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New Binder Systems and Concrete Concepts for Low-Emission Construction

Challenges Regarding Workability of Fresh Concrete

Michail Strijov, July 2019

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Bachelor of Science in Civil Engineering

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Abbreviations Used

ASTM	American Society for Testing and Materials
BMT	Billion metric tons
CCR	Clinker/cement ratio
CCN	Cement chemist notation
d	day
EFNARC	European Federation of National Associations Representing for Concrete
FA	Fly ash
GGBFS	Ground granulated blast-furnace slag
GP	Geopolymer
GPC	Geopolymer concrete
Gt	Gigatons
LC^3	Limestone calcined clay cement
Lig	Lignin (or Lignin-based superplasticizer, respectively)
MK	Metakaolin
OPC	Ordinary Portland cement
P	Plasticizer
PC	Polycarboxylate
PCC	Portland cement concrete
S	Blast-furnace slag
SCM	Supplementary cementitious materials
SP	Superplasticizer
w/c ratio	Water/cement ratio
w%	Weight percentage
WG	Waterglass (sodium silicate, mostly Na_2SiO_3)
yr	Year

Cement Chemist Notation Used

CH	$CaO \cdot H_2O$ (Calcium Hydroxide)
C_2S	$2\ CaO \cdot SiO_2$ (Belite)
C_3S	$3\ CaO \cdot SiO_2$ (Alite)
C_3A	$3\ CaO \cdot Al_2O_3$ (Aluminate)
C_4AF	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (Ferrite)
CSH	$0.6–2.0\ CaO \cdot SiO_2 \cdot 0.9–2.5\ H_2O$ (Calcium Silicate Hydrate)
SH	$Si(OH)_4$ (Orthosilicic Acid)
CS	$CaO \cdot SiO_2$ (Wollastonite)
C_3S_2	$3CaO \cdot 2SiO_2$ (Rankinite)

ABSTRACT

In a world well on its course towards 3 °C of global warming, decarbonization of the economy is a matter of survival. The cement industry produces approximately 5–7% of global anthropogenic CO_2 emissions, and while production efficiency and alternative fuels can help to significantly reduce that footprint, the only way to sustainably decarbonize cement is through alternative binders.

These binders have been in development since the 1970s, and geopolymer cement in particular is a well-researched and efficient material. However, problems persist with the engineering properties of these types of concrete.

This review summarizes the current state of research around concrete made from alternative binders, with a particular focus on fresh concrete workability. Strength and durability aspects are considered as well, with the aim of producing an ambient-cured concrete with sufficient workability and strength properties for general construction purposes.

In this regard, two admixtures (Alccofine and ground granulated blast-furnace slag) have been found to fulfil these requirements; another two admixtures (rice husk-based superplasticizer and waste glass powder) can be used when heat curing is applied.

The use of different precursor/activator combinations and ratios, of different curing regimes and of conventional superplasticizers in order to enhance concrete properties has been analyzed as well, with academic publications reporting positive results for certain materials and procedures.

Those results have been compiled in a comparative and accessible manner in the present review.

1

The Problem with Concrete

Concrete is the second-most used substance on our planet, right after water. By the time you have read this sentence, the global building industry will have poured over 19.000 bathtubs of concrete [1]; between 2011 and 2013, China alone has used more concrete than the US in the entire 20th century [2].

The vast majority of our modern infrastructure utilizes concrete to some degree: houses, roads, bridges, skyscrapers and dams are all built with concrete, often reinforced with steel. The material has everything one could want in construction: it is strong, cheap and it takes on any shape. For many of those structures, using wood, steel or masonry would make them much more expensive, or much more difficult to build, or both.

Hardened concrete is a composite material. In its most basic form it consists of two materials: aggregate (mostly sand and gravel) and binder (almost exclusively cement). Sand and gravel are relatively easy to come by, although concrete-grade sand is increasingly becoming sparse, spawning illegal mining operations [3]. Regular Portland cement, on the other hand, requires limestone and other minerals to be extracted from the soil, ground up and then heated to above 1400 °C – a complex and highly energy intensive process that produces "900 kg of CO_2 for every ton of cement produced (Hasanbeigi et al., 2010) which constitutes approximately 5–7% of the global anthropogenic carbon dioxide emission" [4].

Cement production has been growing extensively for the last half-century, and if that trend continues without substantial abatements, global CO_2 emissions from cement production are projected to hit 2,34 billion metric tons by the year 2050 [5] (up from ca. 1,48 bmt. in 2017).

The year 2050 also happens to be the target year for a net zero emissions economy for Germany [6], the EU [7] and the UN's Intergovernmental Panel on Climate Change [8]. If that target is to be met, it seems clear that our current way of producing cement is not sustainable. We have to either find an alternative or stop using cement at all.

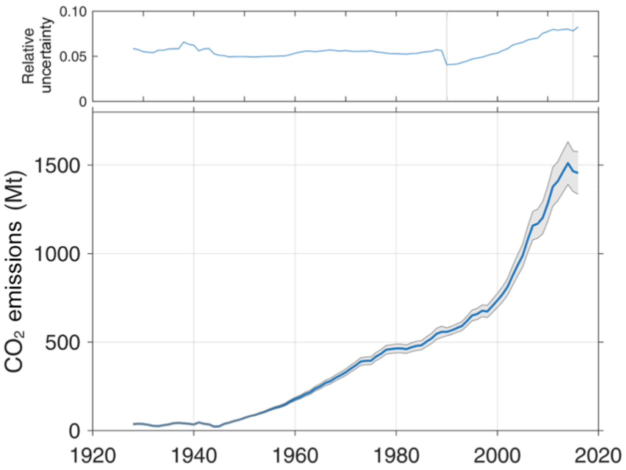

Figure 1: Global process emissions from cement production, with 95 % confidence interval.

Sources of CO_2 in Cement Production

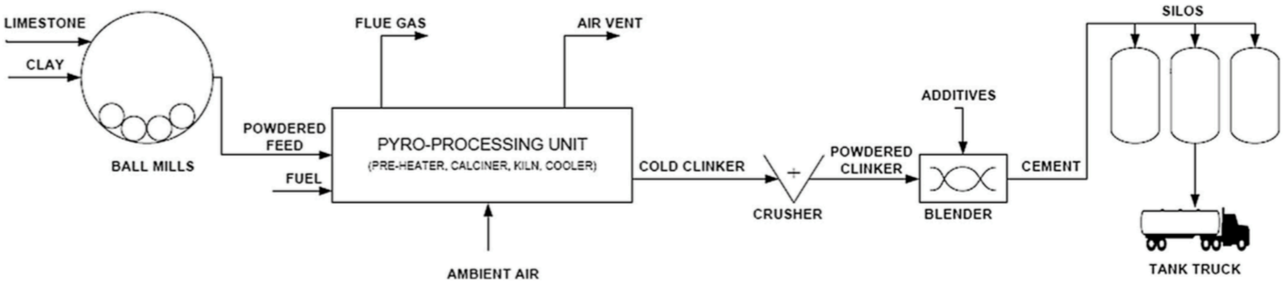

Figure 2: The Cement Production Process

Cement production very roughly consists of three steps: During the first step, raw materials (mostly limestone, magnesium carbonate, silica, alumina and iron oxide) are crushed, ground and mixed. The second step, referred to as pyro-processing, sees the raw material being gradually heated up to 1450 °C in order to form clinker, the main binder component of Portland cement. In the third step, the clinker is finally crushed and mixed with additives in order to obtain the final product.

Mahasenan et al (2002) [9] have identified four major sources of CO_2 in cement production:

1. 40% ● Fossil fuel combustion at cement manufacturing operations
2. 5% ● Transport of raw materials
3. 5% ● Fossil fuel combustion for electricity used in cement manufacturing
4. 50% ● Conversion of limestone to calcium oxide, the primary precursor to cement: $CaCO_3 \rightarrow CaO + CO_2$

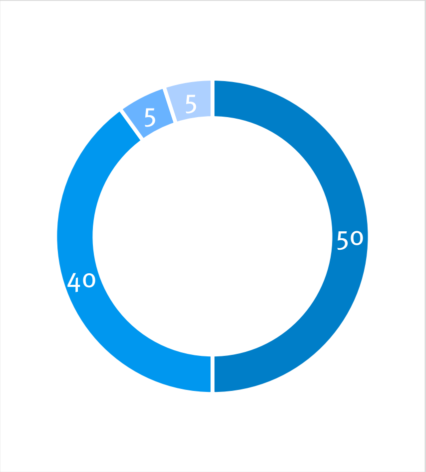

Figure 3: Share of CO2 emissions in cement production in [%]. Legend: on the left.

