2012 ICDC
INTERNATIONAL CONGRESS on DURABILITY of CONCRETE

UNDERSTANDING TRANSPORT PROPERTIES OF GEOPOLYMER MORTAR USING POLARIZATION AND FLUORESCENCE MICROSCOPY

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ABSTRACT

The microstructure of concrete determines the possibility for water to penetrate the material (water transport) and therefore microstructure is a crucial parameter in concrete durability. Because of the intrinsically dense and water impermeable microstructure of geopolymer aluminosilicate reaction products, concrete made with geopolymer has the potential to be very durable. However, geopolymer concrete microstructures consist not only of the hardened, dense geopolymer paste, but also contain the aggregate paste interface, microcracks, air voids etc. These also need to be taken into consideration when trying to understand the (often variable) results of (standard) durability tests on geopolymer concrete and mortars. So far geopolymer durability studies considering the microstructure often have looked at bulk porosity measurements and high resolution techniques such as electron microscopy, thereby missing representative information and an overview of the microstructure, which should include heterogeneities and spatial variations of the hardened paste, microcracks, air voids, aggregate paste interface etc. This study proposes polarization and fluorescence microscopy, a technique often used in cement concrete studies but not yet for geopolymer concrete, to assess the microstructure. For the particular fly ash geopolymer mortar in this study, it is shown that even though a good strength performance is obtained, the microstructure consists of a lot of air voids and microcracks in between the dense geopolymer paste. This type of microstructure allows the geopolymer mortar to absorb water faster compared to Portland cement mortar, which may have implications for the durability of this particular geopolymer mortar. In general, this study shows that polarization and fluorescence microscopy is a useful and straightforward method to deal with the large variety of geopolymer concrete types for which differences in durability are not always easy to explain just by looking at bulk properties or at high resolution nanolevel.

Key-words: fly ash geopolymer, microstructure, polarization and fluorescence microscopy, durability, water transport properties

INTRODUCTION

Driven by an increased demand for sustainability and CO_2 reduction alkali activated cements from waste materials such as slag and/or fly ash (also called geopolymer) are more and more investigated and commercialized. Replacing ordinary Portland cement (OPC) in concrete by alkali activated waste materials leads to an immediate CO_2 reduction related to production of the concrete. Especially the durability of the materials and thus their expected service life is still largely unknown. This hampers their application and their (major) expected benefit, their sustainability, cannot be proven for their entire life cycle. A few durability studies exist but much more work is needed on this relatively new material to reach similar levels of knowledge and experience as for normal (Portland) cement concrete.

Geopolymer is a name for a group of binders consisting of alkali-activated aluminosilicate materials, such as metakaolin, fly ash and other waste materials. Because the generally slow reaction rate, many studies experiment with additions of soluble silicate (waterglass) or calcium containing aluminosilicates such as slag which accelerate early strength development. As such, the group of 'geopolymers' or alkali-activated cements is increasingly variable, not in the least because locally available waste materials are often used. Next to compositional variations, there is no standardized procedure for making geopolymer mortar or concrete. Most studies experimentally derive recipes and procedures for mixing and curing giving reasonable workability and strength development. Their results show that the reaction products, pore structure and in general geopolymer performance largely vary with the recipe, mixing procedure and curing used [1-7]. So far, the few geopolymer durability studies are therefore hard to compare.

While each degradation mechanism depends on its own unique chemical reaction mechanism(s), all are largely dependent on the possibility for water or gasses to enter and move through the material. The microstructure is therefore a crucial parameter that is the key to many durability related issues, regardless of the, for geopolymers still questionable, chemical reaction mechanisms. It has already been shown that geopolymer type binders tend to have a different microstructure than cement type binders, namely their 'glassy', 'amorphous' or 'nanocrystalline' aluminosilicate reaction products have a much denser microstructure compared with the calcium-silicate hydrate microstructure of cement paste [8, 9]. This is one of the reasons why geopolymer concrete has been suggested to be more durable than cement concrete [10]. However, this does not take into account the entire microstructure in mortars or concrete, including not only the hardened paste, but also the aggregate paste interface with the hardened paste, microcracks, air voids etc.

Based on the above considerations, this paper aims to illustrate the potential of polarization and fluorescence microscopy (PFM) to scan and asses microstructure for the variety of geopolymer materials. This technique is widely used in cement concrete quality control and durability studies [11-13], but the authors are not aware of geopolymer publications using this technique. The major advantage of PFM is that it enables to image different scales of porosity and microstructures at once. This paper describes the microstructure of fly ash geopolymer mortar samples of a single recipe, which have relatively high strengths compared to Portland cement mortars. For a first consideration of the possible effect of the observed microstructure on bulk properties that affect durability, capillary suction and electrical resistivity of the material are measured. Both capillary suction and electrical resistivity are related to the possibility of water and ions to move through the material and therefore to durability.

