

Impermeable graphite: A new development for embedding radioactive waste and an alternative option of managing irradiated graphite - 10027

Johannes Fachinger, Karl-Heinz Grosse*, Richard Seemann**, Milan Hrovat**

* Furnaces Nuclear Applications Grenoble, Wilhelm-Rohn-Straße 35, 63450 Hanau, Germany

** ALD Vacuum Technologies, Wilhelm-Rohn-Straße 35, 63450 Hanau, Germany

ABSTRACT

Graphite is a geological stable material proven by its natural occurrence. However its porous structure affects the possible use of graphite as long term stable waste matrix for final disposal because slow corrosion in aquatic phases can be induced by high irradiation dose rates in the range of 2 kGy/hr and resulting in corrosion rates of 10^{-5} to 10^{-7} $\text{gm}^{-2}\text{d}^{-1}$. The porous structure is accompanied by a large surface area and therefore radiation induced corrosion processes cannot be neglected for final disposal. Furthermore aqueous phases will penetrate into the pore system and radionuclides adsorbed on the surface will be dissolved. These problems can be solved with a graphite material with a closed pore system. A graphite composite material with an inorganic binder has been developed with a density $> 99.7\%$ of theoretical density and therefore a negligible porosity. An initial calculation predicts that the lifetime of the graphite will be at least 2 orders of magnitude greater than porous graphite.

This material represents a long term stable leach resistant matrix for the embedding of irradiated graphite (i-graphite). Granulated i-graphite is mixed with natural graphite and an inorganic binder and pressed into a block. Other radioactive wastes can be embedded in this matrix, e.g. coated particles of spent fuel from high temperature reactors (HTR) reactors.

INTRODUCTION

Graphite is an inert high temperature resistant material which is used in industry for many applications e.g. as crucibles for molten metals, fireproof products, fuel cells or electrodes [1-2]. Its long term geological stability is proven by the natural occurrence of graphite formed in the Precambrian age [3] which indicates that it has applicability as host matrix for radioactive waste. Only slow corrosion can be induced by high irradiation dose rates (γ -dose rate ~ 2 kGy/h) due to the formation of aggressive species from water radiolysis. Corrosion rates were observed in the range of 10^{-5} to 10^{-7} $\text{gm}^{-2}\text{d}^{-1}$ [4]. However investigations of the final disposal behavior of HTR fuel elements, which consists of embedded coated fuel kernels in graphite, revealed that the porous structure of graphite affects the utilization of graphite as an embedding material for radwaste [5]. This leads to the conclusion, that graphite with a sealed pore system will be a suitable long term stable waste matrix. Many attempts have been performed to overcoat graphite for this purpose. But considerations of mechanical stability of thin layers as well as corrosion behavior could not guarantee a safe long term enclosure. Impregnation with resins or other organic components leads to a reduction of porosity but not to total enclosure or were in conflict with other disposal requirements, e.g. bitumen with respect to fire hazards [6].

The new development of an impermeable graphite matrix is based on complete filling of the graphite pore system by an inorganic material with the following properties to form a homogeneous matrix material:

- filling the pore system without increasing the volume to obtain densities near theoretical density
- adequate corrosion resistance
- available industrially or easy to produce
- backed by data concerning behavior under final disposal conditions
- able to penetrate into small graphite pores at elevated temperature

Borosilicate glass was identified as the most suitable material to fulfil these requirements and allow the manufacturing of a long term stable impermeable graphite matrix (IGM).

A second advantage of this new development is that it can use irradiated graphite (i-graphite) as feedstock material. About 250,000 tons of i-graphite worldwide must be considered as existing waste or a future waste stream in the next centuries. The major national i-graphite amount is located in UK (~ 80,000 tons) followed by Russia and France. Most of the i-graphite is still in the cores of nuclear reactors which have been shut down (MAGNOX type in UK and UNGG in France). Operational reactors with graphite cores are the Russian RBMKs and the AGRs in UK. All of them will reach their end of life during the next two decades.

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 of these blocks in a container without further conditioning. This requires large volumes because the large cavities in the graphite blocks reduce the packing densities to 0.5 to 0.8 tons per cubic meter.

^{36}Cl and ^{14}C haven been identified as the key radionuclides for long term safety of this disposal option due to their long half life, biocompatibility and mobility [4]. Because the ^{36}Cl inventory in French graphite exceeds the licensed inventory for surface burial an underground disposal site in a depth of 50 to 200 m is proposed for the final repository. In Germany the ^{14}C inventory of graphite core in the prototype HTR reactor AVR would require most of the licensed ^{14}C inventory of the proposed low level disposal site “Konrad”. Additionally the radionuclides are not homogeneously distributed in the graphite matrix. Therefore a preferential leaching cannot be excluded.

