CEMENTATION OF NUCLEAR GRAPHITE USING GEOPOLYMERS

N.A. GIRKE*, H-J. STEINMETZ*, A. BUKAEMSKY*, D. BOSBACH*

* Institute of Energy and Climate Research - Nuclear Waste Management-,
Research Centre Juelich GmbH, D-52425 Juelich, Germany

E. HERMANN**, I. GRIEBEL**

** B.P.S. Engineering GmbH, D-08066 Zwickau, Germany

Abstract

Geopolymers are solid aluminosilicate materials usually formed by alkali hydroxide or alkali silicate activation of solid precursors such as coal fly ash, calcined clay and/or metallurgical slag. Today the primary application of geopolymer technology is in the development of alternatives to Portland-based cements. Variations in the ratio of aluminium to silicon, and alkali to silicon or addition of structure support, produce geopolymers with different physical and mechanical properties. These materials have an amorphous three-dimensional structure that gives geopolymers certain properties, such as fire and acid resistance, low leach rate, which make them an ideal substitute for ordinary Portland cement (OPC) in a wide range of applications especially in conditioning and storage of radioactive waste [1].

Therefore investigations have been initiated on how and to which amount graphite as a hydrophobic material can be mixed with cement or concrete to form stable waste products and which concretes fulfil the necessary specifications best. As a result, geopolymers have been identified as a promising matrix for graphite containing nuclear wastes. With geopolymers, both favourable properties in the cementation process and a high long time structural stability of the products can be achieved.

Investigations include:

- direct mixing of graphite with geopolymers with or without sand as a mechanically stabilizing medium
- production of cement-graphite granulates as intermediate products and embedding of these granulates in geopolymer
- coating of formed graphite pieces with geopolymer

The report shows that carbon in the form of graphite can both be integrated with different grain size spectra as well as shaped in the hydraulic binder geopolymer and meets the requirements for a stable long-term immobilisation.

1. CHEMICAL BASICS

1.1. Geopolymers

The chemical reaction that takes place to form geopolymers follows a multi-step process:

1. Dissolution of Si and Al atoms from the source material due to hydroxide ions in solution;
2. Reorientation of precursor ions in solution; *and*
3. Setting via polycondensation (Figure 1) reactions into an inorganic polymer (actually a crystalline-like lattice).

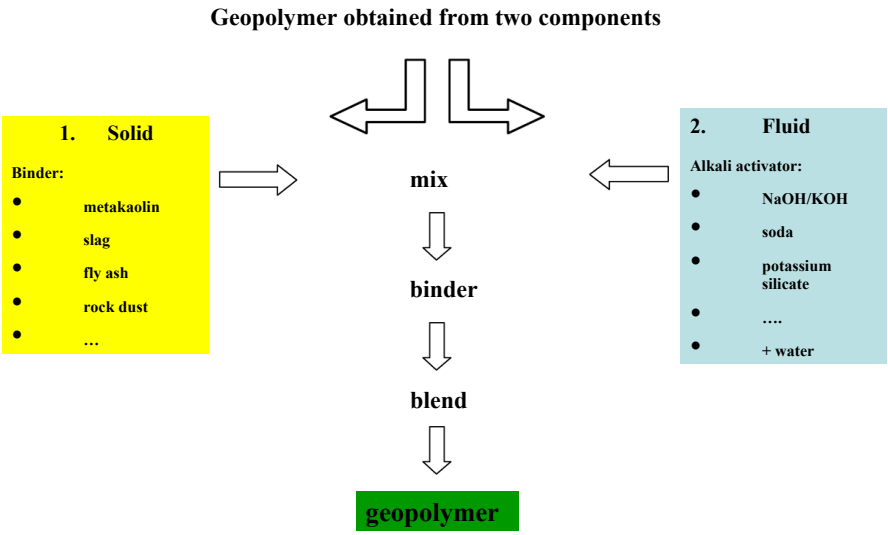

FIG.1 Principle of polycondensation: Geopolymers formed at high pH values (> 12) and room temperatures (about 20 ° Celsius)

The resulting three-dimensional inorganic polymerhydrates are amorphous in nature. The properties arise primarily from the manufacturing method, the concentration of the alkaline activator, and the moisture content.