MATERIAL

The material used in this study is a geopolymer mortar based on a low calcium type fly ash (Table 1) and an alkaline activator consisting of a NaOH with Na-silicate solution (Table 2). Mortars were cast in 40 x 40 x 160 mm steel moulds and were compacted on a vibration table. After casting, the mortars were kept at 20°C and 65 RH, demoulded after 7 days and further cured at 20°C and 65 RH. The recipe (Table 2), mixing and curing procedure was chosen based on mixing tests and unpublished strength experiments (Fig. 1). For comparison with cement type binders, a mortar was made using CEM I 42.5 R following a standard recipe (Table 2) and cured under water. A common water cement ratio of 0.45 is chosen. Hereby it should be taken into consideration that the water cement ratio of cement mortars cannot be directly compared to the solution to binder ratio for geopolymer mortars, especially because water plays a different role in both materials: water is consumed during hydration of clinker and forming capillary pores in cement paste, while water is acting only as a reaction medium and further not taking part in the reaction in geopolymer paste [14, 15]. The mortar prisms have dimensions of 40 x 40 x 160 mm which were cut for microscopy, absorption and electrical resistivity measurements (see below).

Table 1 – mix design and main chemical components of the fly ash

Fly ash (main elements)	%(m/m)
SiO_2	51.7
Al_2O_3	24.5
Fe_2O_3	7.28
CaO	5.92
Na_2O	1.22
K_2O	1.88
Total	92.5

Table 2 – mix design

Cement mortar	**gram**
sand	1350
CEM I 42.5 R	450
water	200
curing	unmould after 1 day - under water
Geopolymer mortar	**gram**
sand	1350
fly ash	473
NaOH (12 M)	101
Na-silicate	101
curing	unmould after 7 days - 20°C RH65
NaOH solution (12 M)	**% (m/m)**
NaOH	29
H_2O	71

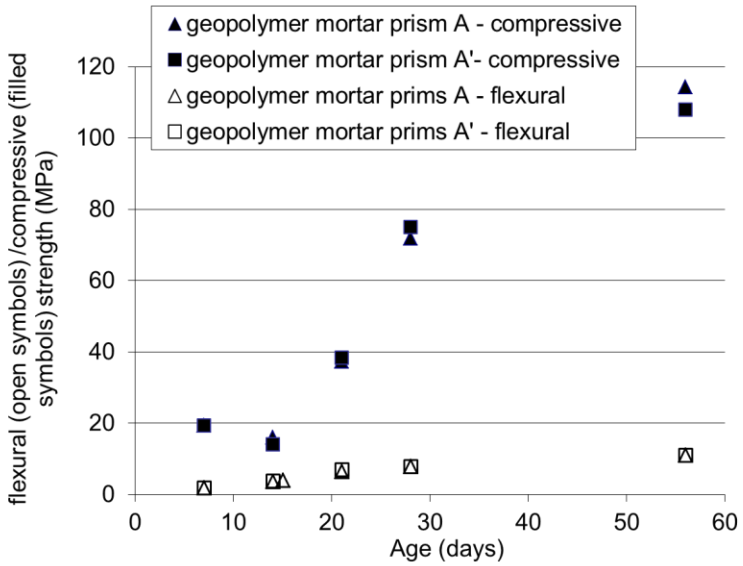

Figure 1 – Compressive and flexural strength with age for the geopolymer mortar made according to the recipe given in Table 2. For each age, duplicate measurements have been done for two mortar prisms of the same batch (A&A')

METHODS

Choice of methods

Polarization and fluorescence microscopy (PFM) is proposed here for evaluating the microstructure because it allows a qualitative assessment of different scales at once. So far scanning electron microscopy (SEM) has mainly been used for qualitatively comparing pore structures [16]. By just using an SEM it is hard to get an overview that is representative for the many local variations of and different scales of pore structures throughout the sample. Transmission electron microscopy could give insights in the finest microstructure [17], but the relation and connectivity with the larger scale pores is lost.

To illustrate the possible effect of microstructural characteristics on bulk properties that affect durability, capillary suction based on NEN-EN 1015-18 [18] is chosen here as a measure for how easily water can enter through capillary forces when the material is not saturated. Capillary suction is important in concrete used in structures above ground.

Another bulk property, electrical resistivity, measured using the two electrode method (TEM) is chosen as a comparison. Resistivity is related to the capacity for electrical current to pass through a sample and therefore related to the amount and connectivity of the water filled pores and their ion content. This two electrode method is a quick and easy method and therefore is useful for measuring the evolution of pore structure through time [19]. Furthermore, the electrical resistivity of concrete is approximately inversely proportional to the chloride diffusion coefficient [20] which can be used in durability models for prediction of steel corrosion in concrete.