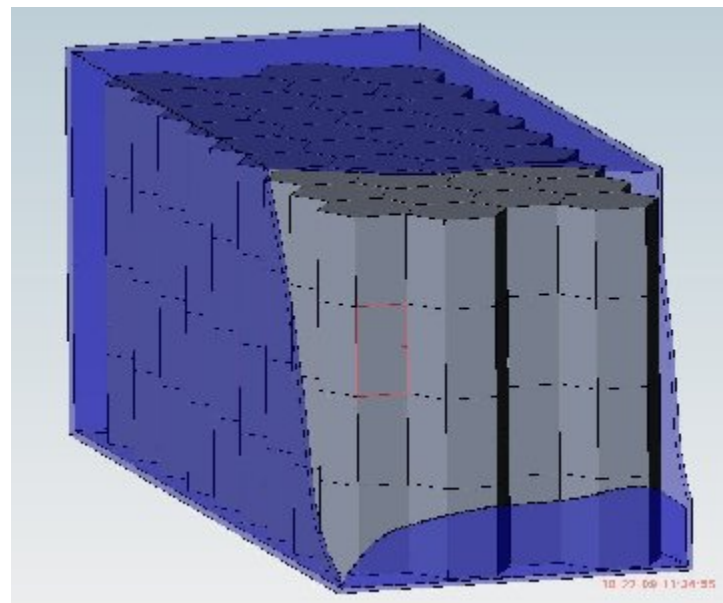
The proposed impermeable graphite material (IGM) would reduce the required disposal volume as well as provides a high leaching resistance and therefore increased safety features.

PRODUCTION OF IGM FROM I-GRAPHITE

The first manufacturing step after retrieval of i-graphite from the reactor will be crushing and milling down to a suitable size which can be mixed with glass powder. Some natural graphite can be added to the mixture to increase the mechanical stability of the final product if required. The mixed powder will be pre-molded to a green body. Next step will be the coating of the green body with a natural graphite glass mixture with a second pre-molding procedure to form a non-

radioactive outer shell around the contaminated inner green body. This outer shell guarantees handling without the risk of contamination during the operational phase and prevents leaching of contaminations from the surface of the green body produced first. The thickness of this outer shell should be in the range of 1 to 5 cm. The final manufacturing step is a hot pressing procedure under vacuum. The vacuum is required to remove air out of the graphite pores which would reduce the required density and increase porosity.

An additional granulation and grinding process could be included before pre-molding to increase the packing density to reduce both the press stroke in the pre-molding step and the anisotropy of the final product.



Initial small scale samples have been produced to demonstrate the principal applicability of the process. The materials and the process parameters are given in Table 1.

The proposed size of the final IGM product will be in the range of 600 mm diameter and 1000 mm length but the dimensions and shape can be adapted to achieve an optimized package density in a waste container (Fig. 1). Hexagonal forms can be produced with a high probability and quadratic may be achievable. Optimized package densities have been estimated as 1.5 to 1.6 tons i-graphite per cubic meter for hexagonal blocks.

Fig. 1: Container filled with IGM blocks

Table 1: Main manufacturing parameters and sample dimensions

Graphite	Natural nuclear grade graphite from GK Kropfmühl, grain size ~ 30 µm
Glass	Type 8250 from Schott, Grain size ~ 30 µm
Press temperature	~ 1150 °C
Pressing force	40 MPa
Vacuum	~ 10 mbar
Sample diameter	80 mm
Samples height	60 mm

PRODUCT PROPERTIES

Mechanical properties

The compressive and transverse bend strength of IGM samples has been measured by RWTH Aachen and GFE Freiberg. Cubic samples with a side length of 20 mm at GFE and 10 mm at RWTH Aachen were used for the measurement of ultimate compressive strength. The compressive strength has been measured parallel and perpendicular to the pressing orientation at the RWTH Aachen. Information about orientation is not given for the samples at GFE. The results of both organizations are consistent in the range of expected error margins (Table 2). However these measurements are not sufficient to give representative material properties which require a statistical representative number of samples. This is also true for the ultimate bending strength values given in Table 3. But the obtained results reveal an increased compressive and bend strength in comparison to A3-3 HTR fuel matrix graphite.

