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GEOPOLYMER CEMENT

a review

by

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1. Introduction

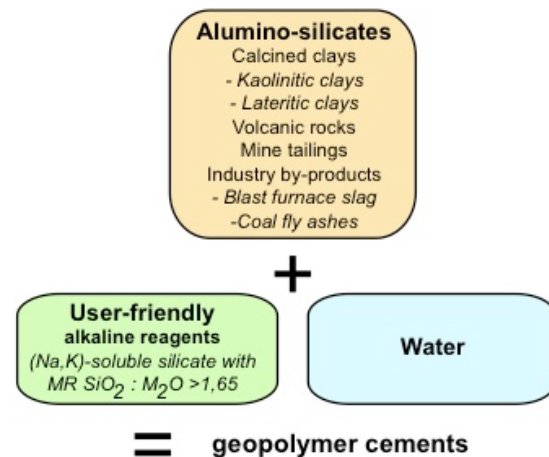
From a terminological point of view, **geopolymer cement** [1] is a binding system that hardens at room temperature, like regular Portland cement. If a geopolymer compound requires heat setting it may not be called geopolymer cement but rather geopolymer binder.

Geopolymer cement is an innovative material and a real alternative to conventional Portland cement for use in transportation infrastructure, construction and offshore applications. It relies on minimally processed natural materials or industrial byproducts to significantly reduce its carbon footprint, while also being very resistant to many of the durability issues that can plague conventional concretes

Creating geopolymer cement requires an alumina silicate material, a user-friendly alkaline reagent [2] (sodium or potassium soluble silicates with a molar ratio $MR \text{ SiO}_2:\text{M}_2\text{O} > 1,65$, M being Na or K) and water (See the definition for "user-friendly" reagent below). Room temperature hardening relies on the addition of calcium cations, essentially iron blast furnace slag.

Geopolymer cements cure more rapidly than Portland-based cements. They gain most of their strength within 24 hours.



However, they set slowly enough that they can be mixed at a batch plant and delivered in a concrete mixer. Geopolymer cement also has the ability to form a strong chemical bond with all kind of rock-based aggregates. On March 2010, the US Department of Transportation Federal Highway Administration released a TechBrief titled *Geopolymer Concrete* that states [3]: *The production of versatile, cost-effective geopolymer cements that can be mixed and hardened essentially like Portland cement represents a **game changing** advancement, revolutionizing the construction of transportation infrastructure and the building industry.*



Geopolymer concrete

There is often confusion between the meanings of the two terms 'geopolymer cement' and 'geopolymer concrete'. A cement is a binder whereas concrete is the composite material resulting from the addition of cement to stone aggregates. In other words, to produce concrete one purchases cement (generally Portland cement or Geopolymer cement) and adds it to the concrete batch. Geopolymer chemistry was from the start aimed at manufacturing binders and cements for various types of applications. For example the British company banah UK (www.banahuk.co.uk) sells its *banah-Cem*TM as geopolymer cement, whereas the Australian company Zeobond (www.zeobond.com) markets its *E-crete*TM as geopolymer concrete.

categories: corrosive products (named here: hostile) and irritant products (named here: friendly). The two classes are recognizable through their respective logos. The table lists some alkaline chemicals and their corresponding safety label [8]. The corrosive products must be handled with gloves, glasses and masks. They are *User-hostile* and cannot be implemented in mass applications without the appropriate safety procedures. In the second category one finds Portland cement or hydrated lime, typical mass products. Geopolymeric alkaline reagents belonging to this class may also be termed as *User-friendly*.

 hostile	friendly 
CaO (quick lime) NaOH, KOH	Ca(OH) ₂ Portland cement, Iron slag
Sodium metasilicate SiO ₂ :Na ₂ O = 1.0	Slurry soluble silicate/kaolin 1.25 < SiO ₂ :Na ₂ O < 1.45
Any soluble silicate SiO ₂ :Na ₂ O < 1.45	Any soluble silicate SiO ₂ :Na ₂ O > 1.45

Unfortunately, the development of so-called *alkali-activated-cements* or *alkali-activated geopolymers* (the latter being a wrong terminology), as well as several recipes found in the literature and on the Internet, especially those based on fly ashes, comprise molar ratio below 1.20, in average below 1.0. Worse, looking only at low-costs consideration, not at safety and User-friendly issues, they propose systems based on pure NaOH (8M or 12M). These are User-hostile conditions and may not be used by the ordinary labor force employed in the field. Indeed, laws, regulations, and state directives push to enforce for more health protections and security protocols for workers' safety.

On the opposite, Geopolymer cement recipes employed in the field generally involve alkaline soluble silicates with starting molar ratio SiO₂:M₂O ranging from 1.45 to 1.95, essentially 1.45 to 1.85, i.e. user-friendly conditions. It may happen that for research, some laboratory recipes have molar ratios in the 1.20 to 1.45 range. Yet, this is only for study, not for manufacture.

3. Geopolymer cement categories

The categories comprise:

- Slag-based geopolymer cement.[9]
- Rock-based geopolymer cement.[10]
- Fly ash-based geopolymer cement
 - type 1: alkali-activated fly ash geopolymer.[11]
 - type 2: slag/fly ash-based geopolymer cement.[12][13] [14]
- Ferro-sialate-based geopolymer cement.[15]

3.1 Slag-based geopolymer cement.

Manufacture components: metakaolin MK-750 + blast furnace slag + alkali silicate (user-friendly).

