

Industrialization of Geopolymers: An Overview of Key Concepts

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1 Introduction

The rate of production of concrete exceeds 3 tons per person per year, which makes it one of the most used resource on the planet, second only to water (Gagg, 2014). The environmental impact of the production of ordinary Portland cement (OPC) is raising concerns due to the important CO₂ emissions caused by the clinker calcination (Levi et al., 2020). As a result, the interest of the scientific community for eco-friendly alternatives is growing exponentially, with one of the most promising materials being geopolymers (Davidovits, 1994; P. Duxson et al., 2007a; Wu et al., 2019). Geopolymers are a semi-crystalline to amorphous three-dimensional material obtained from the reaction of an aluminosilicate source with an alkaline solution (generally NaOH or KOH) (Davidovits, 2015; J. S.J. van Deventer et al., 2007). They were first proposed by the French chemist Joseph Davidovits in 1972 as inorganic polymers for heat resistance applications (Davidovits, 2015). They later found various uses as ceramics, fiber composites, resins and cement materials (Davidovits, 2015). In this work, the focus will remain on geopolymer binders for concrete.

Many literature reviews on geopolymers have been published in the last few years, notably on the parameters affecting their properties (Elie et al., 2021; Farhan et al., 2020; Part et al., 2015), their microstructure (Ng et al., 2018), selected precursors (Liew et al., 2016; Mehta & Siddique, 2016; Zhuang et al., 2016), their environmental impact (Y. H. M. Amran et al., 2020; Habert et al., 2011; Passuello et al., 2017), their durability (M. Amran et al., 2021; Chen et al., 2021) and mix-design approaches (Xie et al., 2020). More general work on the state of the art of geopolymer science and its potential as an alternative for OPC has also been conducted (Duxson et al., 2007a; Provis & Bernal, 2014b; Singh & Middendorf, 2020; van Deventer et al., 2012).

The goal of this literature review will be to provide an overview of a few key concepts for the understanding of geopolymer science, as well as the challenges related to raw sources hindering the large-scale industrialization of this material.

1.1 Rationale for geopolymer use as a construction material

The competitiveness of geopolymers as a binder for concrete is based on its potential to convert industrial waste and other silica and aluminum-rich raw materials into eco-friendly, chemically durable and mechanically performant material (Amran et al., 2020; Chen et al., 2021; Duxson et

al., 2007; Lee & van Deventer, 2002). According to a Life cycle assessment conducted by Bajpai et al. (2020), fly-ash based geopolymers offer a similar performance to OPC in terms of compressive strength, while having a lower environmental impact. However, it has been demonstrated that this success, both on the mechanical and environmental front, rely on several factors related to the mix design and the choices of precursor and alkaline solution, with respect notably to the source location (Habert et al., 2011; Hu et al., 2021; McLellan et al., 2011). As for the durability of geopolymer materials, the short track-record of geopolymers on the field does not allow for strong conclusions, but according to laboratory testing, their performance is similar or even superior to Portland cements' (Chen et al., 2021; Fernández-Jiménez & Palomo, 2009). Furthermore, it has been suggested that ancient concrete's durability could be linked to the synchronous formation of calcium-silicate hydrates (CSH) with alkaline aluminosilicate gels typical of geopolymers (Glukhovsky, 1994; Yip & Van Deventer, 2003). The investigation of archaeological analogues to modern geopolymer concretes (GPC) was conducted by several researchers in order to gain insight on the durability of GPC (Davidovits, 2015; Glukhovsky, 1994; Malinowski, 1988). Strong similarities in nuclear magnetic resonance (NMR) data from certain Roman cement artifacts would suggest that the reaction products are not entirely comprised of lime carbonation products, but would also include aluminosilicate structures resulting from the chemical reaction between calcinated clay and volcanic ash (Davidovits & Davidovits, 1999). With the disintegration of Portland-based concrete infrastructures causing economic and ecological concerns, the durability of concrete becomes paramount (Pacheco-Torgal et al., 2008). The findings depicted earlier, along with the promising resistance to aggressive environments seen in laboratory settings, are thus another argument for geopolymer use as an alternative construction material to OPC.

1.2 More than a toponymic debate: Alkali-activated vs geopolymer

The durability of geopolymers is strongly influenced by its calcium content which is also a central factor in its characterization (Wardhono et al., 2017).

