

LOOKING BACK TO GUIDE US ON HOW TO MOVE FORWARD FOR GEOPOLYMERS

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Key Words: geopolymer, Bayer liquor, XRD, SEM

Making geopolymers and alkali activated materials with specific properties requires skill and a thorough understanding of the process. The trial and error approach used by many researchers may result in an acceptable product but there is little or no understanding of why it worked and how to improve or optimise the product. It also leaves potential producers without quality control of feedstock hence limited quality assurance on product. This presentation will look back at how the geopolymer group at Curtin University improved its understanding of geopolymer technology via development of XRD, SEM and related analytical techniques. Examples on how geopolymers were made with very high compressive strength on one hand and on the other hand with impressive fire resistance will be described.

However, this is not the end of the story. Ultimately the goal is to commercialise geopolymers and for this to happen we must conduct rigorous life cycle analysis and embodied energy assessments to be confident that these materials are competitive and sustainable. One way to ensure low embodied energy is to explore alternate activators and sources of alumina and silica. When alternate precursors such as Bayer liquor have been used to manufacture geopolymers they prove to have a very low embodied energy and are potentially less expensive. The use of Bayer liquor for geopolymers will be described in detail and examples provided on how this approach may be viewed as a way forward for the field of geopolymers for specific products.

INVESTIGATION OF THE RELATIONSHIP BETWEEN THE CONDENSED STRUCTURE AND THE CHEMICALLY BONDED WATER CONTENT IN THE NETWORK OF GEOPOLYMER CEMENTS

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Key Words: Geopolymer cement, chemically bonded water, condensed structure.

The main objective of this work was to investigate the relationship between the condensed structure and the chemically bonded water content in the metakaolin-based geopolymer network. The kaolinite clay used in this work as an aluminosilicate source was transformed to metakaolin by calcination at 700 °C. The powder of the waste glass and the silica fume were used as silica sources for the synthesis of the hardeners. The obtained hardeners were characterized by infrared spectroscopy and MAS-NMR ²⁹Si. The metakaolin and the hardeners were used for producing geopolymers cements. The synthesized products were characterized by X-ray diffractometry, infrared spectroscopy, mercury intrusion porosimetry, scanning electron microscopy, MAS-NMR ²⁹Si and ²⁷Al, thermal analyses (TG and DSC) and compressive strength. The results show that the compressive strength of geopolymer cements using hardener from silica fume and the one from waste glass are 62 and 26 MPa, respectively. The microstructure (SEM observations) geopolymer cements obtained using hardener from silica fume are homogeneous, compact and dense with an average pore diameter around 10 nm. Whereas, the one obtained using hardener from waste glass are heterogeneous and contains larger pores (170 nm). MAS-NMR ²⁹Si and ²⁷Al results show that the specimen obtained using hardener from the silica fume contains more aluminum in four-fold coordination in its network than waste glass geopolymer, GWG. This indicates a higher degree of crosslinking of poly(sialate-siloxo) chains which could lead to a smaller pore sizes and a higher water uptake in the structure of the sample. The amount of chemically bonded water contained in the network of geopolymer cements using hardeners from waste glass and silica fume were 6.82 and 11.23%, respectively, as determined from weight loss in the range 100-300 °C. All these results indicate that the higher content of chemically bonded water in the network of geopolymer obtained using hardener from silica fume is related to the much smaller average pore size diameter and the hydrophilic character of aluminum, which reveals obviously better mechanical and microstructural properties of the specimen. This could indicate here a higher degree of condensation using silica fume based hardeners for geopolymerisation.

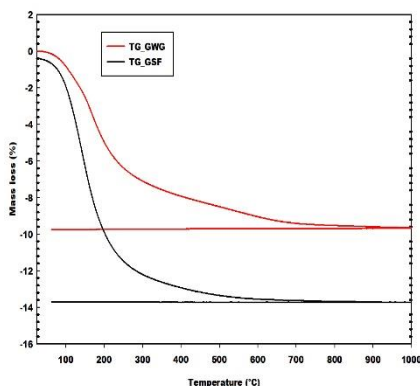


Figure 1 – TG curves of geopolymer cements GSF and GWG

Samples	Cumulative pore volume (mL/g)	Average pore diameter (µm)	Bulk density at 0.52 psia (g/mL)	Apparent density (g/mL)	Total porosity (%)
GWG	0.25	170	1.43	2.27	37
GSF	0.23	10	1.70	2.88	41

Table 1: Mercury intrusion porosimetry of geopolymer cements GSF and GWG.

REAL SOILS VERSUS FAKE SOILS: DOES SOMETHING OTHER THAN CLAY MINERALS INFLUENCE GEOPOLYMERISATION BEHAVIOUR IN REAL SOILS?

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Key Words: Geopolymer; Clays; alkali activation; soil stabilisation

Uncalcined geopolymer-stabilised soils have shown potential for replacing concrete and fired clay as low carbon masonry materials. There is now a good fundamental understanding of how aluminosilicate precursors react to form geopolymer phases in simple systems, but there is a knowledge gap for the more complex systems of real soils where minor phases may influence behaviour. Because the clay minerals and their proportions differ between soils, as well as minor phases present, we are still not able to easily predict which soils are suitable for geopolymer stabilisation. In this study, a comparison was made for the alkali activation of real and 'fake' soils. Three soils from around the world (UK, India, Sudan) of known mineralogical composition were used. From the real soils' known mineralogical compositions, 'artificial soils' corresponding to each one were made. These were made by mixing refined clays in the same proportions, and using quartz sand as a substitute for all other non-clay phases. The soils were mixed with sodium hydroxide activator and cured. The phases formed were characterised using XRD, FTIR and SEM. From the elemental compositions, the most significant difference was the quantities of iron and calcium present in minor phases. The phases and proportions formed by the alkali activation of each real soil broadly match those formed by the fake soils. The implication for the development of geopolymer-stabilised soil materials is that for a fixed activating solution, minor phases have limited influence on the geopolymer reaction. Nevertheless, the complexity of reaction with mixed soils makes it difficult to predict reaction phases and therefore final products.

HYDRATION OF CLINKER PHASES IN ALKALINE CONDITIONS

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Key Words: Clinker phases, alkali hydration, Na_2SO_4

This research is focused on the individual behaviour of calcium silicates (C_3S and C_2S) and tricalcium aluminate (C_3A) when hydrated with water, but in the presence of 4 wt% Na_2SO_4 . Two- and 28-day mechanical strength of pastes were determined and the reaction products were identified by means of XRD, SEM/EDX and ^{29}Si and ^{27}Al MAS NMR. Analysis of C_3A revealed that hydration was favoured in the presence of Na_2SO_4 . This salt governed hydration kinetics while providing the alkalinity required to induce the joint precipitation of carbonated and calcium sulfoaluminate hydrate reaction product, both observed to contribute to the mechanical strength of the resulting material.

In both silicates (C_3S and C_2S), the findings showed that the presence of Na_2SO_4 stimulated mechanical strength development. The synergy among all chemical reactions taking place during the hydration of these calcium silicates favoured a substantial rise in the alkalinity of the pastes formed. In addition, the anion SO_4^{2-} induced the precipitation of cementitious gels with a high percentage of Q^2 units, which leads to a significant increase in the mechanical strength of the materials at 28 day.

MOLECULAR MODEL OF GEOPOLYMERS WITH INCREASING LEVEL OF DISORDER IN THE ATOMIC STRUCTURE.

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Key Words: molecular model; geopolymers; molecular dynamics simulations; X-Ray diffraction; mechanics.

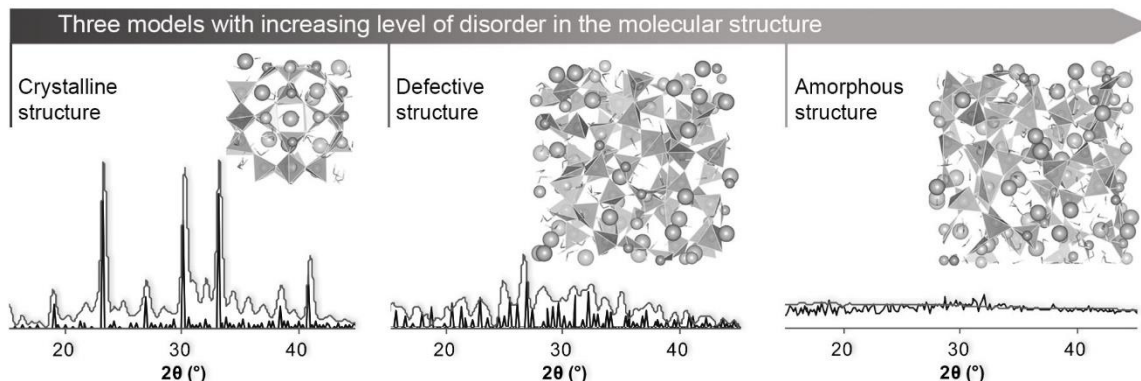


Figure 1 – Three different geopolymers molecular models with increasing level of disorder but with comparable Si:Al. The level of disorder is characterized by the corresponding X-ray diffractions.

Concrete is the most used building material on Earth, but the production of its main binding component, cement, is responsible for 8% of worldwide CO₂ emissions. A greener alternative cementitious material is provided by geopolymers, which can be synthesized from calcined clays and industrial by-products. A key issue, that limits the applicability of geopolymers in the construction sector, is an insufficient understanding of the relationship between their chemistry and development of long-term properties. Reducing these uncertainties requires an integrated approach combining modelling and experimentation. The binding phase of geopolymers often consists of sodium-alumino-silicate-hydrates (N-A-S-H), obtained through the reaction of a sodium silicate solution with an alumino-silicate source. Theoretical models describe this structure at the molecular scale as “pseudo-crystalline” [1] but, the existing models, based on solely amorphous or crystalline structures, are not always in agreement with this definition and with experimental results. For this reason, a defective crystalline structure is proposed here as a baseline geopolymer cell, featuring both amorphous and crystalline attributes (Figure 1). This new structure is created by creating vacancies in a sodalite crystalline cage, which is then stress-relaxed and reorganised to achieve full polymerisation of Al and Si tetrahedra while respecting the Loewenstein's principle. Results are compared with experimental data and with other simulation results for amorphous and crystalline molecular models, showing that the newly proposed structures better capture important structural features with impact on mechanical properties, reconciling experiments with the “pseudo-crystalline” model. Specifically, the comparison with the experiments addresses the effect of Si:Al molar ratio and water content on a range of structural and mechanical properties such as skeletal density, ring structure, bond-angle distribution, X-ray diffraction (Figure 1) and X-ray pair distribution function. The simulation results confirm the necessity of a defective structure able to detect both order and disorder in geopolymers experiments. The proposed defective molecular model provides a starting point for the multiscale understanding of geopolymer cements, as well as for investigating the molecular interactions between geopolymer cements and various adsorbates, e.g. for applications in environmental engineering and nuclear engineering.

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ALUMINOSILICATE NETWORK FORMATION DURING GEOPOLYMERIZATION FOLLOWED BY IN-SITU ²⁷Al NUTATION NMR

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Key Words: Geopolymerization, ²⁷Al NMR.

In classical cement systems, hydration reactions can typically be stopped by a solvent exchange (such as isopropanol) or by drying¹. Subsequently, the chemical reactions are studied by separating and characterizing independently the solid and the liquid phases at different times, to follow their respective compositions and to establish a reaction process by finding chemical intermediates and products. As for geopolymers, they are formed by a dissolution-condensation mechanism resulting from the mixing a solid aluminosilicate source (for example metakaolin) with a highly concentrated alkali-silicate solution. The properties of the suspension do not allow to employ phase separation. This is the reason why the reaction mechanism leading to geopolymers is still said to be unclear, because it has only been studied by indirect methods so far, such as calorimetry, time-resolved rheology or small-angle scattering² for instance.

In-situ static ²⁷Al NMR has already been used as a direct method to probe and quantify the aluminate species in the liquid phase during geopolymerization, using the quadrupolar nature of ²⁷Al nuclei. Aluminum is not present in the liquid state at the very beginning of the process but goes to the initial aluminosilicate powder to the final solid product, naturally making it the nucleus of interest for an NMR study. While dissolved species are mobile enough for the quadrupolar interaction to be averaged, the quadrupolar coupling persists in less mobile species or in solids, leading to different nutation behaviors.

In the present study, it will be demonstrated that a nutation experiment, which simply consists in varying the pulse length and measuring the resulting signal, allows filtering out the reactant aluminosilicate source from the ²⁷Al NMR signal to detect reaction intermediates, and apparently also products. The evolution of the ²⁷Al NMR signal was followed over longer periods of time up to several days during the geopolymerization process of metakaolin-based systems. It was shown that more than two steps can be identified in the geopolymerization process, depending on the frequency of the radiofrequency field applied during the experiment. Simulation of nutation curves at different times of the reactions allowed to follow the evolution of the quadrupolar coupling constant, and gave insight on the aluminate intermediates. Finally, the NMR results were confronted to time-resolved rheology and isothermal calorimetry in order to understand processes occurring on different time scales.

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EXPERIMENTAL STUDY AND NUMERICAL SIMULATION OF THE DISSOLUTION OF BLAST FURNACE SLAG IN ALKALINE SOLUTION

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Key Words: dissolution, blast furnace slag, alkaline solution, numerical simulation, real-shape particle.

Geopolymers are formed by the reaction between an alkaline activator and an aluminosilicate precursor. As any cement-based materials, the reaction starts from the dissolution of aluminosilicate precursor in the alkaline solution. The dissolution kinetics of aluminosilicate precursor determines the reaction kinetics and strength development of geopolymers. In this study, the dissolution of blast furnace slag in alkaline solution will be investigated experimentally and numerically.

In the experimental program, 0.1 gram of blast furnace slag is dissolved in 200 mL of alkaline solution. During the dissolution experiments, the solution is sampled at set time intervals up to 2 hours. The sampled solution is subject to the analysis by the means of inductively coupled plasma-optical emission spectrometry (ICP-OES), by which the concentrations of Ca, Si and Al are determined as functions of time. By studying the concentrations of Ca, Si and Al with time, the influence of the alkalinity of alkaline activator on the dissolution of blast furnace slag are investigated and the dissolution rates of Ca, Si and Al are determined. Furthermore, the relationship between the alkalinity of alkaline solution and the dissolution rates are studied, and the dissolution rate constants are determined.

In the numerical simulation, the dissolution of blast furnace slag in alkaline solution is simulated using real-shape particles of slag [1]. The irregular shape of blast furnace slag is characterized by spherical harmonic series [2]. The Lattice Boltzmann method is used to simulate the transport of aqueous ions and the dissolution rate constants obtained by the experiments are used as input to model the dissolution of blast furnace slag. The numerical model is first applied to simulate the dissolution of blast furnace slag carried out in the experimental program. After validation with the experimental results in terms of elemental concentrations with time, this numerical model is used to study the influence of slag chemistry and temperature on the dissolution of blast furnace slag in alkaline solution.

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SYNTHETIC GLASS WITH HIGH ALKALI-REACTIVITY AND NEAR-ZERO RM-CO₂ EMISSIONS

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Key Words: Synthetic glass, rate of dissolution, alkali activated cement

As cement-related CO₂ emissions increase, alternatives are actively sought. Cement substitution by slag and fly ash is standard practice worldwide and while higher side stream utilization is necessary, their volumes are not adequate to significantly alter global CO₂ emissions. Cement substitution by, and alkali activation of, calcined

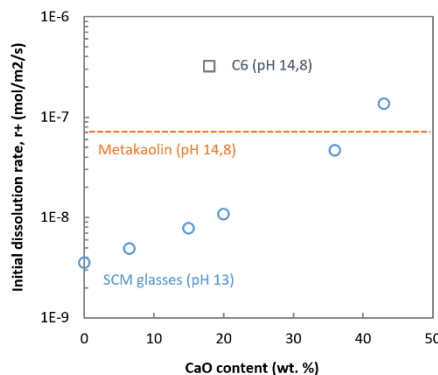


Figure 2 - Initial dissolution rate calculated based on dissolved aluminum in the initial linear phase. Comparison data for SCM from Snellings (2013).

clays offer an alternative with zero raw-material-related CO₂ (RM-CO₂) emissions. The challenge is to achieve adequate reactivity in order to minimize activator content. Another viable option is glass synthesis from silicate minerals, which is considered here. Their RM-CO₂ emissions are zero when using silicate minerals, and in comparison to clays, their feedstocks more widespread. Here, we discuss the requirements for such glasses and report on glass compositions inspired by industrial basaltic stone wool compositions with concurrently low RM-CO₂ emissions and high alkali solubility. The above-expected reactivity of the glasses is thought originate from dilution of the main network-forming species, silicon, and further enhanced by phase separation that drives glass into high-silicon and low-silicon regions, and therefore affects reactivity. Phase separation in the most alumina-rich sample is further studied, and is thought to be caused by moderate cooling rates. The enabling role of glass-glass phase separation is discussed in the context of reactive glasses in cementitious systems. Altogether, our results indicate that controlled phase separation could be an enabling factor in decoupling the CO₂ emissions and reactivity in glassy cement supplements.

