Impermeable Graphite Matrix (IGM) for the Conditioning of Spent Absorbers at Fukushima - 14186

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ABSTRACT

Inorganic absorbers are applied during the purification of the several 100 000 m3 contaminated water at Fukushima Daiichi site. Their preparation for intermediate and later final disposal is challenging:

- They are highly loaded with radioisotopes, like Cs 134/7, with significant dose rates and heat generation resulting;
- They contain sodium chloride and other salts, typical for sea water.

Traditional treatment processes like cementation, melting, vitrification etc. face problems with respect to radiolysis, corrosion, non-compatibility with Chlorides, volatilization of Cs, etc.

The newly developed IGM (IGMImpermeable Graphite Matrix) process has been investigated concerning its applicability on such spent inorganic absorbers. Basically, the IGM process mixes graphite with some percent of borosilicate glass, and compacts the mixture under pressure and temperature of 1,000 bar and 1,000 °C respectively. The resulting matrix is virtually free of pores, and the well-known characteristics of graphite and glass, concerning chemical and mechanical stability, leaching resistance, heat conductivity make it the ideal matrix to embed radioactive waste. During tests with zeolites loadings of 60 % could be reached, maintaining the excellent properties of the matrix for the final product. Addition of Cesium and Chloride does not interfere. The technical application would make use of the HIP (Hot Isostatic Pressing) process, with HIP containers (e.g. 400 L) being filled with premixed IGM/waste, evacuated, and processed through HIP autoclaves.

INTRODUCTION

On March 11, 2011 a seaquake happened on the east side of Japan. The epicenter was 130 km east from the city Sendai on Japan´s main city Honshu. The Tohoku-Chihou-Taiheiyou-Oki seaquake was the strongest ever measured in Japan and 5th strongest worldwide causing a tremor at the magnitude of 9.0 and several tsunamis. Some of the tsunamis were more than 10 meters high, the maximum level reported was almost 40m.
In consequence of the seaquake all power plants on the northeast cost of Honshu disconnected themselves from the grid and turned into the emergency power supply mode, meaning that the emergency diesel generators were switched on in order to remove the residual heat. Among these power plants were also the ones at the Fukushima-Daiichi and Fukushima-Daiini sites.
Until then all events relating the nuclear power plants were in agreement with their design. However the nuclear power plants at the Fukushima sites were hit by a tsunami of 14m height. Due to the fact that the NPPs at both Fukushima sites are only 10 m above sea level and the emergency generators are not secured or sheltered against such flooding the generators were flushed with water and failed. In fact the generators were housed in the basement of the turbine buildings and the doors of the buildings were simple roller shutter doors that collapsed under the pressure of the water pushing against them (Fig. 1).

Due to this loss of power accident and the ongoing production of heat caused by radioactive decay of fission products it was necessary to cool the reactors externally.
Therefor fresh and later seawater were fed in using fire-fighting pumps. However, this measure was started too late and the cladding tube material of the fuel rods overheated, hydrogen was produced and caused explosions, also the uranium fuel melted. [1, 2]

WATER TREATMENT SYSTEM

As a result of the incidents described above thousands of m^3 of highly contaminated sea water flew into the basements of the reactor buildings. The contaminated sea water in the reactor buildings amounts to 400,000. The amount of the contaminated water increases daily due to penetration of rain and ground water into the damaged buildings. [2]
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In addition, similar amounts have been collected in tanks, already. And: the seawater in the harbor gets contaminated, too, and will require treatment.
Already in June 2011 The Tokyo Electric Power Company started water decontamination systems, which initially aimed to remove radioactive Caesium nuclides. In 2012, The Tokyo Electric Power Company has started to build a new treatment system to treat all of the contaminated water. The new system will also remove not only caesium isotopes but a total of 62 radionuclides, among them also Sr-90 [3, 4].
The core of the New Water Treatment System is the adsorption stage which contains 14 towers with ion-exchange media.