Another significant source of CO_2 emissions are “major and minor technical and management problems in the plant which can influence plant performance, requiring additional fuel and electricity consumption“ [10]; these include lack of proper maintenance, low energy efficient processes (e. g. wet, semi-wet cement production) etc.

Currently there is a number of approaches to decrease the amount of CO_2 emitted by cement production, which Benhelal et al (2013) [11] roughly divide in three categories:

1. Fuel and energy saving
2. Carbon separation and storage
3. Utilizing alternative materials (without fully replacing conventional cement).

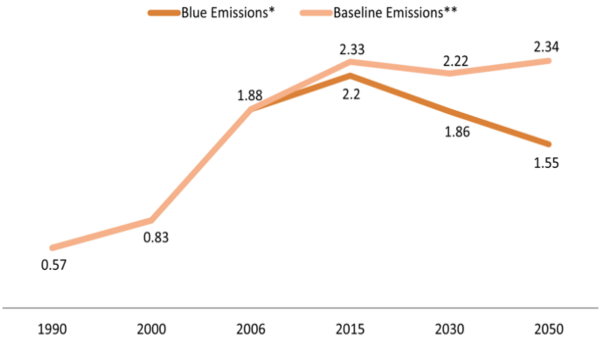

Figure 4: Global CO2 emissions from cement production in Gt. "Baseline Emissions" are expected emissions without mitigation actions; "Blue Emissions" are emissions considering application of mitigation technologies and policies

Taken together, these measures have the potential to reduce CO_2 emissions from cement production from 2.34 Gt/yr to 1.55 Gt/yr by 2050 (see fig. 4). Since that number is still far above zero, the main focus of this review is a different approach: entirely replacing conventional cement with alternative materials.

2

Decarbonization of Conventional Cement

2.1. Cement Chemistry

For clarification purposes, I would like to separate the terms *binder* and *cement*. As mentioned earlier, concrete consists of aggregate and binder. The term *binder* is used here in as “a substance used to make other substances or materials stick or mix together” [12]. The term *cement* is often used synonymously, but in the context of this review, I would like to use it in its more narrow definition: “a powdery substance made by calcining lime and clay, mixed with water to form mortar or mixed with sand, gravel, and water to make concrete.” [13]

The main material for cement is clinker, a phase assemblage of the calcium-based minerals C_3S, C_2S, C_3A and C_4AF [14] (for simplicity, the cement chemist notation is used here. A table mapping CCN to molecular formulas can be found on page 4.)

Clinker phases are obtained from a few basic components mixed in a certain ratio:

- limestone and chalk as a source of $CaCO_3$ (Calcite)
- quartz sand and clay as a source of SiO_2, Al_2O_3, and Fe_2O_3 [15]

This so-called raw feed is then heated step-by-step to evaporate any remaining water and to decompose the minerals into smaller molecules. The maximum temperature of 1450 °C is found in the rotary kiln, where the C_3S clinker phase is formed. A rough overview of the resulting reactions relevant for this review is given in the diagram below:

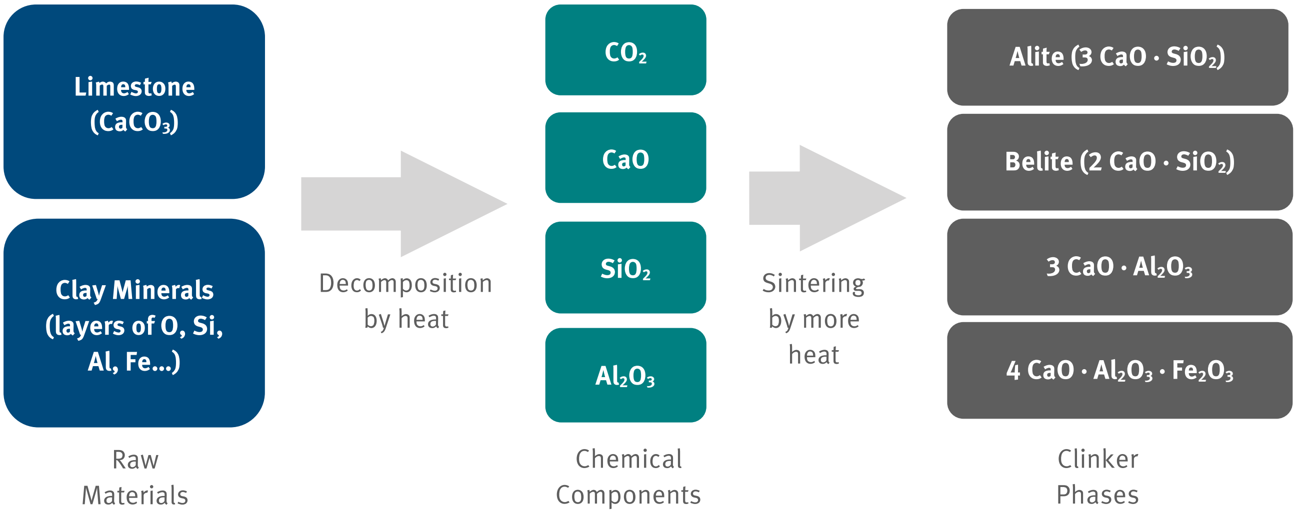

Figure 5: Basic chemical processes in clinker production.

The resulting products are lumps of 1–10 mm diameter which then need to be ground into a fine powder in order to react with water.

As the temperatures imply, clinker production is a very energy-intensive process. The required energy can be reduced through process optimization, and specific thermal energy consumption has already been cut in half in Germany since the 1950s [16]. However, nothing can really be done with the calcination of Calciumcarbonite, which produces some 50% of the CO_2 emissions (except for carbon capture and storage, which is currently nowhere near practicability).

In order to control setting time, a sulfate source is usually added to the clinker before grinding, mostly gypsum or anhydrite [17].

While clinker remains the base material for conventional cement, the industry has developed a few materials that can serve as a (partial) substitute for clinker. Some of them are simply cheaper (because they are byproducts of other industrial processes), and some of them enhance the technical cement properties and allow for constructions that would not be viable otherwise. These are presented in the following chapter.

2.2. SUPPLEMENTARY CEMENTITIOUS MATERIALS

2.2.1. POZZOLANAS

Pozzolanas are "naturally occurring siliceous or silico-aluminous fine-grained materials which at normal temperatures can only harden in the presence of water and calcium hydroxide." [18]

Calcium hydroxide (or CH in CCN) is a compound resulting from residual calcium from the hydratation of C_3S and C_2S to CSH. While CSH is the main hardening constituent of cement, CH increases the water pH, effectively protecting the reinforcing steel from corrosion [19].

A part of the CH contained in the hardening cement can be utilized to for the so-called pozzolanic reaction, where the silicic acid (SH in CCN) reacts with CH in order to produce CSH.

Pozzolanas are usually natural minerals containing at least 25% reactive silica, according to the European Standard specifications [20]. They can be found in volcanic tuff (which has been used since antiquity) as well as volcanic and sedimentary rock; natural calcined pozzolanas are a subgroup that has to be heated to 400 – 800 °C in order to increase their reactivity.

When added to cement, pozzolanas enhance several technical properties such as permeability, hydration heat, workability and cement bleeding [21].

Pozzolanas can be used to reduce the clinker/cement ratio (CCR) to 45 w% (compared to 95 w% in Portland cement) [22].

2.2.2. Fly Ash

Fly ash is a fine-grained residue from the combustion of pulverized coal[23], a waste material produced in copious amounts throughout the world [24].

Two types of fly ash are in use today: siliceous fly ash mainly contains reactive SiO_2 and Al_2O_2 and has pozzolanic properties. Calcareous fly ash additionally contains reactive CaO and has pozzolanic and/or latent hydraulic properties [25].

The clinker/cement ratio of Portland fly ash cement can be as low as 65 w% [26].

2.2.3. Granulated Blast-furnace slag

Blast-furnace slag is a by-product of the smelting of iron ore and other additives in a blast furnace, consisting mostly of SiO_2, Al_2O_3, CaO and MgO [27]. The fluid slag is rapidly cooled off in order to achieve a high glass content, then mixed with clinker and ground up.

Blast furnace slag is a latent hydraulic material, producing CSH with calcium hydroxide as an activator.

The material can make up 95 w% of the final cement, bringing the clinker/cement ratio down to merely 5 w%.

It also offers a range of advantages over Portland cement like higher diffusion resistance, less hydration heat and a higher resistance to sulfate [28].

2.2.4. Limestone Calcined Clay Cement (LC^3)

While pozzolana, fly ash and blast-furnace slag are excellent materials for clinker substitution, the main problem is availability: natural pozzolana are not available in relevant amounts. Blast furnace slag can cover a mere 5%–10% of worldwide cement production, and this number is unlikely to increase since cement production is growing faster than steel production [29]. Fly ash – although available in bigger amounts – mostly cannot match quality requirements, and with the end of coal power on the horizon, availability will probably also decrease.