Geopolymers are characterised by the following properties:

- Curing at room temperature
- Very high compressive strength
- Long term stability
- Resistance to acids and sulfates
- High mechanical stability
- High structural integrity
- Heat resistance

Geopolymers based on high temperature materials with a resistance up to 1200°C are used for fire protection. In the field of fire resistant materials geopolymers are used for casting tools of corrosive aluminium / lithium alloys. Binder in building materials is produced with geopolymers to reduce the proportion of cement or to ensure a faster cure. Another factor is the use as a binder for inorganic compounds and highly toxic radioactive material, because the geopolymer waste products show higher leach resistance. The big difference between geopolymers and regular Portland cement is that their setting mechanism does not depend on hydration, but rather in a polymerization, which happens in a short period of time, while cement's hydration is mostly completed within one month, and fully completed only after one year [2].

In research, different materials for the conditioning of radioactive waste have been studied and used. Today to a large extent, the consolidation is applied with cement. The hydration process is unfavorable because of the requirement for water, which may contribute to container corrosion.

Other materials such as epoxy or bitumen, have a very low thermal stability and low flammability in the case of a fire.

1.2. Nuclear Graphite

Graphite waste arises from different sources such as moderator and reflector of neutrons in more than 100 nuclear power plants and in many research and plutonium-production reactors worldwide. About 250,000 tonnes have already been accumulated worldwide, originating from different reactor types

and retrieval options (MAGNOX, UNGG, AGR, HTR, RBMK, MTR, TRIGA etc.) These graphite may contain various long-lived radioisotopes such as ^{14}C, ^{36}Cl, ^{3}H, ^{129}I, ^{99}Tc, ^{79}Se, ^{135}Cs and others.

Radioactive graphite has to meet special conditions in order to fulfil specific waste acceptance criteria for the disposal. Therefore the treatment of radioactive graphite has become an important issue [3].

^{14}C is one of the main contributors to the total radioactivity of the irradiated graphite. For the KONRAD repository in Germany the ^{14}C inventories of radioactive wastes or waste products are classified according to release rates of volatile ^{14}C under operating and accident conditions of the final repository.

^{14}C transformed to CO_2 may be immobilized by carbonatisation in alkaline media. For this purpose it seems to be favourable to embed reactor graphites in cement matrices. Under appropriate conditions CO_2 should be able to react with in the alkaline pore water or with alkaline functional groups to form carbonates within the waste product [4].

Moreover, for the KONRAD repository, the maximum mass of graphite in a waste package is limited if the waste container (Figure 2) also contains fissile material [5]. The mass of a loaded container must not exceed 20 mg dust. Usually, if containing fissile materials are included, only 42 kg of graphite are permitted in this container and 420 kg if the graphite and the fissile material are not mixed.

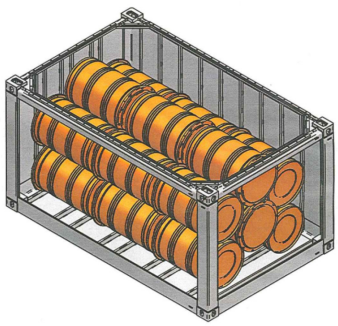

FIG.2. Type V KONRAD-Container netto volume = 10,9 cbm. Permitted graphite load: 42 kg if mixed with fissile material or 420 kg without fissile material

In most cases the free volume in a container is filled with concrete to stabilize the waste package and to utilize higher activity limits. Thereby the volume of the waste may be reduced if the graphite is grained and mixed with the concrete.

The volume of the graphite-containing materials is relatively large compared to the radionuclide inventory and can be used as low-level, non-heat-generating waste. As disposal costs are volume-based, an additional reduction in volume would lead to considerable savings. Furthermore, the total inventory of ^{14}C graphite waste is so high that over 75% of the ^{14}C storage capacity of the KONRAD repository would be exhausted. Thus, the direct disposal of such a waste form does not make sense.