Table 2: Ultimate compressive strength

Sample	Organization	MPa
#2/5*	GFE	52
#3/4*	GFE	71
#3/5*	GFE	63
#1/5-1 II	RWTH Aachen	56
#1/5-2 I	RWTH Aachen	79

Table 3: Ultimate bending strength

Sample	Geometry			Organization	σ_f [Mpa]
	b [mm]	h [mm]	l [mm]		
#2/6 I	5	5	45	GFE	22.4
#2/7 I	5	5	45	GFE	27.7
#2/8 I	5	5	45	GFE	31.8
#1/7 I	10	10	50	RWTH Aachen	19.5
#3/3 II	5	5	45	GFE	19.2
#3/5 II	5	5	45	GFE	18.5
#3/6 II	5	5	45	GFE	10.3
#1/4 II	10	10	50	RWTH Aachen	9.2

Open Porosity

The open porosity of IGM samples has been investigated by mercury porosity measurement. Figure 2 shows the pore volume distribution of IGM in comparison to an A3-3 graphite. The red line represents the detection limit of the measurement as a straight line parallel to the x-axis. This does not represent the increase of the detection limit for small pores and therefore it is a conservative assumption. The main open pore volume of the A3-3 material is related to a pore size of about 2 μm down to 0.8 μm . No open pores have been observed for IGM in this pore size range. Water ingress experiments showed that open pores of this size can be accessed by water whereas smaller pores will not be penetrated [7]. Maybe this will be shifted towards smaller pore sizes under high pressure but a penetration of micro-pores seems to be not probable. In case of IGM a small pore volume of pores < 0.2 μm cannot be excluded by this measurement.

This is probably related to the conservative assumption of the detection limit. But anyhow it is unlikely that pores of this small size will contribute to a water penetration of the IGM.