Depending on the paper, the terms “alkali-activated material”, “geopolymer”, “inorganic polymer”, or even the less common “geocement”, “mineral polymer” and a variety of other names are used alternatively to describe similar materials (Bernal & Provis, 2014). This issue might lead to researchers missing key papers to their topic due to different terminologies and keywords. More

importantly, the absence of a commonly accepted toponomy leads to confusion between two materials: alkali-activated materials and geopolymers. Joseph Davidovits has been defending for many years the restriction of the term “geopolymer” to stable, polymeric materials which can be identified through NMR testing (Davidovits, 2018). Furthermore, the use of N-A-S-H (sodium-aluminum-silicate-hydrate) and K-A-S-H (potassium-aluminum-silicate-hydrate) gel terminologies to describe the reaction products are still argued against by Davidovits, due to the role of water in geopolymers (Davidovits, 2018). As literature is identifying little water chemically bounded in geopolymer gels, the term N-A-S-H for geopolymers might be further criticized, as they are implying an hydrate-dominant microstructure (Liu et al., 2016; Park & Pour-Ghaz, 2018; White et al., 2010). A more chemically accurate term might be the “N-A-S-(H)” proposed by Provis & Bernal (2014), in which the parenthesis indicates that water is not a significant structural component of the gel. The presence of CSH with significant aluminum incorporation seems however to justify the use of “C-A-S-H” when referring to high calcium content aluminosilicates materials (Ismail et al., 2014).

Important differences in gel composition and microstructure are linked with calcium inclusion and can cause the decrease of resistance to chemical attacks (Dombrowski et al., 2007; Ismail et al., 2014; Wardhono et al., 2017; Yip & Van Deventer, 2003). To allow for the distinction of geopolymer consisting of a three-dimensional aluminosilicate gel with alkali-activated materials where a hybrid structure of CSH and aluminosilicate gel can be identified, in numerous works, the term “geopolymer” has been restricted to low-calcium (< 10%) alkali-activated materials (AAM) (Duxson et al., 2005; Garcia-Lodeiro et al., 2011; Ismail et al., 2014; Singh & Middendorf, 2020). In RILEM’S *Alkali-Activated state of the art report* published in 2014, geopolymers are thus defined as a subset of AAMs, with Davidovits’ polymeric structure described as a “highly coordinated [...] pseudo-zeolitic” structure (Provis, 2014).

The question of the belonging of geopolymers in the alkali-activated group will not be addressed in this work, and the terminology of the RILEM report (2014) will be followed, with all alkali-activated materials of low calcium content referred to as geopolymers. However, it is believed that a commonly agreed upon testing to identify geopolymers based on their microstructure should be the subject of further discussion in the scientific community.

2 Geopolymerization

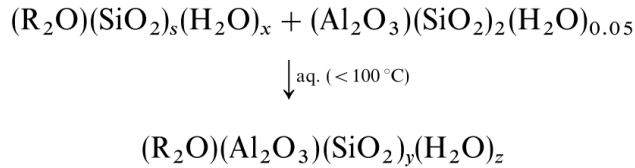
2.1 Models for geopolymerization

The process of formation of geopolymers has been the subject of numerous works over the years and remains to this day a challenge for researchers. Typical methods of analysis are challenged, especially as the complex multistep process involves amorphous raw materials forming mainly amorphous gel phases (Provis et al., 2015; Zhang et al., 2012). However, with the development of characterization techniques, calorimetric, rheological, spectroscopic and diffractometric studies have been performed successfully and improved the understanding of geopolymerization (Provis et al., 2015). Most models developed agree on three main steps: a dissolution step, where silica and alumina monomers from the raw precursors are released in the system, a reorganization step, in which aluminosilicate oligomers form various metastable phases and finally, a polymerization step where final hardening will take place (Duxson et al., 2007; Favier et al., 2015; Provis & van Deventer, 2007).

To the knowledge of the author, the first theoretical model was proposed by Davidovits (1988). This model was based on the known mechanisms of zeolite formation where alkali aluminosilicate species polymerize in basic solutions (Davidovits, 2015). Hypothetical steps of geopolymerization were proposed. The process involved the evolution of molecular structure from monomers to increasingly complex oligomers, and ultimately, from those oligomers, the formation of a complete three-dimensional polymeric network (Davidovits, 1988). The existence of soluble aluminosilicate oligomers such as the ones proposed were later on confirmed by studies from Harris et al. (1996) and North & Swaddle (2000).