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UNDERSTANDING THE RELATIONSHIP BETWEEN MICRO AND MACRO-SCALE PROPERTIES IN SODIUM SILICATE ACTIVATED SLAG-FLY-ASH BINDERS

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Key Words: slag, fly ash, binder, MAS-NMR, UWR

Sodium silicate activated slag-fly-ash binders (SFBs) are room temperature hardening binders that have excellent mechanical properties and significantly lower carbon footprint than OPC. The aim of this study is two-fold. One is to understand setting in slag fly ash binders as a function of slag/fly ash ratio by using two complementary methods namely, Ultrasonic Wave Reflectometry (UWR), and modified Procter penetration test (ASTM C403). The other aim is to develop a method to differentiate and quantify all poorly-ordered phases (unreacted slag, unreacted fly ash, C(A)SH and geopolymer) present in slag fly ash binders as a function of curing time, curing temperature and slag/fly ash ratio. This was achieved by using selective chemical extractions and nuclear magnetic resonance (MAS-NMR) spectroscopy of binders and extraction residues. The results from MAS-NMR were used to explain the observed trend in compressive strength, as a function of the same variables listed above.

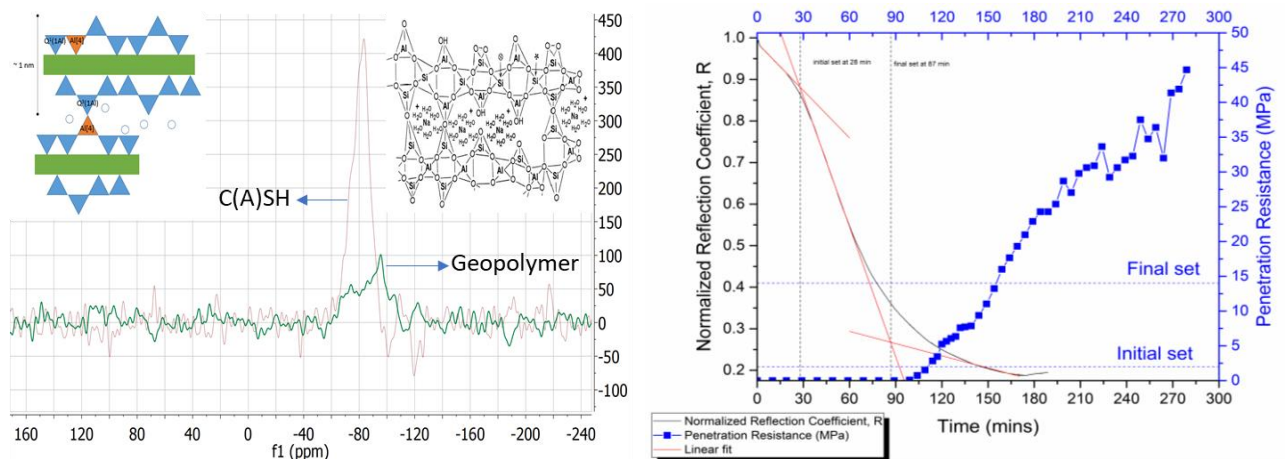


Figure 3 – (left) ^{29}Si MAS-NMR of poorly-ordered phases in SFB (right) UWR and penetration test for monitoring setting in SFB

RETARDATION IN ALKALI-ACTIVATED MATERIALS VIA ZINC OXIDE: MECHANISM AND IMPLICATIONS

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Key Words: admixtures, zinc oxide, retardation, reaction kinetics, X-ray PDF

For ordinary Portland cement (OPC), chemical admixtures and additives that manipulate its hydration and setting are widely available. However, for alkali-activated materials (AAMs) the number of such admixtures that effectively manipulate short-term properties is severely limited. This scarcity of robust admixtures is attributed to the differences in solution and surface chemistry between OPC and AAMs, where existing admixtures are either unstable in the alkaline solution or show mixed/limited efficacy. Here, we utilize zinc oxide, a known retarder for OPC hydration, and investigate its influence on the alkali-activation reaction. We find that ZnO is a robust retarder for alkali-activation of blast furnace slag but has no effect on metakaolin-based AAMs. Using isothermal calorimetry and in situ X-ray pair distribution function analysis, the mechanism of ZnO retardation in alkali-activated materials is uncovered, revealing that calcium plays a pivotal role. Finally, since there is an ongoing debate on the retardation mechanism of ZnO in Portland cements, the results obtained here are significant for developing a fundamental understanding of retarding admixtures in general.

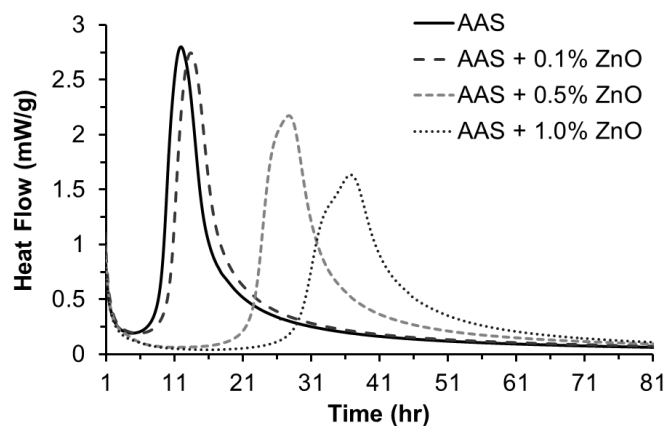


Figure 4 – Isothermal calorimetry data of alkali-activated slag (AAS) pastes with and without various amounts of ZnO.

RHEOLOGICAL BEHAVIOUR OF FRESH INORGANIC POLYMER PASTE: POLYMER BRIDGING EFFECT OF THE ALKALI SILICATE SOLUTION

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Key Words: Inorganic polymers, polymer bridging, ATR-FTIR, Herschel-Bulkley.

Inorganic polymers (IP), produced by alkali activation of a glassy precursor, have been mainly investigated on their microstructure and mechanical strength properties. However, it is important to understand how the IP flow behaves under shear conditions, in particular when pumping is required. The activating solution is one of the main parameters influencing rheology. Therefore, the physical effect of the silicate structure on the rheology was investigated by varying the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio from 1.4 to 2.0 in the activator. The elastic and rheological properties of the IP were measured with a rheometer. In order to investigate the activator silicate structure and IP polymerisation development, Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (NMR) were performed. A decrease in elasticity was monitored for IP with a low $\text{SiO}_2/\text{Na}_2\text{O}$ ratio as a result of the dissolved species, which can be correlated to NMR. The FTIR spectra implied that an activating solution with a higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratio resulted in the formation of a 3D silicate network with Q_3 and Q_4 crosslinks. The presence of a network modifier in the activating solution, such as Na, resulted in more Q_1 and Q_2 crosslinks. A higher stress, at a shear rate of 0.1 s^{-1} , was observed in IP which consisted of a 3D silicate network as a result of the polymer bridging effect between the particles. A stronger shear thinning was observed in an IP with a higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, due to the steric hindrance from the entangled silicates. The rheological data of the IP can be fitted with the Herschel-Bulkley model.

AMORPHOUS, SELF-HEALED, GEOPOLYMERS (ASH-G AND CERAMICS (ASH-C) MADE BY THE GEOPOLYMER PROCESSING ROUTE

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This work describes the cross fertilization of conventional whiteware production by a low energy, geopolymer processing method. Bone china is conventionally made using natural cow bone ash (calcined) of hydroxyapatite (HA). In this study HA and dicalcium phosphate (DCP) particulate reinforcements were investigated in potassium-based geopolymer composites (KGP). Particulate reinforcements of 5, 10 and 15 wt % each of hydroxyapatite and dicalcium phosphate particulate were added to potassium geopolymer to compare with composites made from BASF® Metamax metakaolin (KGP MT), Mymensingh clay metakaolin, KGP(MW) and synthetic Mymensingh clay metakaolin, KGP(MW-SYN). Microstructural properties using SEM, XRD and mechanical properties using Instron were investigated for the geopolymer samples at both room and high temperature. The XRD of pure and reinforced geopolymer samples at RT confirmed the formation of geopolymer analogues with the characteristic X-ray amorphous hump at 28° in 2θ , along with the crystalline peaks observed in KGP (MW), as well as in potassium geopolymer reinforced with hydroxyapatite and dicalcium phosphate. Thermally treated geopolymer composites at $1150^\circ\text{C}/1\text{h}$ exhibited crystalline peaks of leucite, kalsilite, monetite and quartz confirming the signature of geopolymer ceramics at elevated temperature. SEM revealed fully reacted and homogenous aluminosilicate matrix in all the geopolymer samples cured at room temperature for 7 days. Geopolymer composites KGP (MT)-15 DCP, KGP(MW)-15DCP and KGP(MW-SYN)-15DCP after thermal exposure at 1150°C revealed microstructural integrity with the formation of phosphate glass, while a self-glazed surface was developed in KGP (MW) after being heated at $1125^\circ\text{C}/1\text{h}$. Their high temperature properties are superior to RT properties due to amorphous self-healed glass formation (ASH) from the DCP phosphate glass. Their high temperature properties were superior to RT properties due to amorphous self-healed glass formation (ASH) from the DCP phosphate glass. The optimum DCP content was 10 wt % which gave flexure strengths of ~ 32 MPa after heat treatment at $1150^\circ\text{C}/1\text{h}$.

EFFECT OF CHEMICAL STRUCTURE ON THE EFFICIENCY OF SHRINKAGE REDUCING ADMIXTURES IN ALKALI ACTIVATED SYSTEMS

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Key Words: alkali activation, blast furnace slag, shrinkage, shrinkage reducing admixtures, chemical structure

Alkali activated binders, especially those based on alkali activated blast furnace slag (AAS), have the potential to become an alternative construction material to ordinary Portland cement binders. Nevertheless, AAS has some disadvantages which prevent its broader practical applications. An extensive shrinkage is one of the main limiting factors. Therefore, the study of chemical admixtures mitigating especially the drying shrinkage is necessary to be performed. The efficiency of suitable shrinkage reducing admixtures depends on the chemical structure of used surfactants. The study is consequently focused on the molecular architecture of amino alcohol surfactants which are closely associated with their ability to effectively reduce shrinkage. The molecular structure of used chemical compounds is shown in Figure 1. The influence of different substituents bounded to the secondary amine group was studied in terms of their effect on alkali activation, mechanical properties, microstructure arrangement and in particular on the enhancement of drying shrinkage reduction. It was determined that the addition of any tested admixture delayed the CASH gel formation which negatively influenced the flexural as well as compressive strengths in the early stages of hydration process (1 – 7 days). However, only slight decrease in strengths compared to reference sample was measured after 28 days of curing. The deeper insight into the microstructure (Figure 2) confirms previous results. It is obvious that in the case of reference sample the consistent matrix of binding phase is created after 24 hours. On the other hand, only thin layer of hydration products is formed in samples containing the admixture, which increases the porosity of material and tends to the deterioration of mechanical properties. Finally, the study confirms that the reduction of surface tension in pore solution occurs primarily with admixtures containing branched substituents, which further decreases the capillary tension responsible for the shrinkage according to Young-Laplace equation. The presented study highlights the essential role of molecular structure of shrinkage reducing admixtures contributing to the development of a new range of additives designed especially for alkali activated materials.

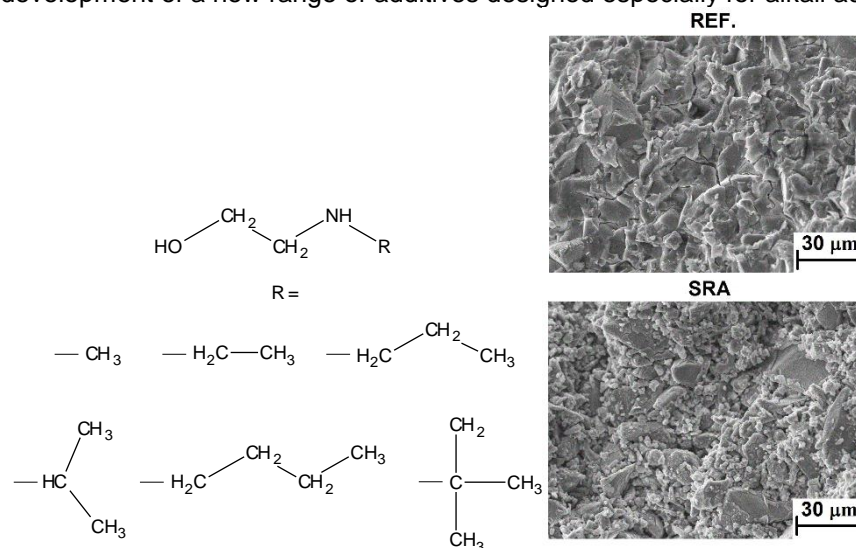


Figure 5 – Molecular structure of used amino alcohol surfactants

Figure 2 – SEM fracture areas of AAS without (REF.) and with shrinkage reducing admixture (SRA) after 1 day of alkali activation

INFLUENCE OF DIFFERENT TYPES OF SUPERPLASTICIZERS ON ONE-PART ALKALI-ACTIVATED SLAG MORTARS

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Key Words: Ground Granulated Blast Furnace Slag (GGBS); Alkali-Activated Materials; Alternative Binders; Mortars; Superplasticizers.

This paper presents an experimental study carried out to investigate the influence of different types of superplasticizers on the fresh and hardened properties of one-part alkali-activated slag mortars. Three different admixtures were added to the mixes at the level of 1.3% by binder mass. In particular, sulphonated polymer-based, polycarboxylates-based and lignosulfonates-based high-range water reducers were used. In addition, a hardening accelerator was added to the mixes up to 1.0% respect to binder mass. Ground granulated blast furnace slag (according to EN 15167-1) as precursor and sodium metasilicate pentahydrate: potassium hydroxide : sodium carbonate = 7:3:1 in powder form as activator were used to produce different mortars with the dosage of activator between 2% and 16 % vs binder mass. The water was adjusted in order to attain the same workability at the end of the mixing procedure, equal to 160 mm \pm 10 mm by means of a flow table. The specimens were cured in climatic chamber at 20°C and R.H. 60%. The effectiveness of the admixtures has been investigated in terms of percentage of water reduction, workability loss over time and compressive strength.

The experimental data show that all superplasticizers provides a reduction in mixing water. The admixtures are influenced by the presence of the activator. In fact, the water reduction, at the same initial workability, is maximum in mortars manufactured without activators. However, the ability of water reducers is not influenced by the activator/precursor. Moreover, results indicated that as consequence of superplasticizer addition, the pot-life of reference mortars manufactured without superplasticizer (60 minutes) is extended up to 160 minutes. The addition of high-range water reducers does not delay the development of 1-day compressive strength. On the other hand, it causes a little reduction of mechanical properties at 7 and 28 days respect to the reference mortars, regardless of superplasticizers employed. Finally, the use of hardening accelerator admixture does not determine a reduction in workability loss over time while no improving was detected on the mechanical strength at early and long ages.

DEVELOPMENT OF GEOPOLYMER COMPOSITES REINFORCED WITH FIBER FELTS USING AN INDUSTRIAL APPROACH

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Key Words: Geopolymer, composites, fibers felt

Geopolymers are synthetic inorganic alumino-silicate materials generally formed by reaction of an aluminosilicate with an alkali (Na,K) silicate solution. The reaction occurs at room temperature, so geopolymer can be considered as a type of bi-component inorganic resin.

Considering their inorganic structure, geopolymer composites have better thermal properties than organic resins, which typically decompose by oxidation starting from ~400°C.

In collaboration with Trucker Subforniture s.r.l., geopolymer based composites reinforced with different kinds of felt, have been developed as alternative to GFRP, for applications where a high thermal resistance is required. Glass and basalt fibers were considered as reinforcement; using felts based on recycled fibers it is possible to keep the cost lower than that of virgin fibers for basalt fibers. Geopolymer composites were developed using an industrial technology. In order to have a good infiltration of the felts, the composition of a potassium based geopolymer resin was optimized in terms of water and alkalinity to tune the rheology and the reactivity in function of the temperature.

Density, mechanical properties and thermal stability of the different composites were tested.

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DRYING SHRINKAGE BEHAVIOR OF METAKAOLIN-BASED AND BAMBOO FIBER REINFORCED GEOPOLYMERS

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Key Words: Durability, sustainable composites, MOR, E.

This Brazil-USA collaborative research uses bamboo cultivated in the Amazon region and metakaolin attained from calcined Amazonian kaolin. The durability of sustainable geopolymer materials is studied by means of the drying shrinkage aging behavior. Scanning electron microscopy and energy dispersive x-ray fluorescence were used to investigate the microstructure of the composite materials. X-ray diffraction was used to confirm the formation of geopolymer. The water treated geopolymer matrix (GP) samples dried at room conditions for the periods of 3-7-14-21-28-56-112 days showed very close and increasing weight and length changes. The GP reinforced with bamboo fiber (GPBF) treated samples weight and length changes increased from the 3-day sample up to the 21-day, then it dropped down to the 112-day. The GP water treated samples dried at room conditions for the aging periods showed increasing flexural strength (MOR) and modulus of elasticity (E). The GPBF treated samples MOR were higher and very close to each other.

ENVIRONMENTALLY FRIENDLY IMMOBILIZATION OF RADIOACTIVE WASTES IN AN ALKALI ACTIVATED CEMENT MATRIX

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Key Words: alkali activated cement, cement matrix, solidification, immobilization, zeolite-like.