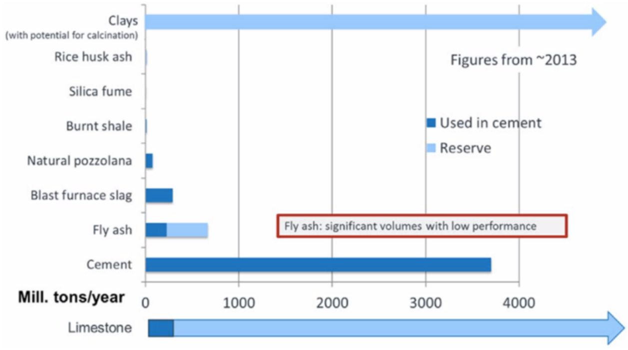

Figure 6: Availability of Common SCMs

Clays, however, are the most abundant minerals in the earth's crust, together with limestone [30];

Clays before calcination are hydrous phyllosilicates, and kaolinite in particular is composed of tetrahedral silica sheets and octahedral alumina, linked by oxide bonds. The sheets among themselves are connected through weaker hydrogen bonds. During calcination, the hydroxide is lost and the alumina and silica layers lose their long range order; also, the alumina transform to a tetrahedral coordination. The resulting material is referred to as metakaolin ($Al_2Si_2O_7$) and is a much more reactive aluminosilicate. Metakaolin then serves as a pozzolan to react with calcium hydroxide to form CSH, contributing to strength and durability [31]. Due to its aluminum content, it also forms "carbo-aluminates that continue to reduce the porosity and therefore increase the strength of cement pastes" [32].

According to Scrivener et al (2018) "Clays having a significant proportion of kaolinite have proven to be highly pozzolanic if calcined between about 700 and 850 °C" [33] and produce mechanical properties comparable to Portland cement when mixed with clinker and limestone. At the same time, they reduce the clinker/cement ratio to 50 w% and can be used "by untrained workers with similar water to cement ratios and superplasticizers" [34]. Furthermore, the clays can be calcined in existing equipment without the need for investing in new production infrastructure [35].

The high availability and easy production of calcinated clay, as well as the high rate of clinker substitution with comparable quality make LC^3 appear like a feasible way to significantly reduce CO_2 emissions from cement production in the near future.

3

DECARBONIZATION OF CONCRETE USING ALTERNATIVE BINDERS

3.1. SOLIDIA

Solidia Cement is a non-hydraulic calcium silicate binder consisting mostly of wollastonite ($CaO \cdot SiO_2$, or CS in CCN) and rankinite ($3CaO \cdot 2SiO_2$, or C_3S_2 in CCN). In an interesting turn, it sets and hardens through carbonation with CO_2. It permanently binds up 300 kg of CO_2 per tonne of cement used [36], effectively making it a carbon sequestration process.

While the Solidia concept seems promising, the following information is to be taken with some caution – Independent sources describing the material are scarce. There was some research done about non-hydraulic calcium silicates in the late 70s [37], and in the 90s Low et al. released a paper describing the enhancement of flexural strength of OPC through wollastonite addition [38]. The only detailed sources regarding Solidia are whitepapers and other materials released by Solidia Technologies, Inc. in New Jersey. While they appear to be results obtained in over a decade of production and use of Solidia cement, the methodology used is never laid out in detail; some of the characteristics of Solidia, such as the carbonation behavior [39] and the microscopic structure [40] have been investigated and confirmed in separate studies. Others, like compressive strength, could not be verified externally.

Just like Portland cement, Solidia Cement relies on a raw feed of limestone and clay/sand as sources of calcium and silicium oxides. However, due to the lower lime content, Solidia can be produced from lower-grade limestone and does not require bauxite and laterite addition [41].

The lower Calcium content required for Solidia also has two effects on the CO_2 emissions: first, less calciumcarbonate needs to be calcined, with less CO_2 as a by-product. Second, the required kiln temperature is 1200 °C, some 250 °C lower than what is required for Portland cement production. These two factors reduce CO_2 emissions in Solidia production by 30% per tonne when compared to Portland cement [42].

In order to cure, the CS and C_3S_2 components of Solidia need to be exposed to water and gaseous CO_2 simultaneously. They then form a three phase substance of $CaCO_3$, amorphous

SiO_2 and unreacted $CaO{\cdot}SiO_2$ (see figure 6). Compressive strengths of up to 70 N/mm² have been achieved in Solidia concrete parts [43].

There is no information to be found considering the workability of fresh concrete produced with Solidia. The curing time is nonetheless noteworthy: depending on the thickness of the part, Solidia concrete fully cures within 10 – 24 hours – considerably less than the 28 days needed for Portland cement concrete.

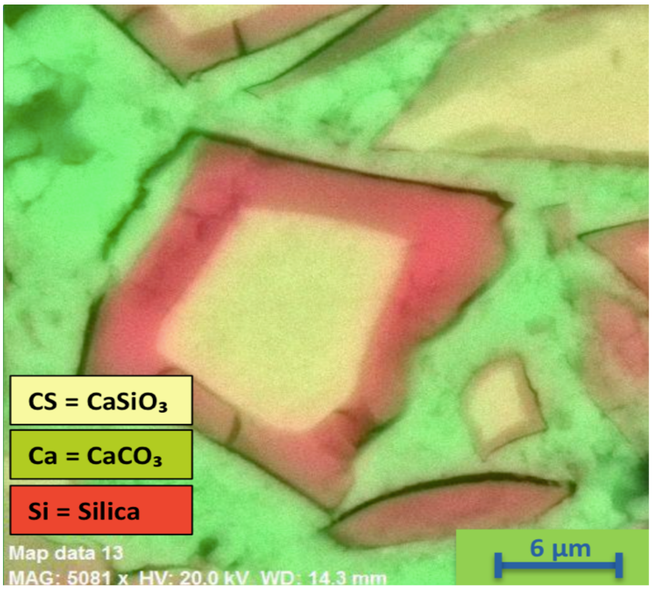

Figure 7: Microstructure of Solidia Cement

All in all, when considering the lower emissions for clinker production as well as the sequestration through carbonation, Solidia has total net emissions of about 265 kg per ton of cement – almost 70% below the net emissions of Portland cement.

However, as noted earlier the sources describing Solidia are scarce and should be taken with caution.

3.3. GEOPOLYMER BINDER

The term *Geopolymer* goes back to the 1970s and was coined by JOSEPH DAVIDOVITS, one of the foremost researchers in this field. While there is no universally accepted definition, in the context of this review I would like to define it as a solid and stable aluminosilicate material formed by alkali activation of an aluminosilicate precursor [44].

3.3.1. GP PRECURSORS AND ACTIVATORS

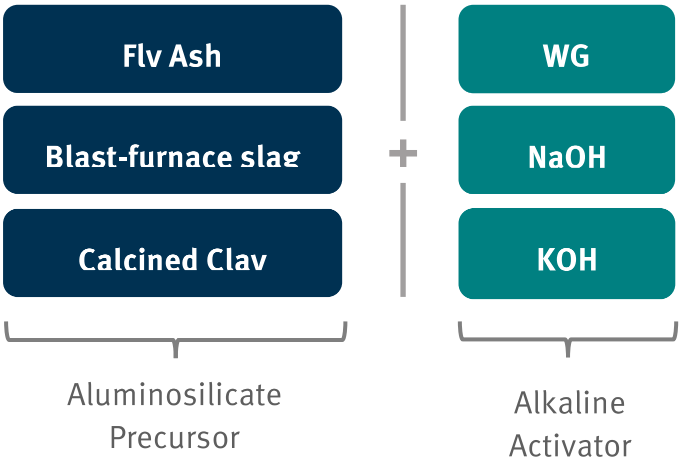

Figure 8: Common precursor and activator materials for geopolymer cement

As fig. 9 illustrates, GP is produced by taking an aluminosilicate precursor (left) and adding an alkaline activator (right). All of the publications considered in this review use only three types of precursor and activator, combining them in different ways: For aluminosilicates it is either fly ash (FA), blast-furnace slag or calcined clay; for alkaline activators it is either sodium silicate (waterglass, or WG), sodium hydroxide (NaOH) or potassium hydroxide (KOH). Finally, water serves as a reaction medium.

In developing countries, both fly ash and blast-furnace slag are often disposed of as waste and could be utilized for GPC production. However, clays are the only precursor material available in amounts that would suffice to replace OPC.

