

SOLIDIFICATION OF VARIOUS RADIOACTIVE RESIDUES BY GÉOPOLYMÈRE® WITH SPECIAL EMPHASIS ON LONG-TERM-STABILITY

SOLIDIFICATION DE DIFFÉRENTS RÉSIDUS RADIOACTIFS AVEC LE GÉOPOLYMÈRE POUR UNE STABILITÉ À LONG-TERME

PART I: LABORATORY INVESTIGATIONS PART II: PILOT-SCALE EXPERIMENT

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Abstract

Sludges containing radionuclides, toxic heavy metals and hydro-carbons can be solidified by Géopolymère® with excellent long-term structural, chemical and microbial stability, satisfying high standards of contaminant retention. The novel technology gives a monolithic product which can be easily handled, stored and monitored. It requires only simple mixing and moulding technology known from conventional solidification methods.

Extensive laboratory investigation has been carried out to demonstrate the performance of the novel solidification method under adverse stress conditions. In particular, the sludges of a treatment facility for uranium mining effluents and sludges from a settling pond, contaminated organically, radioactively and by heavy metals, have been treated. An optimized two-step technology, known as Geopolytec®, was successfully adapted to the specific characteristics of these sludges. Moreover, the Geopolytec® process has been shown to deliver excellent results for radioactive and arsenic-loaded sludges from municipal drinking water purification plants that are sensitive with respect to public risk perception and regulatory policy.

Pilot-scale experiments that show the method's maturity for industrial use and to provide realistic material and operation cost estimates were done for the uranium mine sludges. Several tons were solidified in WISMUT's Schlema-Alberoda water treatment plant in 1998. Our results clearly show that Géopolymère® solidification is a prime candidate to fill cost-efficiently the gap between conventional concrete technology and vitrification methods. Due to the reduced effort to prepare, operate and close the landfill, solidification by Géopolymère® leads to approximately the same unit

cost as by conventional portland cement, but provides in most aspects the performance of vitrification.

The paper is divided into two parts. Part I describes in detail the basic principles of Géopolymère® and the laboratory investigations carried out to develop a viable solidification technology. After briefly introducing the basic principles of the Geopolytec® process and comparing it to conventional solidification methods, our paper shows promising results that were obtained for the long-term stability and contaminant retention of under several testing procedures. Subsequently, the experience from the pilot-scale experiment in the water treatment facility of WISMUT is presented. It shows that the Geopolytec® process is now mature for industrial application.

Part II is devoted to a pilot-scale experiment in which about 10 tons of radioactive and toxic sludges were solidified by the Geopolytec® process.

Finally, the prospects and market potential for the solidification of sludges by Geopolymer® are discussed, and an outlook to future activities is given.

Résumé

On peut solidifier avec le ciment géopolymérique (K,Ca)-Poly(sialate-siloxo) des boues contenant des radionuclides, des métaux lourds toxiques et des hydrocarbures; on obtient une excellente stabilité à long-terme tant du point de vue structurale, chimique que microbienne, qui satisfait aux normes les plus exigeantes. Cette nouvelle technologie fournit un produit monolithique qui peut très facilement être manipulé, stocké et surveillé. Il suffit seulement d'utiliser des méthodes conventionnelles de solidification, par simple mélange et coulée dans une forme.

On a réalisé énormément d'essais sous des conditions très dures pour bien démontrer les performances de cette nouvelle méthode de solidification. On a par exemple traité spécialement les boues produites par une unité de traitement des eaux provenant de mines d'uranium et les boues de bassin de décantation contaminées par des produits organiques, radioactifs et des métaux lourds. Pour cela on a mis au point une méthode comprenant deux phases de traitement, connue sous le nom de Procédé GEOPOLYTEC®, bien adaptée au traitement de ces boues. En plus, le procédé GEOPOLYTEC® a donné d'excellents résultats sur des boues radioactives contenant de l'arsenic, résultant du traitement des eaux potables, donc dans une approche plus sensible aux problèmes liés au service public et aux normes s'y affaissant.

L'expérimentation pilote faite sur des boues de mine d'uranium montre que la méthode est opérationnelle et qu'elle permet d'obtenir des prévisions réalistes sur les coûts en matières premières et de transformation. En 1998, on a solidifié plusieurs tonnes de boues dans l'unité de traitement des eaux de Schlema-Alberoda, WISMUT. Nos résultats montrent clairement que la solidification avec le ciment géopolymérique (K,Ca)-Poly(sialate-siloxo) permet de remplir économiquement le vide qui se trouvait situé entre la technologie du béton et les méthodes de vitrification. Comme le Procédé GEOPOLYTEC® permet de réduire les coûts de manutention, d'opération et de fermeture des décharges, le coût total de l'opération est identique à celui de la méthode conventionnelle au ciment Portland, mais en plus le procédé fournit des caractéristiques finales dont les performances sont identiques à la vitrification.