The paper presents data on efficiency of immobilization of low level radioactive wastes of nuclear power stations using the alkali activated cements as a binding agent in comparison with Portland cement. Much higher efficiency of the alkali activated cements is attributed to abilities of the alkali activated cement matrix, on the contrary to the Portland cement one, to bind radioactive nuclides not only physically and adsorptionally, but chemically. As a result of specific features of the alkali activated cement hardening processes the conditions occur, under which the zeolite-like phases (analogues to natural zeolites) with the crystalline lattices in which Cs and Cr can be disposed, to form, for example, Na-Sr-analcime – wairakite, Na-Cs-analcime – pollucite, gismondine (with the higher adsorption capacity) occur. Compositions of the alkali activated cements and those of the final products using real nitrate- and borate-containing wastes of various composition were chosen experimentally at the nuclear power stations after preliminary work with the waste imitators at the laboratory. Properties of the final products, these were: leachability, biological resistance, freeze/thaw resistance, water resistance, strength, were tested and the results are discussed. A conclusion was made that all above properties of the final products in which the alkali activated cements were used were at least by 10–20 % higher than those of similar products made using Portland cement, and in leachability (leach rate) exceeded by 5–10 times.

The paper also includes description of solidification processes used at the nuclear power plants with using of alkali activated cements.

ACID GEOPOLYMER MATERIALS BASED ON DIFFERENT ALUMINOSILICATE SOURCES

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Key Words: metakaolin, phosphoric acid, geopolymer, composites.

Geopolymers synthesized from the reaction of metakaolin (or aluminosilicate) in an alkali medium are studied since decades [1]. However, in order to develop composites, alkali medium is undesirable due to the detrimental effect of alkali ions on fibers. As an alternative, the use of an acid medium seems promising as some authors demonstrated an increase of mechanical properties with acid-based geopolymers [2, 3]. The aim of this work is to investigate the various formulations and to understand the reactional mechanisms.

The work is based on the activation of an aluminosilicate source with phosphoric acid to obtain geopolymer. The various formulations consist to determine the Al/P ratio leading to consolidation at various temperatures (from 20 to 70°C). The samples were characterized by Fourier Transform Infrared and Nuclear Magnetic Resonance spectroscopies and X-Ray Diffraction measurements in order to study their structure. The thermal and mechanical properties were correlated with the microstructure [4].

Consolidated geopolymers were synthesized with different Al/P ratios. The consolidation time decreases with increasing Al/P ratio. For instance, the material realized with Si/Al=1,17 consolidates at 20°C in 15 and 8 days with Al/P=4 and 1, respectively. Two behaviors can be distinguished: samples presenting good fire resistance (Si/Al=1,17 and Al/P=1) or presenting poorly water resistant (Si/Al=1,17 and Al/P=4). Consequently, the impact of the reactivity of the aluminosilicate source on the geopolymerisation kinetics leads to different types of structures (secondary and metastable phases) in relation with the phosphorus content.

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STUDY OF GEOPOLYMERIZATION MECHANISMS BY ^{27}Al -NMR AND CALORIMETRY CORRELATION

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Key Words: geopolymer, metakaolin, ^{27}Al NMR, calorimetry, mechanisms

Geopolymers are alumino-silicate binders prepared by reacting a powdered alumino-silicate source (metakaolin) with an alkali silicate “activating” solution. The geopolymerization reaction is a complex process but it is consensual that geopolymers are formed by dissolution of the metakaolin and condensation reactions between silicates and aluminates initially in solution or as dissolution products. However, those two processes occur concomitantly during the geopolymerization. It makes it difficult to study geopolymerization mechanisms in detail for kinetics or thermodynamics purposes. This could explain why detailed mechanistic descriptions are scarce in the literature and why this topic is still a matter of debate.

In this study, an experimental method highlighting the different mechanisms involved in the geopolymerization is proposed, allowing the determination of a thermodynamic parameter of the system. The different processes constituting the geopolymerization were dissociated by varying the metakaolin content in geopolymers, for a given activating solution. Reactivity of such mixes was investigated by isothermal conduction microcalorimetry (ICC). Time resolved ^{27}Al static Nuclear Magnetic Resonance (NMR) was used to monitor the concentration of aluminate centers in solution during the reaction.

The correlation as function of time of the total heat release measured by ICC with the aluminate centers concentration in solution exhibited the existence of a master curve allowing the determination of a reaction enthalpy. The influence of alkali cations, silicate species and aluminate ions on this reaction enthalpy was then investigated. For the first time, the dependence of the geopolymer thermodynamics over the initial composition of the system was highlighted

USE OF SODA LIME GLASS WASTE AS SILICA SUPPLIER IN FLY ASH BASED GEOPOLYMERS

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Key Words: Fly ash-based geopolymers; waste glass; leaching test; machinability.

Geopolymers have been primarily proposed for the construction industry as a substitute for Portland cement considering the lower CO₂ emissions associated with their production. The relatively high compressive strength and chemical inertness of geopolymers, in addition to the possibility to incorporate in the network hazardous waste materials, increase the current interest in this technology. Geopolymers are usually composed of an aluminosilicate source activated with a solution of sodium silicate and sodium hydroxide. The present study evaluates the feasibility of using waste glass as silica source instead of water glass in geopolymer production, using sodium hydroxide as the only non-waste material. The samples were developed changing the SiO₂/Al₂O₃ molar ratio and the molarity of the sodium hydroxide solution.

Fig. 1 shows that the compressive strength tends to rise as the molarity of the solution as well as the SiO₂/Al₂O₃ molar ratio increase. The compressive strength values, around 45 MPa, are comparable to those of traditional Portland cement and they are remarkable considering the high amount of waste glass (70% wt.) incorporated in the matrix. SEM pictures demonstrated the formation of a compact matrix indicating the high reaction degree of the raw materials.

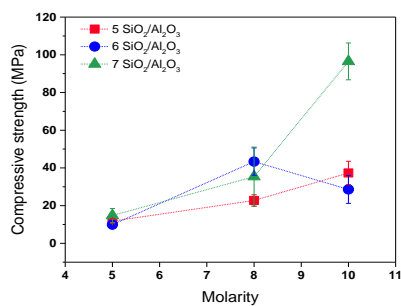


Figure 6 – Compressive strength of the samples, after 28 days.

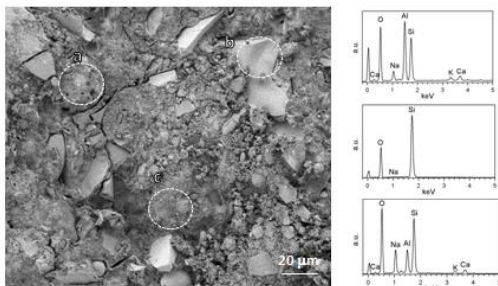


Figure 2 – SEM image and EDX spectra of geopolymers fabricated with 6 SiO₂/Al₂O₃ molar ratio and 8 NaOH molarity.

In Fig. 2 the EDX analysis for sample with 8 NaOH molarity and 6 SiO₂/Al₂O₃ molar ratio, shows that the relative height of peaks related to Al and Si is consistent with a Si/Al molar ratio as expected from the formation of a geopolymer material. The results from leaching tests verified the excellent chemical stability of the present samples, confirming the capacity to produce a valuable robust and chemically durable product from waste materials. Moreover different processing technology such as 3D printing and machinability were evaluated to obtain a more versatile material to expand the range of possible applications

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PERFORMANCE OF SODIUM CARBONATE/ SILICATE ACTIVATED SLAG MATERIALS

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Keywords: alkali-activated slag, sodium carbonate, mechanical strength, durability, shrinkage

Alkali-activated slag (AAS) materials are acknowledged as environmentally friendly due to the reduced embodied energy associated with their production. However, the use of highly alkaline solutions such as sodium silicate to promote the chemical reactions that lead to their hardening, poses potential human and environmental hazards that might constrain their utilization beyond specialized applications.

It is possible to use less alkaline solution based on near-neutral salts as activators, such as sodium carbonate, to produce alkali-activated slag binders with desirable properties. However, to achieve this, the 'right match' between slag chemistry and activation conditions is required. The use of sodium carbonate presents several advantages compared with using sodium silicate when producing AAS, including reducing alkalinity to values comparable to that of Portland cement, and extending the setting time and improving workability, which facilitates the casting of these materials. Sodium carbonate-activated slag binders do not always meet the setting time and strength requirements for on-site concreting, which has limited the application of these materials. A recent study in pastes demonstrated that the addition of sodium silicate in these binders significantly improves the compressive strength development, while effectively controlling the kinetics of reaction, which makes AAS binders produced with a blend of activators an attractive candidate for producing concretes.

In this study we report compressive strength, water absorption and durability properties of AAS concretes produced with a blended sodium carbonate/silicate activator. Shrinkage microcracking of these materials was also studied, by drying the specimens for 8 weeks at 65% relative humidity (RH) and 23°C. The results obtained are compared with concretes produced solely using sodium silicate as alkali activator.

EFFECT OF RECYCLED GEOPOLYMER CONCRETE AGGREGATE ON STRENGTH DEVELOPMENT AND CONSISTENCE OF PORTLAND CEMENT CONCRETES

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Key Words: Recycled aggregates, geopolymers concrete, calorimeter.

Numerous studies have shown that production of geopolymer cement concretes can have lower carbon emissions compared to Portland cement concretes. However, for a full lifecycle assessment of environmental impacts, scenarios for the end of structures' design life must be considered, including reuse options. The work presented here is part of a wider study investigating the recyclability of fly ash-slag geopolymer cement (GC) concrete as an aggregate in Portland cement (PC) concretes.

Three types of GC concretes with varying Na_2O % per mass of precursor and $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio were produced in the laboratory. All other mix design parameters were kept constant. The concretes were investigated thoroughly through physical and mechanical testing and chemical characterization at various ages and then crushed mechanically to form recycled geopolymer concrete aggregates (RGCA).

Two series of PC concretes with 20% aggregate replacement by RGCA were produced – one of S1 consistence class and one of S3 consistence class (design slumps of 10-40mm and 100-150mm). The effect of RGCA on PC concrete fresh properties was investigated. The compressive strength development was assessed by testing at 7, 28 and 90 days. All results were evaluated against concretes with recycled Portland cement concrete aggregates (RCA) and natural limestone aggregates. These results were paired with calorimetric studies of pastes produced with recycled concrete aggregate leachate.

Although mix designs were adapted according to water absorption requirements, the consistence of concretes appeared to be largely dependent on the type of aggregate. The results showed that strength trends remained unaltered between the two concrete series and were mostly influenced by the aggregate type. Mixes with RGCA presented overall higher strengths than the RCA and limestone aggregate concretes. Tests at 90 days showed a continuous increase of compressive strength, while the trends between the concretes remained unaltered. Overall, this study has shown that RGCA affect new concretes in a different way to RCA. However, none of the factors investigated here should prevent the use of RGCA in new concretes.

FACTORS INFLUENCING SETTING TIME OF ALKALI ACTIVATED BLAST FURNACE SLAG

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Key Words: alkali activation, blast furnace slag, soda, setting time

Fast setting of geopolymers and alkali activated materials is often presented as an advantage. However, if setting is so fast that forming and molding becomes problematic, this turns into a disadvantage. In most civil applications a setting time between 1 and 2 hours is the minimum for proper and safe operation. Especially when using blast furnace slag based alkali activated materials, the setting time can be in the order of minutes only, and therefore there is a need for ways of extending the setting without compromising the resulting final strength.

Activation of blast furnace slag with a water glass solution results in short initial setting times in the order of 10 to 40 minutes. The setting time slightly increases with increasing $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of the water glass (M_s), but optimal final strength of around 50 MPa is found for M_s -values in the order of 1 to 1.6.

Addition of borax gives hardly any improvement if the borax is added as powder to the solids. However, if borax is first dissolved in the activator solution, 5% w/w addition of borax is capable of almost doubling the initial setting time.

Addition of soda showed an increased setting time from 45 minutes with no soda up to 90 minutes with 5% soda. Compressive strength also shows an increasing trend with increasing soda addition. Higher soda additions decreased both setting time and compressive strength.

Instead of adding new components to the mixture design, changing the physical conditions of operation can as well have an effect on the setting time. By cooling the activator solution to 5 °C and then mixing with the precursor at 20 °C, the initial setting time was already extended from 30 minutes (for everything at 20 °C) to 50 minutes. Conversely, preheating the activator solution to 30 °C decreased the initial setting time to 20 minutes. Further heating up to 50 °C resulted in instantaneous setting. In general, the relation between activator temperature and setting time follows a linear trend. Temperature has also a significant influence on the viscosity of the solution, which may have an impact on the extent of mixing. However, within the range of 5 °C and 30 °C, at laboratory scale the same compositions could be mixed for the same mixing times without any practical problems.

AUTOGENOUS SHRINKAGE INDUCED STRESS OF ALKALI ACTIVATED SLAG AND FLY ASH CONCRETE UNDER RESTRAINT CONDITION

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Key Words: Autogenous shrinkage, Stress, Creep, Restraint condition, Elastic modulus

Autogenous shrinkage is an important engineering property for construction materials since it can induce internal tensile stress and consequent micro- or macro- cracking of the concrete. Alkali activated slag and fly ash (AASF), as a promising alternative to ordinary Portland cement (OPC), has shown many interesting properties such as high early age strength, good durability and fire resistance, but it also shows high autogenous shrinkage in the meantime, which hinders a wider application of this eco-friendly binder material. However, high autogenous shrinkage doesn't necessarily mean high stress of the material under restraint condition, since there are creep and associated stress relaxation happening simultaneously. Therefore, the creep of AASF needs to be considered in order to better understand the stress induced by autogenous shrinkage. In this study, the autogenous shrinkage induced stress of AASF concrete (with a liquid/binder ratio of 0.5) under restraint condition is measured by Thermal Stress Testing Machine (TSTM). The free autogenous shrinkage of a twin specimen is measured by Autogenous Deformation Testing Machine (ADTM). The elastic modulus of AASF concrete is tested on prisms. The creep coefficient of AASF concrete is calculated based on the stress, free autogenous shrinkage and elastic modulus. It is found that the creep coefficient of AASF concrete is much higher than that of OPC concrete, and creep plays an important role in relaxing the shrinkage induced stress and thus reducing the cracking potential of AASF concrete.

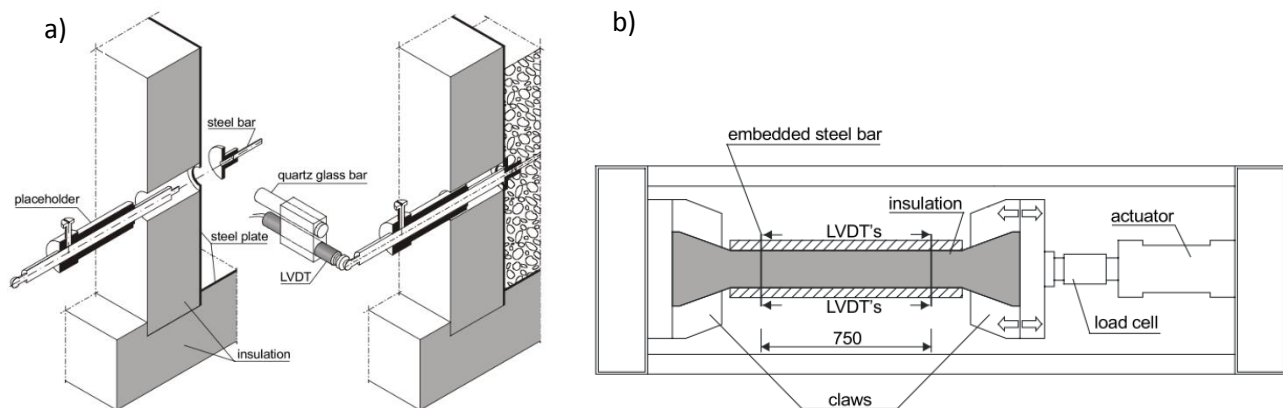


Figure 7 – (a) Detail of experimental setup for the measurement of the free deformations of concrete (ADTM) and (b) top view of experimental setup for the determination of stress development in concrete (TSTM)

ULTRA-HIGH PERFORMANCE ALKALI ACTIVATED MATERIAL WITH SILICA FUME AND NANOSILICA

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Key Words: UHPC, rheology, capillary porosity, compressive strength, microstructure

Based on the principles of ultra-high performance concrete a cement free, alkali-activated system was optimized in order to enhance the strength and durability. This system is based on a ground granulated blast furnace slag and the activator is a combination of potassium water-glass and potassium hydroxide. Furthermore, inorganic fines were used for enhancing the packing density. As aggregates, quartz sand (0-2 mm) and quartz powder are added. The rheological properties could be improved by adding a certain amount of silica fume. A water/binder ratio of 0.25 was realized using a certain mixing procedure on a high-intensity mixer. The compressive strength reaches 150 MPa after 14 days, which lies in the range of an ultra-high performance concrete. The rheology was measured by using a rotation rheometer depending on time and silica fume content. Different silica fumes were tested in order to vary the grain sized distribution and the chemical composition. Beneath silica fume with a d50-value of 2 μm also nanosilica with a d50 value of 0.2 μm was tested in terms of gaining higher strength and durability and as well in terms to enhance the rheological properties. The silica fume could be substituted by nanosilica, which proofs that the improving rheology is not only due to the ball bearing effect of silica fume. The microstructure of the hardened AAM was investigated using SEM, FTIR, XRD and MIP.

This material was used as basic material in different applications: as face concrete of paving slabs, chemically foamed light weight concrete (600 kg/m^3 - 4 MPa) and high performance lightweight concrete (1800 kg/m^3 – 100 MPa).