3.3.1. The Geopolymerization Process

The kinetics of geopolymerization are not yet understood in detail and have been the topic of significant discussion in the past decade. A sound understanding and a reliable mathematical model of the reaction mechanisms is necessary in order to accurately adjust the curing process. That would make the material usable for a variety of applications. However, the characteristics of GP (corrosiveness, stickiness, X-Ray amorphous structure) make it hard to find a technique that would provide a good understanding of what exactly is going on during polymerization [45].

A simplified model of the geopolymerization process was described by Provis and van Deventer (2007). In a first step, the crystalline aluminosilicate precursor is dissolved by the alkali activator and water, forming AlOH and SiOH monomers. Those in turn form aluminosilicate oligomers, releasing the water added in the first step. Then they are further condensed into aluminosilicate polymers (amorphous) and aluminosilicate ‘nuclei’ (quasi- or nano-crystalline), releasing more water, which also enhances the workability of the GP paste. Those materials form the base for the hardened GP, consisting of amorphous aluminosilicate gel and a nanocrystalline zeolitic phase [46]. Depending on the mix and curing environment, the reacting slurry can set almost instantaneously or over the course of a few days. Reaction processes, however, still occur over some time as can be seen in the increasing strength [47].

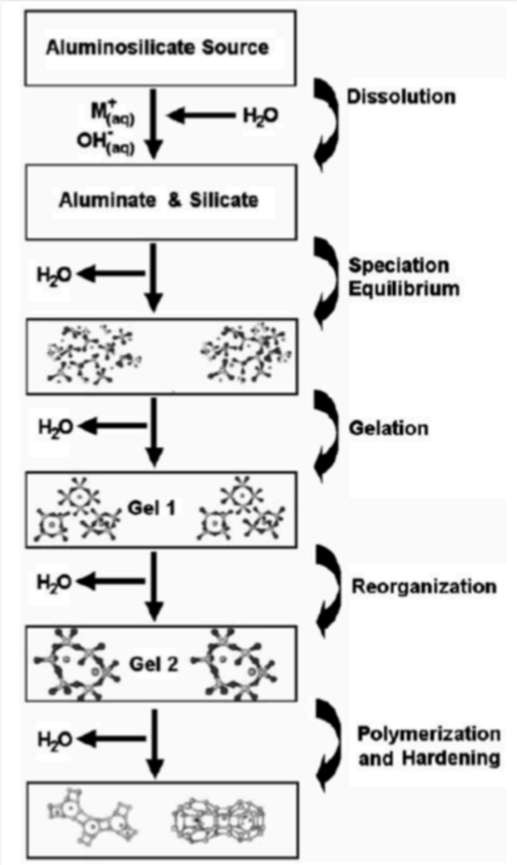

Figure 9: The geopolymerization process

The hardened aluminosilicate polymer gel consists of AlO_4 and SiO_4 tetrahedra, linked with bridging oxygen atoms in four (or less) corners, thus forming a three-dimensional amorphous web; the water used for dissolution of the aluminosilicates in the initial reaction is released into the gel pores [48]. It furthermore contains zeolites, a crystalline outgrowth of aluminosilicates.

4

CONCRETE PROPERTIES ACHIEVED WITH ALTERNATIVE BINDERS

4.1. WORKABILITY

A central aspect of concrete technology is workability, defined as the effort "needed to manipulate a freshly prepared concrete mixture with minimum loss of homogeneity" [49].

In order to properly investigate workability, one needs to find a measure for it. For practical purposes, this is done in-situ with slump and table flow testing, giving a good (relative) idea of whether a concrete batch fulfills certain requirements. Slump was also the main parameter that was used to measure workability in most of the publications reviewed. These tests, however, provide a rather limited picture of the rheological properties. Slump and flow table results are "related to the flow resistance (and yield stress) which governs the 'static' flow behaviour of the material." [50] However, in GPC pastes, the yield stress is often not correlated with plastic viscosity (see fig. 9 on the right). Thus, a GP paste may show a low yield stress and high slump, implying a high-workability, but still be highly viscose and thus not suitable for many applications [51].

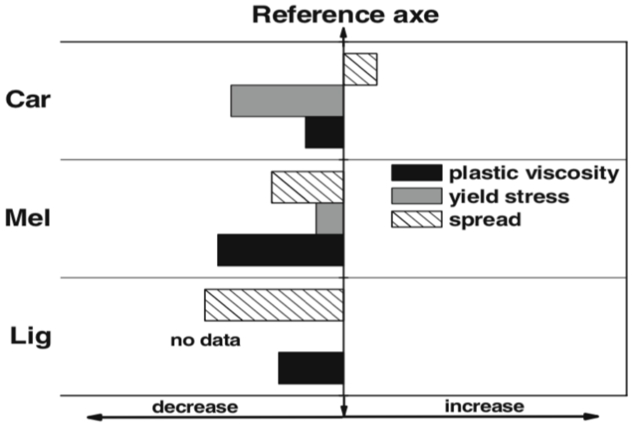

Figure 10: Correlation between flow and rheological parameters. Car: Modified polycarboxylic ethers; Mel: Melamine-derived synthetic polymers; Lig: Purified lignosulphonate

For these reasons, testing with a rotational cylinder rheometer provides more accurate measurements: a rheometer applies a certain shear rate (moving plate in fig. 8) to a fluid and then measures the resulting stress τ exerted by the fluid on the stationary plate (stationary plate in fig. 8).

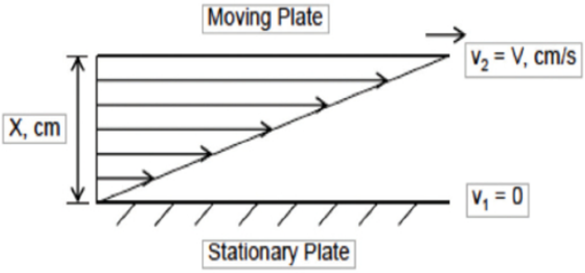

Figure 11: Basic model of a rheometer

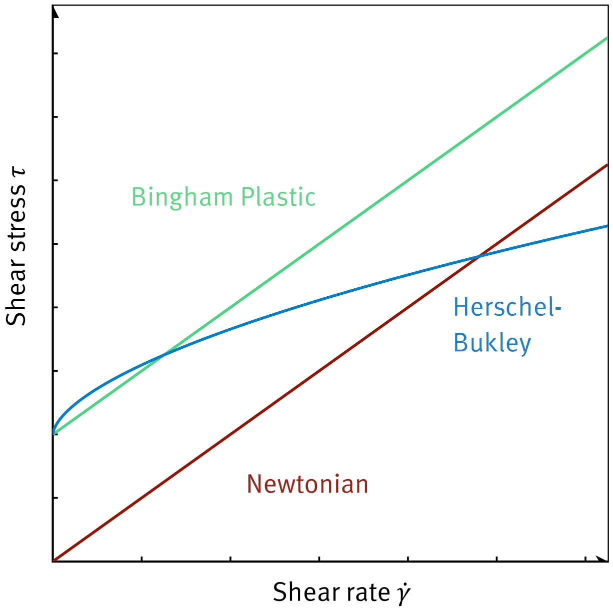

Figure 12: Shear rate / shear stress graphs for Newtonian, Bingham plastic and Herschel-Bulkley liquids.

This experiment provides a shear rate/shear stress graph as shown in fig. 9. The red graph describes a Newtonian liquid (e. g. water) – as soon as the moving plate applies a certain force to the liquid, it induces a movement, and a speed gradient. The Bingham plastic model is commonly used for cement, drilling liquids and slurries: these substances behave like a solid at first. When the moving plate exerts a force, they absorb the shear through elastic deformation. This behavior is due to solid particles in the liquid which form bonds. When the yield stress τ_0 (equals the y-axis offset in fig. 12) is reached, these bonds are broken up and the liquid starts flowing. Under certain circumstances, the dynamic viscosity (equals the slope of the graphs in fig. 12) of GP pastes will decrease with an increasing shear rate, a behavior described by the Herschel-Bulkley model. This was shown to be the case for slag pastes activated by sodium silicate [52].

Accordingly, the fluids can be described by the following formulae:

Newtonian fluid: $\boldsymbol{\tau = \mu\dot{\gamma}}$

Bingham plastic fluid: $\boldsymbol{\tau = \tau_0 + \mu\dot{\gamma}}$

Herschel-Bulkley fluid: $\boldsymbol{\tau = \tau_0 + k\dot{\gamma}^n}$

τ : shear stress

$\dot{\gamma} = \frac{\delta v}{\delta x}$: shear rate

μ : dynamic viscosity

τ_0 : yield stress

k : consistency index

n : flow index

Generally, one of the main problems with GP binder is its poor workability: Alkali-activated Fly Ash has a much greater plastic viscosity than OPC [53] and is prone to fast setting. In a matter of minutes, it can produce “highly viscous, unmanageable concrete mixtures” [54]. Generally, the slump values are around 40 mm (which is low) and the compressive strength at 28d is around 30 – 35 N/mm^2 (which is also considerably low). Alkali-activated metakaolin (MK) has a very high specific surface and needs a lot of water to ensure workability. In both cases, increasing the w/c ratio improves workability but also increases the cement porosity. The pores in turn greatly reduce compressive strength and lead to durability issues.

