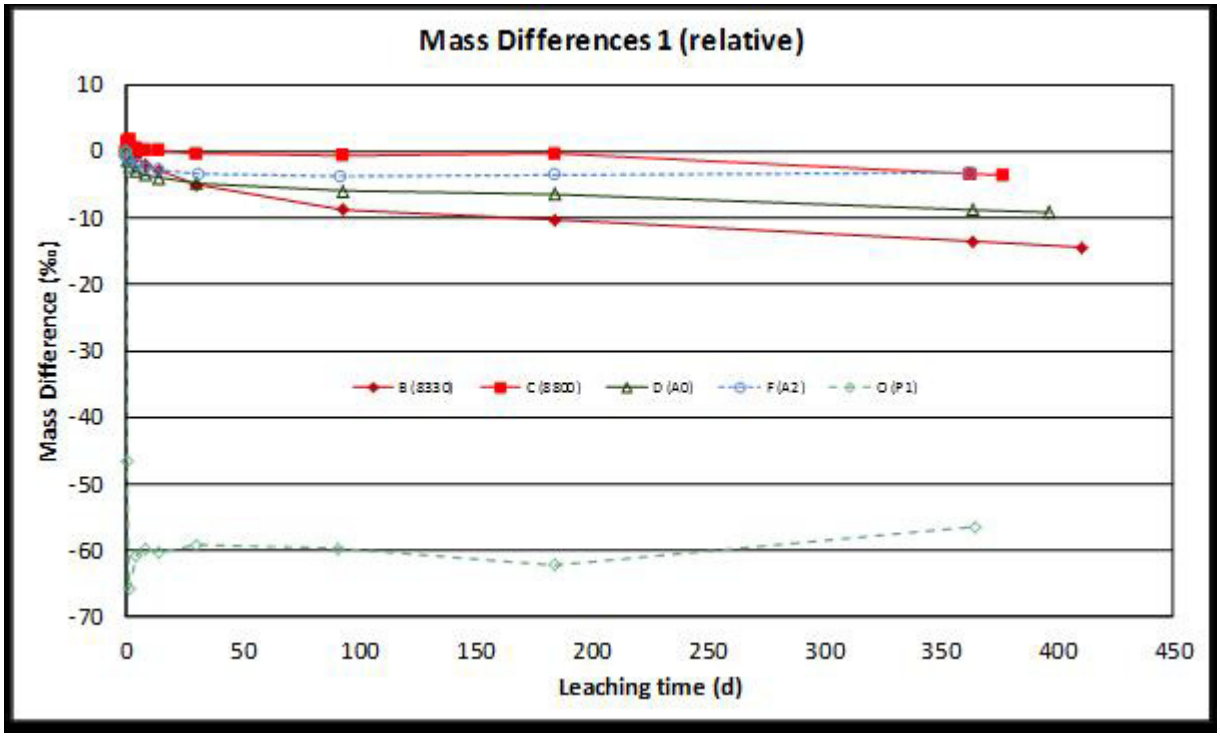

Figure 21: Mass loss of different IGM types in de-ionsed water (Part 1)

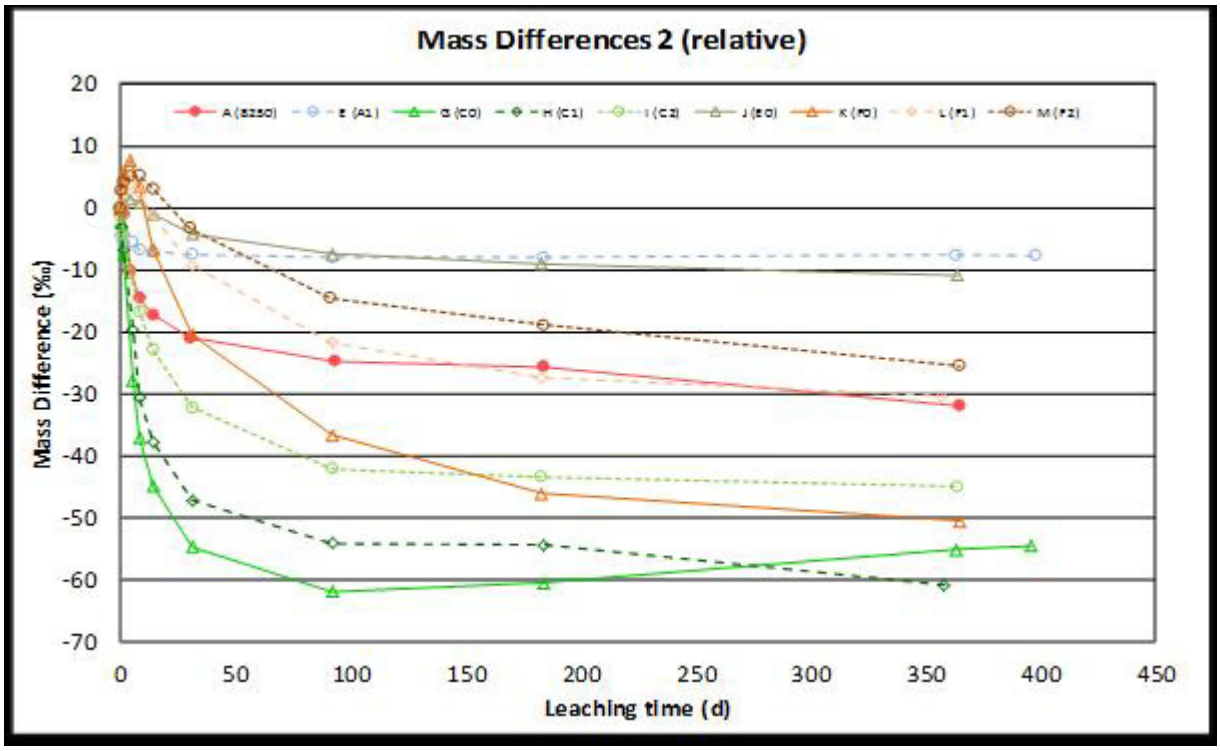

Figure 22: Mass loss of different IGM types in deionsed water (Part 2)

7. SUMMARY AND OUTLOOK

The investigations performed have shown with inactive simulants the irradiated graphite can be transformed into an impermeable graphite matrix suitable for embedding radioactive waste streams. The manufacturing can be performed with different manufacturing system whereas HIP seems to be

the most promising method for industrialization and HVP has been identified as a simple lab method to obtain small scale samples of comparable quality.

The encapsulation of different potential waste stream like spent fuel, inorganic ion exchangers or volatile nuclides like Cs-137 has been successfully demonstrated by with inactive analogues.

Furthermore, the determined physical and structural properties prove the save enclosure from surrounding host system. Especially the selection of the added glass binder has been reduced to four promising long term resistant glass types for further investigations under conditions more similar to potential disposal sites.

However, the final improvements must be performed with radioactive samples. Therefore it is foreseen to install a HVP in an isotope lab. This will allow the manufacturing of small samples with irradiated graphite and other radionuclides as tracers. The HVP is actually installed at FNAG Grenoble for inactive commissioning. The commissioning in an isotope lab is proposed for the first half of 2014. This work will be a collaborative project of ENRESA, CIEMAT and FNAG.

The set up HIP for radioactive material is planned by NNL in 2018. A collaboration contract of FNAG and NNL will be signed in January 2014 for the manufacturing of larger IGM samples with irradiated graphite and other radioactive waste materials.

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