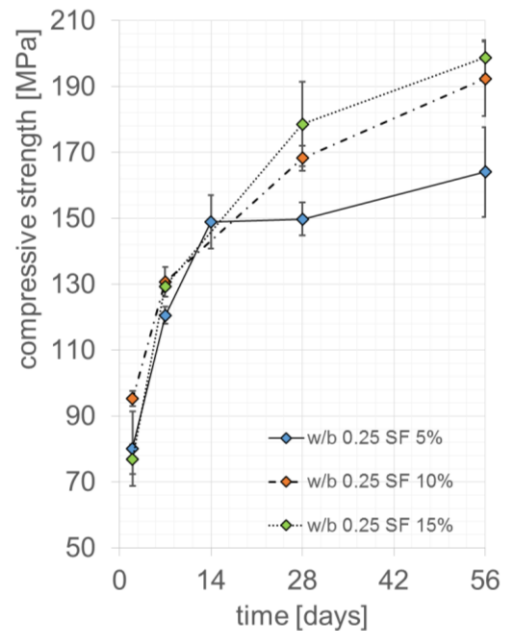


Figure 8 – Compressive strength of UHPAAM

EFFECT OF GEOPOLYMER COMPOSITION AND CURING CONDITIONS ON EFFLORESCENCE IN LIGHTWEIGHT POROUS GEOPOLYMERS

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Key Words: Geopolymers, lightweight, foaming, efflorescence

Lightweight geopolymers are more readily produced and give higher fire resistant performance than foam cement concrete. The fly ash-based lightweight geopolymers stones could be used for decoration due to the similarity in appearance and color to natural vesicular basalts. Efflorescence can be even more nettlesome issue in commercialization of lightweight porous geopolymers. Lowering the density of solid geopolymers can be achieved by inducing chemical reactions that entrain gases to foam the geopolymer structure. The apparent density of lightweight porous geopolymers has a range from 0.7 to 1.2 g/m³ with 0.025, 0.05 and 0.10 wt% of Al powder concentration, which corresponds to about 37~60 % of the apparent density, 1.96 g/cm³, of solid geopolymers. The compressive strength of cellular structured geopolymers decreased to 6~18 % of the compressive strength, 45 MPa of solid geopolymers. The microstructure of geopolymers gel was equivalent for both solid and cellular structured geopolymers. The efflorescence can be controlled by reducing targeted Na/Al molar ratio less than 1.0 or water content in geopolymers or curing at high temperature.



Figure 9 – Solid (a) and cellular structured fly ash-geopolymer cylinders ((b)-(d)). Aluminum concentration is 0.025 wt% (b), 0.05 wt% (c) and 0.10 wt% (d).

Acknowledgement

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UNDERSTANDING THE AUTOGENOUS SHRINKAGE IN ALKALI-ACTIVATED SLAG/FLY-ASH BLENDS

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Key Words: Autogenous shrinkage, chemical shrinkage, self-desiccation, condensation shrinkage, Polymerization degree.

Alkali-activated materials offer the potential for more durable, sustainable and low-CO₂ construction and building materials with reduced environmental footprints when compared to Portland cement concrete. However, this new concrete technology suffers substantially from early-age autogenous shrinkage and micro cracking. The aim of this work is to illuminate the intrinsic reasons that are responsible for larger autogenous shrinkage in alkali-activated slag/fly-ash (AASF) blends by understanding the essential link between solidification process (reaction mechanism, kinetics, phase formations and binder structures) and early-age autogenous shrinkage deformations.

In this study, six different compositions of AASF are studied by varying the type and the concentration of three different activators: sodium metasilicate, combinations of sodium metasilicate with sodium carbonate and sodium sulfate. The results show that the solidification process strongly depends on both the alkalinity and anion type of the alkaline solution. A higher alkalinity (high amount of Na₂O) accelerates the reaction process, as the presence of OH⁻ ions enhances the dissolution of slag and also increases the solubility of silica and alumina. Therefore, the intense autogenous shrinkage of alkali-activated slag at early-ages can be attributed to the high amount of chemical shrinkage. Autogenous shrinkage of alkali-activated slag is not only caused by well-known self-desiccation process in hardened state, but related to the condensation shrinkage. The larger autogenous shrinkage in AAS may also be attributed to refined pore structure and silica polymerization, which is controlled by the nature of anion presence in the solution.

COMBINING CHEMICAL AND MECHANICAL FOAMING IN GEOPOLYMER FOAM CONCRETES

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Key Words: Geopolymer foams, H_2O_2 , chemical foaming, mechanical foaming,

Chemical and mechanical foaming techniques have been successfully used in foam concrete technology for introducing voids in concrete, enhancing their thermal insulating properties, and reducing their weight. The combination of both foaming techniques have been proved useful in reducing the pore size and narrowing the size distribution of the pores in foam concretes. However, there is no clear understanding regarding the impact of combined foaming on structural properties and thermal performance of geopolymer foams. In this study, different geopolymer foams are made by various combination of chemical and mechanical foaming technique and the impact of pore distribution on thermal and mechanical performance of concretes is investigated. It is concluded that the pore size distribution is not the key factor affecting the performance of foam concretes, and the concrete expansion regime and pore connectivity are more critical aspects.

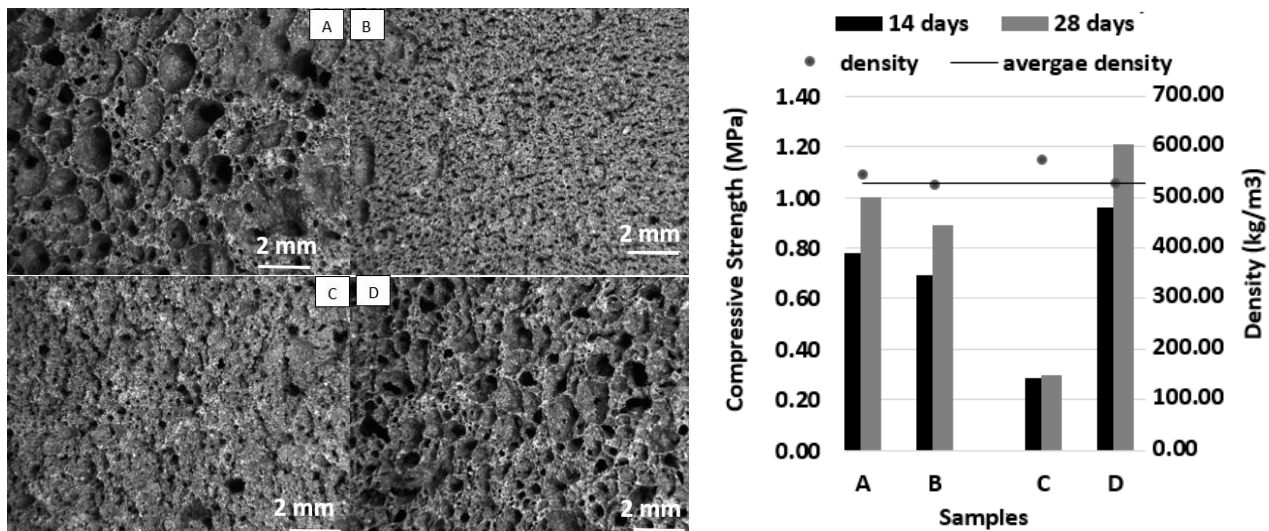


Figure 10 – The impact of combined foaming techniques on pore size distribution and mechanical properties of geopolymer foams

STEEL CORROSION IN DIFFERENT ALKALI-ACTIVATED MORTARS

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Key Words: Alkali-activated Materials, Corrosion in Cementitious Materials, Corrosion Monitoring, Electrochemical Measurements, Concrete Pore Solution

One of the potential alternatives to Ordinary Portland Cement (OPC) are Alkali-Activated Materials (AAMs) [1]. The service life of reinforced concrete structures greatly depends on the corrosion resistance of embedded steel reinforcement. Due to the wide range of AAMs with their diverse properties, corrosion processes of steel in these materials are relatively unknown. Corrosion monitoring methods or their interpretations in certain cases cannot be directly transferred from the ones for OPC materials, and therefore results of different corrosion studies are sometimes contradictory [2]. The chemical composition of pore solution in different AAMs are influencing the results of electrochemical measurements and their interpretation, e.g. the presence of sulphides reduces the redox potential of the pore solution, but enables the steel to remain in an apparently passive state [3]. The aim of this paper is to compare electrochemical parameters measured on steel reinforcement in different alkali-activated and OPC mortars.

Ordinary carbon steel reinforcing bar was installed in three different alkali-activated mortar mixtures, based on fly ash, slag or metakaolin. Specimens were exposed to wet/dry cycles with saline solution and periodic measurements of electrochemical impedance spectroscopy (EIS). Measured parameters were analyzed and compared to the ones measured in reference OPC mortar. The propagation of corrosion damages on embedded steel bars was also followed using x-ray computed microtomography (MicroCT). In addition to corrosion tests, information on pore water chemistry was obtained, as well as general mechanical and physical properties of tested AAMs. In certain specimens also Electrical Resistance (ER) probes were implemented, which can successfully detect corrosion initiation and monitor general corrosion rate [4].

It was concluded that EIS method can follow the evolution of corrosion processes on steel reinforcement in AAMs, although the caution is needed when interpreting the results. The additional use of the MicroCT can provide verification of ongoing results obtained by electrochemical methods, and deeper insight in corrosion processes in AAMs.

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STEEL REINFORCEMENT CORROSION IN ALKALI-ACTIVATED FLY ASH MORTARS

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Key Words: Alkali-activation; Reinforcement corrosion; Carbonation; Chloride attack; Leaching

Corrosion of steel rebars in concrete presents one of the main deterioration mechanisms limiting service life of the reinforced structures. The corrosion is accompanied by an expansion of the corrosion products causing high pressures, concrete cracking and finally spalling of a cover layer. Critical chloride concentration, loss of alkalinity and modeling of the steel corrosion are in researchers' spotlight for decades, however reinforcement corrosion in alkali activated materials is insufficiently described and understood yet.

In this work, the steel reinforcement corrosion in alkali-activated fly ash mortars is investigated in terms of electrochemical behaviour of the reinforced mortars exposed to aggressive environments such as leaching, carbonation and chloride ingress. A selected geopolymer mixture based on hard coal fly ash activated with sodium hydroxide and sodium silicate solutions is used for the steel reinforcement-corrosion experiments. The formation of passive layer on the steel rebars is observed after approx. two weeks of hardening at laboratory temperature. However, alternative heat-treatment at 80°C for several hours leads to immediate formation of the passive layer as well as to a faster strength gain (80 MPa after 24h at 80°C). Chloride-induced corrosion, leaching and carbonation resistance of the alkali activated fly ash-based concrete is studied, where leaching in deionized water or carbonation under natural conditions ($\sim 0.04\%$ CO_2) for 300 days did not lead to corrosion of the embedded steel. On the other hand, accelerated carbonation under 100 % CO_2 atmosphere lead to depassivation within two weeks.

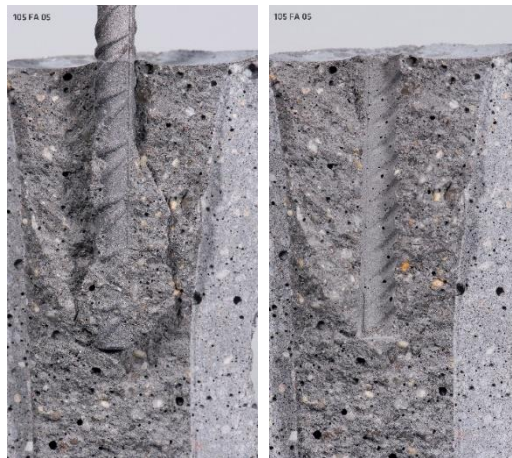


Figure 11 – Carbon steel reinforcement in alkali-activated fly ash mortar after passivation – two weeks of ambient curing.

ON THE ACID RESISTANCE OF ALKALI-ACTIVATED CEMENTS: WHAT ROLE DOES MAGNESIUM PLAY?

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Key Words: Microbial-induced concrete corrosion (MICC), acid degradation, alkali-activated cements, electron microprobe analysis.

Sewer infrastructure worldwide is being affected by microbial-induced concrete corrosion (MICC). This major durability challenge occurs when biogenic sulfuric acid, produced within sewer environments, deteriorates ordinary portland cement (OPC) concrete. While acid-resistant alkali-activated cement (AAC) concrete is a proposed potential solution to this pervasive challenge, all factors contributing to acid resistance are not fully understood. This work addresses current gaps in knowledge by elucidating the role of magnesium on the acid resistance of AACs. A central composite experimental design was utilized to evaluate the effect of (1) silica content, (2) sodium content, and (3) the presence of a magnesium mineral addition on the structure (i.e., mineralogy) and properties (i.e., porosity, acid resistance) of AACs. The mineralogy, porosity, and acid resistance of AACs were explored via X-ray diffraction, ethanol vacuum-intrusion, and electron microprobe analysis, respectively. Results demonstrate that addition of unreacted magnesium minerals yields a decrease in porosity and a decrease in the amount of leached silicon and aluminum during acid exposure, leading to an overall improvement in acid resistance. Furthermore, statistical analysis of experimental data enabled construction of surface response models that aid in prediction of acid resistance. The results presented from this study permit a greater understanding of the acid resistance of AACs and enhance their value as a potential solution to MICC.

STRUCTURE, ACID-RESISTANCE AND HIGH-TEMPERATURE BEHAVIOR OF SILICA-BASED ONE-PART GEOPOLYMERS AND GEOPOLYMER-ZEOLITE COMPOSITES

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Key Words: one-part geopolymers; zeolites; acid-resistance; heat treatment; rice husk ash

One-part geopolymers (OPGs) are a sort of alkali-activated materials (AAMs) which production avoids the use of highly-alkaline activator-solutions and contributes to a better acceptance of alternative mineral binders in terms of safety-related and economic aspects. In the present contribution OPGs were synthesized by blending silica sources (two industrial silicas and two biogenic silicas) with sodium aluminate and only water must be added to initiate the hardening, *i.e.* mixing is performed in the same way as for conventional Portland cements. The OPGs were characterized by XRD, and SEM and the degrees of reaction of the silicas were determined by a chemical dissolution method.

The industrial silicas led to the formation of geopolymer-zeolite composites, that contained, besides geopolymeric gel, crystalline tectosilicates (e.g. zeolite A and hydrosodalite) and depending on the starting composition also unreacted silica. The biogenic silicas provided a higher reactivity and avoided the formation of crystallite by-products. The differences in the microstructures caused differences in the mechanical strength of the specimens [1, 2].

The treatment of the OPG composites at moderate elevated temperatures revealed promising behavior on thermal dehydration in terms of shrinkage and residual strength up to 700 °C. Above 700 °C sintering and partial melting occurred, and new phase formation commenced. After exposure to 1000 °C the specimens appeared virtually amorphous or formed stuffed silica structures of nepheline- or carnegieite-type type [3].

The investigations of the OPG based mortars on their resistance against sulfuric acid in accordance with DIN 19573 (Appendix A) revealed very high residual strengths up to 78 % after treatment with H₂SO₄ (pH 1) for 70d. A mechanism of dissolution of the primary aluminosilicate reaction products of the pastes and the precipitation of a silica gel that protects the remaining aluminosilicates and decelerates further corrosion was found to be the main reason for the good performance under acidic conditions. The addition of CaO-containing feedstocks enhanced hardening, but at a certain content the resistance against sulfuric acid decreased, due to the formation of gypsum on exposure to sulfate.

In addition, the mortars exhibited excellent shrinkage behavior as well as good bond to concrete substrates with pull-off strength up to > 3 MPa. The workability of the fresh mortars provided very good manual applicability; automatic applications such as sprayed and spun mortars will require further optimization regarding rheological properties. In summary, the studied OPG are promising materials for the construction and the repair of concrete structures, such as sewers, that are affected by biogenic sulfuric acid corrosion.

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ASSESSING THE LONG-TERM STRUCTURAL CHANGES OF METAKAOLIN GEOPOLYMERS ENCAPSULATING STRONTIUM LOADED ION-EXCHANGER

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Key Words: Metakaolin geopolymer, nuclear waste, mineral structures, strontium

Zeolite-type inorganic ion-exchangers are extensively used in the nuclear industry to remove fission product radionuclides from contaminated process water and in groundwater cleanup. A significant amount of ion-exchangers loaded with concentrated radioactive isotopes of Sr are generated every year, and this is a particularly pressing issue in the Fukushima Daiichi site, where minimising the environmental release of these radioisotopes is currently the focus of much work. Encapsulation of these granular radionuclide-loaded ion-exchangers, which are often stored as slurries, into a stable solid waste form (as required for disposal) with a low leaching rate of toxic ions is challenging but critical for the safety of long-term geological disposal. Metakaolin geopolymers are attracting interest in the immobilisation of nuclear wastes. However, only limited information is available from the literature regarding the stability of key ion-exchangers in geopolymer binders, and the potential modifications occurring in the binder materials as a function of interactions with the ion exchangers. In this study, an ion exchanger representing those used in the Fukushima Daiichi wastewater treatment process, loaded with inactive isotopes of Sr, was encapsulated using metakaolin-based geopolymers. Different alkali cations were used as activators and the effects of different reaction temperatures were also assessed. The phase evolution, dimensional stability, and changes in microstructure of the geopolymer binders containing Sr-loaded ion-exchanger were characterised up to 1 year, to provide important information for evaluating the partitioning of Sr between the pore solution, ion-exchangers, and the binder.