Nous présenterons ici brièvement les principes de base du procédé GEOPOLYTEC® et le comparerons avec les méthodes conventionnelles de solidification. Puis nous monterons les résultats très prometteurs obtenus quant à la rétention des éléments toxiques soumis à des tests très

sévères de durabilité à long-terme. On montrera ensuite l'expérimentation pilote effectuée dans l'unité de traitement des eaux de WISMUT. Elle montre que le procédé GEOPOLYTEC® est opérationnel et prêt pour l'application industrielle.

Part I Basics and Laboratory Investigations

1 Introduction

During the past decade geopolymerisation has emerged as a possible technological solution for the effective stabilisation and immobilisation of toxic and radioactive materials. Despite the fact that this technology is based on a very old principle, surprisingly little is known about the nature of these reactions or their products. It is only in the last fifteen years that it has been rediscovered and attention has been drawn to its useful chemical and physical properties [1]. Meanwhile, a number of patents have been granted, among them those cited in [2].

Geopolymerization is a geosynthesis (a reaction that chemically integrates minerals) that involves naturally occurring silico-aluminates. Silicon and aluminum atoms react to form molecules that are chemically and structurally comparable to those binding natural rock.

The European research project GEOCISTEM [6] successfully tested this technology in the context of the East-German mining and milling remediation project, carried out by WISMUT. Another research project into the solidification of radioactive residues was jointly carried out by Cordi-Géopolymère and Comrie and is documented in Ref. [7]. Relevant information on the basic principles and the performance achievable can be found there.

In more recent investigations, special emphasis had been laid on the solidification of sludges contaminated by decay products of the U-238 and U-235 series, arsenic, and a variety of hydrocarbons. These sludges stem from existing sedimentation ponds (e.g., near Drosen) and, more importantly, from water treatment plants (e.g., Pöhla and Schlema-Alberoda) which remove radioactive and heavy metals from mine effluents prior to their discharge into rivers.

The disposal of radioactive and toxic sludges must meet at least two conditions:

- safe chemical encapsulation of the contaminants, i.e., prevention of their release into ground and seepage water in order to minimize the health risks via the water path. Contaminant release is controlled by the leaching properties of the immobilisation matrix.
- structural stability with respect to adverse environmental conditions such as rapid changes of temperature and humidity, microbial and chemical aggression and mechanical stress, in order to guarantee safe handling during operation time and minimize the risk of uncontrolled spread of contaminated matter over the next several hundred years

For the Schlema-Alberoda water treatment plant, conventional Portland cement/fly ash solidification was initially chosen. However, it is not proven to meet the above requirements satisfactorily. Neither can structural stability be guaranteed (as evident from a few freeze-thaw and wet-dry cycles), nor are the contaminants safely retained in the structurally eroded material (as shown in subsequent leach tests) [11]. A technology was therefore sought for, which on one hand satisfies the afore-mentioned standards and, on the other hand does not require significant changes to the cement mixing equipment already installed in the water treatment plant. Furthermore, the cost figures projected for sludge conditioning and disposal must not be intolerably overrun. Géopolymère® can be shown to provide a solution under these conditions. Laboratory tests

including artificial ageing experiments have demonstrated that the stability requirements are met even under extreme conditions. Subsequent pilot-scale tests and cost estimates derived indicate that the appropriate use of inorganic geopolymer binders in the Geopolytech® process is providing an economically viable alternative to traditional systems.

High-alkali (K-Ca)-Poly(sialate-siloxo) binders which have been coined Géopolymère®, result from an inorganic polycondensation reaction, a so-called geopolymerisation yielding three dimensional zeolitic lattices. The corresponding reactions are shown in Figure 1. High-tech Géopolymère K-Poly(sialate-siloxo) binders, whether used pure, with fillers or reinforced, are already finding applications in all fields of industry. These applications are to be found in the automobile and aeronautic industries, non-ferrous foundries and metallurgy, civil engineering, plastics industries, etc. The solidification technology on the basis of Géopolymère® has been coined Geopolytec® Process.