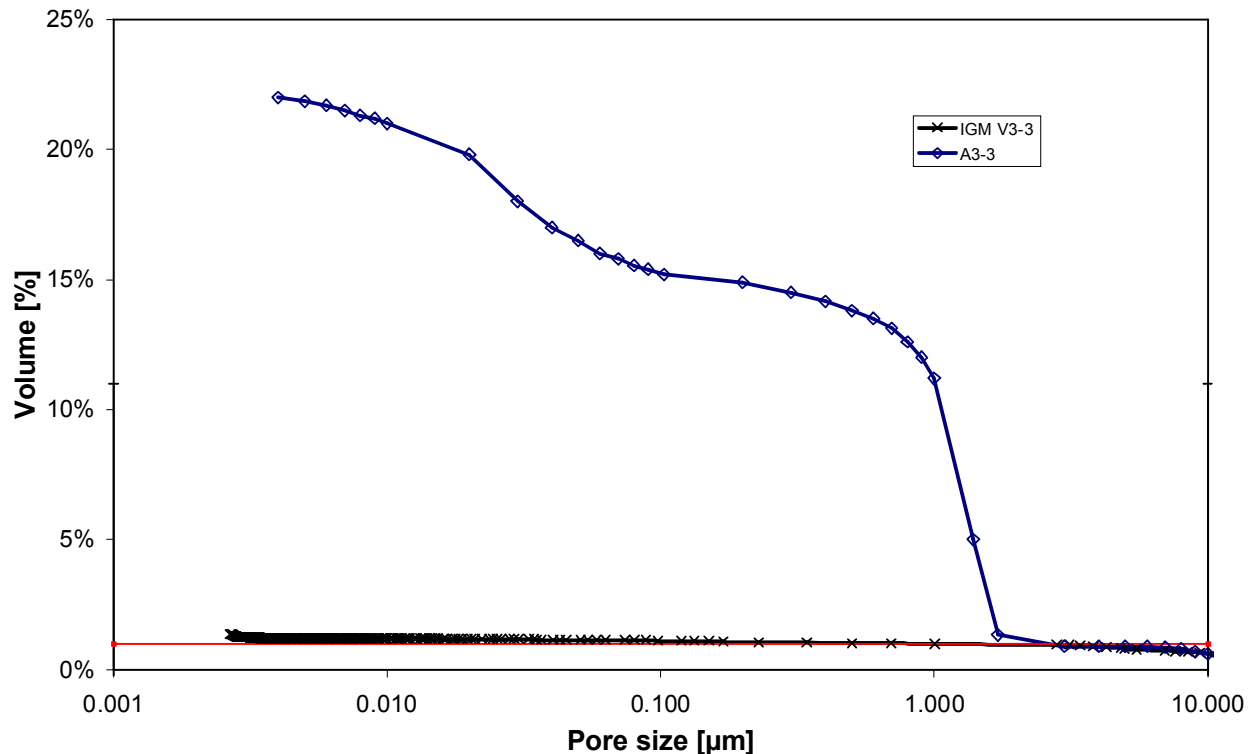


Fig. 2: Mercury porosity measurement of IGM and A3-3 graphite

Structure

Raster electron microscopy (REM) investigations and energy dispersive x-ray examinations (EDX) has been performed at GFE, RWTH Aachen and FZ Jülich. REM investigations of IGM samples at FZ Jülich showed that the glass is percolated between graphite particles and confirmed the pore free structure already obtained by the mercury porosity measurement. Small in-homogenous zones were observed with REM and EDX investigations at GFE. Figure 3 shows such an area with an increased carbon and decreased glass concentration which is related to single larger graphite particle. The carbon and silicon distribution shows the penetration of glass into microcracks of the graphite. This indicates that the glass wets the graphite as well as the percolation of glass into the graphite.

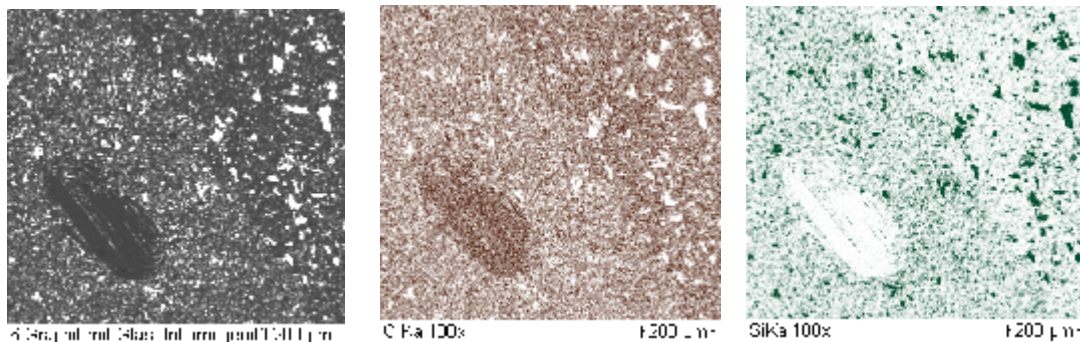


Figure 1: IGM with a larger graphite particle inhomogeneity

MODELLING THE CORROSION BEHAVIOUR

Graphite corrosion has been determined on fine graphite powders under final disposal conditions for the lifetime prediction of HTR fuel spheres. No graphite corrosion was observed in aqueous phases without irradiation. Measurable corrosion rates from 10^{-5} down to 10^{-7} g/m²d were only found in with high γ -dose rates in the range of 2 kGy/h [4] as a result of the formation of aggressive species formed by radiolysis. High chlorine concentrations lead to higher corrosion rates as result of the formation of reactive oxychlorine species.

To model the lifetime of a 6 cm fuel sphere, the pore system of the graphite was simplified by representing it as tubes with a diameter of 6 cm length and a diameter of 1 μ m whilst conforming to a pore volume of 20%. The model neglected any transport phenomena and corrosion rates from graphite powder have been applied for the calculations. This leads to total calculated carbon corrosion of a 6 cm A3-3 graphite pebble in 1000 to 100000 years on whether the presence of chlorine was assumed or not. This is shown in figure 4 by the open symbols.