All of the mentioned water purification systems did produce and will produce huge amounts of spent absorbers, loaded with radionuclides of Cs, Sr, Co, TRU, and so on. In addition, some of the treatment processes (pH adjustment, flocculation, precipitation) generate radioactive sludge.
The amounts are not exactly known; for sure some thousand tons of such materials are to be expected.
The challenges in connection with the treatment of these materials are manifold:

- Activities up to 10^{15} Bq/t
- High content of Cs, which is volatile at high temperatures
- Heat loadings up to 0.3 W/kg
- High salt content (mainly sodium chloride) from the sea water

The spent materials are contained in vessels or cartridges, not ready for long term intermediate and final disposal.
The well-known and technically applied treatment processes and matrices like cementation, melting, vitrification etc. face problems with respect to radiolysis, corrosion, non-compatibility with Chlorides, volatilization of Cs, etc., clearly there is a need for a new matrix material.

MANUFACTURING OF IMPERMEABLE GRAPHITE MATRIX (IGM)

The base material for the manufacturing of Impermeable Graphite Matrix 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 even irradiated graphite e.g. from reflectors of graphite moderated power plants can be used as feedstock material.
Various glass types are under investigation which will be shown later. The final choice will be influenced by price and availability but the most important parameter should be the long term corrosion stability in aquatic phases. The glass 8800™ for Schott is recommended based on the available corrosion studies shown in the chapter on IGM properties.

The preparation of the IGM base mixture will be performed in batch or continuous mixer. Additionally the mixture can be granulated to obtain a higher filling density in the pressing die. The formation of the IGM is performed by hot pressing of the graphite glass mixture under vacuum at temperatures near to the softening point of the glass.

The inclusion of the radioactive waste can be achieved by mixing of a radioactive waste granulate with the IGM base material or insertion of lager waste parts into the moulding die partially prefilled with IGM base mixture. The direct mixing of the IGM granulate is the preferential method for ion exchange resins. Up to 60 vol. % of resin can be mixed with the IGM granulate.

The vacuum is required to avoid gas inclusions which would lead to porous structures. Several options are available to perform the pressing process:

- Hot vacuum pressing in an axial die (HVP)[5]
- Spark plasma sintering in an axial die (SPS)
- Hot isostatic pressing in a can (HIP) [6]

It has been shown that all methods will lead to an acceptable IGM. However the HIP has been chosen as best process for industrialising the manufacturing. Figure 1 shows the general scheme of the process.

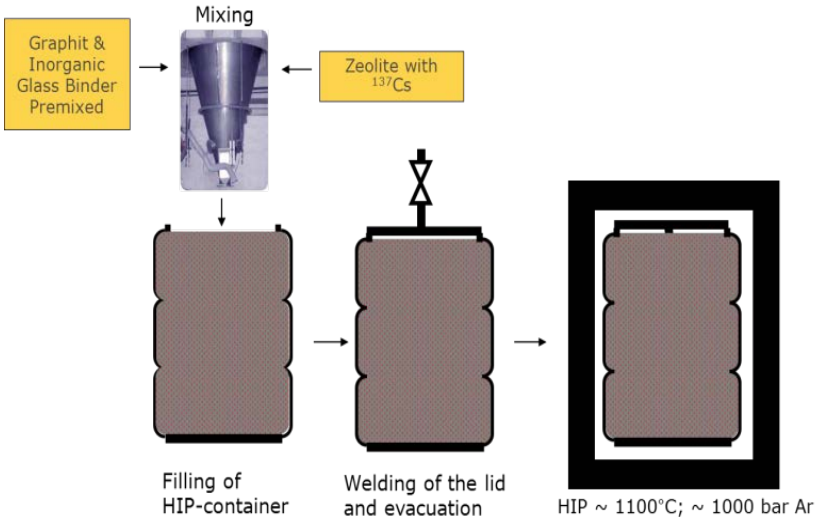

Fig. 1: HIP Process scheme

First of all HVP and SPS require complicate filling processes and open handling of filled moulding dies. This can be avoided in the HIP process where the IGM granulate mixed with the waste in filled into a metal can under vacuum and the can is sealed by welding directly after filling. Such a filling processes has been developed and already operated by ALD for filling of reactive metal powders into cans. Another advantage is the availability of large industrialised HIP systems with sizes of 2 meters diameter and 3 meters height as working space.