The same problem was routinely faced in OPC technology, and a set of admixtures was developed to achieve a low water demand, good workability and high strength at the same time. However, GP chemistry and synthesis is vastly different to OPC chemistry and hydration. Conventional plasticizers and superplasticizers have limited applications in GP technology.

In the context of this review, I would like to concentrate on producing a GPC that, for general construction purposes, has

a) **reasonable workability** – at least 50 mm slump – class S2 according to DIN EN 12350-2

b) **adequate compressive strength** – at least 30 N/mm^2

4.1.1. INFLUENCE OF PRECURSORS, ACTIVATORS AND WATER RATIO ON WORKABILITY

Even without any admixtures, very different results can be achieved with different combinations of aluminosilicate sources and activators, and with different ratios.

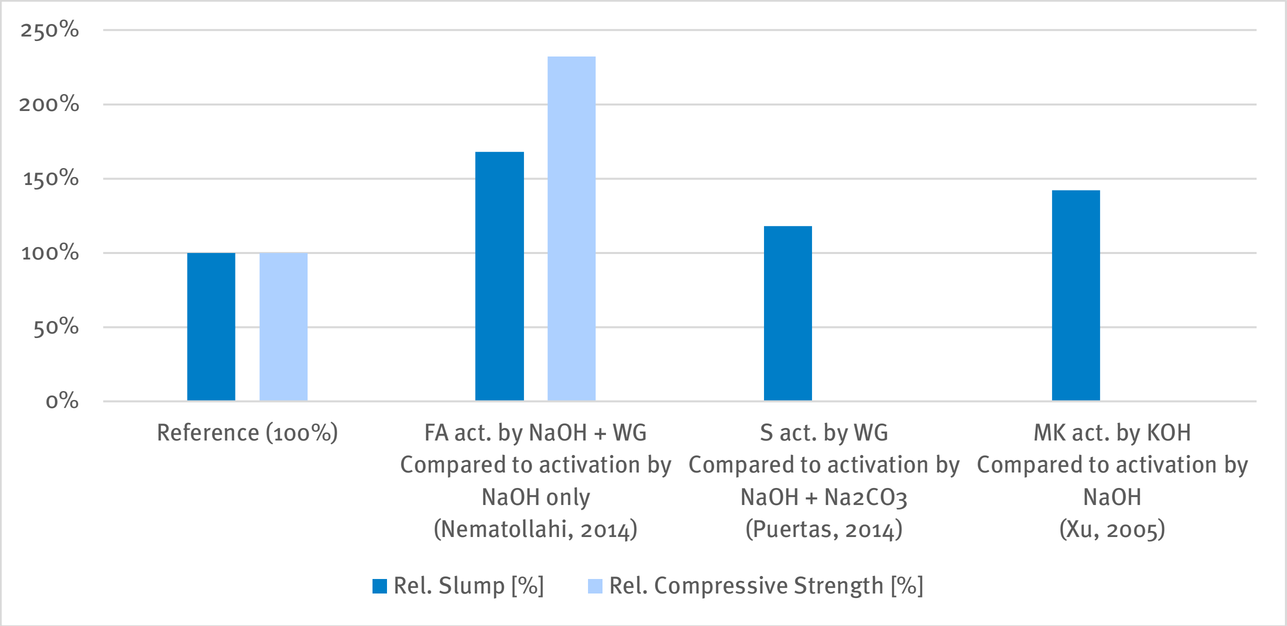

Figure 14: Relative slump and compressive strength values for different activators used on the same precursor. Exact values can be found in Annex A table 1.

For instance, NEMATOLLAHI et al. (2014) compared slump and compressive strength in **fly ash** activated with a) NaOH only and b) NaOH + WG. They found that activating the paste with both NaOH and WG increased slump by 68% and compressive strength at 3d by 131% when compared to activation by NaOH only [55].

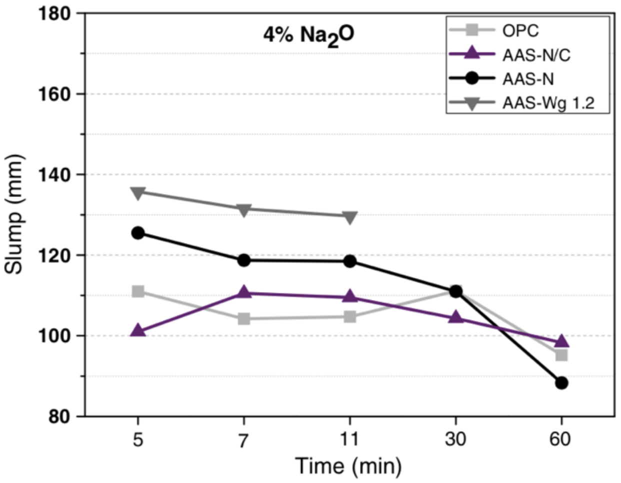

Figure 15: Minislump values for OPC and slag activated by NaOH + Na2CO3 (AAS-N/C), NaOH only (AAS-N) and waterglass (AAS-Wg 1.2)

Similarly, Puertas et al. (2014) used **blast-furnace slag** paste activated by a) NaOH, b) NaOH + WG or c) NaOH + Na_2CO_3 to investigate the effect of different activators, activator concentrations and activator ratios; their specimens showed the highest slump with WG, then NaOH, and the lowest with NaOH + Na_2CO_3 activation (18% less than WG at 11 min). Their findings also suggest that “higher activator concentrations induced speedier loss of fluidity. That finding is related to the formation of more reaction product at shorter test times.” [56] For instance, WG-activated slag with 1,5% SiO_2/Na_2O ratio resulted in a 18,6% lower slump when the activator ratio was raised from 3% to 5% (Na_2O by slag mass) [57].

Furthermore, WG-activated slag showed a high early yield stress at around 15 min, which, the authors suggest, is due to formation of a CSH phase using the Ca^{2+} ions dissolved from the slag and the silicate ions from the activator. This CSH could be broken up by constant mixing of the concrete, although the instruments used were unable to break it up at concentrations over 5% Na_2O [58], with the paste hardening after that. Similarly, the CO_3 ions present in the Na_2CO_3 activator “tend to form AFm (calcium aluminate monosulfate) and sodium–calcium carbonate compounds, which may induce higher shear stress in these AAS-NC [fly ash activated with NaOH + Na2CO3] pastes” [59].

For **metakaolin**, Xu et al. have shown in 2005 that metakaolin activated by KOH has a 42% higher compressive strength than metakaolin activated by NaOH. Furthermore, an admixture of silicate solution to the alkaline activator was shown to “generate the best homogeneous geopolymeric paste and so to create the GP with the highest compressive strength.” [60]

Regarding the addition of extra water, Ahmed et al. (2011) used fly ash as a precursor and achieved the following results, in a parallel to PCC:

> As it was expected, the addition of water improved the workability characteristics of freshly prepared concrete mixtures; however, the addition of water beyond certain limit resulted in bleeding and segregation of fresh concrete and decreased the compressive strength of the concrete significantly. [61]

These results are generally mirrored in the reviewed literature [62], with additional water increasing workability and decreasing compressive strength. However, since an increase in activator ratio generally decreases workability and increases compressive strength [63], there is a theoretical potential to combine these two effects in order to produce a GPC with better properties. Curing, precursor fineness and binder/aggregate ratios may also serve as avenues for increasing strength, as explained in 4.1.2.

4.1.2. Influence of curing temperature, curing time, precursor fineness and binder/aggregate ratio

Heat curing does not have a direct influence on GP workability, but it can offer a remedy for strength problems. For instance, one could add additional water in order to increase GP workability, which would result in reduced strength; this could then be compensated by heat curing the concrete in order to increase the strength to an acceptable level.

Research results regarding heat curing indicate that the effects largely depend on the precursor/activator combination, as the below figure illustrates.