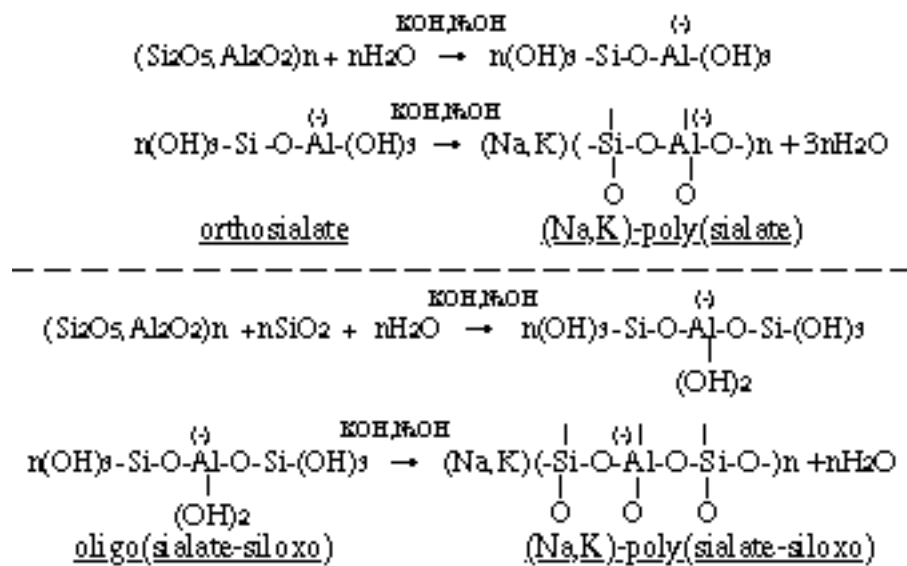


Figure 1: Reaction equations for poly(sialate) and poly(sialate-siloxo) geopolymerization

Géopolymère® hardens rapidly at room temperature and provides compressive strengths in the range of 20 MPa, after only 4 hours at 20°C, when tested in accordance with the standards applied to hydraulic binder mortars. The final 28-day compressive strength is in the range of 70-100 MPa. The behaviour of geopolymeric binders is similar to that of zeolites and feldspatoids; 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 and wet-dry resistance, sulphate and corrosion resistance, make them ideal for long term containment in surface and subsurface disposal facilities. These high-alkali cements do not generate any Alkali-Aggregate reaction.

X-rays diffraction spectra of hardened geopolymeric materials do not provide accurate information (amorphous structure). However, high-resolution MAS-NMR spectroscopy of ^{29}Si and ^{27}Al is a very powerful tool that provides useful structural data. Preliminary study involving ^{27}Al and ^{29}Si MAS-NMR spectroscopy and the proposed structural model shown in Figure 2, reveal that geopolymeric cements are the synthetic analogues of natural tecto-alumino-silicates [4, 5].

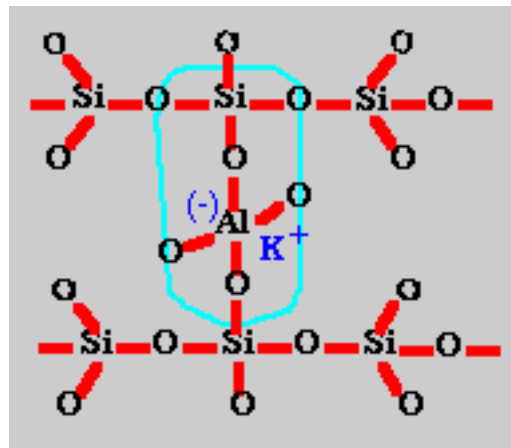


Figure 2: Poly(sialate-siloxo) structural framework of the Géopolymère[®] used in the solidification of radioactive and toxic sludges

In some aspect, solidification of hazardous residues by Géopolymère[®] is comparable to vitrification. Like vitrification, the Geopolytec[®] process offers

- high strength
- acid resistance
- long term durability
- geological and archaeological analogues

But unlike vitrification, it does not require energy-consuming drying and melting. Geopolytec[®] requires only simple mixing equipment (such as for concrete solidification) and hardens at room temperature.

It is evident from the comprehensive references cited in [1] that some factors governing the formation of geopolymers are still not completely understood, although the physical and chemical properties suggest that these matrices are well suited for the immobilisation of toxic materials and specifically radioactive and toxic matter. It is finally concluded that geopolymers offer attractive options towards simple industrial applications where large volumes of waste materials need to be stabilised.

The remaining part of this paper is structured as follows: Chapter 2 briefly characterizes the sludges that were treated using our technology. In Chapter 3, the technology is outlined and an optimized recipe is given which could serve as a “reference case“ for the Geopolytec[®] solidification. The results of an extensive investigation programme regarding long-term stability and leaching behaviour are shown in Chapter 4, while Chapter 5 provides conclusions future prospects.

2 The sludges

The sludges that have been solidified by Geopolytec[®] originate from the following sites:

- Drosen sedimentation pond (WISMUT GmbH, Thuringia) [9]
- Surface water treatment facility (Waterworks of Zwickau, Saxony) [10]
- Water treatment plants Pöhla and Schlema-Alberoda (WISMUT GmbH, Saxony) [8]

The sludges can roughly be characterized by the parameters listed below (Table 1).