Polarization and fluorescence microscopy (PFM)

Polarization and fluorescent microscopy is a two-fold integrated method, which allows the mineralogy and the internal structure of hardened cement-based materials to be characterized. In the present study, thin sections were prepared by first sawing small prisms from each of the samples. Each prism measured about 50 mm x 30 mm, with a thickness of about 15 mm. The sawn specimens were then dried at 40°C and subsequently impregnated under vacuum at about 40°C with an epoxy resin containing a fluorescent dye. After hardening of the resin, a thin section with a surface area of about 50 mm x 30 mm and a thickness of about 25 µm was prepared from each prism by grinding and polishing. Impregnation with a fluorescent resin makes it possible to study thin sections by means of both transmitted-light and fluorescent-light microscopy. In fluorescent mode, pores, air voids, microcracks and their local variations can be clearly distinguished. Furthermore, the fluorescent light intensity of the hardened paste is determined by the amount of resin that could enter the very fine pore structure of the paste and therefore is directly related to the amount and permeability of the fine (capillary) pores of the hardened paste. The fluorescent light intensity can be quantified using image analysis techniques, which is used in normal concrete to deduce and compare capillary porosity and estimate the water-cement ratio [21, 22].

Two electrode method (TEM) resistivity experiments

In the TEM test, rectangular mortar specimens are placed between two steel plates. A piece of wet cloth is used between the mortar and each steel plate to ensure good electrolytic connection and a weight is placed on top of the upper metal plate. The electrical resistance of the mortar is determined using 120 Hz alternating current (AC) by imposing a small voltage over the steel plates and measuring the current. From the measured resistance and the dimensions of the specimen the resistivity can be calculated [20], which is called ρ_{TEM}. It is important to make sure that the samples are fully saturated with water such that drying effects are restricted to a minimum. However, because no continuous water layer should exist along the mortar surface, the specimens need to be left shortly in open air such that the surface dries, but only superficially. This may cause a slight increase in resistivity. Furthermore, during the submersion in water for ensuring water saturation, some leaching may occur causing an increase in resistivity (because there are fewer ions in the sample to transmit the current). In this study, it was seen that especially geometries with a large surface connected to the steel plates and a short distance between the plates are sensitive to these drying and leaching effects and as such showed relatively large variations in resistivity. Therefore, a relatively small measurement surface (40 x 40 mm) and a longer distance between the steel plates (80 mm) was chosen such that the electrical current was running through a large bulk part of the material relative to superficial drier or leached area. For this geometry, reproducible results were obtained at an age of 4, 5 and 6 weeks.

Absorption and drying experiments

The capillary suction test was set up based on the standardized method described in NEN-EN 1015-18 [18]. The only difference with the standard method was the geometry of the samples: because of possible curing effects on the microstructure, the top, middle and bottom part of the sample were tested separately on thin slices of 40 x 80 x 11 mm. The net absorbed amount of water until constant mass is compared for the geopolymer mortar and cement mortar at an age of 44 days. In order to be

able to compare the capillary suction of different samples without a possible effect of different amounts of water already present in the pores, the specimens (originally water saturated) were dried until constant mass. The drying was done at 40°C in order to prevent any structural breakdown of minerals. The drying time is also used as an indication of the speed of water release of the geopolymer compared with the cement mortar.

RESULTS

Polarization and fluorescence microscopy (PFM)

Young (21 days) geopolymer mortar and cement mortar
In general, the aggregate appears well distributed throughout the hardened paste for the geopolymer as well as the cement mortar (Fig. 2a & Fig. 3a). The fine pores of the geopolymer paste cannot be visualized individually with light microscopy, but their presence can be deduced from the fact that fluorescent resin could enter the hardened cement paste resulting in a dark green light. The geopolymer paste has a lower fluorescent light intensity than the hardened cement paste (Fig. 2b & 3b). In other words, the hardened geopolymer paste has a finer pore structure than the cement paste allowing less resin to penetrate the geopolymer paste. However, next to a dense hardened paste, the geopolymer mortar contains a lot of air voids, some compaction voids and tiny curved microcracks which are not seen in the cement mortar (Fig. 2b & 3b). A large part of the air voids is related to hollow fly ash particles.