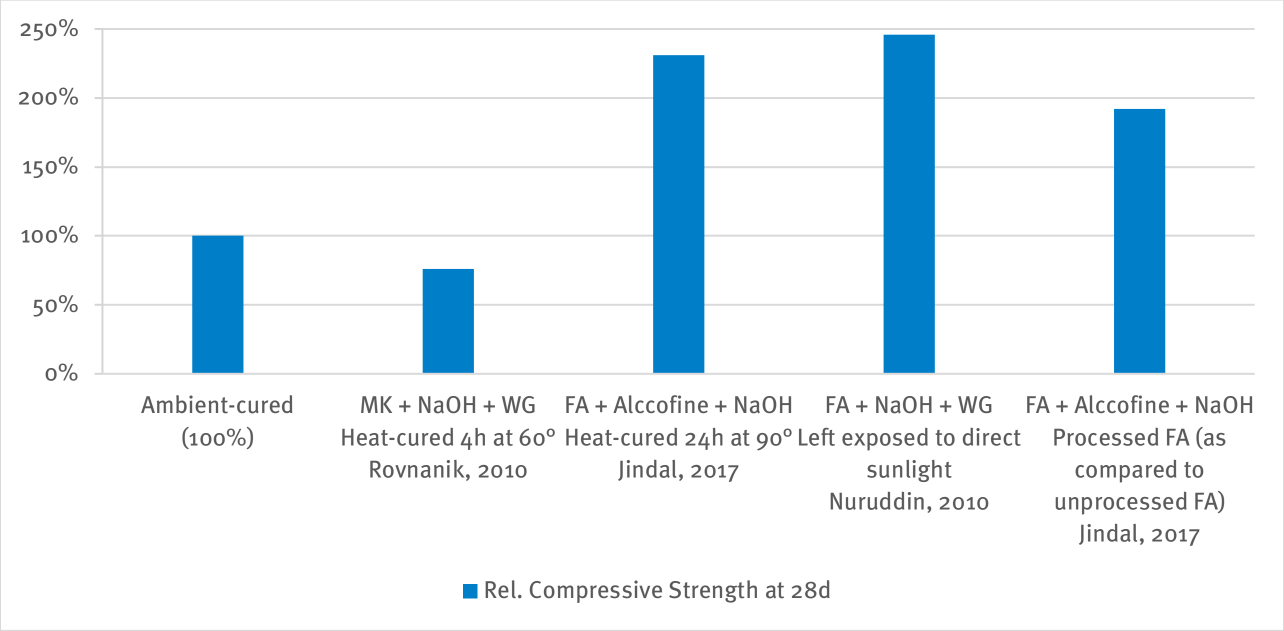

Figure 16: Relative compressive strength values for heat curing, as compared to ambient-cured GPC.

For **metakaolin**-based GP, Rovnanik (2010) showed that MK activated by NaOH+WG hardened earlier when heat cured, and could even develop target strength at 1d. However, heat curing appeared to have a substantial negative impact on 28d-strength (-23,81%) compared to specimens cured at ambient temperatures [64].

For **fly ash** precursors, Jindal et al. (2017) used FA with so-called Alccofine, activated by NaOH, and observed an 131% increase in 28d compressive strength when heat curing at 90 °C, when compared to specimens cured at ambient temperatures [65]. Hardjito and Rangan (2005) showed a substantial increase in 7d compressive strength through heat curing, and a positive relation between curing time and compressive strength. Interestingly, Nuruddin et al. (2010) demonstrated that in warm climates FA-based GPC could be heat cured by leaving it in the sun, which yielded a 113% increase in compressive strength in their study [66].

Furthermore, JINDAL et al. (2017) have found that an increase by 25% of the specific surface (and thus the fineness) of FA yielded a substantial increase in both workability [67] and compressive strength [68]. Somewhat obviously, but still noteworthy, they also showed that slump increased significantly the higher the binder/aggregate ratio was in their study [69].

4.1.3. EFFICIENCY OF CONVENTIONAL SUPERPLASTICIZERS

Again, the efficiency of conventional plasticizers (P) and superplasticizers (SP) can be put in relation to the precursor/activator combination.

With regards to **slag-based geopolymer**, the effects of conventional SPs has been broadly studied. It should be noted that research results are somewhat inconsistent due to certain differences in experimental conditions (additions such as FA and MK, different activators, activator ratios and concentrations). Generally, when activated by WG or NaOH+WG, both Lig- and N-based SPs either had no considerable effect on workability or reduced concrete strength, or both [70], which might be due to their instability in those (alkaline) environments. Vinyl and polyacrylate copolymers also failed to improve workability for these activators; However, PALACIOS and PUERTAS (2004, 2005) were able to show that N-based SPs are chemically stable when using NaOH activator and thus increase workability, delay setting time and enhance compressive and flexural strength [71]. These results were mirrored by PALACIOS et al. in 2009, where N “was the only type of SP that affected the rhelogical parameters of the slag pastes when the activator was 2.57 M NaOH” [72]. However, once the activator molarity was changed to 0,005 M NaOH, vinyl copolymer produced the highest reduction in yield stress.

Efficacy of SPs in **fly ash geopolymer** is less explored, however, congruent research results can be found here, too.

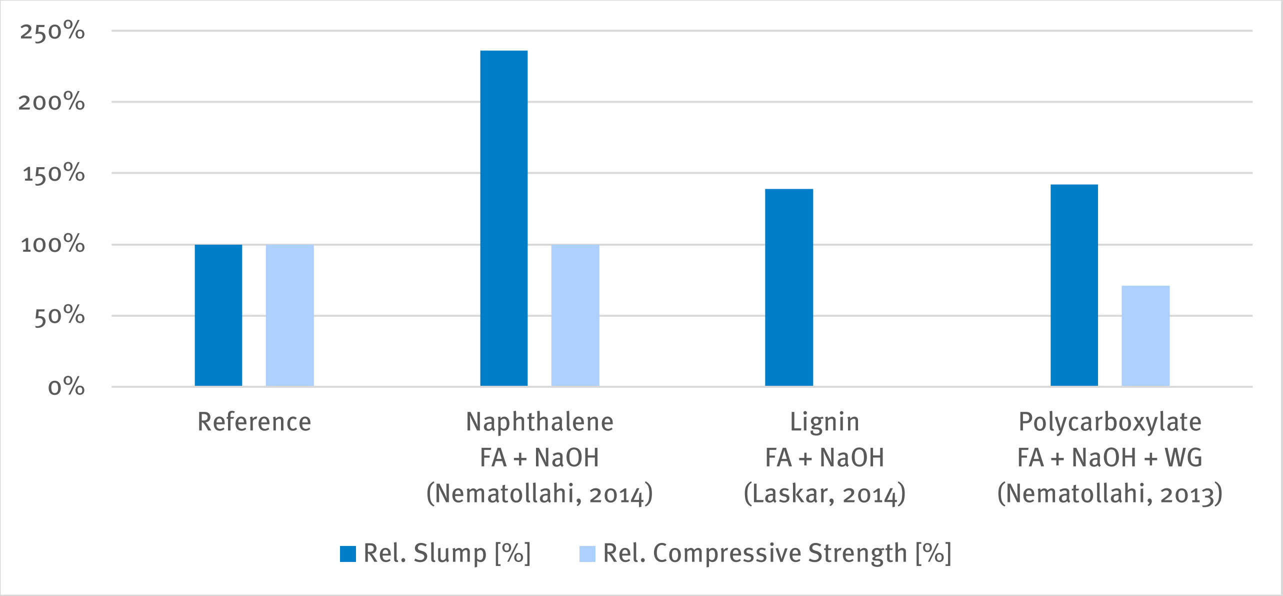

Figure 18: Relative slump and compressive strength values achieved with different SPs for FA-based GPC

When activated by NaOH only, vinyl copolymer and polyacrylate copolymer SPs seem to be ineffective; however, N-based SP is effective in this case according to NEMATOLLAHI et al. (2014), increasing relative slump by 136% with no negative effect on compressive strength [73]. LASKAR et al. (2014) have found that Lig-based SP is effective for this type of activator, improving relative slump by 39% [74] (strength was not evaluated in this study).

When activated by NaOH+WG, N increases workability and has no negative impact in compressive strength up to a concentration of 2% by mass of fly ash [75], according to HARDJITO et al. (2004, 2005). CRIADO et al. (2009) found that PC-based SPs were effective in increasing workability in these mixtures (however, strength was not evaluated) [76]. The efficiency of PC-based SPs was also confirmed by NEMATOLLAHI et al. (2013), with an increase in relative slump of 39–45% and a decrease in compressive strength of 29% at most [77].

For KOH + WG activators, there is only one study covering this topic. KONG and SANJAYAN (2010) did not find that N- or PC-based SPs had any effect on workability, while having a pronounced negative effect on strength [78].

4.1.4. DEVELOPMENT OF NEW ADMIXTURES AND SUBSTITUTES

As shown above, the use of conventional Ps and SPs in GPC is fairly limited. In order to create a binder comparable to Portland cement in terms of versatility and adjustment, new ways need to be found to increase workability.