Table 1: Characterization of the sludges treated by the Geopolytec® process

Specific content of elements	
Radionuclides	Toxic
U _{nat} (U-238, U-235): 1000...7000 ppm	Arsenic: 100...9000 ppm
Ra-226: 1...15 Bq/g	Chloride
	Antimonium
	Molybdenum
	Sulphates
Other characteristics	
Grain size distribution	e.g., 95% < 63 µm
Dry matter content	10...45 %, typ. 40% water partly bound in macro flocks
Dewatering behaviour	hard to dewater, filter press needed
Rheological properties	strongly thixotropic (e.g. hydroxide sludges)

Additionally, the Drosen sludges contain 6000 ppm hydro-carbons which was initially expected to interfere with the solidification process. However, the geopolymerization process itself and the performance of the end product were not noticeably affected.

While the technology has been shown to work for all sludges, we will focus in the remaining part of this article on the solidification of sludges from the Schlema-Alberoda mine water treatment plant.

3 Solidification technology, Geopolytec® process

In principle, mixing the wet dewatered sludges with Géopolymère® leads to acceptable results. This one-step technology was successfully deployed when treating the Drosen sludges contaminated by radionuclides, arsenic and hydro-carbons.

In the course of experimenting with Géopolymère® as potential solidification material for the water treatment sludges of the Schlema-Alberoda plant, a two-step technology (the Geopolytec® process) has been elaborated:

1. producing a granular pre-product of the sludge and ordinary portland cement which can be stored some days
2. binding the granular pre-product with Géopolymère® and filling the resulting end-product to Big Bags or moulds

The intermediate step of producing a pre-product has turned out to be advantageous for at least three reasons:

- better immobilization results for some heavy metals such as arsenic due to the moderate pH of portland cement as compared to Géopolymère®,
- optimized structural long-term stability as compared to a pure Géopolymère® matrix, since the granules act effectively as fillers,
- lower cost due to the smaller portion of Géopolymère® needed to solidify a given amount of sludge.

The technological scheme of the two-step process is shown in Figure 3. It is obvious that the equipment used is the same as known from conventional concrete mortar methods. The process, too, is very similar, the only difference being the intermediate storage of the granular pre-product

which is fed again into the equipment and mixed with Géopolymer® and potassium silicate acting as hardener.