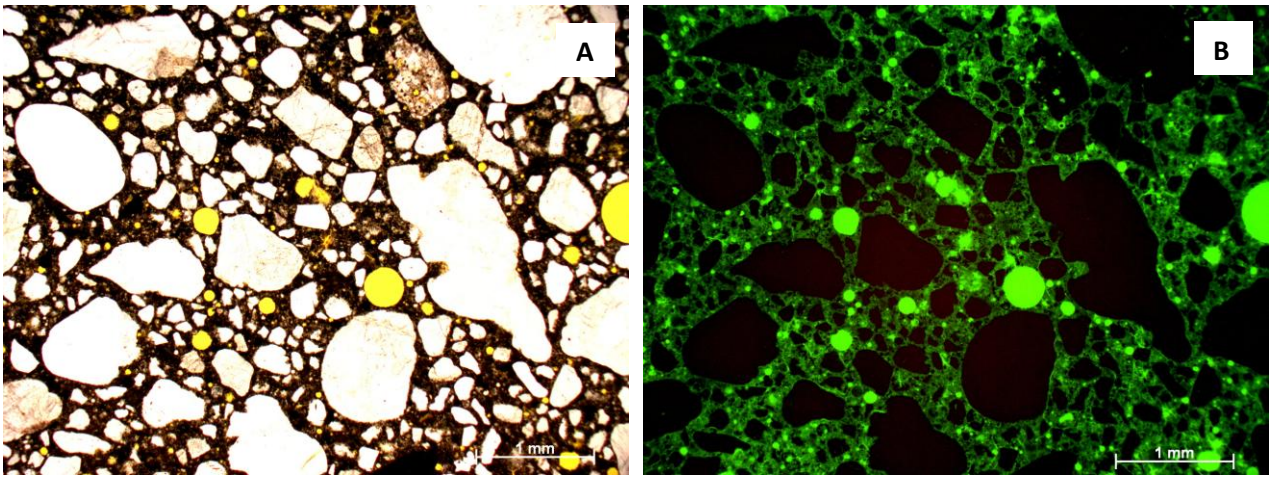

Figure 2(a&b) – Micrographs (25x) showing an overview of the geopolymer mortar of the same area, but in different light mode. 2a: parallel polarized light mode: the aggregate is white to brown, pores and air voids are yellow and hardened paste is dark grey to black. 2b: fluorescent light mode: aggregate is black, pores, air voids and microcracks are light green and the hardened paste including fine pores is darker green

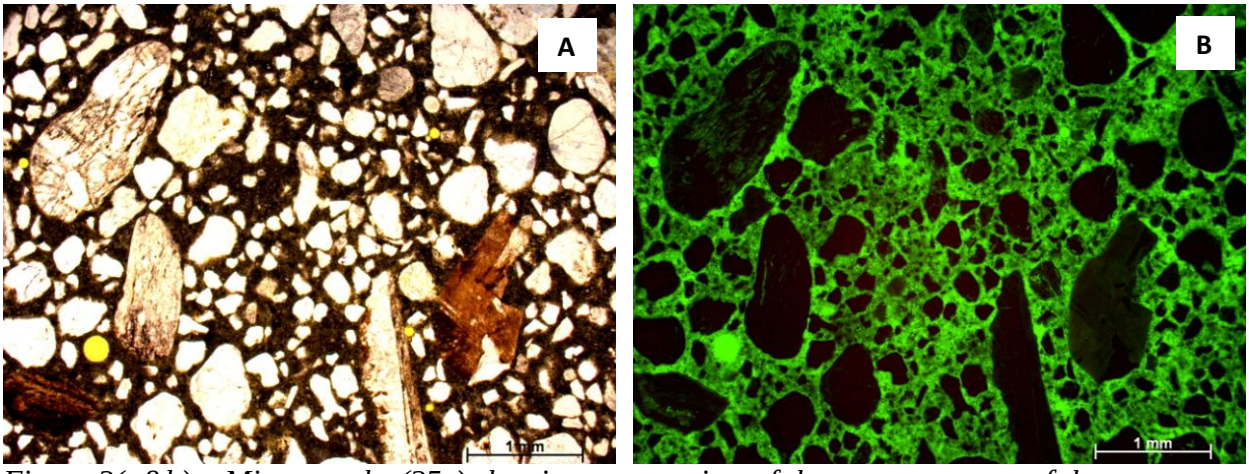

Figure 3(a&b) – Micrographs (25x) showing an overview of the cement mortar of the same area, but in different light mode. 3a: parallel polarized light mode. 3b: fluorescent light mode. For explanation on the colours is referred to Fig. 2