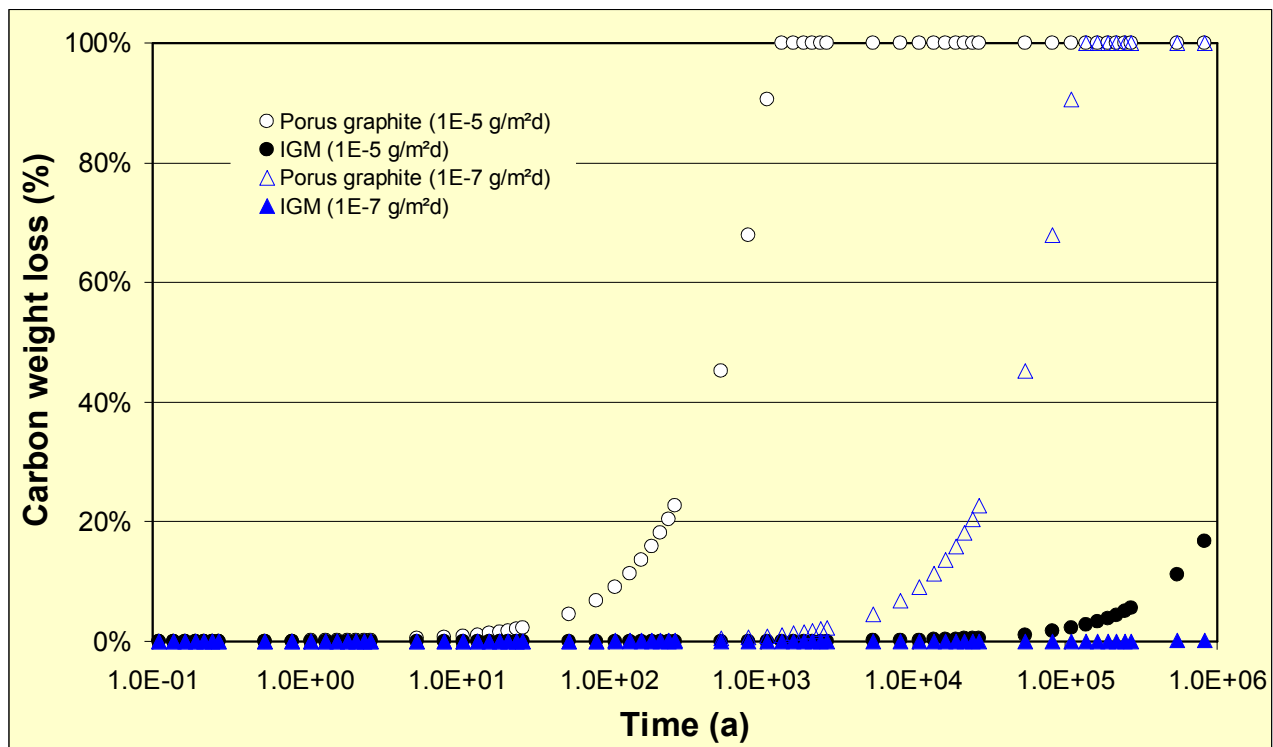


Fig. 4: Simplified model calculation for the corrosion of graphite with a closed pore system.

For the carbon loss of the IGM material the model was modified by assuming a total filling of the pores by glass. This reduces the carbon surface accessible for corrosion to the geometric surface minus the surface of the pores. Then a glass corrosion rate of 10^{-4} g/cm²d was assumed. As before no transport phenomena or secondary phase formation of the glass has been considered for the glass corrosion. This leads to a slow opening of the pore system and the carbon surface increases. The effect on carbon corrosion is shown in figure 4 by the closed symbols.

Only 20% of the carbon would corrode in 10^6 years. This simple model does not claim to describe the reality or the lifetime of IGM but it shows clearly the prolongation of the life time of the IGM material under disposal conditions.

CONCLUSIONS

The work reported in this paper illustrates the principal application of the IGM material for long term safe disposal of i-graphite. The first important step, the manufacture of pore free graphite material, has been demonstrated.

Future work is connected to the demonstration of the long term stability of the material. As a result experiments with nonradioactive IGM materials are foreseen by the production of laboratory scale samples with i-graphite for leaching experiments. These will be accompanied by the development of improved glass materials and the optimization of the production process. For example hot isostatic pressing is considered as an alternative to vacuum hot pressing.

In the longer term IGM blocks with cavities are in discussion for the incorporation of other waste material such as Iodine bearing materials or metal slurries from reprocessing. In addition the direct embedding of HTR fuel pebbles, coated particles or CANDU fuel elements is considered as a possible future option for the use of IGM.

REFERENCES

1. Graphit – Wikipedia. <<http://de.wikipedia.org/wiki/Graphit>>
2. Graphit Kropfmühl AG <<http://www.graphite.de/englisch/index.php?menueID=74>>
3. E. Crespo et al.; Significance of graphite occurrences in the Aracena Metamorphic Belt, Iberian Massif. Geological Magazine 146, 687-697(2004).
4. J. Fachinger; Inventory of Reactor Graphite and Treatment for Disposal. Proceedings of the RADWAP 2008 in Press(2008)
5. J.Fachinger et. al.; Behaviour of spent HTR fuel elements in aquatic phases of repository host rock formations. Proceeding of the HTR 2004, Peking (2004).
6. B. Marsden, A. Wickham; Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors. IAEA TEC DOC 78(IAEA: Vienna, 2006) <http://www-pub.iaea.org/MTCD/publications/PDF/te_1521_web.pdf>
7. J. Fachinger; Aqueous phase ingressions into non-irradiated graphite. Internal report of the EC Project “RAPAEL” (FZJ: 2005).