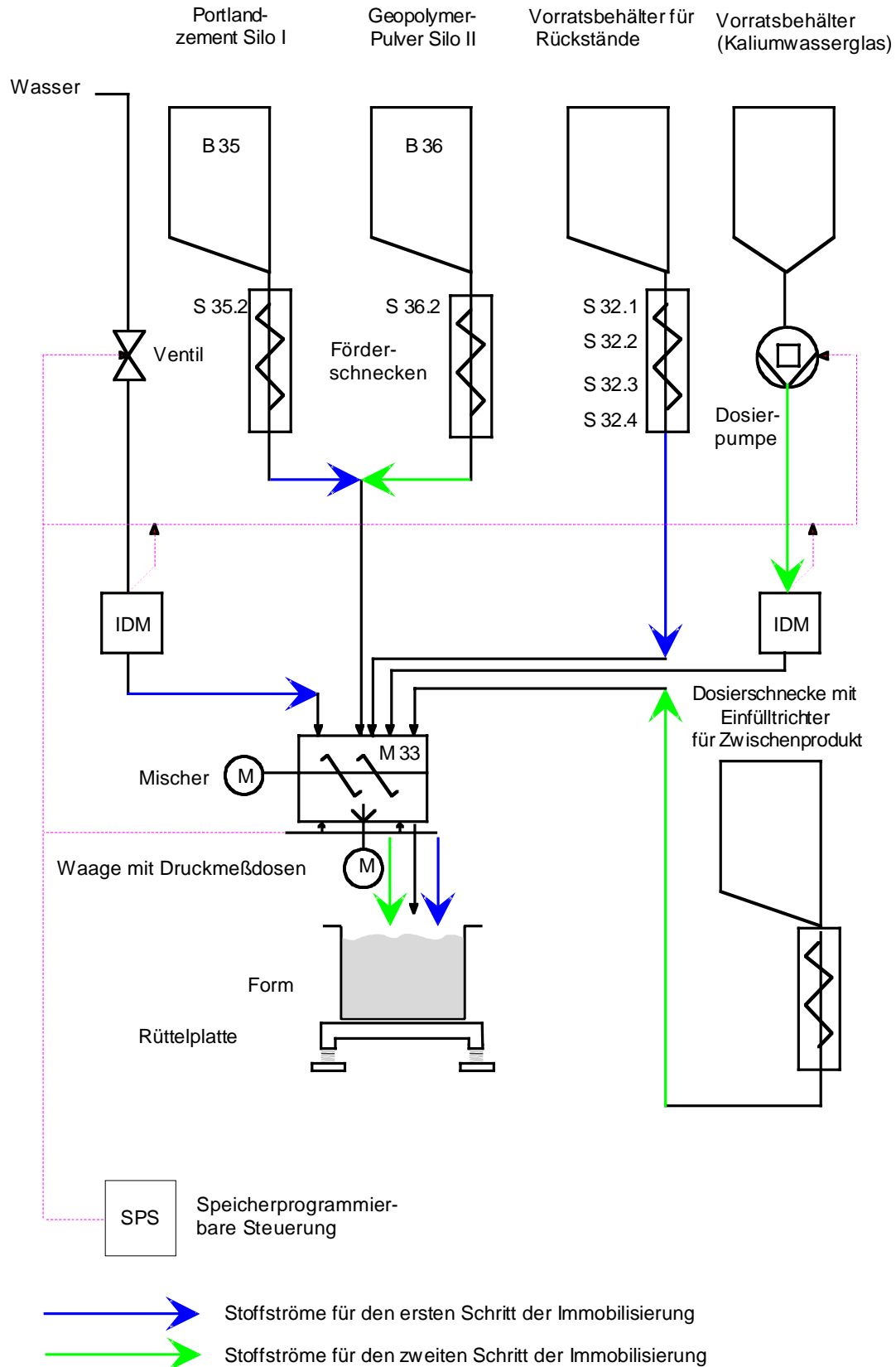


Figure 3: Two-step Geopolytec® solidification technology

In a series of variations of the relative portions of sludge, cement pre-product and geopolymer, a standard range of recipes has been identified which gives the best results with respect to chemical retention of contaminants (i.e., leaching behaviour), long-term stability, and cost. It is given in Table 2.

Table 2: „Standard“ mixing recipe for Geopolytec® solidification

Component	Mass [kg]	Remarks
dewatered sludge from filter press	1	35% dry matter content
dry matter	(0.35)	
water	(0.65)	
portland cement	0.75	
water	0	no water needed in this step
pre-product	1.75	
↓		
Géopolymère® (reactive clays, GGBF slag + potassium silicate)	0.81	
water	0.25	
end-product	2.81	

The density of the monolithic end product is about 1.8 t/m³ which is higher than that of portland cement products (1.4 t/m³). It can go as a rough estimate that 1 ton dry matter (equivalent to 2.5 tons sludge of 40% dry matter content) results in about 4.4 m³ of the end product. This is well comparable to conventional cement methods.

4 Results

To demonstrate the performance of the new technology, a large number of standardized and adapted tests were carried out. The most relevant results are discussed below.

- Handling and hardening of the Géopolymère® mortar

Immediately after mixing the pre-product with the Géopolymère® and hardener, the mortar flows easily into moulds or big bags. Mechanical energy input (such as vibration tables) can be used to keep the mortar liquid.

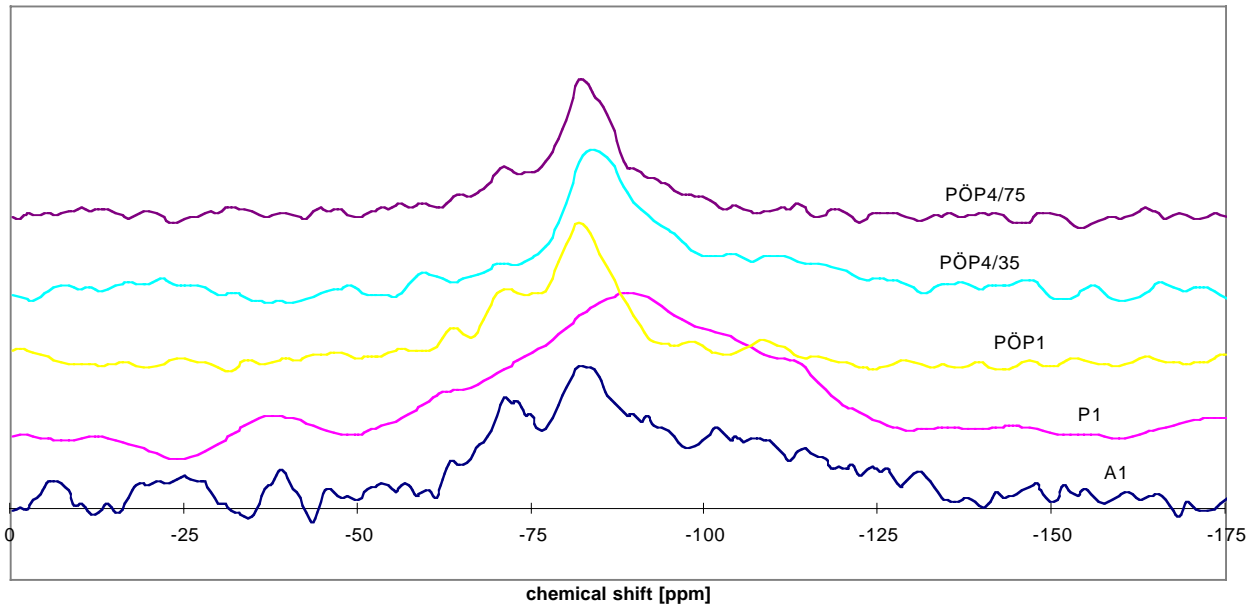
Form-stable demoulding is possible after 2 hours at room temperature. After 2 days, 90% of the final compressive strength are reached, the final compressive strength of about 20 MPa is reached within 28 days. It is interesting to note that shrinkage is well below < 0.5% (detection limit) and exothermic heat is considerably lower than that of cement.

