

# Recommendations for geopolymer raw materials

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## Summary:

In a CO<sub>2</sub>-storage system, normal wellbore sealants based on Ordinary Portland Cement may be a vulnerability that can lead to leakage of CO<sub>2</sub>. Geopolymers and similar alkali-activated materials provide an attractive alternative, with improved durability and other beneficial properties. This report gives an overview of the key properties of geopolymers and similar materials, and, based on that, recommends raw materials for the creation of a geopolymer tailored for use as a wellbore sealant for CO<sub>2</sub>-storage applications.

## 1. Background Introduction

Depleted reservoirs or saline aquifers are recognized as the most promising candidate for CO<sub>2</sub> storage. Current wellbore cementing is commonly performed using sealants based on Ordinary Portland Cement (OPC). However, leakage of CO<sub>2</sub> through or along wellbores has been identified and viewed as one of the main challenges to such subsurface CO<sub>2</sub> storage. This means that OPC-based cements can be a major vulnerability.

Geopolymers, a group of alkali-activated materials (AAMs), have been researched during the past few decades as an alternative to sustainable construction materials, which can minimize CO<sub>2</sub> emission for its use of industry by-products [1-4]. Numerous research publications have reported that geopolymers have advantages over OPC regarding fire resistance [5], chemical corrosion resistance [6], high mechanical strength and satisfying durability over OPC materials [7].

The Cementegrity project aims to develop a novel geopolymer material that can be used in wellbores to prevent the leakage of CO<sub>2</sub> as well as satisfying other required properties. Geopolymer is produced by the alkali activation of silica and alumina-rich materials (precursors) using alkaline activators. Precursors can be natural materials such as clay and laterite soil; processed natural materials such as metakaolin; or waste products such as ground granulated blast furnace slag (GGBFS), fly ash (FA), biomass ash and waste incineration bottom ash, etc. [8]. Among them, GGBFS and class F-FA has often been used due to their availability and economy advantages.

In this report, the properties as well as the influential factors on the properties of geopolymers made by (GGBFS) and/or class F-FA will be briefly reviewed. General recommendations for the raw materials and mix design will then be given by considering the required properties for the wellbore cementing.

According to the calcium content, the raw materials for preparing AAMs can be grouped into the following two categories: low calcium systems (CaO w% <10%) and high calcium systems. GGBFS belongs to the high calcium system. FA could be classified into 2 categories: C-FA (high calcium FA) [9], which is rarely used as a precursor because of too fast setting properties [10], and F-FA (low calcium FA). By FA in the continuation of this report, it represents the F-FA, which is mostly used in applications.

## 2. Properties of GGBFS and/or FA (class F) based geopolymers

### 2.1 Mechanical properties

The mechanical properties of GGBFS-FA-AAMs as well as the controlling factors have been detailed in [4]. Generally, the 28d mechanical strength of BFS/FA-AAMs system increases with the increasing BFS content in the system, while decreases with the increasing water content. An optimal value of Na<sub>2</sub>O / precursors ratio has been found for obtaining a highest mechanical strength. In GGBFS-AAMs, this optimal value is between 5.5% and 8%. In FA-AAMs, it is between 7% and 10%. Similarly, an optimal value of SiO<sub>2</sub>/Na<sub>2</sub>O ratio is also found for obtaining a highest strength for both GGBFS-AAMs and FA-AAMs. Temperature has been found to accelerate the strength gain of GGBFS-AAMs in the early stage but leads to a lower strength in the later stage. However, in FA-AAMs system, strength increases with increasing temperature. The strength development of GGBFS-AAMs cured at room temperature normally finishes at 28 d, while for FA-AAMs, it gradually increases until 90 d.

### 2.2 Shrinkage

Based on the different mechanisms by which shrinkage develops, the shrinkage of materials can be characterized as plastic shrinkage, carbonation shrinkage, autogenous or chemical shrinkage, and drying shrinkage. Plastic shrinkage happens instantly when the mixture is poured into a mould, and it stems from the evaporation of water solution. Carbonation shrinkage happens when CO<sub>2</sub> from the environment permeates through the outer surface of the specimens and interacts with Ca(OH)<sub>2</sub> in the hydration

products to produce  $\text{CaCO}_3$  and water molecules. Autogenous shrinkage is an unavoidable reduction in volume caused by the self-desiccation of the composites and is particularly likely to form at a low water-to-cement ratio [71]. Drying shrinkage is the change in volume resulting from the evaporation of water from the gel pore surface and occurs primarily in the hardening process of the mixtures.