A few years later, a second model was proposed by Rahier et al. (1996a). The mechanism of geopolymer formation was modelled by the change in composition of an aluminosilicate glass made of metakaolin and sodium silicate. In a first study, the mechanical resistance, short-range (molecular scale) and long-range (distances larger than 1 nm) order, as well as the evolution of heat flow during the formation of the glass were investigated (Rahier et al., 1996a). The chemical reaction found was later generalized.

Equation 1: Geopolymerization chemical equation (Rahier et al., 1997)



In this equation, R represent the cation from the alkaline solution (Na or K), y is the ratio of SiO₂ to Al₂O₃ and z is the amount of water bound in the final polymeric network (Rahier et al., 1997). Further work was then accomplished regarding the impact of rheological behavior, of silicate solution composition and of particle size on the final aluminosilicate glass properties (Rahier et al., 1996b, 1997, 2003). A two-step process for geopolymerization was also proposed. The authors first observed the disintegration of metakaolin grains, followed by a recombination of the products of this first reaction with sodium silicate to form the final inorganic polymer (Rahier et al., 2003).

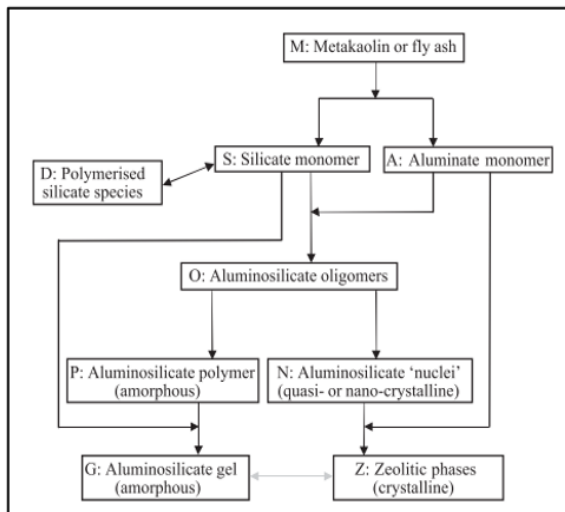


Figure 1: Geopolymerization process (Provis & van Deventer, 2007c)

Rahier's work could only identify the two steps depicted due to the limits of the sole use of calorimetric and rheological techniques. To improve furthermore the understanding of the geopolymerization process, diffractometric techniques started generating interest as an additional method for investigating the first steps of reaction (Olanrewaju, 2002; Provis & van Deventer, 2007b, 2007a). Similarly to previous models, a mechanistic approach was adopted by Provis et al. (2005). However, since more attention was given to the early kinetics (dissolution and reorganization steps), this new model was based on the process proposed by Faimon et al. (1996) for the weathering of aluminosilicates in alkaline environment (Provis et al., 2005).

As can be seen from Figure 1, both the presence of gel and zeolitic phases in the final geopolymer matrix were explained through this process. The order observed on a nanoscale by the early work

of Rahier et al. (1996a) was found to be caused by the presence of zeolites “nuclei” around which larger zeolite phases might crystallize over time (Provis et al., 2005; Provis & van Deventer, 2007c).

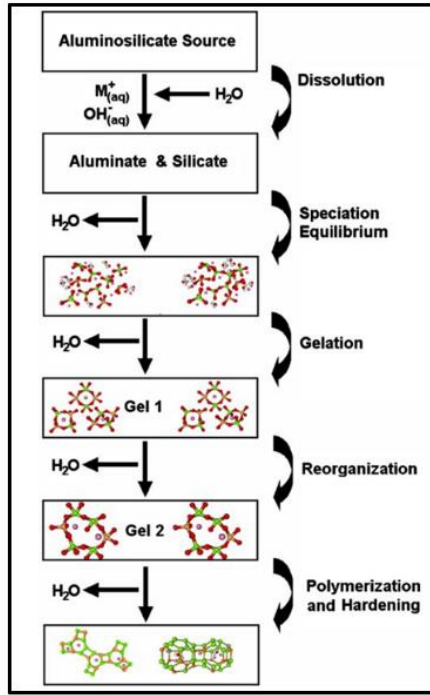


Figure 2: Model for geopolymerization (Duxson et al., 2007b)