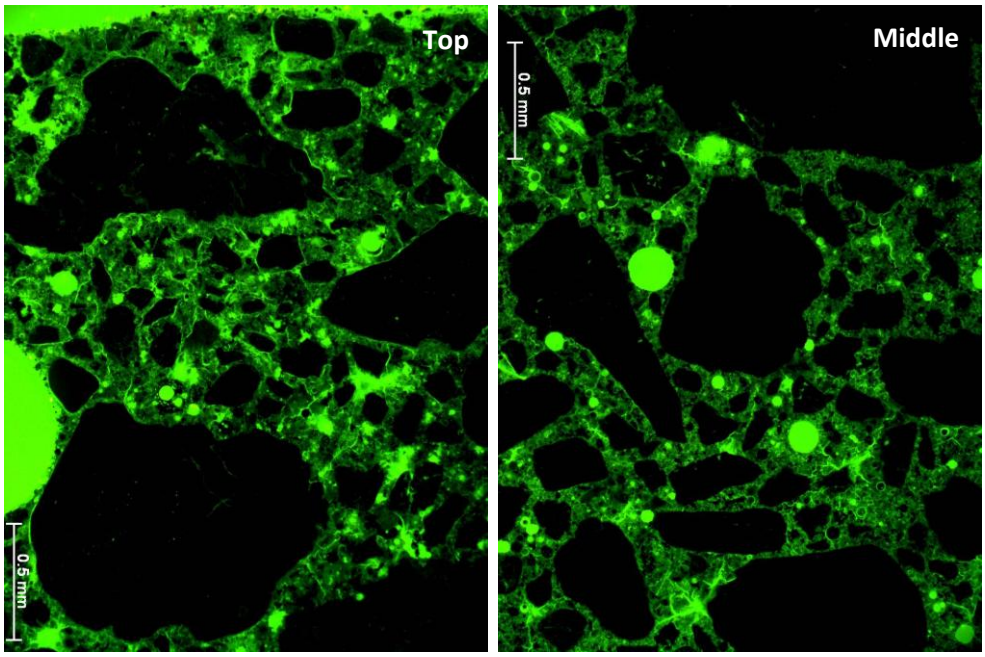

Figure 4 – Micrographs (50x) for comparison of pore structure with depth in a 21 day geopolymer mortar (left: top of the sample; right: middle of the sample). For explanation of the colours of the fluorescent light mode is referred to Fig. 2. The top of the sample is more porous than the middle of the sample (for more explanation, see text)

Spatial variations in micro- and pore structure of the geopolymer mortar

Looking more in detail at larger magnifications, local variations in pore structure of the geopolymer mortar are seen. At the top (the only side that was exposed to air during the first 7 days of curing in the mould), a more open pore structure is seen (Fig. 4). Many small microcracks can be seen. Most of them are somewhat perpendicular to the top surface. Also in the top zone, tiny microcracks show sometimes a disconnected interface between aggregate and paste and of open space appears where few reaction products have developed. In the middle zone, the overall structure looks more dense, less microcracks and open space occur and the aggregate interface is well connected with the hardened paste (Fig. 4).

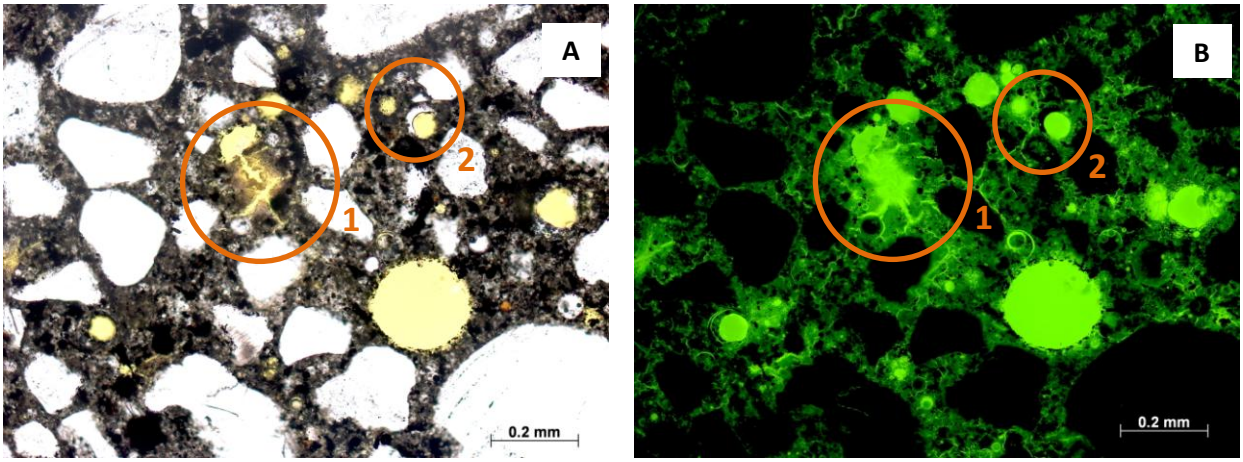

Figure 5(a&b) – Detailed micrographs (100x) of a 21 day geopolymer mortar: Fig. 5a: parallel polarized light mode, Fig. 5b: fluorescent light mode. For an explanation on the colours see Fig. 2. The area indicated with 1 is a concentration of dried gel with shrinkage cracks. Note that in fluorescent light mode, these shrinkage microcracks create some 'over luminescence' at the centre of the gel zone, such that the central void seems larger. Circular holes smaller than the air voids are the imprint of reacted fly ash particles (e.g., area 2)