It is reported that there is approximately 2–4 times shrinkage for AAMs than OPC at early stage [11-12]. The variation in shrinkage can be outlined as the differences of the pore size distribution and reaction products in the paste matrix, which is detailed in [13]. In summary, the high shrinkage of GGBFS-AAMs is predominantly attributed to the larger capillary pressure arising from the mesopores (1.25nm-25nm) in the GGBFS-AAMs, which is much higher than that in OPC. The low Ca/Si products in AAMs also prefers to develop higher shrinkage. Besides, the content of fine crystals (CH, Aft, AFm etc) in AAMs, which can serve as fine aggregate in the slurry structure to mitigate shrinkage, is much lower than that in OPC. In addition, the structural insertion of alkali metal ions in C-A-S-H gels in AAMs also reduces the regular arrangement of C-A-S-H layers, which allows the C-A-S-H gel more susceptible to collapse and redistribute in drying processes. Furthermore, there are more silica-rich or silica gel in alkali-activated products. Silica gels containing high water content are vulnerable to dehydration in dry environment, causing large shrinkage of alkali-activated composites.

The addition of fly ash is considered to effectively reduce the dry shrinkage of AAMs system. This is because with the increase of calcium content in the raw material, the hydration products may transform from N-A-S-H gels to C-A-S-H gels, which is beneficial to the denseness of the pastes and the improvement in the mechanical behaviour for the composites, but this also increases the shrinkage of the composites. In GGBFS-FA-AAMs system, the drying shrinkage increases with increasing BFS/binder ratio, while decreasing with increasing  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio. In GGBFS-AAMs, autogenous and drying shrinkage increases with increasing both  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  as well as  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio. In FA-AAMs, shrinkage decreases with increasing  $\text{Na}_2\text{O}/\text{precursors}$  ratio. Increasing the contents of both  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  has also been reported to result in higher autogenous and drying shrinkage in FA-AAMs. Increasing temperature has been found to decrease the shrinkage of AAMs.

## 2.3 Durability

Research in [14-15] has demonstrated in detail that geopolymer concrete generally has better durability than OPC concrete in most cases.

### Fire resistance [15]

AAMs are fire-resistant because they are inorganic polymeric materials and are therefore incombustible. It is found that AAMs with high calcium content have lower fire resistance. This is the case because CaO changes the stoichiometry of the system, forming compounds that increase the temperature gradient, pore pressure, and the phases inside the material, causing cracks that significantly decrease fire performance of the material. In addition to fire resistance, AAMs may increase mechanical performance after being subjected to high temperatures. This occurs because at temperatures around 600 °C, the AAMs matrix undergoes sintering and densification.

### Resistance to acid attack [15]

AAMs shows a better acid corrosion resistance compared with OPC. This occurs because of the lower calcium content in AAMs compared to OPC, and consequently a lower Ca/Si ratio. Regarding the different acid types, acetic acid showed the highest aggressiveness toward AAMs, compared with nitric, sulfuric, and hydrochloric acids. Higher stability of GGBFS-AAMs under acetic acid attack is attributed to the lower initial permeability, higher alkalinity of the pore solution, and low CaO/SiO<sub>2</sub> ratio in the alkali-activated slag system compared to OPC.

Sulphuric acid is more aggressive than acetic acid in low-calcium AAMs. It was also suggested that the durability properties of FA-AAMs depend on the type of alkali-activator solution used.

### **Sulfate resistance**

AAMs has been found to perform better for sulfate resistance than OPC because of its different chemical composition, and consequently its different mechanism of sulfate attack [15].

Regarding the alkali activator in the high-calcium alkaline binders, mortars activated with sodium silicate perform better after exposure to the sodium sulfate solution than those activated with sodium hydroxide. Traces of expansive ettringite and gypsum were detected in the samples activated with sodium hydroxide. In high sulfate solutions, the compressive strength of high calcium AAMs increases which is associated to the porosity reduction caused by the formation of reaction products between geopolymer and sulfate solution or by the extended alkali-activation reaction because of high pH [15].

Low-calcium alkali-activated systems generally show excellent sulfate resistance. For low calcium alkaline binder, a fluctuation in flexural strength following by an increase in strength was observed. No significant differences were observed in sulfate resistance of the alkali-activated fly ash samples prepared with sodium hydroxide and sodium silicate solutions as activators.

MgSO<sub>4</sub> has been found to cause server damage in high-calcium AAM than Na<sub>2</sub>SO<sub>4</sub>. While for low-calcium AAM, it is the opposite.