The model on the left corresponds to simplified representation of this geopolymerization process (Provis et al., 2005; Provis & van Deventer, 2007b, 2007c). Aluminosilicate monomers are assumed to be released in solution and to form various oligomers until the formation of a first Al-rich gel (“Gel 1”) (Duxson et al., 2007b). The increase in silica availability over time would allow for partial substitution of Al by Si in “Gel 1”, which would result in the formation of a Si-rich “Gel 2” (Favier et al., 2015). The reorganization of “Gel 1” into “Gel 2” was challenged a few years ago after an NMR study on the interstitial phases revealed that direct polymerization of “Gel 1” might be more plausible (Favier et al., 2015). According to the authors, the evolution of “Gel 1” and oligomers in solution into “Gel 2” would be the result of a major precipitation of aluminosilicate species rather than the single reorganization of “Gel 1” (Favier et al., 2015). Some degree of reorganization could however be possible in the polymerization phase. As a matter of fact, it was found that the polymerization step was associated with an exothermic peak which may be due to more cross-linking in the final amorphous aluminosilicate gel and thus reorganization of this final gel into a more stable structure (Z. Zhang et al., 2012).

The impact of several factors on the geopolymerization process were better understood through this model, but no precise quantification of the reaction extent was yet achieved (Duxson et al., 2007b; Zhang et al., 2012). Insight on this topic was gained a few years later with studies conducted by Zhang et al. (2012, 2013). Indeed, the representation of metakaolin-based geopolymer structures through zeolites of the analcime family allowed for the estimation of the thermodynamic parameters of the final amorphous and zeolitic phases (G, Z: Figure 1) (Z. Zhang et al., 2012). The geopolymerization process could thus be simplified into a single equation from which the theoretical maximum heat release could be computed. Through calorimetric testing, it is now possible to estimate the reaction extent by comparing the experimental heat release at chosen moments in time with the theoretical maximum.

3 Precursors

The term precursor has been used in geopolymer's literature to describe raw aluminosilicate sources which will effectively dissolve in an alkaline medium to form the 3-dimensionnal polymeric gel. Their careful examination is of great importance for geopolymer science. The variability of raw sources, especially for waste-based geopolymers, and the large impact of multiple physicochemical factors greatly limit the predictability that can be attained in mix-designs (Xie et al., 2020). In this section, an overview of the main findings related to precursors reactivity and physicochemical characteristics will be given. The purpose will remain on highlighting the most critical factors for the following common precursors: metakaolin, fly ash and ground granulated blast furnace slag.

3.1 Reactivity

The development of a simple, yet reliable method for quantifying the reactive oxide amounts from the raw sources is still a topic of ongoing research (Ko et al., 2014; Sanalkumar et al., 2019). Even though no general agreement has been reached, various techniques have been proposed. One of the most efficient among them is the dissolution of aluminosilicate precursors in 1% hydrogen fluoride (HF) (Fernández-Jimenez et al., 2006; Ruiz-Santaquiteria et al., 2011). However, the health and safety issues related to the manipulation of HF limits its applicability (Ko et al., 2014). Attempts to transfer this methodology to other acid (e.g. HCL) and basic (e.g. NaOH) solutions have been done and found some degree of success (Buchwald et al., 2009; Sanalkumar et al., 2019;

Xu & Van Deventer, 2000). XRF and XRD analysis to quantify amorphous/reactive content have also been conducted in numerous works as a sole method or to compare the results of another novel technique (Buruberry et al., 2019; Sanalkumar et al., 2019; Williams & Van Riessen, 2010). Reactivity techniques based on the final gel composition rather than precursors composition have also been developed. In this regard, Rietveld X-ray powder diffraction and NMR have proven to be effective but can be technical and expensive (Fernández-Jimenez et al., 2006; Gao et al., 2017; Vogt et al., 2019). Furthermore, quantification of reactive content by NMR may be complexified by the overlap between resonances of some precursors and their reaction products (Gao et al., 2017).

Future work should be oriented toward the inclusion of calcium addition and activator characteristics as factors to consider in reactivity testing. A methodology based on the mineralogical composition of the raw sources and accounting for molarity and composition of the activator solution might present potential in this regard (Xie et al., 2020).

3.2 Physicochemical characteristics

As can be deduced from the broad definition given earlier for a “suitable” precursor, a large family of materials of varying mineralogy, physical and chemical characteristics is embedded in the term.

3.2.1 **Metakaolin**

Metakaolin (MK) is generated by the calcination of kaolinitic clays at temperatures varying between 600 and 900°C (Liew et al., 2016). In the family of calcinated clays, metakaolin geopolymers are undoubtedly the most common ones, but studies have been conducted on less reactive clays and promising results have been obtained in this area (Buchwald et al., 2009; Khalifa et al., 2020; Seiffarth et al., 2013). Similarly to other clay-based geopolymers, properties of MK geopolymers are highly dependent on the pre-treatment of the initial clay. To increase clays’ reactivity, dehydroxylation is achieved by mechanical, chemical or heat treatment (Liew et al., 2016). Heat treatment (aka calcination) is the most efficient among those techniques. In the case of metakaolin, it allows for a large fraction of the kaolinite crystalline content to be converted into pozzolanic amorphous phases (Liew et al., 2016).