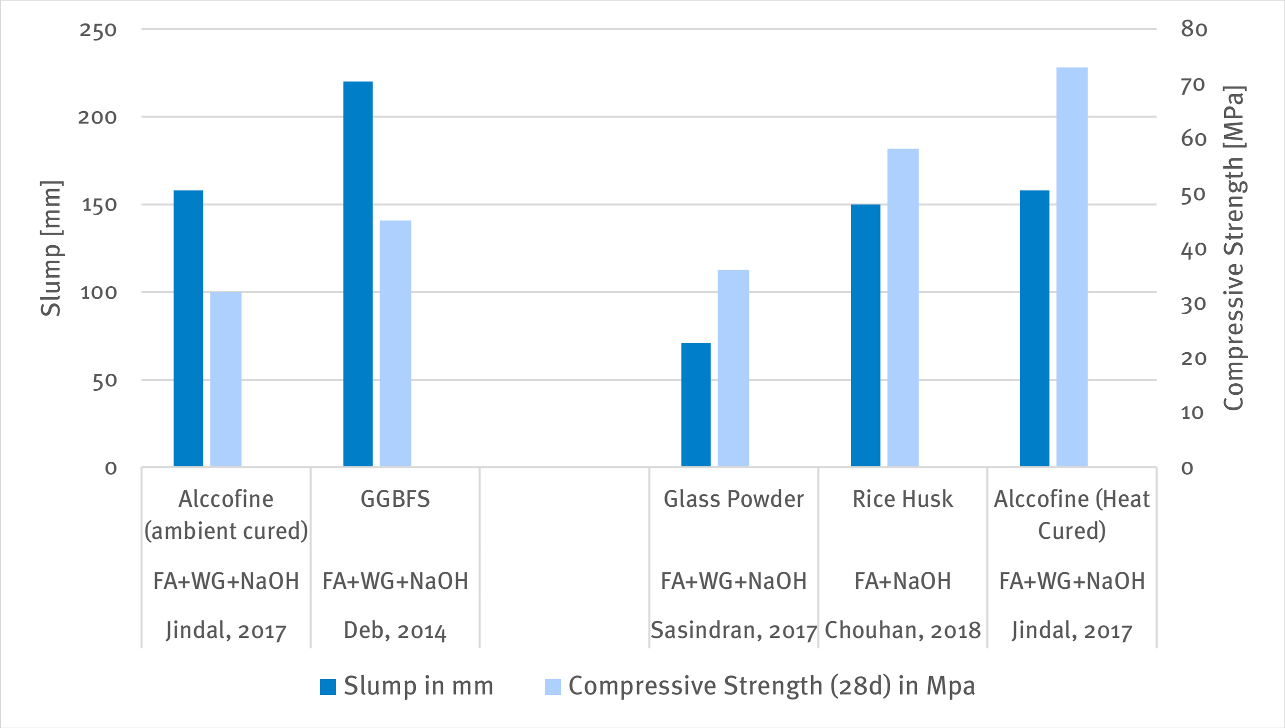

Figure 19: Slump and Compressive Strength (28d) Values Achieved With Different Admixtures / Substitutes

There is a handful of studies focusing on developing new admixtures and substitutes for that purpose, and I would like to focus on four of them; they all used FA as a precursor.

Figure 18 shows a comparison of slump and compressive strength at 28d, with ambient-cured specimens on the left and heat-cured specimens on the right-hand side.

Alccofine is “a specially processed product based on slag of high glass content with high reactivity obtained through the process of controlled granulation.” [79] It consists mostly of silicium, aluminum, calcium and magnesium oxides and has a very fine particle size. The addition of Alccofine to the fly ash precursor (at about 10% of fly ash mass) produces a GPC with 158 mm slump and 32 N/mm^2 compressive strength after 28d [80]. This would put the concrete into the high workability category (S3 according to DIN EN 206-1) and make it usable for most general construction purposes.

When heat-cured at 90 °C for 24h, the paste can reach a compressive strength of 73 N/mm^2 and can then be used for high-strength construction purposes [81]. The authors generally trace this to a) higher reactivity due to the presence of aluminum oxides, and b) the ultra-high fineness of Alccofine and subsequent plugging of micropores in the gel.

Adding **ground granulated blast-furnace slag** (or GGBFS) to the FA precursor can also significantly enhance its properties. DEB et al. (2014) found that the addition of GGBFS (around 20% of the fly ash content) decreased the workability, “mainly because of the accelerated reaction of the calcium and the angular shape of the slag” [82]. However, it also increased the compressive strength significantly, which they attribute to “to the formation of more compact microstructure of the binder.” [83] Additional water was then added in order to enhance workability.

With an optimum ratio (2/8 GGBFS to FA) the authors were able to produce an ambient-cured GPC with a slump of 220 mm and 45 N/mm^2 of compressive strength at 28d, thus putting it in the fluid category (S5), and making it usable for general construction purposes. Furthermore, the hardening reactions continued in the cement after 28d, often increasing compressive strength by about 27% to 57 N/mm^2 at 175 days [84].

Another interesting development was made by CHOUHAN et al. (2018) in Bhopal, India. They obtained a new superplasticizer by boiling **rice husk** in NaOH solution for an hour, then adding that admixture in regular SP amounts (up to 1% of binder) to the FA precursor and WG+NaOH activator and curing it at 60 °C for 48h. The highest slump was recorded at 200 mm, with 1% admixture; however, the optimum amount with regards to compressive strength was found to be 0,5%. The GPC at that rate showed a slump of 150 mm and a compressive strength at 28d of 58,1 N/mm^2 [85]. These numbers would generally put it in the high workability (S3) class and very close to being a high-strength concrete [86]; the authors attribute these effects to in-situ synthesis of lignin, a substance often used as a base for superplasticizers.

Another way to increase both workability and compressive strength was found by SASINDRAN et al. (2017). Using **waste glass powder** as a partial substitute for FA, they leveraged the pozzolanic qualities of the substance. At a concentration of 15% and heat-cured for 24h, the glass powder increased slump to 71 mm and compressive strength at 28d to 36 N/mm² [87]. that would put the GPC in the mid-workability range (S2) and make it suitable for general-construction purposes.

4.1.5. DEVELOPMENT OF SELF-COMPACTING GEOPOLYMER CONCRETE

AHMED et al. (2011) used low calcium FA with a WG+NaOH activator to produce self-compacting GPC. This was achieved by a PC-based SP as well as additional water increasing the flowability of the GPC. The concrete was then heat cured in order to compensate for reduced strength.

Numerous tests were conducted for filling and passing ability as well as resistance to segregation; all but one of ten mixtures fulfilled the EFNARC criteria for self-compacting concrete (however, two specimens showed segregation); all but two specimens demonstrated compressive strengths of more than 40 N/mm² [88]; FA was thus shown to be suitable for production of self-compacting concrete, when heat curing is utilized.

4.2. DURABILITY

GPC is generally more durable than PCC [89]. This is explained by the very different chemistry involved in GP synthesis: many durability problems usually encountered in PCC "are associated in one way or another with the calcium content of its phases" [90] – and calcium is hardly found at all in GPC.

As a result, hardened GPC has been reported to be much more resistant against acids [91] (acetic, sulphuric, nitric, hydrochloric), conventional sulphate attack (e. g. from ground water), ASTM sea water and sodium sulphate [92]. Again, these resistances depend on the mix design.

One very important practical aspect of GP materials is resistance to corrosion of steel reinforcement. The capacity of GPC to passivate steel reinforcement is essential to its application in general construction. However, few studies regarding passivation have been conducted. In general, it appears that FA can passivate steel as effectively as OPC [93]. The passive state is more stable and lasting when the FA is activated with WG or NaOH; similarly to OPC, the presence of chlorides significantly increases corrosion rates. Furthermore, fluctuations in relative humidity can change the passive state in FA. In general, more research needs to be conducted with regards to this critical aspect.

One of the original applications of geopolymers was for heat-resistant materials. As such, there is general agreement that they show better resistance to fire than OPC [94].

Results regarding frost durability of GPC are somewhat contradictory. It can show much better frost resistance than OPC, or much worse, depending on its microstructure [95] (which, in turn, depends on the precursor/activator combination and curing temperature/time).

Degirmenci et al have found that "no body disintegration or deformation could be detected after 25 of freeze-thaw cycles" [96]. In particular, GPC containing GGBFS had shown no loss of compressive strength.