### **Alkali silica reaction resistance**

Compared with OPC, the high-calcium binder is more likely to suffer from expansion because of ASR, while low-calcium binder shows a better performance than OPC.

### **Carbonation**

In high-calcium AAMs, atmospheric CO<sub>2</sub> reacts with the C-A-S-H gel formed during geopolymerization, producing CaCO<sub>3</sub>. In high-calcium precursors, especially slags, Mg content is fundamental for carbonation resistance. This occurs because the product of the interaction of atmospheric CO<sub>2</sub> with the MgO is a layered double hydroxide, which can absorb CO<sub>2</sub>.

The presence of silicate on the activator increases carbonation depth in GGBFS-AAMs. This occurs because the Ca/Si ratio of C-A-S-H formed with sodium silicate is smaller than that activated with sodium hydroxide. Therefore, higher availability of calcium in the C-A-S-H activated with sodium hydroxide favors the formation of carbonated products to fill pore spaces, which affects the diffusivity of CO<sub>2</sub> within the material. The carbonation depth is also dependent on the activator concentration. A higher concentration of alkalis in the pore solution is likely to attract a higher concentration of CO<sub>2</sub>, favouring the formation of carbonic acid and carbonates, thereby accelerating the carbonation reaction [15].

For low-calcium AAMs, because the primary product is a N-A-S-H gel, without decalcification, the primary carbonation process transforms the pore content from high-alkalinity to high-alkalinity high-Na<sub>2</sub>CO<sub>3</sub> solution, and the microstructure of the matrix only changes slightly [15].

## **2.4 Workability**

AAMs has been found to have lower workability than OPC. This occurs because, in addition to different rheology of these materials, the activators contribute to their sticky appearance, like the water glass and sodium silicate, and have higher viscosity. Many studies have shown that AAMs made from high calcium precursor show smaller workability than AAMs made from low calcium precursor. The slump and flow of AAMs decrease with increasing Na<sub>2</sub>SiO<sub>3</sub>/NaOH because of the highly viscous nature of sodium silicate. Workability of AAMs increases with water/b ratio [15].

High calcium-activated materials show a shorter setting time compared to low calcium materials. This occurs because calcium is rapidly dissolved in an alkaline solution. Longer setting times were observed when using the NaOH activator compared to  $\text{Na}_2\text{SiO}_3$  activator. With other mixing variables unchanged, increasing the  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  ratio can reduce the setting time. The initial and final setting times increased considerably with the increased molarity of the NaOH activator [15].

## 2.5 Summary

The properties of AAMs are affected by a lot of factors. But from a general perspective, it can be concluded that low-calcium AAMs ( $\text{CaO} \leq 10\%$ ) show better performance in terms of durability and fresh properties. By contrast, high-calcium AAMs exhibit better performance in terms of mechanical properties. With the increase of calcium content in the raw material, the hydration products may transform from N-A-S-H gels to C-A-S-H gels, which is beneficial to the denseness of the pastes and the improvement in the mechanical behaviour for the composites, but this also increases the shrinkage of the composites.

## 3. Raw materials recommendation for Cementegrity Project

Regarding the sealing materials used for the Cementegrity project, required properties includes proper volume stability to resist thermal expansion, proper mechanical properties to resist high pressure, and proper resistance to acid attack formed by the impurities contained in the industrially derived  $\text{CO}_2$  streams such as  $\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_x$  and  $\text{NO}_x$ . Carbonation may happen during the injection of  $\text{CO}_2$ , but the expansive reaction product may help enhance the bonding strength between the sealing materials and casting, thus, resistance to carbonation is not considered as a reference property.

A high-volume stability and good durability require the use of low-calcium precursors, while high mechanical properties require the use of high-calcium precursors. Thus, we recommend that a combination of high-calcium raw materials such as GGBFS and low-calcium materials such as class F FA should be adopted to achieve the above requirements. Similarly, a combination of sodium hydroxide and sodium silicate as an activator is also recommended. To keep a balance between the mechanical properties and durability, some importance controlling factors should be considered when determining the specific mix design including the GGBFS/precursors ratio, the  $\text{Na}_2\text{O}$ /precursors ratio, the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio, the water/precursors ratio as well as the curing temperature.

Recently, a rock-based geopolymer has been developed in UiS for well cementing applications [16-17]. The precursors of this rock-based geopolymer are a combination of granite with selected other chemical admixtures. Good fresh properties and better shrinkage as well as high mechanical properties than OPC were found. This can also be considered as a candidate for Cementegrity Project.

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