2. INVESTIGATIONS

2.1. Graphite mixtures

For the investigations the following samples were available (Figure 3):

- powder with an average grain size of 7 µm - 10 µm
- granules max. grain sizes of 1 cm - 1.5 cm
- a spherical form with a diameter of 6 cm

- granules max. grain sizes of 1,25 mm - 4.0 mm

With the amount of available material, specimens in a cylindrical shape could be produced. The average dimensions are: diameter about 3 cm and height about 5 cm (Figure 6). As the immobilization process is initiated by the geopolymer formation of the alkaline activators, i.e. the geopolymer basic mixture has a high pH value and the alkaline potential breaks down very slowly, the chemical stability of graphite over the alkaline activators was studied. The graphite samples were exposed for more than 30 days in the activator mixture outsourced. The resistance is given for all graphite grades. For the products commonly used the powder and activator components are processed by intensive mixing to form a homogeneous mass / mortar. In this mortar then for immobilization graphite is added by intensive mixing. This mixture can then be poured into any form. This was implemented with the available graphite grades.

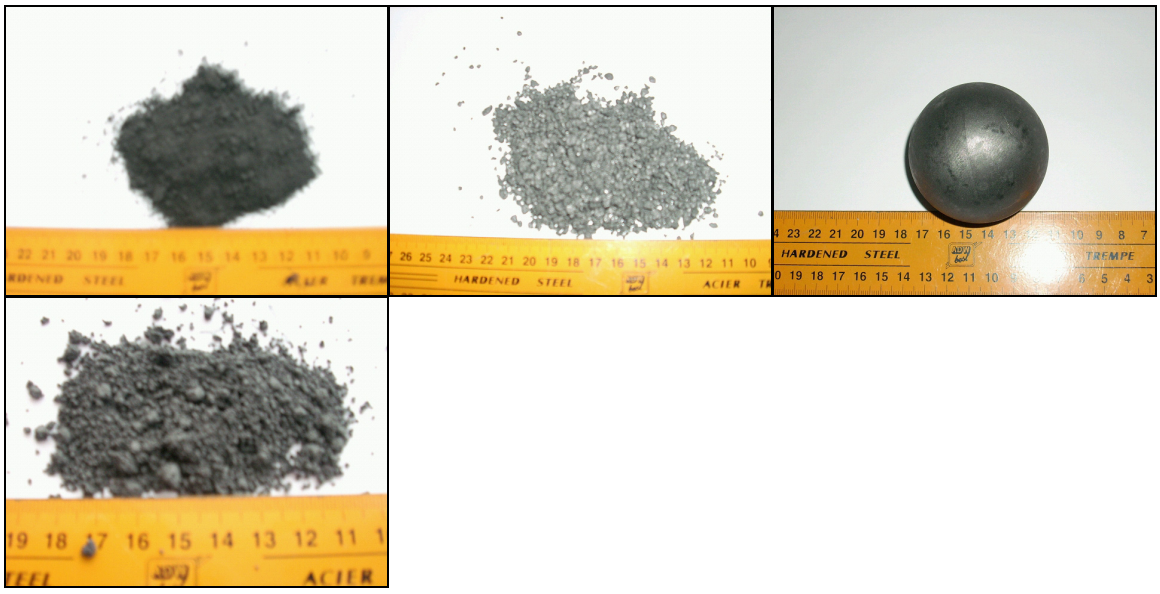

FIG.3: top left: powder (size 7-10 µm) top right: granules (max. size 1,5 cm) bottom left: spherical form (ø 6 cm) bottom right: geopolymer mixed with sand (J50)

2.2. Graphite absorption capacity of the basic geopolymer mixture

The capacity of a mortar / hydraulic binder is also dependant upon the aggregate size spectrum. For granular graphite powder amounts this statement is also applicable. Most effective and with largest amounts, samples can be processed in a wide range of grain sizes.

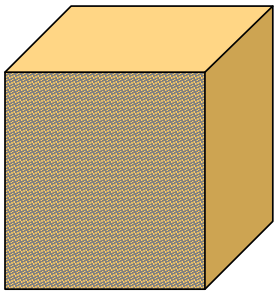

FIG.4:Sketch for the direct involvement of graphite powder or granules in geopolymer

2.3. Special case graphite forms

For formed graphite, like cylinders or spheres, direct mixing of the forms is considered. Graphite forms can be included bt mixing with a support structure made of sand into a geopolymer, when the densities of the basic mixture and the graphite forms are similar. The density of the geopolymer basic mixture can be influenced by the choice of the support structure. If the density is not taken into account, there is a demixing of the mortar of the graphite form possible.