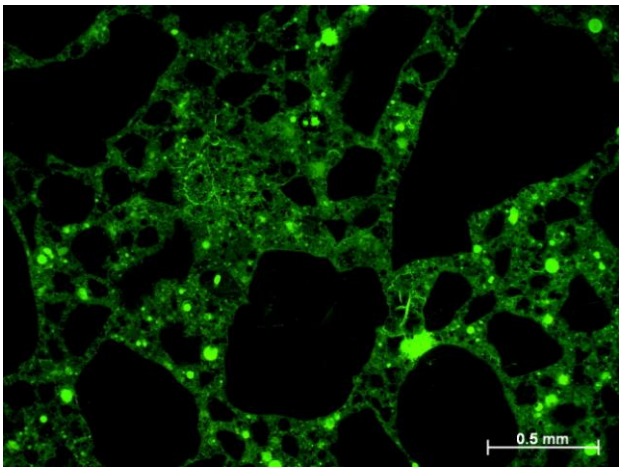

Figure 6 – Micrograph (50x) of a 1 year old geopolymer mortar. For an explanation on the colours in the fluorescent light mode see Fig. 2

In Figure 5, a detail is shown of the hardened geopolymer paste in the middle of the sample, showing local heterogeneity. Concentrations of Na-silicate glass with few fly ash particles occur between areas rich in unreacted fly ash (Fig. 5). The Na-silicate glass zones are dense but have shrinkage microcracks. In the zones rich in unreacted fly ash particles, also small light green fluorescent spheres appear indicating the place of former, now fully reacted fly ash particles. Overall, many of the larger size fly ash particles still are largely unreacted. Hereby it should be noted that fly ash particles smaller than 5 µm can hardly be distinguished using light microscopy.

Comparison with one year old geopolymer mortar

In a one year old sample, most of the small microcracks and open space seen at 21 days are not visible anymore, and bonding between aggregate and geopolymer paste is good (Fig. 6). Also areas with segregated water glass seem to have densified and shrinkage microcracks are less obvious (Fig. 4). Fine porosity of the hardened paste itself shows the same fluorescence, indicating the fine

porosity is similar to that of 21 days (Fig. 3, 6).

Two electrode method (TEM) resistivity

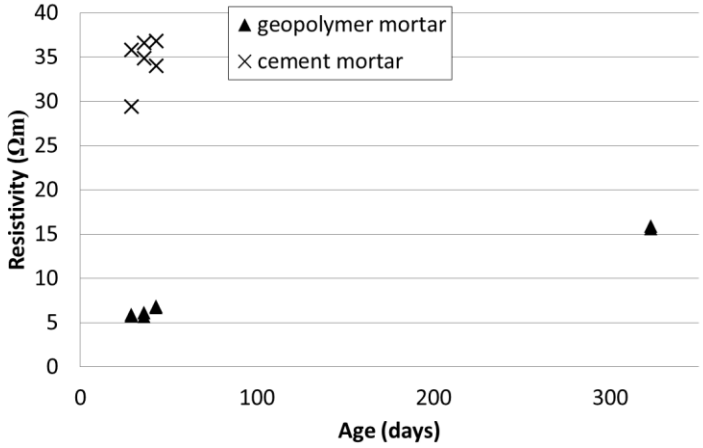

Figure 8 – TEM resistivity versus age for the geopolymer mortar made according to the recipe given in Table 2 and for the cement mortar

On Figure 8 it is seen that the electrical resistivity of the geopolymer mortar is significantly lower than for the cement mortar. It should be noted however that the chemical composition of the pore liquid may be quite different in the cement and geopolymer mortar. Consequently, resistivity should not be compared directly between the cement and geopolymer mortar, but in one and the same sample resistivity can give an idea of its development through time. While the resistivity of the geopolymer mortar increases slightly each week, the cement mortar's resistivity remains roughly similar at young ages. After one year, the resistivity of the geopolymer has increased. Unfortunately there was no reference cement mortar sample available of one year old to compare with.

Absorption experiments

The drying time at 40°C for a water saturated geopolymer mortar was several times faster (less than one day) than for the water saturated cement mortar (three days). After drying, it is seen in the capillary suction experiments that the geopolymer sucks up water very quickly and the total net absorbed amount of water (relative to the dry weight of the sample) already stabilizes after a few minutes to 2.5 g in the top sample and to 3 g in the middle and bottom samples of the geopolymer (Fig. 9). On the other hand, the capillary suction of the cement mortar samples goes more slowly and takes at least 60 minutes to reach a similar level to a slightly larger amount of water absorption as the geopolymer (Fig. 9).