The Figure 2 shows a block scheme for a production line to embed radioactive ion exchange resins into IGM. The required production capacity is proposed with one IGM waste package of 200 l per hour. This is an equivalent on 200 t ion exchange resin per year.
The system contains of the following components:

- Mixer
- Filling station for HIP container
- Welding and evacuation station
- HIP vessel
- Cooling station

Total space requirement

- 100 m^2, 4 m height (8 m for HIP station)

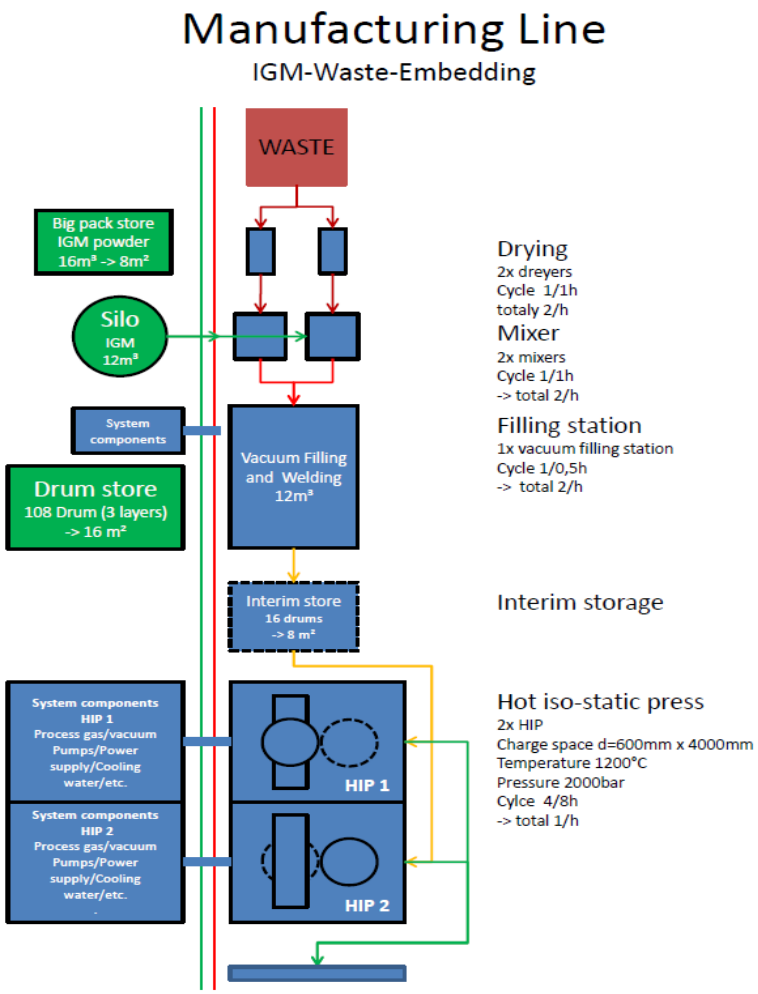

Fig. 2. Process line for embedding ion exchange resins into IGM

PROPERTIES OF IMPERMEABLE GRAPHITE MATRIX

Lab scale samples have been manufactured for investigation of the IGM properties by all three methods. For HIP the powder mixture was prepressed in the HIP can before evacuation and sealing of the can in order to increase the loading of the canister. Figure 3 shows a DB1 can with a volume of ~ 200 ml after HIP processing. Figure 4 shows the main parameters of the HIP process. The maximum pressure was 100 MP and the process temperature 1000 °C. This temperature was increased to 1100 °C for a second samples series