- MAS-NMR spectroscopy

The magnetic angle spinning (MAS) NMR can be used to confirm that the polycondensation process leading to Géopolymère® has occurred. This gives a first hint that the physical and chemical properties expected for Géopolymère® will be achieved.

The graph shows the spectra for ²⁹Si. If silicon is properly co-ordinated in the solid, the chemical shift is expected to lie at approx. -85...-90 ppm. This is actually true for the plots shown in the

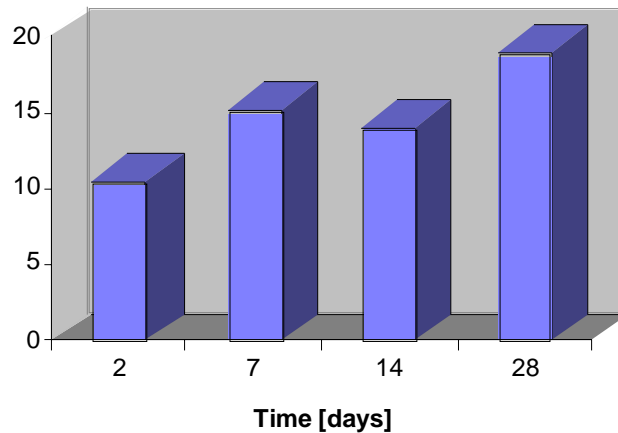
figure. For comparison, a MAS-NMR plot of conventional Portland cement is shown with a ^{29}Si peak shifted towards 70 ppm. This peak is visible in all curves with more or less intensity and is due to the first granulation step with portland cement.



MAS-NMR spectra of ^{29}Si for Géopolymère® and Portland cement

- Uni-axial compressive strength (DIN 18 136, 20°C, 60% air humidity)

Compressive Strength [MPa]



Static compressive strength (MPa) vs. hardening time (days)

The final compressive strength reached after 28 days was 18.8 MPa. Note that the technology has not been optimized to attain higher compressive strengths. This is, however, no principal problem if desired.

- Hydraulic conductivity (DIN 18 130)

The hydraulic conductivity was measured to be in the range 10^{-10} ... 10^{-12} m/s or below, since most of the tests were below the detection limit.

- Leaching behaviour

Several leach tests were carried out in order to cover a large range of environmental stress conditions that may possibly occur over the next centuries. Standard leach tests according to (DIN 38 414-S4, 24 hours, intact 7 cm cubes) were performed to get information about the overall containment, while sequential leach tests according to ANS 16.1 (slightly adapted to locally relevant conditions) provide an estimate of the diffusive transport in the Géopolymère[®] matrix. The diffusion constant D can under certain simplifying assumptions be determined from the relationship $Q_{tot}(t) = A \cdot c_{sol} \cdot (4D \cdot t / \pi)^{1/2}$ where Q_{tot} is the total contaminant mass leached over time t , A is the surface of the specimen, c_{sol} is the specific contaminant content in the solid.

The results of the tests are summarized below.

Leachate concentrations according to DIN 38 414-S4

Element	Leachate concentration
U_{nat}	1...6 µg/l
Ra-226	< 10 mBq/l
As	< 100 µg/l, typ. 10 µg/l

Diffusion constants for uranium as calculated from sequential leach tests according to ANS 16.1

	pH 3	pH 5
D(Uranium)	$3,8 \times 10^{-16} \text{ cm}_2/\text{s}$	$1 \times 10^{-16} \text{ cm}_2/\text{s}$

The diffusion constants are expected to be independent of the leachate pH, as diffusion should exclusively be determined by solid state processes within the Géopolymère[®] matrix. The slight difference of D between pH 3 and 5 may be explained by the tolerance of the leachate concentration measurement which sensitively enters the equation for D .