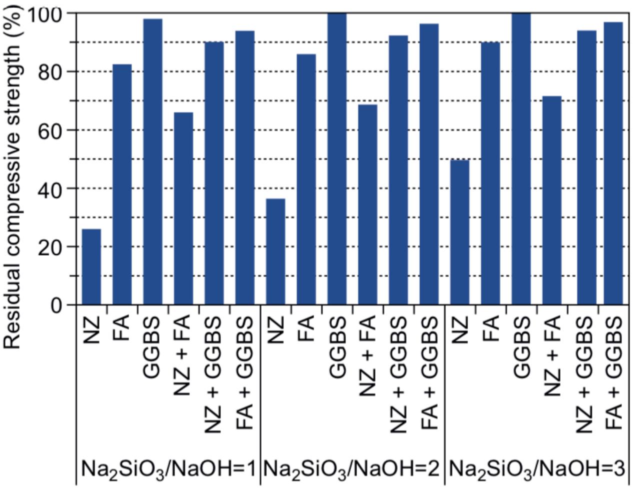

Figure 20: Residual compressive strength of geopolymer mortars after 25 of freeze-thaw cycles. NZ = Neozyolytes, FA = Fly Ash, GGBS = Ground granulated blast-furnace slag

5

CONCLUSION

5.1. SUMMARY

Cement production contributes 5–7% of CO_2 emissions worldwide. This footprint can be reduced – particularly in developing countries – through optimization of production processes (which make up 40% of the footprint), transport and electrical energy (5% each). However, the remaining 50% originate from the calcination of $CaCO_3$, an inevitable part of clinker production.

The cement industry already utilizes a range of supplementary cementitious materials in order to reduce the clinker/cement ratio (and thus the CO_2 footprint) of its products. However, these materials cannot fully replace Portland clinker.

The most developed and researched technology for clinker-free concrete production was found to be geopolymer binder. One feasible way to produce geopolymers is through alkaline activation of industrial by-products like fly ash and blast-furnace slag. These materials are widely available in the developing world – where coal power is still rapidly growing and where cement demand will perhaps be the highest in the decades to come. Another way of producing geopolymers is from metakaolin, a material obtained through low-temperature calcination of kaolinite clays.

Due to the immediate availability, the majority of studies into the rheology of GPC uses fly ash and blast-furnace slag as precursors. They suggest the following conclusions:

- It is reasonable to divide GP chemistry by precursor (fly ash, slag or metakaolin) and then further subdivide it by activator (NaOH, KOH and/or WG). Depending on the precursor and activator, admixtures and procedures used to adjust concrete properties can have a very different effect.
- Different combinations of precursor and activator produce different rheological and strength properties.
- The chemistry of GP synthesis can lead to the unexpected formation of certain compounds when adjusting these parameters, which may then have an adverse effect on fresh/hardened concrete properties.

- The activator-to-precursor ratio and activator-to-activator ratio can be used to enhance workability as well as strength of GPC within certain limits. The same can be achieved through different aggregate-to-binder ratios and water-binder ratios.

- Increasing the fineness of the material also had a beneficial effect on concrete properties in one study.

- Heat curing can, in some cases, substantially increase GPC compressive strength. Water can be used to enhance fresh concrete properties, with heat curing compensating for the ensuing decrease in strength.

- Conventional SPs can be effective in GPC. However, efficacy again depends on the precursor and activator used:

  - In slag-based GPC activated by NaOH, N-based SP enhances workability and strength, according to two studies.

- In fly ash geopolymer activated by NaOH only, N- and Lig-based SPs were found to be effective; when activated by NaOH+WG, N- and PC-based SPs were found to be effective.

- Two newly developed admixtures for ambient-cured FA-based GPC produce a concrete with good workability and strength:

  - Alccofine, a fine-ground slag-based product, produces a slump of 158 mm and a compressive strength of 32 N/mm² at 28d when added to a fly ash precursor. When heat-cured, the compressive strength can reach 73 N/mm².

  - Ground granulated blast-furnace slag can produce a fly ash-based GPC with a slump of 220 mm and a compressive strength of 45 N/mm² at 28d (the strength further increased to 63 N/mm² at 175d).

- Another two papers report promising results for heat-cured GPC:

  - Rice husk boiled in NaOH produced 150 mm slump and 58,1 N/mm² compressive strength at 28d.

  - Waste glass powder produced 71 mm slump and 36 N/mm² compressive strength at 28d.

- The above admixtures produce a geopolymer paste with high workability and sufficient strength for general construction purposes.

- One paper reported on producing a self-compacting FA-based GPC fulfilling the EFNARC criteria by using a PC-based SP, additional water and subsequent heat curing.

- GPC durability is generally comparable or superior to PCC durability.

5.2. PERSPECTIVES

The publications reviewed for this thesis suggest that there are admixtures and procedures already available that produce an ambient-cured GPC with good to very good workability and adequate strength properties for general construction purposes. In the case of ground granulated blast-furnace slag, the subsequent strength development at 28d–175d is even sufficient for high-strength applications.

GGBFS appears more preferable, both technically and economically, with an additional cost of merely 0,83 EUR per dry ton of concrete (based on the mix proportions detailed by the authors [97] and current wholesale rates [98]). The cost of Alccofine is not particularly high either, with 13,01 EUR per dry tonne of concrete [99] [100]. Both materials are abundant as industrial waste in developing countries, and are often dumped in the environment. However, that abundance might not last for the (very) long term since it is not entirely clear how the iron and steel industries will change with the climate.

Heat curing can further improve the strength properties of GPC. When heat is applied, additional water can increase the workability, enabling the production of self-compacting GPC with sufficient minimum strength. Admixtures like rice husk-based SP and waste glass powder can also be used with heat curing. They, too, are cheap and easy to obtain, and will probably remain so for a long time to come. However, heat curing is somewhat impractical in some applications. Pre-fabricated GPC parts could be used in those cases.

However, the above results should be taken with caution. While both GGBFS and Alccofine have been used as an admixture to OPC and in other construction applications for some time, more research needs to be done regarding their use in GPC. This could serve to a) replicate the findings obtained by JINDAL et al. and DEB et al. and b) further investigate the differences among their use with different precursors and activators.

More research is also required for the use of (old or new) SPs with metakaolin-based GPC. Metakaolin is the only material abundant enough to cover the entire global cement demand in the long run. However, there is currently only one available publication dealing with its rheology, and it generally seems to receive little attention besides its use as a supplementary cementitious material.

The general impression is that cement has the potential to dramatically reduce its carbon footprint without much restructuring. GPC production does not require extensive re-training or radically different facilites. The cost is also hardly an argument: as THAARRINI (2016) has shown, producing one ton of grade M30 GPC in India costs merely 1.7% more than producing grade M30 PCC. For grade M50, it is even cheaper by 11% [101].

The general impression is also that the cement industry is somewhat inertious to change (as is any industry). Perhaps political action is needed to move away from the status quo. But politics is beyond the scope of this review.

ANNEX A — DATA TABLES

Author	Precursor	Activator	Compared to	Rel. Slump [%]	Rel. Compr. Strength [%]
Nematollahi (2014)	FA	NaOH + WG	NaOH	168 %	232 %
Puertas (2014)	S	WG	NaOH + Na2CO3	118 %	n. a.
Xu (2005)	MK	KOH	NaOH	142 %	n. a.

Table 1: Relative slump and compressive strength values for different activators with same precursor (Fig. 14)

	Precursor	Activator	Heat curing regime / difference in precursor	Rel. Compr. Strength at 28d
Rovnanik (2010)	MK	NaOH + WG	4h at 60°	76,19 %
Jindal (2017)	FA + Alccofine	NaOH	24h at 90°	231,00 %
Nuruddin (2010)	FA	NaOH + WG	Left exposed to direct sunlight	246,00 %
Jindal (2017)	FA+ Alccofine	NaOH	Processed FA (higher fineness)	192,00 %

Table 2: Relative compressive strength values for heat curing, as compared to ambient-cured GPC (Fig. 16)

	Precursor	Activator	SP	Rel. Slump [%]	Rel. Compr. Strength [%]
Nematollahi (2014)	FA	NaOH	N	236 %	100 %
Laskar (2014)	FA	NaOH	L	139 %	n. a.
Nematollahi (2013)	FA	NaOH + WG	PC	142 %	71 %

Table 3: Relative slump and compressive strength values achieved with different SPs for FA-based GPC (Fig. 17)

	Precursor	Activator	Admixture/partial substitute	Slump	Compr. Strength at 28d
Jindal (2017)	FA (ambient-cured)	WG+NaOH	Alccofine (ambient cured)	158 mm	32 N/mm^2
Deb (2014)	FA (ambient-cured)	WG+NaOH	GGBFS	220 mm	45 N/mm^2
Sasindran (2017)	FA (heat-cured)	WG+NaOH	Glass Powder	71 mm	36 N/mm^2
Chouhan (2018)	FA (heat-cured)	NaOH	Rice Husk	150 mm	58,1 N/mm^2
Jindal (2017)	FA (heat-cured)	WG+NaOH	Alccofine (Heat Cured)	158 mm	73 N/mm^2

Table 4: Slump and Compr. Strength (28d) Values Achieved With Different Admixtures / Substitutes (Fig. 18)

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