SYNTHESIS OF GEOPOLYMER FOAMS FOR DECONTAMINATION OF LIQUID NUCLEAR WASTE

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Key Words: monolithic foams, blowing agent, copper hexacyanoferrate, cesium decontamination

Liquid radioactive waste is produced in the nuclear industry and has to be treated to firstly minimize their impact on environment and secondly to propose an ultimate confinement matrix. One way to decontaminate these waste is to synthesize inorganic monolithic filters that are less sensitive to radiolysis phenomena than organic ones. Geopolymer cements are good candidates to fulfill these specifications since intrinsically they are mesoporous with high specific surface area [1] and compatible with specific grafting agents which allow to trap selectively radionuclides of interest (especially the cesium) [2]. For this purpose, a monolithic geopolymer with good mechanical resistance and hierarchical porous network (tailored open macroporosity) was synthesized.

From this geopolymer foam, the precipitation of copper hexacyanoferrate into the porous network has been performed in order to trap selectively the cesium. The functionalized foams were characterized and the trapping capacity of Cs was assessed. After having determined the sorption kinetics, sorption isotherms were performed and the maximum sorption capacity, $Q = 120 \text{ mg/g}$, was measured. Tests in a radioactive environment were also carried out in order to validate the performance of the material in real conditions (traces of Cs in fresh water). The results show that the functionalized material is capable of selectively trapping Cs with a distribution coefficient K_d of $2.37 \cdot 10^5 \text{ ml/g}$. The results demonstrate remarkable potential of this innovative material for Cs removal from liquid nuclear waste.

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RETENTION OF RE IN METAKAOLIN BASED GEOPOLYMER IN THE PRESENCE OF AN ORGANIC REDUCTANT – AN EXPERIMENTAL STUDY

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Key Words: geopolymer, metakaolin, rhenium, oxidation, leaching

The goal of this research was to examine the change in redox sensitive contaminant retention and leaching behavior from a model geopolymer system, during oxidation and carbonation, in the presence of an organic reductant. The behavior of redox sensitive elements under variable environmental conditions is specifically important for understanding the leaching of radionuclides retained in geopolymeric materials (e.g. Tc) that are soluble when oxidized and insoluble under reducing conditions.

An alkali-activated metakaolin geopolymer with high silica/alumina ratio was selected as a model material. Rhenium was selected as the model redox sensitive element, which exhibits a large valence (-3 to +7) and solubility range. Rhenium was introduced in its most oxidized form (VII) as Re_2S_7 . Ascorbic acid was used as a reducing agent during geopolymer casting due to its high solubility and homogeneous distribution within the matrix. Cylindrical monoliths were cured for 90 days under an inert atmosphere (N_2) and then aged for 60 days under 98% N_2 + 2% CO_2 or CO_2 deficient air, at a constant relative humidity (68%). The samples were then subjected to EPA 1313 pH dependent leaching test and EPA 1315 monolith leaching test. Leachates were analyzed using DOC and ICP techniques. XRD and SEM – EDS imaging and analyses were used to characterize the solids

Results show that Re has precipitated as ReS_2 (IV) in the matrix. The pH dependent leaching test shows that Re was released homogeneously throughout most of the pH range (3-12). However, the retention of the material aged under CO_2 deficient air was three times lower, indicating that the main effect on leaching from this material is of the oxidation process. The natural pH values were 11.3 and 12 for the material aged under 2% CO_2 and for material aged under CO_2 deficient air respectively, indicating minor carbonation in the former, however, no carbonate minerals were detected in the matrix.

Monolith leaching results show that the geopolymers aged under CO_2 deficient air have retained significantly less Re (0.24% leaching) relative to the sample aged under 2% CO_2 (0.07wt % leaching). $-\log(\text{diffusivity})$ values were in the order of 15 and 16 for CO_2 deficient air and 2% CO_2 respectively. There is a clear positive correlation between the amount of Re and DOC released from the samples, where their amounts are significantly larger for the samples aged under CO_2 deficient air, indicating that the main Re-release mechanism from these samples is related to chelation to organic species under oxidizing conditions.

STABILIZATION OF SULPHIDIC MINE TAILINGS WITH MGO ACTIVATED BLAST FURNACE SLAG

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Key Words: tailings, stabilization, magnesite, blast furnace slag.

The mining industry is the biggest producer of waste materials in the form of waste rock and tailings. Tailings ponds create potential ecological risks due to hazardous substances the tailings themselves and the toxic additives used in the metal processing phase include (1). For example, in China, tailings storage is rated to be 18/93 among the most dangerous environmental risk sources (2). Serious environmental accidents worldwide, increased public awareness and increasingly stringent environmental regulations have promoted research to develop new innovative approaches to mitigate the risks caused by tailings.

The Pyhäsalmi mine in Finland is one of the largest massive sulphidic ore mines in the world. The tailings potentially generate acid, mostly due to oxidation of iron sulphides (58 %). The total area of the tailings ponds is 150 ha which has mainly been covered with conventional methods at the beginning of the millennium. The mine will be closed in the near future, and the principal aim of the tailings recovery plan is to decrease environmental risks in the long-term by restricting acid generation caused by water and oxygen ingress. Several tailings pond cover liner options are currently under consideration. This study compares tailings stabilization with two alternative binder materials; alkali activated blast furnace slag (AAC) and Portland cement (PC).

Stabilization is a commonly used technology to prevent the leaching of hazardous substances into the natural environment. Stabilization encapsulates hazardous substances both chemically and physically. In the research, MgO-activated blast furnace slag was compared with PC as a stabilization binder using a dosage of 10 w%. According to the literature, MgO activated BFS binder has not been studied or used earlier in the stabilization of tailings while PC is the most commonly used stabilization binder.

However, the long-term durability of PC, especially in highly sulphidic environments, is questionable due to its vulnerability to sulphate attack and ecological impacts. These vulnerabilities are significant due to the need for high binder amounts and consequently required investments. In addition, commonly used liquid alkali activators, for example sodium and potassium hydroxides and silicates, have safety, cost and ecological issues.

In this research, by-product based MgO was used as an activator in BFS instead of liquid alkali activators. The laboratory studies tested hydraulic conductivity, compression strength, oxygen diffusion, leaching, freeze-thaw resistance and water resistance, in addition to chemical, mineralogical, microscopic and thermal analysis. The Life Cycle Assessment (LCA) method was used to compare environmental impacts of the used binder materials. A stabilized tailings layer with a thickness of 300 mm was constructed as a part of the advanced hardpan cover pilot structure of 100 m² in the tailings pond area.

According to the tests, the hydraulic conductivity (6.08E-09 m/s) and compressive strength (11.5 MPa/28 days) of AAC were better than when using the corresponding amount of PC (2.04E-08 m/s and 10.3 MPa/28 days) indicating better immobilization efficiency and thus improved technical performance, in addition to competitive costs. LCA shows clear ecological benefits when using AAC instead of PC: a 35 % lower amount of generated greenhouse gas emissions due to the use of waste based binders. In addition, using the stabilization method in tailings storage reduces the need for natural moraine in the cover structure. The video script illustrates the use of AAC binder in the pilot structure.

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MK-GGBS FOAMS: RELATION BETWEEN MECHANICAL PROPERTIES AND MORPHOLOGICAL PARAMETERS

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Key Words: Foam concrete, porous structure, alkali-activated material, morphological parameters

This study aims to link the thermomechanical properties of blended metakaolin-ground granulated blast furnace slag (MK-GGBS) foam concrete (FC) to their morphological parameters. The AAM FC matrix is composed of MK, GGBS and an alkaline solution. The binder is composed of 62.5% of MK, 12.5% of GGBS and 25% of dry extract of alkaline solution. Water came from the alkaline solution and additional water to reach a water/binder ratio of 0.36. The AAM paste was aerated with different H_2O_2 contents (1, 1.5 and 2%) and stabilized with surfactant. The surfactant content ranged from 0.002 to 0.05 %. Lightweight AAMs were obtained with density from 264 to 480 kg/m³. The analysis of the sectional view pictures revealed that AAMs FC porous structure is highly influenced by both H_2O_2 and surfactant contents. The H_2O_2 content modify the FC density while the surfactant content mostly modified the bubble distribution at a constant density.

The thermal conductivity of the AAMs FC mostly depended on the FC density and ranged between 0.084 and 0.139 W/(m.K). FC compressive strength ranged between 0.53 and 3.34 MPa. It mainly depended on H_2O_2 content. However, at constant density, FC compressive strength also depended on surfactant content. An optimized surfactant content (0.004%) maximizing FC compressive strength at constant density was found. The analysis of the cross view of the FC enables to do a quantitative analysis of the relation between FC composition (H_2O_2 and surfactant contents), porous structure and mechanical performances. However, a more precise quantification of the porous structure was required.

X-ray tomography was performed on several FC samples. The 3D geometries were rebuilt using a software (iMorph) in order to precisely characterize FC morphological parameters. As expected with the sectional view analysis, the FC porosity mostly depends on H_2O_2 content. Bubble size distribution was highly modified by the surfactant content. The analysis also revealed slight bubble shape anisotropy linked to their formation process. The cells had an ellipsoidal shape that can be described by 3 orthogonal axes a , b and c ($a > b > c$) in a 3D referential O,x,y,z . The bubble connectivity was also investigated and it significantly depended on both H_2O_2 and surfactant content. The X-ray tomography enabled to quantify the relation between FC composition and 3D morphology.

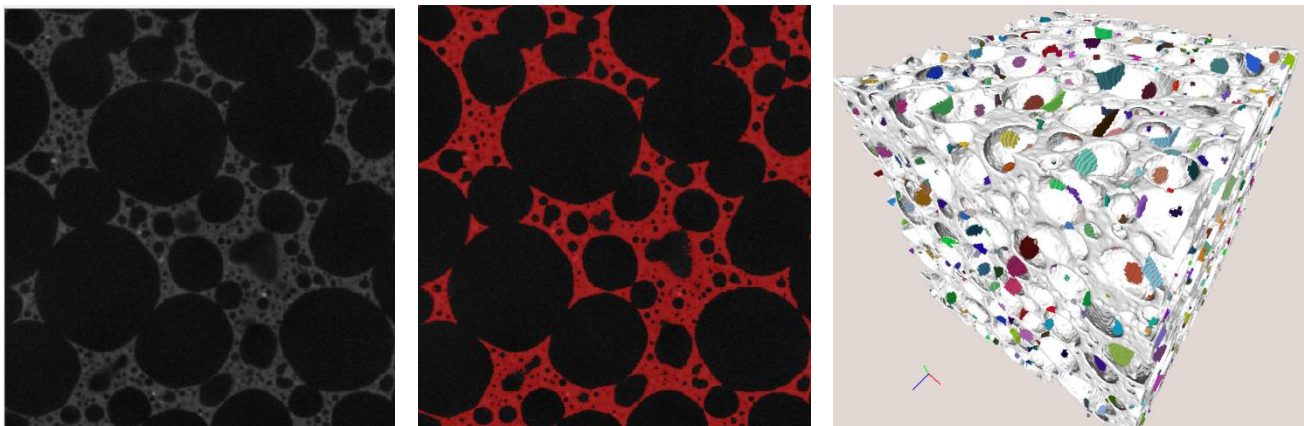


Figure 1. Raw image (left), binarized image (center) and segmentation of each throat on a 3D view (right).

EVALUATION OF ALKALI-ACTIVATED BINDERS SUITABILITY FOR THE STABILIZATION/SOLIDIFICATION OF TUNNEL BORING MUDS

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Key Words: alkali-activated slag, subgrade layer, stabilization/solidification, compressive strength.

In Europe, two major civil engineering projects, the “Grand Paris” automatic metro lines and the “Lyon-Turin” high speed railway tunnel, brought forth for the construction industry an unprecedented prerequisite within schemes of this scale: the necessity to recycle all forms of waste that comes out of the excavation process. By 2030, up to 100 million tons of muds retrieved from the boring operations, likely contaminated with sulphate and heavy metals, will have to be dealt with.

One application that would engage large volumes of these tunnel muds is the development of a stabilized subgrade layer for road construction. Common practices of the road industry dictate the stabilization of soils for subgrade layer design to be performed essentially with quicklime or Portland / Slag based cement. In addition to a proven low carbon footprint, alkali-activated slag binders could turn out to be relevant candidates for a subgrade layer application as their durability in such aggressive environments had already been demonstrated. Following this approach, we assessed the performances of four different types of binder: two alkali-activated slag binders, respectively with NaOH and sodium silicate, a Portland cement and a blended slag cement containing up to 90% of GGBS. Standard mortars were prepared with these four different binders as well as prismatic samples of stabilized mud containing about 90% of mud and 10% of binder. All samples were then cured in sealed bags at 20°C until compressive strength testing.

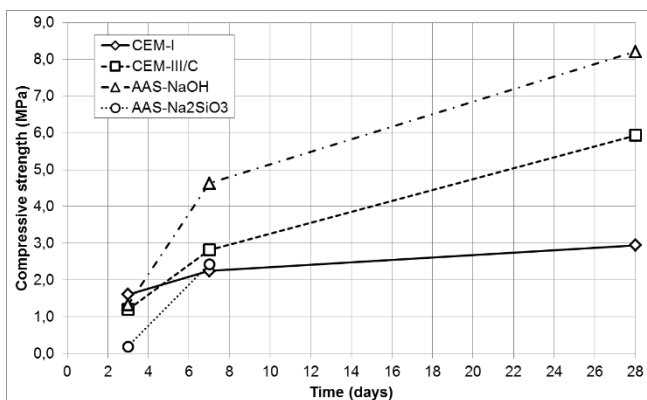


Figure 12 - Compressive strength evolution with time of stabilized mud with 4 different binders.

As shown in Figure 1, even though the exclusive use of Portland cement for mud stabilization provides a higher compressive strength after three days of curing (1.6 MPa), its evolution with time was rather limited after 28 days of curing. On the contrary, using either slag-rich or soda activated slag binders, the three days requirement of 1 MPa has been reached while the strength development with time was significantly higher, with

values respectively of 6 and 8 MPa after 28 days. Finally, when proceeding with the sodium silicate activated slag binder, sufficient solidification does not occur after three days of curing as it could have been expected from results obtained on mortars samples.

In addition, measurement of ultrasonic pulse velocity through freshly mixed samples during seven days has enabled us to follow their macroscopic structuring and estimate quantities of significance like the setting time. Furthermore, the hydration kinetics of each binder, when mixed with a mud sieved beforehand, has been inspected by the means of isothermal calorimetry. For both methods, the results obtained are in good agreement with the compressive strengths highlighted in Figure 1, displaying the limits of a stabilization based solely on Portland cement compared to the use of a CEM-III/C or a NaOH activated GGBS.

NaOH alkali-activated GGBS was shown to be a suitable alternative solution to the traditional binders, such as Portland cement or even a CEM-III/C, for the stabilization/solidification of the studied mud within the specific set of requirements of road applications and especially in the design of sustainable subgrade layers.

GEOPOLYMERS FOR HAZARDOUS CATIONS AND ANIONS INERTIZATION

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Key Words: metakaolin based geopolymers, inertization, chlorine, chromium, soluble salts.

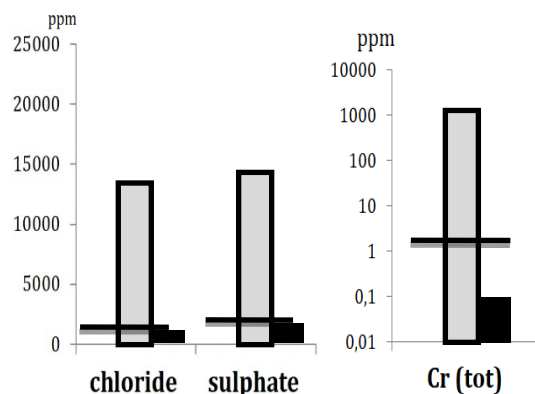
Several waste liquors are classified as toxic or hazardous waste and represent a real burden for companies in terms of costs and treatment time. One of the most difficult to treat is the tannery waste water that represent a high pollution risk if not treated and collected properly.

Geopolymeric matrix based on metakaolin has been used to treat tannery waste water without any post use treatment. The as received waste water containing tannins, chromium soluble salts, phenols, bicarbonates, and a mixture of organic compounds have been added to a geopolymeric formulation which was optimized for Cr^{+3} liquor [1].

The addition of toxic water was added with weight ratio 40:100 to metakaolin powder. The final geopolymer structural integrity was test after 24h and 72h in water. Four week after the synthesis of the geopolymer, the waste-leaching-compliance test was performed according to the European norm EN 12457: the dry sample was washed and weighed, the granular material was poured into bi-distilled water in a flask, with solid/liquid ratio 1/10; the heterogeneous liquid/solid mixture is left to stir for 24h, and, finally, the solid was filtered and the solution analysed via ICP-AES.

The ions released from the material were below the limit fixed by Italian regulation DLGS 152/2006, in the case of chloride (limit 1200 ppm), sulphate (limit 1000 ppm) and total chromium content (limit 2 ppm) see Figure 1. The test indicated that geopolymerization is an efficient and a low cost inertization technique when compared to actual treatment technologies available in the industry.

We are completing the mechanical properties tests, but we can already suggest that the final geopolymeric material can be used as building materials for floorings and non-structural applications.



[1] L. Barbieri, E. Kamseu, I. Lancellotti, C. Leonelli, C. Ponzoni, Procedure for the inertization of liquid waste IT 0001410758, 19 Sept. 2014.

Figure 13 – Content of Cl^- , SO_4^{2-} and Cr in the leachate before (grey bar) and after geopolymerization (black bar); curing time 28 days.