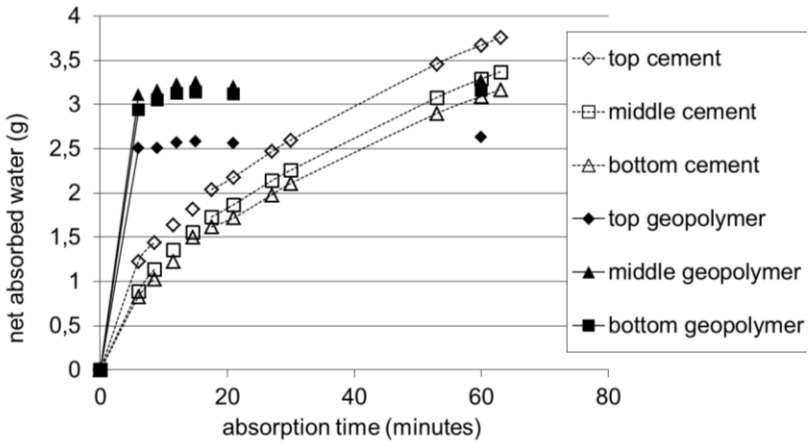

Figure 9 – absorption data from capillary suction experiments on 40 x 80 x 11 mm slices from top, middle and bottom of the geopolymer and cement mortar prisms

DISCUSSION

Microstructure development

At young ages the microstructure in the geopolymer mortar in this study is a combination of a hardened geopolymer paste with a very dense fine pore structure and in between a larger pore structure mostly consisting of air voids and microcracks with a curly shape. The air voids are likely related to the escape of air during the use of the vibration table. The microcracks and their particular curly shape is probably due to the fact that the paste was not yet fully hardened when some segregation took place between excess water (water is only used as a reaction medium during geopolymerization) and the reacting geopolymer paste. Considering the above, adding more water to increase workability and as such avoid the air voids may lead to more segregation, slower reaction rates and therefore slower strength build up. On the other hand, using low amounts of water and low workability for obtaining high strengths may lead to an apparently poor microstructure with a lot of air voids and microcracks.

After one year, the larger pore structure of air voids and microcracks has largely disappeared. It is suggested that continuous reaction of the paste has been able to close the open space and microcracks. This continued formation of reaction products can also be deduced from the resistivity which slowly increases in time due to the fact that microcracks and pores have closed and less connected water is able to transmit the electrical current.

Cement mortar shows a more homogeneous pore structure with fewer air voids and microcracks, but larger capillary pores. This is deduced from the significantly higher fluorescent light intensity of the hardened paste itself at similar ages. It is not possible to compare this difference in capillary porosity between the cement and geopolymer mortars in relation to a difference in amount of water in the mix (as is usually done for cement mortars) because an entirely different reaction process takes place with a different role of water.

Significance of microstructure for strength development

Even though the young geopolymer mortar contains a relatively high amount of microcracks and air voids on a larger scale, the hardened geopolymer paste with its high density is still connected well enough to transmit forces resulting in a higher 28 day strength than for the cement mortar which has less microcracks and voids but a higher capillary porosity of the cement paste. Furthermore, the continued reaction of the geopolymer paste results in a continuous, significant strength increase through time (to over 100 MPa after 56 days).

Significance of microstructure for durability

From the absorption experiments it is seen that the geopolymer mortar in this study takes up and transports water faster than cement mortar and this is probably related to the combination of a relatively open larger scale pore structure of connected air voids and microcracks on the one hand and a dense geopolymer paste with probably a high capillary suction force on the other hand. At first sight, this ease of taking up water suggests that this geopolymer is less durable. Certainly, for a degradation mechanism mainly dependent on water ingress such as chloride induced corrosion of steel or freeze-thawing in concrete, easy water ingress would probably result in more severe degradation. Indeed it has been reported in literature that geopolymers may be more sensitive to freeze-thawing.