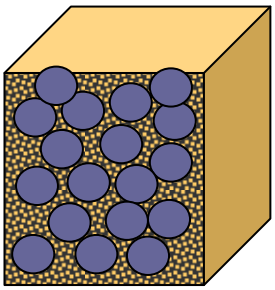

FIG.5: Graphite cylinder in geopolymer mixture

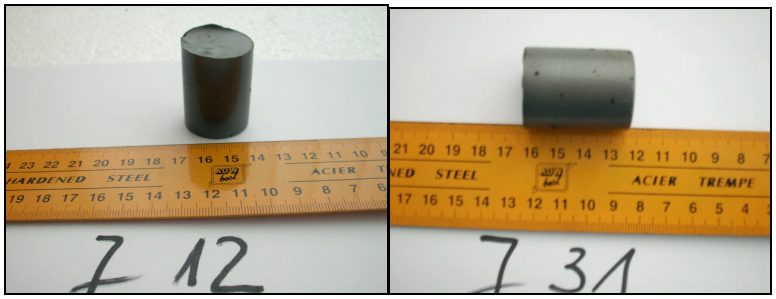

FIG.6: Geopolymer cylinder with 10% graphite (left) and 13% graphite (right)

3. RESULTS

3.1. Observation

Graphite in principle can be immobilized in the hydraulic binder geopolymer. Stable true to size pieces can be made. The stability in the strongly alkaline activator is observed. The filling level of a geopolymer base mixture is dependent upon the grain size distribution of the graphite.

With the tested powder or granules specifications for the direct mixing of the following recipes could be identified:

- 10% graphite (7 µm) to 90% geopolymer basic mixture (J12)
- 9.1% graphite (7 µm) to 54.5% and 36.4% geopolymer base mix sand (J31)
- 40% graphite (1.0 cm - 1.5 cm) to 60% geopolymer basic mixture (J71)
- 47% graphite (1.25 mm - 4 mm) to 53% geopolymer basic mixture (J81)

3.2. Uniaxial compressive strength and density

The filling ratio and the grain composition define the mechanical stability, intended as the uniaxial compressive strength and density of the immobilized body. With the available powder specification and the grain size, compressive strengths could be reachede in the range between about 5 $N.mm^{-2}$ (pure geopolymer) and 60 $N.mm^{-2}$ (geopolymer with a support structure made of sand).

- geopolymer-graphite mixture 5-26 $N.mm^{-2}$
- geopolymer-graphite-sand-mixture 22 - 30 $N.mm^{-2}$

The following Table shows the results:

TABLE 1: RESULTS

Recipe - Number	Compressive strength [$N.mm^{-2}$]		density [$g.cm^{-3}$]
	from	to	
J12	5*	22*	1,8
J31	22*	30*	1,9
J41	7*	22*	1,7
J51	5*	30*	1,9
J71	5*	23*	1,7
J81	21,7**	26,3**	1,7**
For comparison:			
Geopolymer, clean	5	15	1,9
Geopolymer with sand	30	61	1,9 - 2,1

** in B.P.S procedure ** according to DIN 18136, DIN 52 105, DIN 1048*

The compressive strength of geopolymers embedded in test samples (sphere diameter 6 cm) by the cover, consisting calculated from the geopolymer-sand mixture. It can be assumed that 30 Nmm^{-2} can be safely reached. For the generation of stable elements with graphite powder (<100 µm) the addition of an additional support structure component is effective. The smaller the grain size, the more the compressive strength approaches that of the pure geopolymer. To some extent this has been studied with the J30/J31 mixture.