CESIUM INCORPORATION IN METAKAOLIN-BASED K-GEOPOLYMER

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Keywords: K-geopolymer, Cs ions, adsorption, zeta potential, exchange, radioactive waste

Recently, considerable attention has been paid to using synthetic zeolites and titanates for cleanup of the waste water containing Cs and Sr radionuclides from Fukushima Daiichi Nuclear Power Plant. It has been considered that geopolymers have high potential for immobilization of Cs- and Sr-loaded zeolites and titanates, but more studies are needed to validate the geopolymers for radioactive waste disposal. The interaction of cesium with metakaolin-based K-geopolymer is studied in this paper. Geopolymers with composition of $\text{SiO}_2/\text{K}_2\text{O} : \text{Al}_2\text{O}_3/\text{K}_2\text{O} : \text{H}_2\text{O}/\text{K}_2\text{O} = 1:1:11$ were synthesised and characterised based on ref. [1]. The binding of Cs and release of K in varying CsOH concentration were determined using ICP-AES (Figure 1). At very low concentration, the same amount of K is released for the binding of Cs, but the release of K is much higher than binding of Cs at high concentration of Cs. It is suggested that CsOH solution may promote the dissolution of geopolymer at high concentration. The results of zeta potential measurement indicate that there is no specific adsorption of Cs on geopolymer because the absolute value of zeta potential is increasing slightly with Cs concentration (Figure 2). Thus, the primary mechanism for Cs incorporation in geopolymer is exchange with K.

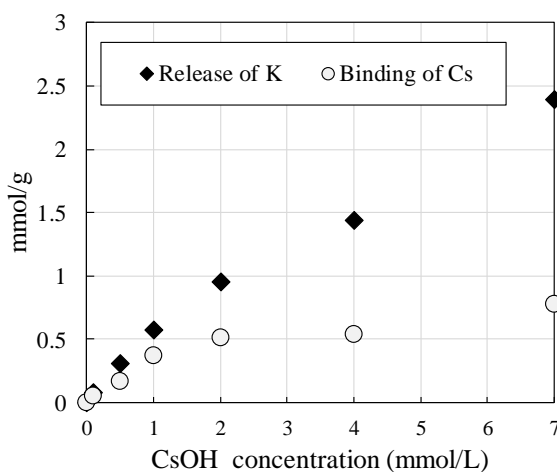


Figure 14 – Binding and release of Cs and K respectively as function of CsOH concentration (the leaching of initial K in the absence of Cs is deducted in each measurement)

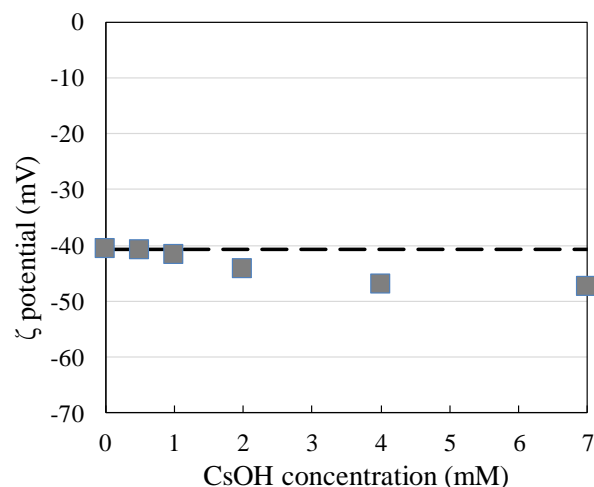


Figure 2 – Zeta potential of geopolymer suspension in CsOH for a constant ionic strength of 10 mM. Ionic strength was adjusted by KNO_3

References

[1] P. Duxson, J. L. Provis, G. C. Lukey, S. W. Mallicoat, W. M. Kriven, and J. S. J. Van Deventer, "Understanding the relationship between geopolymer composition, microstructure and mechanical properties," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 269, no. 1–3, pp. 47–58, 2005.

HYBRID CONCRETE: ALTERNATIVE FUTURE

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Key Words: hybrid concrete, abrasion resistance, shrinkage, durability.

Hybrid concrete is a combination of hydrate and polycondensation products to produce crystalline and amorphous gels such as C-A-S-H, C-S-H, C-A-S-Š and C-F-A-S-H.

Several physical and chemical characteristics of these products have being analysed and summarized in this thesis based on the practical application on commercial and industrial sites in Southern Africa since 2010.

There are several distinct advantages of these type of products;

- lower costs environmentally
- lower costs economically
- better abrasion resistance
- lower heat of hydration
- crystalline formations in lieu of amorphous gels

The base materials for these eco-binders that have being applied on several sites are ground granulated corex slag, ground granulated blast-furnace slag, pulverised fuel ash, mineral sand slimes, small amounts of Portland cement in some cases and other wastes that are used to activate the eco-binders.

The site summary combines the use of Portland cement replacement concretes of 60 – 100% with the above wastes or by-products and the physical nature of the products over periods up to 4 years

DEVELOPMENT OF ALKALI ACTIVATED ADHESIVE APPLICABLE FOR ALKALI ACTIVATED PANELS

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Key Words: slag, fly ash, alkali activation, adhesive

The overall goal of InnoWEE project (Innovative pre-fabricated components including different waste construction materials reducing building energy and minimising environmental impacts), is the development of optimized reuse of construction and demolition waste - CDW (concrete, bricks, mortars, glass, and wood) into prefabricated alkali-activated panels to be used in energy-efficient buildings. Moreover, one of the tasks is the development of an alkali-activated adhesive that would bond together different types of alkali-activated panels (high-density panel - HDG and low density, wood-based alkali-activated panels - WGD).

The following parameters are important for the efficiency of the adhesive:

- chemical bonding between the AAM layer and the adhesive;
- matching between shrinkage and expansion, and
- mechanical interlocking (improved by a rough surface).

For alkali-activated adhesives it is known that the adherence of alkali-activated mortars to the cement-based substrate is poor (Vanconcelos et al., 2011). It was assumed that if the sand-to-binder ratio was low, then high shrinkage caused micro cracks on the contact surface, which decreased the bond strength. Zhang (Zhang et al., 2010) has also proposed a mechanism of chemical bonding where the dissolution of hydrated cement takes place and a new alkali-activated gel containing calcium is formed so that good adherence is achieved.

Within the present study, the precursors selected for the adhesive preparation were slag and fly ash. KOH and K-silicate were applied as alkali activators. Samples were mixed using the standard procedure for ceramic tile adhesives and then evaluated for shrinkage and compressive strength. Other parameters important for its application in real conditions are consistency and open time, were also determined.

As expected, it was found that shrinkage mainly depends on the water in the mixture, but also on the amount of added fly ash, and it amounted to 1.8 and 1.4% for the two mixtures that were selected for application on different substrates. Both mixtures have the same ratio of slag to fly ash; i.e. 1:2, but in the first mixture (No. 28) the activator is only K-silicate, and in the second one (No. 42) the activator is a mixture of KOH and K-silicate. The compressive strengths were 21.5 and 54.1 MPa, respectively.

These two mixtures (No.28 and No. 42) were then applied on different substrates (ceramic tiles, concrete plates, alkali-activated plates), and after 3 days the pull-off strength was determined.

The bonding strength depends very much on the substrates; results are presented in Table 1.

Table 1: Pull-off strength of the selected adhesives on different substrates

Mixture	Ceramic tiles/concrete tile (MPa)	Concrete tile/concrete tile (MPa)	Concrete tile/alkali-activated panel – HDG (MPa)	HDG/WGD panels (MPa)
28SL FA KS (SL:FA 1:2)	1.1	1.8	0.1	0.5
42SL FA KS KOH (SL:FA 1:2)	≈ 0.01	1.8	0.2	≥0.4*

*failure in sub-layer

For comparison, the bond strength for repair mortar (EN 1504-3) should be min. 0.5 MPa; for ETICs, the requirements for the bond between the adhesive and the wall min. 0.25 MPa; between the external layer (mortar) and the insulation min. 0.08 MPa.

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30 CUBIC METERS BATCHING, DELIVERING, AND POURING OF ACTIVATED FLY ASH CONCRETE

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Key Words: concrete, Fly ash, Compressive strength, Alkali-activated fly ash, construction site

ABSTRACT: Mae Moh power plant (Thailand) has expelled fly ash more than 1.5 million tons each year for almost 2 decades. Around two thirds of them was managed to sale in cement and concrete industry. The Minority of fly ash was sale to other industries such as fertilizer. The deeper coal mine lead to the fly ash become high CaO and free. The leftover fly ash has sent to landfill because it failed to meet Thai standard specification of using fly ash in concrete. Electricity Generating Authority of Thailand (EGAT) has sought the sustainable way to maintain the use of fly ash in cement and concrete industry. So, EGAT begin pay attention to alkali-activated fly ash concrete as pilot project. It aims to enhance the turning research to be commercial product.

The pilot project was set up in the power plant area with 120 square meters (30 cubic meters) of alkali-activated fly ash concrete. It was planned to overlay in a truck yard which was 20 minutes far away from the batching plant. Several mixtures were pretested in laboratory to achieve the compressive strength more than 28 MPa at 28 days while provided at least 10 cm slump after pouring 2 hours. The mix required 4.5 tons of NaOH 6M and 1.7 tons of sodium silicate to be prepared and stocked in the existing OPC ready mixed plant. These two chemicals had to be well mixed in activator tank to reduce the temperature then rise to ambient before discharging to the batch.

The project underwent some problems the process of mixing, delivering, pouring and finishing. The mix of chemical solution in activator tank has condensed and settled due to dramatically temperature drop at night. High moisture in sand made the NaOH more caustic. Problems and solutions are report in this paper. The result showed that the slump of concrete is 22 cm and after 2 hours, it lose to 10 cm. The compressive strengths of concrete at 3, 7 and 28 days in air cured condition were 8.7, 18.8 and 36.3 MPa respectively. Moreover, this project is the first alkali-activated fly ash concrete construction in Thailand.



Figure 1 – Batching Plant



Figure 2 – Pouring Process



Figure 3 – Overlay in truck yard

GEOSIL – READY TO USE ALKALINE ACTIVATOR SOLUTIONS FOR GEOPOLYMERS

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Key Words: alkaline activator solution, waterglass, potassium silicate, sodium silicate, soluble silicates

Soluble silicates, also known as waterglass represent one of the oldest anthropogenic chemicals in the world. Waterglass not only has one single stoichiometric structure. It more or less stands as collective name for glassy frozen melts of alkali silicates with varying compositions as well as their solutions.

In Geopolymer applications a large number of activator solutions were tried out, such as alkali hydroxides, sulfates, aluminates and other oxides but none of them is comparable to waterglass with its unique properties. Unfortunately the majority of research laboratories don't focus on waterglass which has been produced under industrial conditions and is industrial available in future. But especially for future industrial applications and for bringing Geopolymer products broader into the market these requirements are essential. Furthermore qualified production processes ensure a constant product quality over the time for materials available in bulk.

With this awareness of the needs of the customers and the market, Woellner started to develop its new ready-to-use liquid alkaline activator solution production line for Geopolymers called "Geosil®".

Woellner is one of the biggest waterglass producers in Europe and is connected with Geopolymer projects for more than 30 years. Within the last 10 years, the number of inquiries, projects and customers has increased significantly.

Waterglass in AAM (alkali activated materials)

Basically there are two common types of waterglass which can be used as activator solutions. Sodium silicate, potassium silicate as well as mixtures of both. Lithium waterglass usually shows minor reactive properties and consequently only seldom is used for research. Depending on the application, a thorough selection of the corresponding type of Geosil® product has to be performed.

For building materials applications, especially at visible parts and surfaces, Geosil® products based on potassium silicate are commonly used. Sodium silicate based Geosil® products show their main advantages for example in the application of waste material immobilization. Geopolymer-based mineral foams are mainly produced by Geosil® products based on blended waterglass.

Geosil® products are adopted to your specific needs and ensure excellent working properties. The different products can be used in high solid systems as well as in binder dominant formulations and lead to end products with optimized mechanical and chemical properties.

Commercial available soluble silicates usually show the following molar ratios ($\text{SiO}_2/\text{Me}_2\text{O}$, $\text{M}=\text{Na}, \text{K}, \text{Li}$):

Sodium silicate: molar ratio: 1,7 – 4,0

Potassium silicate: molar ratio: 1,0 – 4,0

Lithium silicate: molar ratio: 2,5 – 5,0

For Geopolymers the most effective molar ratio lies between 1,5-1,7.

From practical point of view a molar ratio above 1,6 should be favoured as this leads to products without dangerous goods transport classification.

Geosil® products represent user-friendly, storage stable, ready-to-use formulations based on soluble silicates. They are produced via a quality controlled production process. Woellner ensures the high purity of raw materials via defined chemical parameter and makes the products available in many countries worldwide in different packaging sizes.

PQ Curesil™ - ALKALINE SILICATE ACTIVATORS FOR GEOPOLYMER

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Silicates play a vital role in geopolymer science and applications. Silicate chemistry matters and understanding the links between silicate properties and geopolymer attributes/performance is crucial to the enhancement and development of geopolymer applications. With this in mind, this paper will attempt to highlight the manufacturing process of silicate, type of silicates available, relationship between silicate composition and structures, effect of different grade of silicates on geopolymer properties, safety and stability aspects of silicate and their implications especially to geopolymer scale up operations. In addition, work carried out to produce geopolymers at both pilot and plant scales will be illustrated.

PRACTICAL APPROACHES FOR THE DEVELOPMENT OF ALKALI ACTIVATED CONCRETE - A DURABILITY- AND SUSTAINABILITY-DRIVEN OPTIMIZATION

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Alkali activated concrete can gain high strength, nevertheless the advantage is seen in its high durability, which is related to the aluminosilicate network. Due to this and the opportunity to use high amounts of (or even primarily) industrial wastes for the binding material, alkali activated concrete represents a material with a high sustainability potential. But a broad utilization beyond special applications can only be achieved, if the cost side can compete with conventional cement concrete.

This paper discusses the strong relationship between material selection, mixture composition, and durability. Nevertheless, the final evaluation takes place concerning costs. For evaluating durability, the resistance against freezing and thawing and deicing chemicals (as one of the main criteria of concrete use in Germany) were investigated by means of CDF-test device. In addition, the production costs and the life cycle impact (LCA) were analyzed.

In extensive laboratory test series the influences of different binding material qualities including different ratios of granulated ground blast furnace slag, fly ash and a waste material from ore processing on the concrete durability were investigated, as well as evaluated concerning costs and environmental impacts. Furthermore, different activator solutions, combinations of these, as well as different alkalinity and water/binder ratios were included into the investigation and evaluation.

While in the first step, the technical results decide for the mixture to be chosen for a certain application, in the second step the costs are the tongue on the scales. Also it will be explained, that it is worth to invest into e. g. chemical admixtures, which improve technical quality and durability. A longer lifetime of the geopolymer concrete implies increased economic and ecological advantages. These result in a higher sustainability, which includes also lower total costs.

From the practical point of view it will be strongly suggested that alkaline-activated concrete compositions are to be developed with focus on the final technical product parameters, such as durability and costs, instead of theoretically calculated concrete compositions e.g. in terms of activator use.

LOW-TEMPERATURE ALKALINE ACTIVATION OF FELDSPATHIC SOLID SOLUTIONS: DEVELOPMENT OF HIGH STRENGTH GEOPOLYMERS

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Keywords: solid solution, amorphous, crystalline, geopolymers, porosity, pore-size distribution.

Most of the natural solid solutions, as a result of the history of their formation and crystallization, present a fraction of amorphous or metastable materials that may easily be dissolved or activated in alkaline media. In this work, trachyte, granite, pegmatite and sand for comparison are used as principal solid precursors for the design of high strength geopolymers. The particularity of the solid-solution based geopolymers is the high fraction of crystalline phases incongruently dissolved that may react essentially at the surface, thus developing very resistant bonds. While working with 100 wt% of solid solution is almost unrealistic for the production of geopolymers, it was found that 15 to 30 wt% of metakaolin in replacement of the solid-solution powder conducts to low porosity (10 vol.%), high flexural strength (20-30 MPa) and compact microstructure. Preliminary resonance-based mechanical tests showed that the elastic modulus of the investigated samples ranged between 11-15 GPa, as also confirmed by instrumented micro-indentations. It was concluded that a high strength and durable matrix are a result of chemico-mechanical equilibrium of phases contained within the composites including the pore volume and pore-size distribution, which are significant for the life cycle of geopolymer composites.

DEVELOPMENT OF A NEW ALKALI-ACTIVATED BINDER INCORPORATING DREDGED SEDIMENTS

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Key Words: Alkali activated materials, Blast furnace slag, sediments.

Alkali activated materials (AAMs) are known to be alternative binders to Ordinary Portland Cement (OPC) since the latter has the disadvantage of emitting large amounts of CO₂ during its manufacture. Indeed, industrial by-products such as blast furnace slag (BFS) have been the main precursors in the alkali-activation reactions. On the other hand, dredging operations in the marine ports result in the formation of large volumes of sediment. In Europe, 100-200 Mm³ of sediment are dredged annually, and future regulations tend to restrict their immersion at the sea. The valorisation of a part of these sediments as raw materials in the composition of binders would contribute to limit the depletion of natural resources.

So the aim of this work is oriented towards the development of a new type of alkali-activated mineral binder, based on blast furnace slag, incorporating dredged sediments. This study aims to assess the effects of sedimentary additions on the properties of the new binder.