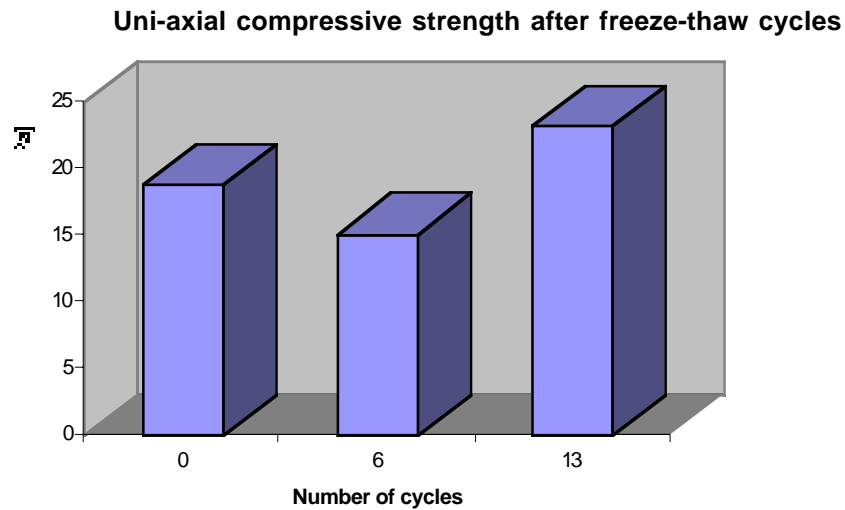
More leach tests have been carried out for various pH values, especially in the acidic range. Every hour, the pH was kept at pH=3 by adding sulphuric acid. The leachate concentrations, measured according to DIN 38414-S4 remained unaffected. After the test, the compressive strength was determined and showed no decrease.

- Structural stability tests

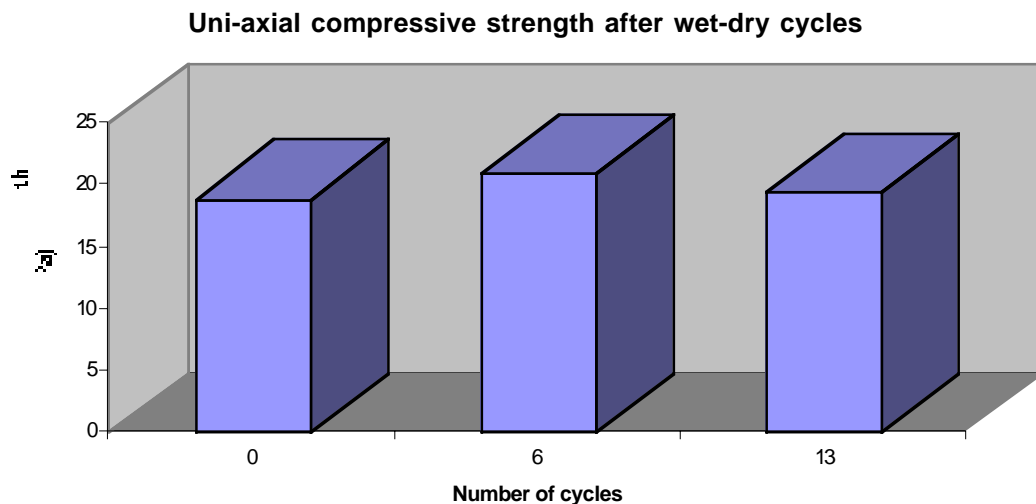
The samples were subjected to structural stability tests according to ASTM D 4842 (wet-dry cycles) and ASTM D 4843 (freeze-thaw cycles). In both cases, no decrease in the compressive strength is observed, as evident from the figures below (start value, after 6 and 13 cycles, respectively).

No deterioration of the surface (cracks, fissures, increased roughness or the like) was observed. The loss-of-weight was 0.06% after both tests.

In addition, Endell's Decay Index (a rather traditional measure mainly known from construction material testing) was determined over a total duration of 60 days. The loss-of-weight was well below the detection limit of 0.01%.



Compressive strength [MPa] vs. number of cycle (start, 6, 13) during freeze-thaw cycles



Compressive strength [MPa] vs. number of cycle (start, 6, 13) during wet-dry cycles

- **Microbial stability**

Microbial stability was determined according to DIN 53739 and the ASTM G 21/22 procedures. The specimen were flushed and then doped with fungi, bacteria and a combination of both. The samples were then stored in a humid and dark environment over 4 weeks. An undoped reference sample was stored under equal conditions for comparison.

The specimen were then visually evaluated, compressive strength and leach tests followed. The surface remained unaffected, and no noticeable changes occurred to compressive strength and leachability. No microbial or fungal growth was observed. Géopolymère® can thus be rated microbially stable.