Metakaolin-based geopolymers have been extensively used as a simpler model for the geopolymerisation process (Liew et al., 2016; Provis et al., 2009) as well as a very efficient material for toxic waste encapsulation (Cheng et al., 2012; Davidovits, 2015). However,

metakaolin particles have a large surface area and plate-like shape that typically leads to high water demand and porosity of the geopolymer system (Li et al., 2010; Provis et al., 2010). Those physical characteristics significantly limit their applicability as a single precursor.

3.2.2 Fly ash

During the combustion of coal, fly ash, a fine particulate residue from the coal, is produced and retained by the power plant (Keyte, 2009). They typically resemble small and spherical glass particles (Duxson, 2009). Therefore, fly-ash based geopolymer have less viscosity in the paste, which allows for the design of geopolymers with lower water to binder ratio and better pore refinement (Duxson & Provis, 2008; Provis et al., 2010). Fly ash-based concrete have shown great mechanical performance, as well as excellent chemical resistance. Though fly ash is commonly used in Portland concrete, its inherent variability may raise challenges in the mix-design of geopolymers (Rangan, 2009; Zhuang et al., 2016). [...]

Furthermore, the glassy phase of fly ash particles causes some proportion of the aluminum they contain to be in crystalline phase. As a result, the amount of reactive aluminum is limited, and the formation of the geopolymer matrix can be strongly affected (Fernández-Jimenez et al., 2006). Their reactivity is also lower than metakaolin's, which typically raises the need for curing if no calcium is added as an accelerating additive (Chithiraputhiran & Neithalath, 2013; Hajimohammadi & van Deventer, 2016).

3.2.3 Ground granulated blast furnace slag

Ground granulated blast furnace slag (GGBFS) is a calcium-rich by-product of the iron industry (Duxson, 2009). Its composition can be mainly described with the CaO-MgO-Al₂O₃-SiO₂ system, with some impurities depending on the iron ore (Bernal et al., 2014). The high amorphous content of this precursor and its composition leads to the formation of strong cross-linked and non cross-linked tobermorite-like structures (Myers et al., 2013; Puertas et al., 2011; Shi, 2003). Low to medium amounts of GGBFS can be used as a precursor for geopolymerization due to the co-existence of C-A-S-H and N-A-S(H) phases (Garcia-Lodeiro et al., 2011; Yip & Van Deventer, 2003). Moreover, their addition to the geopolymer system accelerates setting time (Zhu et al., 2021), improves compressive strength and other precursors' reactivity (Samson et al., 2017; Zhu et al., 2021), and decreases of porosity due to better water binding (John et al., 2021; Zhang et al., 2020).

3.2.4 Blended mixes

As demonstrated in the present discussion, raw aluminosilicate source for geopolymer formation differ greatly and can present limitations. To answer the issues raised by single precursors, many authors have successfully studied blended systems (Bernal et al., 2011; Buchwald et al., 2007; Samson et al., 2017; Xu & Van Deventer, 2002; Yang et al., 2017; Z. Zhang et al., 2014). Promising results have been found in this area, especially regarding intermediate calcium system (Palomo et al., 2019; Provis & Bernal, 2014a). Nonetheless, the added level of complexity of those blends raises the need for development of a unified and systematic approach to mix-design.

4 Conclusion

In this work, a brief overview of geopolymer chemistry and of precursors-related challenges has been given. From the information presented, the following conclusions can be drawn:

- The definition of geopolymers should be based on a commonly accepted testing rather than a calcium threshold which may not uphold for all alkali-activated materials
- Geopolymer science has evolved significantly in the last decades and the better understanding of chemistry related to geopolymers has facilitated research in this area. However, intermediate steps in geopolymerization are still not fully understood and thus further studies are needed.
- Drawbacks from the use of single precursors could be answered by the development of rigorous design for blended mixes. Success in this area is strongly dependent on the appropriate characterization of the reactivity of raw sources and on predicting the impact of their properties on the final geopolymer matrix.
- Intermediate calcium content geopolymers/alkali-activated materials present great potential, notably in terms of durability, and should be the subject of more research

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