Parameters affecting the alkali-activation of BFS were fixed (nature of the activator: a solution of Na₂SiO₃ and NaOH with 5% Na₂O and an activator modulus M_s equals to 1.45, while the Water/Solid ratio is set at 0.45). Then, variable percentages of sediments between 0 and 30% were incorporated into the studied formulations of the alkali-activated materials (MAAs), while W/S varied in order to maintain a constant workability. The effects of these sedimentary additions on the properties of the obtained material were studied.

SUSTAINABLE ALKALI BINDERS: WASTE ACTIVATING WASTES

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Key Words: Low cost activators, fly ash, blast furnace slag

Alkaline binders usually requires two main components, namely the solid precursor, rich in alumina and silica (preferably in an amorphous state); and the activator solution, based on an alkali metal (usually sodium or potassium). The role of the precursor is commonly assumed by a residue, usually fly ash or blast furnace slag with significant economic and environmental benefits. However the activator is frequently prepared with first grade commercial reagents (usually sodium or potassium hydroxide and sodium or potassium silicate), which significantly increases the financial costs and severely dilutes the environmental initial advantages, due to the high CO₂-eq released during the production of the reagents. These drawbacks associated with the activator severely hinder the wide spreading of this technology severely making the development of low cost activators a major research target. Therefore, a strong expectation regarding the application of industrial residues as the main (or even the sole) constituent of the activators – and not just as the precursor – is rapidly growing. The aim of the present paper is thus to analyse the potential application of some by-products, in this case from the aluminium foundry industry, as the alkali activator of two different precursors: fly ash type F (FA) and blast furnace slag (BFS).

ALKALI ACTIVATION OF FLY ASHES, PART I: MECHANICAL PRE-PROCESSING FOR THE IMPROVEMENT OF THE FLY ASH REACTIVITY

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Key Words: Pre-mechanical treatment fly ash

Fly ashes use to be heterogeneous materials as a function of the mineral origin of the coal burned in the power plant. The control of particle size distribution of fly ashes by a pre-mechanical treatment can improve the reactivity of some fly ashes and help to produce homogeneous materials for the fabrication of alkaline cements. In this paper original and pre-mechanical activated fly ashes (from different countries) were studied. The alkali activator used in all cases was an 8-M NaOH solution. The reaction rate was determined through conduction calorimetry. Paste mechanical strength was determined on 1x1x6-cm prismatic specimens. Both the starting ash and the reaction products were characterised by means of XRD and SEM/EDX. The results obtained show that effectively the pre-mechanical activation can help to obtain a good quality fly ash independent on the mineral origin of coal.

ALKALI-ACTIVATED MINERAL WOOLS

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Key Words: Mineral wool, stone wool, glass wool, man-made mineral fibers, alkali-activated cement, geopolymer

Mineral wools –a general term for stone wool and glass wool– are the most common building insulation materials in the world. The amount of mineral wool waste generated in Europe totaled 2.3 Mt in 2010 – including wastes from mineral wool production and from construction and demolition industry. Unfortunately, mineral wools are often unrecyclable due to their fibrous nature (Figure 1) and low density. Thus, the utilization of mineral wool waste in post-consumer products remains low.

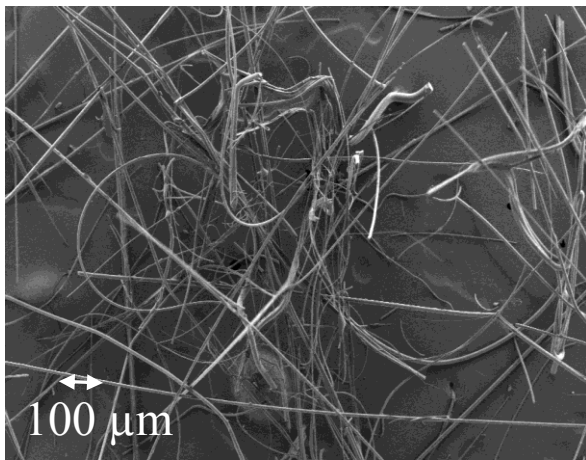


Figure 15 – Mineral wool fibers before milling.

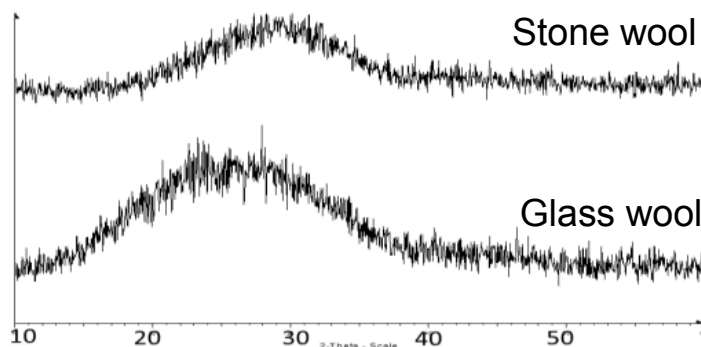
Interestingly, as mineral wools are synthetic glasses designed to dissolve in lungs, they have favorable chemical and mineralogical composition also for alkali activation (Figure 2). However, in order to successfully mix mineral wools with alkali activators they must be processed to destroy the fiber structure.

Here, we show that with careful processing of mineral wools and reaction mix formulation, mineral wools may be alkali-activated to form sustainable cements with excellent mechanical properties.

The results show that mineral wools are highly soluble in alkaline conditions (up to 60% solubility in 24h) which promotes the formation of strong binders (>100 MPa compressive strength and flexural strength up to 20 MPa). Depending on the mix design different types of amorphous, NASH, CSH and hydrotalcite phases are formed. Finally, we discuss some problematic issues regarding the overall

process and our suggestions to overcome them.

Mineral wool could turn out to be very valuable raw material for AAMs as itself or as co-binder as they have very constant chemical and physical properties compared to many other AAM precursors. Alkali-activation of mineral wools therefore offer an attractive route for waste valorisation and production of low-CO₂ cements with excellent mechanical properties.



	Stone wool	Glass wool
CaO, [%]	18	8
SiO ₂ , [%]	40	56
Al ₂ O ₃ , [%]	16	2
Fe ₂ O ₃ , [%]	9	1
Na ₂ O, [%]	1	15
K ₂ O, [%]	1	1
MgO, [%]	11	2

Figure 2 – X-ray diffractogram showing the amorphous nature of the mineral wools. On the right typical chemical compositions of stone wool and glass wool are presented.

SILICA SOURCE FOR FORMATION OF C-S-H IN WASTE SEDIMENT-STEEL SLAG MIXTURES

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Key Words: volcanic glasses, diatom flustures, industrial byproduct, waste soil, C-S-H

Dredged soils, which results from marine and waterfront engineering work, are soft and unfavorable physical properties, and often landfilled as wastes. However, when it is mixed with alkali activating material, in this case steel slag, it develops strength by chemical reaction forming hydrates, resulting in cementation and developing strength. This mixture is awaited to be used for undersea constructions such as making reclamation in place of cement, but its utilization is limited due to the un-predictableness of the mixture's strength development due to the variation in components of the steel slags and dredged soils. The cementation is hypothesized to be occurring by calcium silicate hydrate (C-S-H) formation (Kiso et al., 2008) by pozzolanic reaction, and calcium is stated to be supplied from Ca(OH)_2 , but especially the source of silica is not being clarified. Revealing the source and clarifying the effect of them to the formation of secondary hydrate phases quantitatively would enable to predict strength development of the mixture by simple steps of characterization of starting materials, which would enable the utilization of the wastes as construction resources.

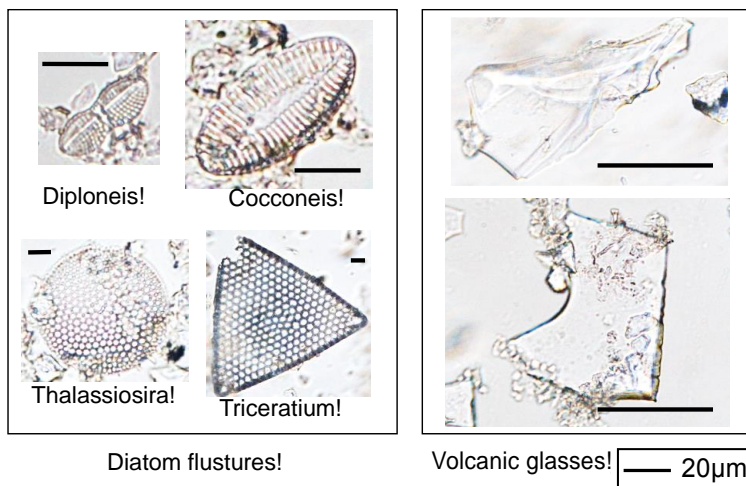


Figure 1. The optical microscopic observation of amorphous silicates incorporated in dredged soils

In this study, the clarification of silica supplying phases in dredged soils were conducted with detailed characterization. Two steel slags produced from different ironworks and four dredged soils from various ports were used for the investigation to compare the components affecting the formation of C-S-H.

Simulation of the kinetic steel slag-dredged soil interaction with geochemical modeling was also conducted. Amongst all silicate phases characterized in all dredged soils, we confirmed the main silica supplier to be not crystalline silicates and clay minerals but amorphous silica such as volcanic glasses and diatom flustures (Figure 1).

When comparing the difference in mixtures made with various dredged soils and a slag with sufficient Ca(OH)_2 supply, the variation of the formation of C-S-H appeared to be controlled by amount of amorphous silica. Dredged soils or any waste soils that contains amorphous silica, which readily dissolves at early curing stages under high pH condition, are clarified to be the major silica source to enable the utilization of them as construction resources.

LIGHTWEIGHT FOAMED GEOPOLYMER

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Key Words: Foamed geopolymers, Aluminium, Polyethylene glycol, structural and insulating concrete

Foamed cementitious materials are becoming more commonly used as an alternative to organic polymer foams in the insulation of buildings. Foamed geopolymers are a promising alternative to other foamed cement-based materials, potentially offering attractive performance with reduced environmental footprint in both manufacturing and operational phases of the material lifecycle. To produce a geopolymer foam derived from metakaolin with a very high strength/density ratio, flash calcined metakaolin was mixed with a sodium silicate activator solution, foamed using aluminum powder and with the addition of polyethylene glycol (PEG) as a bubble stabilising agent. After curing, the densities of the obtained materials ranged from approx. 997 kg/m³ to 1016 kg/m³, with 7-day compressive strengths of up to 14 MPa. The foamed geopolymers produced here have desirable mechanical properties and performance as a construction product, and could potentially be used as a lightweight material for walls or partitions.

STUDY ON SURFACE DEGRADATION OF LCFA-GGBF GEOPOLYMERS BY PARTIAL WATER ABSORPTION AND SILANE IMPREGNATION TECHNIQUES

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Keywords: Geopolymer, Fly ash, Ground granulated blast furnace-slag, Efflorescence, Surface roughening

When the pore solution becomes supersaturated in Portland cement hardened bodies due to evaporation of moisture, temperature change and so on, salts dissolved in the pore solution precipitate and the surface whitening (efflorescence) and surface roughening may occur. Similar phenomena also occur in hardened geopolymer (GP) (Fig.1). Formation process and resultant minerals are different from those of Portland cement and there are a few studies on GP so far on these events. In this paper, efflorescence and surface roughening were studied using low calcium coal fly ash (LCFA) / ground granulated blast furnace-slag (GGBS) type GP. Primarily, these phenomena were studied by partial water immersion technique (Fig.2). Subsequently, surface impregnation technique by a silane was performed and effective results were obtained as follows:

- (1) Since efflorescence and surface roughening were promoted in the refrigerator rather than in the constant temperature room (20°C, 60%RH), deterioration of the surface layer of GP is more likely to proceed as the temperature and humidity are lower. In addition, repetition of temperature change promotes deterioration of the surface layer.
- (2) Efflorescence and surface roughening of GP impairs not only aesthetic appearance of the structure but also sometimes lowers proof stress, so certain measures are necessary.
- (3) Efflorescence and surface roughening of GP can be suppressed by increasing the GGBS substitution rate (Fig.3).
- (4) Adjustment of the concentration of alkaline solution may suppress efflorescence and surface roughening.
- (5) The silane-based surface impregnating material for OPC concrete has the effect of reducing the rate of efflorescence and surface roughening of GP.



Figure 16 – Degraded GP walkway boundary block placed on strongly acidic soil (Beppu Myoban Spa, Oita, Japan)

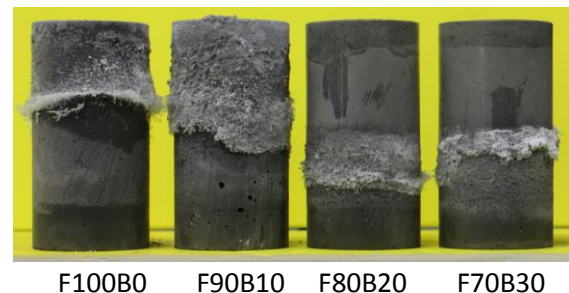


Figure 3 – Comparison of appearance by GGBS substitution rate (After 8 week storage in refrigerator)

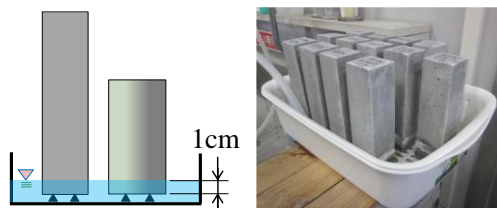


Figure 2 – Partial water absorption test

GEOPOLYMER-BOUND INTUMESCENT COATINGS FOR FIRE PROTECTION

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Key Words: Fire protection; Fire testing; Intumescent coatings; Oscillatory rheometry

Intumescent coatings for fire protection offer advantages over (non-intumescent) cementitious coatings and boards regarding speed of construction, architectural aesthetics, sometimes costs, and other features [1]. However, conventional organic intumescent coatings as well as soluble silicate (waterglass) coatings form foams with low mechanical stability, and the latter coatings generally suffer from low resistance against humidity. Therefore, the search for novel intumescent coatings for more demanding conditions (e.g., abrasive environments) is a necessity in the context of steadily increasing requirements of society and industry.

In this contribution, we present results on intumescent aluminosilicate coatings for fire protection that form foams with significantly increased mechanical strength [2]. Two base formulations, a metakaolin/silica-based mix, adapted from Krivenko *et al.* [3], and a silica/corundum-based mix, developed at Curtin University, as well as formulations modified with additives ($\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, B_2O_3 , $\text{Na}_2\text{B}_4\text{O}_7$), were applied to steel plates (75 mm x 75 mm) and exposed to simulated fire conditions (fire curve according to ISO 834-1:1999). Temperature-time curves were recorded to assess the degree at which the coatings insulated the substrate. In addition, XRD, TG, oscillatory rheometry, and SEM were employed to characterise the coatings.

The coatings were observed to partly expand during hardening due to H_2 formation. When the hardened coatings were exposed to elevated temperatures they intumesced as expected, with the degree and nature of expansion dependent on the formulation. Oscillatory rheometry provided insights into the intumescent processes in an apparently brittle material. It revealed that the hardened aluminosilicate coatings became viscous (loss factor > 1) at 75–225 °C, in the temperature range of major water release, as opposed to a “standard” metakaolin-based geopolymer, which continued to behave as a solid. This explains the intumescent behavior of the coatings, *i.e.* further expansion and foam formation. Microstructural analysis confirmed pore expansion and coalescence; XRD showed that the phases formed after heating (max. temperature ~840 °C) were of ceramic-type.

The fire protection (defined here as the time for the steel substrate to reach the critical temperature of 500 °C) depended mainly on the thickness of the fully expanded coating, *i.e.* after intumescence. An aluminosilicate coating free of additives with an original thickness of 12 mm was able to protect the steel for >30 min. The addition of 10 % anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$) caused a significant improvement, such that an original coating thickness of only 6 mm was sufficient to protect the steel for ~30 min. This was caused by the formation of sodium metaborate dihydrate ($\text{NaB}(\text{OH})_4$) in the coating that led to a significantly extended dehydration plateau in the temperature-time curve at ~100 °C during the fire exposure.

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ACHIEVEMENT AND EXPLOITATION OF POROUS GEOPOLYMER-BASED SPHERES

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Key Words: geopolymer, spheres, injection-solidification, porosity, adsorption

Several spherification processes were applied to obtain porous geopolymer spheres, different in term of porosity, specific surface area and adsorption properties.

The processes are based on the formulation of metakaolin-based geopolymer slurries, produced using a potassium- or sodium-based alkaline activating solution, and exploiting an injection-solidification method in different mediums, i.e. polyethylene glycol (PEG), liquid nitrogen or calcium chloride, to produce the spheres. When liquid nitrogen was used, the geopolymer slurries underwent a maturation step (several hours at room temperature) to trigger the geopolymerization without reaching a complete chemical consolidation. Spheres were obtained injecting in liquid N₂ the mixture as it is or mixed with water, to modulate the final porosity (ice-templating process). The spheres were then freeze dried to remove the solidified water and complete the chemical consolidation of the geopolymer.

Conversely, with the PEG solutions, the slurries were directly injected in the solutions heated at different temperature (60-80°C). After the consolidation, the spheres were rinsed with water and left in a heater to complete the geopolymerization.

Geopolymer slurries were also mixed with a solution of sodium alginate and then dropped off in a hot CaCl₂ solution to obtain spheres by means of a ionotropic gelation.