Part II Pilot-scale Experiments

In November/December 1998, a pilot-scale experiment was carried out in WISMUT's Mine Water Treatment Facility at Schlema-Alberoda. This facility has been built to remove Uranium, Radium, Arsenic and other toxic metals from the flooding water of the Schlema-Alberoda Uranium mine. The technological principle is a consecutive selective precipitation/flockulation. At a flow rate of about 450 m³/h, approximately 3.5 to 4 tons of dewatered hydroxide sludges have to be solidified and disposed of every day.



Mine water treatment facility of WISMUT at Schlema-Alberoda

The original technology design for solidification was based on a conventional Portland cement (P.C.) technique in which cubic blocks of 1 m³ volume are cast into steel moulds, demoulded after hardening and then transported by trucks to a specifically prepared disposal site. The disposal site is situated on a former waste rock pile. Regulatory requirements that are mainly dominated by the standards of radiation protection have led to an extensive encapsulation of the landfill. The most expensive landfill encapsulation cell components can be dropped if Geopolytec[®] blocks are produced instead of P.C. blocks. The latter are insufficient with respect to their short- and long-term structural stability, particularly their freeze-thaw and wet dry resistance. This renders additional measures necessary to

- ensure geotechnical stability during the construction and disposal phase and long-term geotechnical stability,
- preclude the hydraulic transport of fine grain fractions due to the structural instability of P.C. blocks, which would be critical due to the high content of radionuclides.

The cost savings on this side clearly offset the higher material costs of Geopolymer[®]. This and the drastically improved short- and long-term stability lead WISMUT and regulators to commission the pilot-scale experiments.

The existing P.C. mixing and moulding equipment was used. Feeding technology for the binders and dosing pumps for the Potassium waterglass (activator) were available in the water treatment facility. The photographs below show the different steps of the Geopolytec[®] process.



Granular pre-product (Sludge + P.C.) after hardening



The final product filled in Big Bags



Final product, hardening in steel moulds



Demoulded Big Bags with hardened blocks



Big Bags with Geopolymer® blocks on prepared landfill

From the pilot-scale experiment, the following lessons have been learned.

- Systematically optimizing recipes in the laboratory and testing the sensitivity of the technology with respect to changes in the recipes is necessary to be able to react quickly to unforeseen situations. For example, if the residual water content of the dewatered sludges decreases,

additional water must be added and the mixing time must be longer. If the Arsenic concentration in the leachate is rising, less Geopolymer[®] must be added, and so on.

- The real-size technology fully reproduces the lab results.
- The chemicals needed for the Geopolytec[®] process can be safely handled.
- The solidification equipment was designed for Portland cement. For the pilot-scale experiment it worked satisfactorily. However, the liquid mixture did not easily flow into the steel moulds. More vibration energy would have been needed to keep the mixture fluid (due to its thixotropy), but the vibration table was insufficient. As a makeshift, we added slightly more water.

The pilot-scale experiment impressively demonstrated the technological maturity of the Geopolytec[®] process for the solidification of hazardous sludges.

5 Conclusions and Outlook

A new method for the solidification of sludges containing radionuclides and heavy metals as well as organics has been developed and shown to meet high standards with respect to long-term stability and contaminant retention. The innovative technology which is based on the use of inorganic Géopolymère[®] binder is very easy to handle and requires basically the same equipment as conventional cement mortar methods. It fills the gap between concrete-based solidification methods which do not satisfy the requirements of long-term structural stability, and vitrification which is too expensive for most cases in which larger amounts of sludges have to be treated.

The excellent performance of Géopolymère[®] and the Geopolytec[®] process has been shown by extensive laboratory work simulating aggressive environmental conditions including chemical, microbial and physical stress. A pilot-scale experiment to solidify radioactive and toxic sludges from one of WISMUT's mine water treatment plants was successfully carried out, more tests with other partners will follow soon. It has been shown that Geopolytec[®] now provides a mature and cost-efficient solution to many problems where hazardous residues must be treated and stored under critical environmental requirements.

The next step will most probably be the solidification of approximately 6 tons of radioactively contaminated hydroxide and sedimentation sludges from the drinking water purification. Due to the higher standards for the arsenic concentration in drinking water, removal technologies are being refined by many of Germany's public water suppliers. An unwanted side-effect however, is the higher content of Uranium and Radium which are present in the water in some regions. Under certain circumstances, the sludges are classified as radioactively contaminated which prompts the need for special but affordable treatment. Among other fields, it is here where we see an application for Geopolytec[®].

Geopolytec[®] process and Géopolymère[®] are registered trademarks of Cordi-Géopolymère SA.

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