Variability of geopolymer microstructure and durability: using PFM

While the results of the particular geopolymer mortar in this study show an easy water uptake compared to cement mortar, in other studies geopolymer materials have been shown to have a lower permeability and denser pore structure than cement based materials [23, 24]. These variations in (water) transport properties may result in significant variations in durability, making it impossible to make general statements on geopolymer durability. Indeed, it has been noted that in geopolymer durability studies testing several degradation mechanisms (acid, sulphate and frost-thaw attack), clearly contrasting results were obtained [10 and references therein]. The variations in microstructure and in (water) transport properties, which could be the main cause of variations in durability, are, amongst others, related to the following:

- Variations in chemistry of the source material:
  Practically all geopolymer durability studies depart from chemically different mix constituents. The geopolymer mortar in this study was based on fly ash containing virtually no calcium and an activator containing a relatively large amount of Na-silicate. This resulted in a high strength of the geopolymer mortar at 28 days, and a microstructure consisting of a dense geopolymer paste and in between water channels and local shrinkage microcracks. In many other geopolymer studies, calcium rich aluminosilicates (such as blast furnace slag) are added to speed up the early strength development. In this case, apart from aluminosilicate geopolymer type reaction products, also cement like (CSH) reaction products may be formed or other hydrates containing water. It is hypothesized that this may prevent water segregation to take place and result in more homogeneous microstructures without water channels and a permeability more comparable or lower than normal concrete [24, 25]. In still other studies, no fly ash but metakaolin is used as aluminosilicate source [9]. This leads to entirely different paste microstructures as metakaolin tends to dissolve more easily and the unreacted metakaolin particles have a totally different packing density than fly

ash particles.

- Variations in mix design, mixing and curing procedure:
  Apart from chemical variations of the mix constituents, many other factors play a role. In this study it was seen that the specific mix design with a relatively low solution to binder ratio leads to a low workability which, together with vibrations during the filling of the mould results in a large amount of entrapped air and water channels. In other studies it has also been demonstrated that water content, alkaline solution content, chemical composition of the alkaline solution, aggregate to binder ratio, aggregate grading etc. largely affect the microstructure and pore structure [4, 23, 26, 27]. Furthermore, some studies base their conclusions on geopolymer paste, while others on mortar and still others on concrete although it is known that pastes have different water to binder ratios, different workability, shrinkage patterns etc. resulting in significantly different pore structures and permeability compared to geopolymer mortars or concrete.

As discussed above, many durability related issues may be related to differences in microstructure and (water) transport properties. Therefore, methods to assess the microstructure and transport properties are indispensible for making comprehensive comparison of the different geopolymer materials possible. Because of the different levels of porosity as seen in this study and also stated elsewhere [23] the bulk porosity techniques that are often used may not give the entire picture of the pore microstructure. For example, mercury intrusion porosimetry may be biased towards the enormous amount of fine pores, resulting in a very low average pore size and a skewed pore size distribution, which masks the possible presence of larger air voids connected by microcracks. PFM can give useful additional information to understand where differences in bulk measurements like porosity and permeability actually come from. PFM is often used for normal concrete durability studies, but not yet for geopolymer concrete or mortars. Especially when upscaling geopolymer pastes to geopolymer mortars and concrete, PFM is a useful microscopy technique additional to SEM because it provides a larger overview of heterogeneities and different scales of the pore structure. Furthermore, the amount and connectivity of fine pores in a hardened geopolymer paste can be quantitatively compared relative to other geopolymer materials using image analysis on fluorescent light images [22, 28]. Measuring resistivity is a useful additional method, in particular for monitoring development of (water) transport properties in time because it is quick and non-destructive.

CONCLUSIONS

When trying to understand the (often variable) results of (standard) durability tests on geopolymer concrete and mortars, the geopolymer concrete microstructure can reveal crucial information because it determines (water) transport properties. So far, geopolymer durability studies considering the microstructure often have looked at bulk porosity measurements and high resolution techniques such as electron microscopy, thereby missing representative information and an overview of the entire microstructure (including heterogeneities and spatial variations in hardened paste, microcracks, air voids, aggregate paste interface etc.). This study proposes polarization and fluorescence microscopy, a technique often used in normal Portland cement concrete studies but so far not for geopolymer concrete, to assess the entire microstructure including larger scale features and spatial variations. For the particular fly ash geopolymer mortar in this study, it is shown that even though a good strength performance is obtained, the microstructure consists of a lot of air voids and microcracks in between the dense geopolymer paste, especially at young ages. This microstructure allows water to penetrate faster than a Portland cement mortar, which may have

implications for the durability of this particular geopolymer mortar. In general, this study shows that polarization and fluorescence microscopy is a useful and straightforward method to deal with the large variety of geopolymer concrete types for which differences in durability are not always easy to explain just by looking at bulk properties. Measuring resistivity is a useful additional method, in particular for monitoring development of (water) transport properties in time because it is quick and non-destructive.

ACKNOWLEDGEMENT

The authors would like to thank Mehdi Zarkhoshk, MSc. of TU Delft for the strength experiments, Peter Laugesen of Pelcon for the useful discussions on thin section preparation and TNO colleagues Jeanette Visser, Mario de Rooij, Timo Nijland and Hartmut Fischer for fruitful discussions.

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