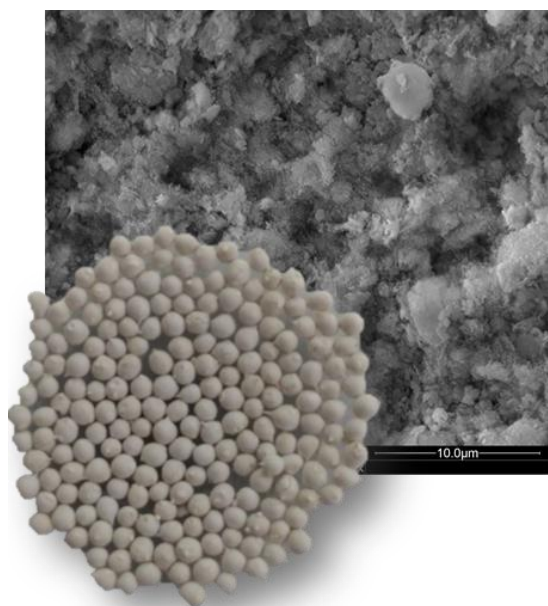


Figure 17 – Geopolymer spheres and microstructure obtained by injection-solidification in PEG.

The object of the work was to synthesize geopolymer spheres with hierarchical porous structures differing in term of intrinsic mesoporosity and architecture, which means distribution of voids/material within the spheres (Fig. 1).

The production process parameters were deeply investigated together with the different geopolymer slurry compositions in order to design the final porous structures of the spheres; indeed the tuning of the water content in the starting mixtures allows to affect the intrinsic mesoporosity of the geopolymer matrix (water is a pore former during the geopolymerization), moreover, the porosity can be further tailored adding organic templates as the alginate.

The design of the porosity in the final spheres is important to find potential applications, indeed, beads and spheres have received attention for their potential use as adsorbents, microreactors, catalysis supports, etc., thanks to the good mobility, flow-ability, high packing density, ease of separation and reuse after regeneration.

Hence, the most performing spheres were selected and characterized in term of morphology, macro- and microstructure, composition-stoichiometry, porosity distribution and specific surface area together with the adsorption properties towards, for example, gaseous CO₂ or dyes and heavy metals in aqueous solution.

MULTI-SCALE ANALYSIS ON SOIL IMPROVED BY ALKALI ACTIVATED FLY ASHES

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Key Words: Soil improvement, alkali activated binders, multi-scale analysis, chemo-mechanical behaviour.

The development of soil treatment techniques using alkali-activated binders is a relevant issue since the increasing interest into the use of new binders as an alternative solution for geotechnical engineering applications, such as soil improvement.

Alkali activated binders are formed by alkaline activation of an aluminosilicate source, containing precursor materials like fly ash, silica fume, steel sludge, which chemically react with an alkaline solution (i.e. sodium hydroxide, sodium silicate) forming a three-dimensional aluminosilicate gel with cementitious properties (Duxon et al. 2007, Provis and van Deventer 2014, Davidovits 1991, Xu and van Deventer 2000, Shi et al. 2006). Recycling of waste materials such as by-product from industrial process to synthesize a new binder favors a closed loop of material use, which minimizes the generation of waste and reduces the costs of production. Alkali activated binders represent a viable sustainable alternative to the use of ordinary binders for soil improvement (Vitale et al. 2017a; Vitale et al. 2017b).

In the present study, an insight into the mechanical improvement induced by alkali-activated binders based on the activation of two different type of fly ashes on a clayey soil has been presented. An experimental multiscale analysis on chemo-physical evolution of the systems and its influence on microstructural features of treated soil has been developed highlighting the link between alkaline activation processes and macroscopic evolution of soil properties. Mechanical tests have been performed and interpreted taking into account the chemo-physical evolution of alkali activated fly ashes. Effects of binder content and curing time have been also considered. Addition of alkali-activated binders increases shear strength of the treated samples since the very short term. A reduction of compressibility and an increase of yield stress of treated samples have been also detected, whose extent depends on the curing time and on the binder content. Macroscopic behaviour of treated soil has been linked to the experimental evidences at microscale. Mineralogical and fabric changes induced by alkali-activated binders have been monitored over time by means of X ray diffraction (XRD), thermogravimetric analysis, ^{29}Si NMR spectroscopy and Mercury Intrusion Porosimetry (MIP). Test results showed a high reactivity of alkali activated fly ashes as alumino-silicate source promoting precipitation of new mineralogical phase forming chains and networks with cementitious properties, responsible of the mechanical improvement of the treated soil. The efficiency of treatment has been also highlighted by comparing the mechanical performance induced by alkali-activated binder with the one promoted by ordinary Portland cement.

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IMMENSE POTENTIAL OF GEOPOLYMERIC NANOMATERIALS FOR SUSTAINABILITY APPLICATIONS

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Key Words: Geopolymerization; Nanomaterials; Porous materials; Sustainability; Nanostructured zeolites

Geopolymer has been extensively studied and utilized as “green cement” in addressing global warming issues, one of the most challenging problems in human sustainability. It is one of the few inorganic material systems that can be produced in a large scale and thus has a potential to truly address such large-scale problems. In connection to the innate “nano” properties of geopolymer materials, we present some of our new progresses in the pursuit of new geopolymeric aluminosilicate nanomaterials and their sustainability applications. We will first briefly describe syntheses and properties of three different types of the new nanomaterials (Figure 1) and will illustrate their uses. For example, nanoporous geopolymer materials could be produced and used as an excellent arsenic absorbent for ground water purification and as a highly effective biodiesel catalyst. High-structure geopolymer nanoaggregates can be synthesized with controlled zeolicity for polymer nanocomposite applications with excellent energy-saving performances. Highly-crystalline hierarchical zeolites have been discovered to show an exceptional CO₂ capacity, sorption kinetics, selectivity and regeneration capability essential for cost-effective CO₂ separation. Superior ion exchange kinetics of the material has been observed for silver-ion zeolite with a superb antibacterial efficacy against antibiotics-resistant MRSA bacteria. Their out-of-the-lab usages are currently being realized in industry with future goal of megatonic production.

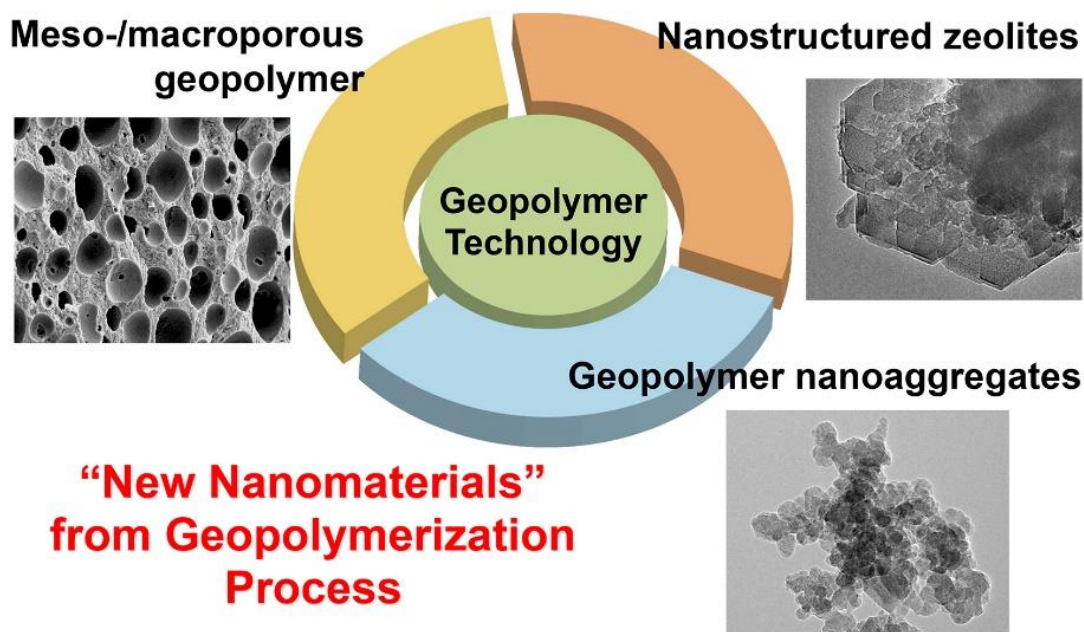


Figure 1. Three different types of aluminosilicate nanomaterials produced through geopolymerization process.

GEPOLYMERS AS INORGANIC BINDER IN 3D PRINTING APPLICATION IN CONSTRUCTION

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Key Words: 3D Printing, inorganic binder

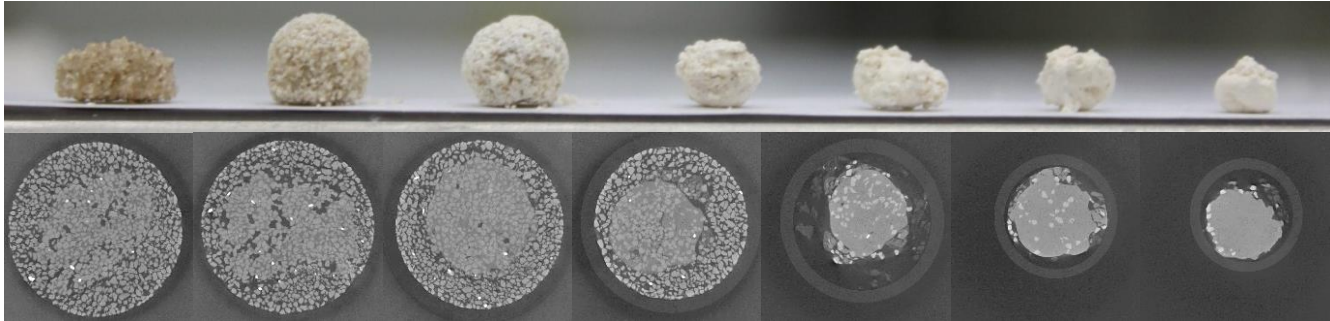


Figure 18: Top: Droplets of 20 μ l of sodium silicate solution dropped on different sand/metakaolin mixes: increasing metakaolin content from left to right (0wt%, 10wt%, 20wt%, 40wt%, 60wt%, 80wt%, 100wt% metakaolin). Bottom: Microtomography images of dry geopolymer droplets, increasing metakaolin content from left to right (0wt%, 10wt%, 20wt%, 40wt%, 60wt%, 80wt%, 100wt% metakaolin).

Digital fabrication and more specifically, 3D printing allows the production of very complex shapes with no extra cost for complexity and customization. This mass customization revolution opens new possibilities for the construction industry [1]. For instance, structural elements can be designed with the exact amount of materials positioned in the right place. Recently 3D printing has been used to produce a formwork for high performance fiber reinforced concrete [2], which would reduce the environmental impact of the structure, by one third. However, this large scale binder-jet technology with organic binders (phenolic and furanic resins) causes serious problems for the indoor environmental quality of buildings through the release of volatile organic compounds when they are used as building structure.

Therefore, in this study, we replaced the organic binder with a geopolymer in a custom-built binder jet 3D printer. The sand bed of the printer contains a mix of metakaolin and silica sand, on which we print with a sodium silicate solution. The prominent Al(IV) band in an Al-NMR measurement of a printed part confirmed that a geopolymer was built during the printing process.

The printer allows adjusting the layer height, the printing line spacing and the ejection speed.

In order to find the optimal settings of the printer, test bars with varying amount of binder, line spacing and layer thickness were printed. The bars were tested in 3-point bending and compression tests, where they reached up to 1 kN and 8.5 MPa respectively, which is higher than the parts printed with the organic binder.

The immersion of silicate droplets into powder beds with different metakaolin contents was studied with micro tomography to get an insight of the spreading of the liquid in the powder bed (See Figure 18 on the bottom). The analysis of the weight of the single droplets shows that the Si/Al ratio remains constant, independently of the alumina content of the sand bed. The amount of metakaolin in the sand bed does not change the Si/Al ratio of the final part, but it changes the size of the droplet (See Figure 18 on top). Therefore, the optimal layer height can be changed by adjusting the metakaolin to sand ratio.

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INVESTIGATION OF LIGHTWEIGHT GEOPOLYMER MORTARS AS FIREPROOFING COATINGS

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Key Words: Fly ash; Fire resistance; Geopolymers; Passive fire protection; Thermal conductivity

Fireproofing coatings are passive fire protection (PFP) systems adopted to increase the fire safety of structural components in several civil and industrial applications. They are generally spray-applied systems that behave like thermal barrier for heat transfer to the substrate. Their use is aimed at slowing down the temperature rise of the substrate and maintaining the temperature of the component below its critical temperature (e.g. steel loses about one-half of the strength at 500 °C), thus providing time to control or extinguish the fire. When good resistance to high temperature is required, geopolymers are considered highly competitive materials thanks to the intrinsic thermal resistance of their structure. For this reason, this study investigates the possibility of using fly ash-based geopolymers, activated at room temperature, as fireproofing coatings for steel components.

Lightweight geopolymer mortars (LWGs) were synthesized at room temperature using low-calcium coal fly ash as precursor and 8 M NaOH and sodium silicate solutions as activators. The weight ratio between the sum of the alkaline solutions and the fly ash was maintained constant, whereas the amounts of 8M NaOH and sodium silicate solutions in the mix were varied, thus obtaining two different geopolymer matrices with different compositional $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ ratios. The mix design was completed using expanded perlite (EP) as aggregate and hydrogen peroxide solution as foaming agent to increase thermal insulation properties and to decrease products density, both essential features for fireproofing coatings.

Physical, mechanical and thermal properties of the lightweight geopolymers were investigated as a function of the compositional parameters and of the amount of lightweight aggregate and foaming agent. Furthermore, considering that the performances of a fireproofing coating are temperature dependent, the variation of thermal conductivity and specific heat as a function of temperature were studied to provide data on the heat transfer to the substrate during heating.

Thermogravimetric analysis confirmed the remarkable weight stability at high temperature of all the investigated geopolymers, which showed a total mass loss always lower than 8% at 900°C. Results showed that the use of expanded perlite as lightweight aggregate, combined with the foaming agent, allowed obtaining lightweight geopolymer mortars characterized by bulk density of 0.77 g/cm³ and thermal conductivity of 0.23 W/mK at T = 20°C. These features are comparable to the ones of commercially available cementitious-based fireproofing coatings.

Results obtained from the experimental characterization were used to simulate the performance of the most promising LWG as fireproofing coating during a fire accident. A finite volume software set-up was used to simulate the temperature rise of steel components covered by different thickness (15, 20, and 25 mm) of the selected LWG, under cellulosic and hydrocarbon fire curve conditions. The performance of a commercial Portland cement-based fireproofing mortar (LWC) was also simulated for comparison.

The simulations confirmed that the selected lightweight geopolymer mortar was effective in delaying the increase of the steel temperature, providing a protection for the steel substrate for at least 30 minutes in the case of cellulosic fire conditions. In addition, the thinnest layer (15 mm) of LWG coating considered in this study exhibited the same behavior of a 20 mm layer of cementitious-based product.

LIGHTWEIGHT INSULATING GEOPOLYMER MATERIAL BASED ON EXPANDED PERLITE

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Key Words: Alkali-bonded, Perlite, Lightweight, Thermal insulation

Expanded perlite, owing to its lightweight and excellent thermal insulating properties, has been extensively used in different industrial sectors to produce self-standing insulating boards bonded with various organic polymers or calcium-silicates. In order to improve the high temperature behavior and mechanical performances of such materials inorganic binders, such as geopolymers, can be regarded as a promising alternative.

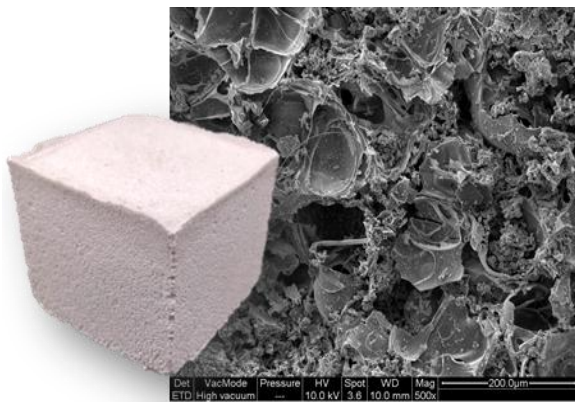


Figure 19 – Alkali-bonded perlite block and its microstructure

In this research work we investigated the possibility to use alkali silicates to bind expanded perlite by promoting the formation of a highly stable and resistant geopolymer interface phase, exploiting the partially reactive aluminosilicate nature of perlite. The material was produced using fine granules of expanded perlite as raw powder and potassium di-silicate aqueous solution as alkaline activator. After consolidation, the thermal and mechanical properties of the obtained material were investigated in correlation with its microstructure and physical properties. Bulk and true density measurements, pore size distribution analysis as well as water stability tests were firstly carried out. Structural characterization of the alkali bonded perlite was then performed through ESEM investigations, FT-IR and XRD analysis, while the evaluation of the thermo-mechanical performances was made by compressive strength tests, dilatometric analysis up to 1200 °C and thermal conductivity

measurements by Laser Flash Method up to 550 °C. Our findings confirmed that, besides the action of potassium di-silicate as an alkali binder, expanded perlite granules reacted on the surface forming geopolymer nano-precipitates. The obtained material had a density of 467 kg·m⁻³ and a total porosity of 80 vol. % with a corresponding compressive strength of 1.6 MPa, while the measured thermal conductivity was between 0.084 and 0.121 W·m⁻¹K⁻¹ in the range 25-550 °C. Results showed that the use of potassium disilicate as an inorganic binder promoted the partial activation of the expanded perlite granules, creating a mechanically strong bond within the particles, ensuring at the same time satisfactory thermal insulating properties and stability at high temperatures.