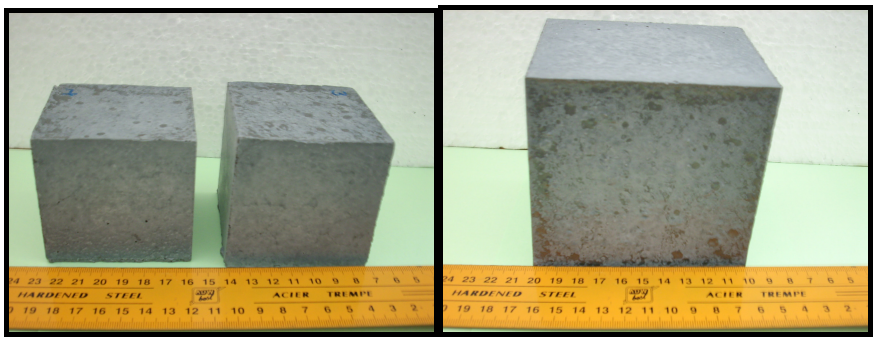

FIG.7: Left: cube (10 x 10 x 10) cm with graphit granulates (1,25-4mm); right: cubes (7x 7 x7) cm to determine the uniaxial compressive

3.3. Long term structural stability

The long-term resistance and structural stability were obtained by freeze-thaw resistance (following ASTM D4842):

TABLE 2: OVERVIEW OF THE RESULTS OF THE FREEZE-THAW RESISTANCE

cycle	J12	J31	J41	J51	J71	Control body Geopolymer
Start weight	43,905	49,192	65,424	64,182	51,469	100,312
End of the cycle	o.k.	o.k.	o.k.	o.k.	o.k.	o.k.
	43,91	49,108	65,457	63,95	51,272	100,106

The results for long-term resistance can be summarized as follows:

During the run of the 12 cycles of tests, visually no changes are observed on the surfaces of the test pieces. The samples were not destroyed. No crishing or splintering at the edges of the specimens were seen at the end of the investigation. The masses of the test samples were mostly unchanged. Fluctuations of the masses in the second and third decimal place are based in how well the adherent surface water could be removed before weighing.

4. CONCLUSIONS

Geopolymer cement, high-alkali polysilicate cement, results from an inorganic polycondensation reaction, a so-called geopolymerisation yielding three dimensional zeolitic frameworks. High-tech Geopolymer K-Poly(silacate-siloxo) binders, whether used pure, with fillers or reinforced, are already finding applications in all fields of industry. These polymers can be used in a variety of different application such as, cementing agent, immobilization systems for heavy metal containment, radioactive waste, and fire resistant composites in buildings. The behaviour of geopolymeric cements is similar to that of zeolites and feldspathoids; they immobilize hazardous materials within the geopolymeric matrix, and act as a binder to convert semi-solid wastes into adhesive solids. Their unique properties which include high early strength, low shrinkage, freeze-thaw resistance, sulphate resistance and corrosion resistance, make them ideal for long term containment in surface disposal facilities. These properties favored the cementation of nuclear graphite using geopolymere.

Finally, it is at present being debated whether geopolymers could have been used to build the pyramids. The pyramids have existed thousands of years while the normal Portland cement or concrete is known to last only for two centuries! It is therefore very probable that the geopolymer was used [1].

REFERENCES

[1] PROVIS J.L., STEPHANUS J. and VAN DEVENTE J**,** *'Geopolymer: Structure, Processing, Properties and Industrial Applications'*; Oxford : Woodhead ; Boca Raton, FL : CRC Press (2009)

[2] HERR R., SCHUBERT K. and HILLEMEIER B: 15th Internationale Baustofftagung IBAUSIL, Weimar 2003, Tagungsberichte, Band 1, S. 0933-0941 (2003)

[3] ADAM K., *ESEM-Untersuchungen an Geopolymerbindern*; BAM Berlin, Fachgruppe IV.2, (2004)

[4] HERR R., LUTZ W., RITZMANN A., HILLENEIER B. and SCHUBERT K.', *Neue Erkentnisse über die Struktur von Geopolymerbindern mit Hilfe der Molybdatmethode';*Vortrag Tagung Bauchemie der GDCh, Erlangen, 07th-08th October, 2004 (2004)

[5] BRENNECKE P., *Endlagerungsbedingungen KONRAD*; BfS Salzgitter (October 2010)