Fig. 2. DB1 can after HIP process

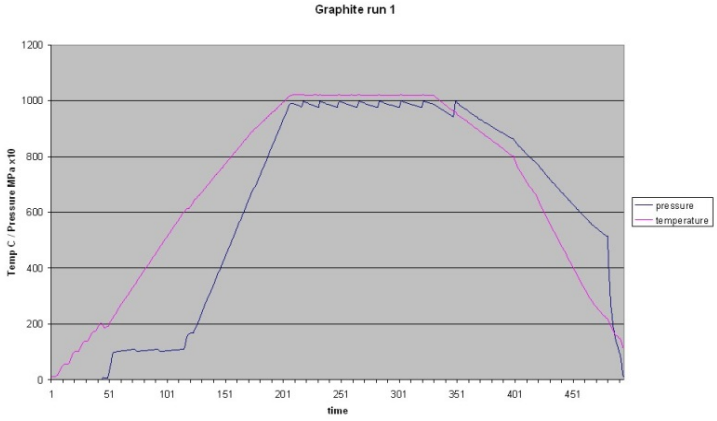

Fig. 4. Pressure and temperature during the HIP process of sample series 1 Density

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 7 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.

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 7 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.

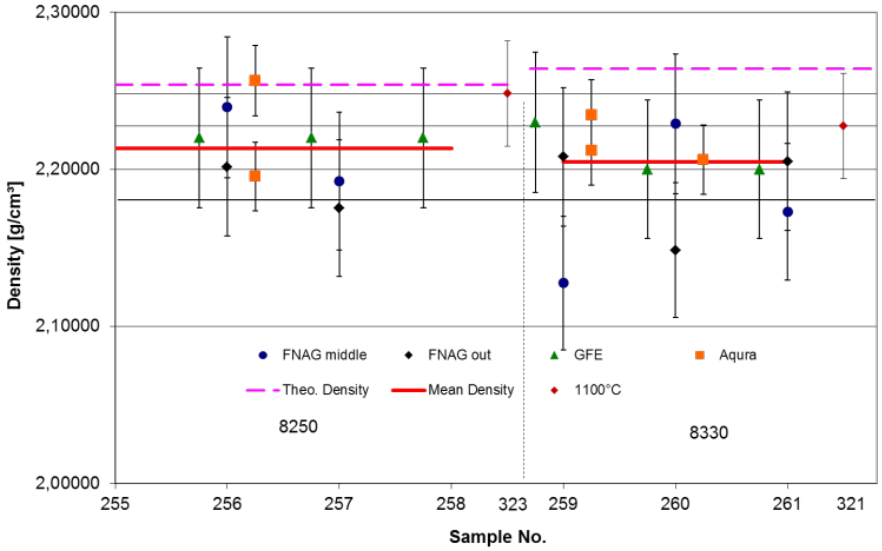

Fig. 5. Density of IGM samples

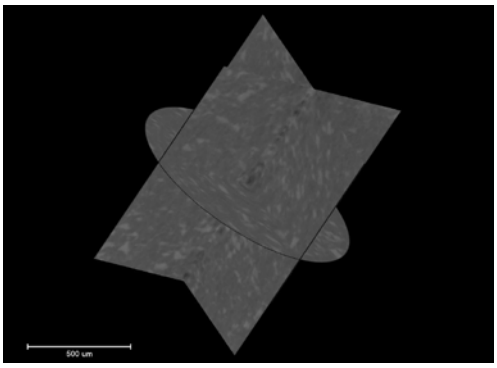

Fig. 3. Central orthoslices of sample NS321

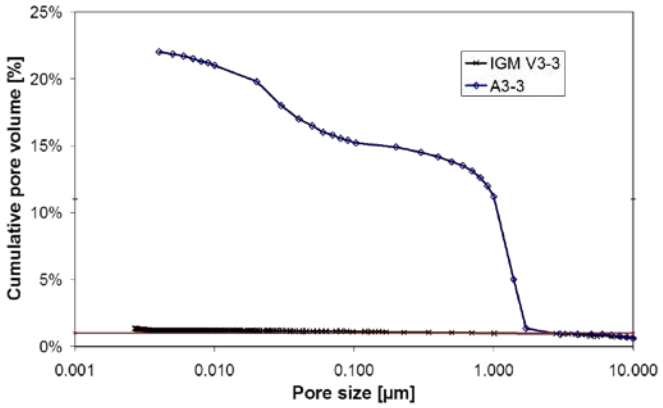

Fig. 4. Mercury porosity measure of IGM sample V3-3 and HTR fuel matrix material A3-3

This is in accordance with mercury porosity measurement performed with IGM samples prepared by VHP show in Figure 8. This IGM sample had density of 99.1 % of theoretical density. No pores were detected larger than 0.1 µm. Figure 8 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 [2]. 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.

CsCl Distribution

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 8** shows an EDX map of chlorine from an area near the edge of a slice and from an area in the centre of the slice. The intensity of the chlorine distribution shows no significant difference and indicates a homogenous distribution.
WDX analyses were performed along a line across a slice cut out of the middle of the sample. This method of detections has a higher sensitivity than that obtained by EDX mapping. The results are shown in Figure 9. A reference sample without CsCl shows no signal for Cs and Cl. The spiked sample shows a homogeneous distribution of Cs and Cl across the sample slice within the uncertainty of the method. The violet line for Cs may indicate a slight increase in concentration in the centre and outer regions.
These results indicate that Cs remains in the IGM matrix even during the processing at 1000°C.
Additional investigations showed that IGM with a load of 50 volume % of sea salt can be produced with an homogenous distribution of the salt in the IGM matrix.

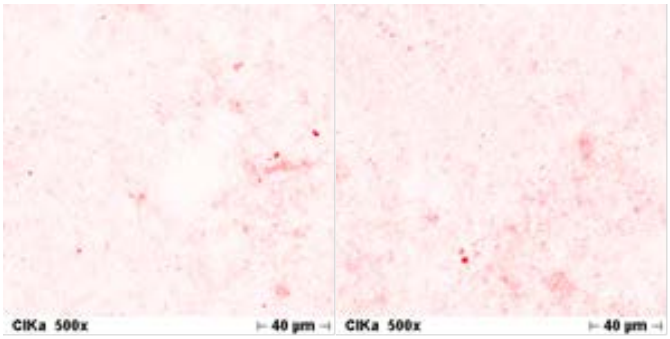

Fig. 5. EDX Cl map of sample NS 327
a) outer region b) central region of the sample

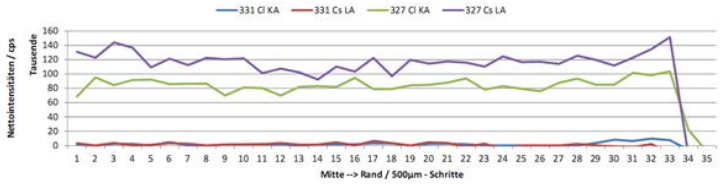

Fig. 6. WDS of across a slice cut from NS327 and NS331

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 center only by Zeolith):

Load	65 kg	130 kg
Temperature can surface	27°C	28 °C
Temperature in center	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 center	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.

CONCLUSIONS

The properties of IGM indicate that this new matrix material is an ideal material for the embedding of inorganic absorbers applied during the purification of the several 100 000 m3 contaminated water at Fukushima Daiichi site. The IGM is also capable to enclose larger amounts of sea salt as well as retain ^{137}Cs even the manufacturing is performed at elevated temperatures.

No radiolysis problems are expected same as for vitrified waste. Surface temperatures will low lower than for vitrified waste because of the high thermal conductivity of the IGM matrix.

The manufacturing of zeolite embed in IGM has been proved. Large HIP system are commercial available and industrialization of the process will be easy to achieve.

The ion exchanger embedded IGM will be a long term stable waste package suitable for interim storage and final disposal.

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