Geopolymeric make-up: Si:Al = 2 in fact solid solution of Si:Al=1, Ca-poly(di-sialate) (anorthite type) + Si:Al =3, K-poly(sialate-disiloxo) (orthoclase type) and CSH Ca-disilicate hydrate.

The first geopolymer cement developed in the 1980s was of the type (K,Na,Ca)-poly(sialate) (or slag-based geopolymer cement) and resulted from the research

developments carried out by J. Davidovits and J.L. Sawyer at Lone Star Industries, USA and yielded to the invention of the well known Pyrament® cement. The American patent application was filed in 1984 and the patent US 4,509,985 was granted on April 9, 1985 with the title 'Early high-strength mineral polymer'.

3.2 Rock-based geopolymer cement.

The replacement of a certain amount of MK-750 with selected volcanic tuffs yields geopolymer cement with better property and less CO₂ emission than the simple slag-based geopolymer cement.

Manufacture components: metakaolin MK-750, blast furnace slag, volcanic tuffs (calcined or not calcined), mine tailings and alkali silicate (user-friendly).

Geopolymeric make-up: Si:Al = 3, in fact solid solution of Si:Al=1 Ca-poly(disialate) (anorthite type) + Si:Al =3-5 (Na,K)-poly(silate-multisiloxo) and CSH Ca-disilicate hydrate.

3.3 Fly ash-based geopolymer cements

Later on, in 1997, building on the works conducted on slag-based geopolymeric cements, on the one hand and on the synthesis of zeolites from fly ashes on the other hand, Silverstrim et al.[16] and van Jaarsveld and van Deventer [17] developed geopolymeric fly ash-based cements. Silverstrim et al. US Patent 5,601,643 was titled 'Fly ash cementitious material and method of making a product'.

Presently two types based on Class F fly ashes:

- *Type 1: alkali-activated fly ash geopolymer (user-hostile):*

In general requires heat hardening at 60-80°C and is not manufactured separately and becomes part of the resulting fly-ash based concrete. NaOH (user-hostile) + fly ash: fly ash particles embedded in an alumino-silicate gel with Si:Al= 1 to 2, zeolitic type (chabazite-Na and sodalite).

- *Type 2: slag/fly ash-based geopolymer cement (user-friendly):*

Room-temperature cement hardening. User-friendly silicate solution + blast furnace slag + fly ash: fly ash particles embedded in a geopolymeric matrix with Si:Al= 2, (Ca,K)-poly(sialate-siloxo).

3.4 Ferro-sialate-based geopolymer cement

The properties are similar to those of Rock-based geopolymer cement but involve geological elements with high iron oxide content. The geopolymeric make up is of the type poly(ferro-sialate) (Ca,K)-(-Fe-O)-(Si-O-Al-O-). This user-friendly geopolymer cement is on the development and pre-industrialization phase [18].

4. CO₂ emissions during manufacture

Concrete (mixture of cement and aggregates) is the most commonly used construction material; its usage by communities across the globe is second only to water. Ever grander building and infrastructure projects require prodigious quantities of concrete with its binder of Portland cement whose manufacture is accompanied by

large emissions of carbon dioxide CO₂. According to the Australian concrete expert B. V. J. Rangan, this burgeoning worldwide demand for concrete is a great opportunity for the development of geopolymer cements of all types, with their much lower tally of carbon dioxide CO₂ [19].

4.1 CO₂ emission during manufacture of Portland cement clinker

Ordinary cement, often called by its formal name of Portland cement, is a serious atmospheric pollutant. Indeed, the manufacture of Portland cement clinker involves the calcination of calcium carbonate according to the reaction:



The production of 1 tonne of Portland clinker directly generates 0.55 tonnes of chemical-CO₂ and requires the combustion of carbon-fuel to yield an additional 0.40 tonnes of carbon dioxide.

To simplify: 1 T of Portland cement = 0.95 T of carbon dioxide

The only exceptions are so-called 'blended cements', using such ingredients as coal fly ash, where the CO₂ emissions are slightly suppressed, by a maximum of 10%-15%. There is no known technology to reduce carbon dioxide emissions of Portland cement any further.

On the opposite, **Geopolymer cements** do not rely on calcium carbonate and generate much less CO₂ during manufacture, i.e. a reduction in the range of 40% to 80-90%. Joseph Davidovits delivered the first paper on this subject in March 1993 at a symposium organized by the American Portland Cement Association, Chicago, Illinois [20].

The Portland cement industry reacted strongly by lobbying the legal institutions so that they delivered CO₂ emission numbers, which did not include the part related to calcium carbonate decomposition, focusing only on combustion emission. An article written in the scientific magazine *New Scientist* in 1997 stated that: *...estimates for CO₂ emissions from cement production have concentrated only on the former source [fuel combustion]. The UN's Intergovernmental Panel on Climate Change puts the industry's total contribution to CO₂ emissions at 2.4 %; the Carbon Dioxide Information Analysis Center at the Oak Ridge National Laboratory in Tennessee quotes 2.6 %. Now Joseph Davidovits of the Geopolymer Institute... has for the first time looked at both sources. He has calculated that world cement production of 1.4 billion tonnes a year produces 7 % of [world] current CO₂ emissions [21].* Fifteen years later (2012), the situation has worsened with Portland cement CO₂ emissions approaching 3 billion tonnes a year.[22].

The fact that the dangers to the world's ecological system from the manufacture of Portland cement is so little known by politicians and public makes the problem all the more urgent: when nothing is known, nothing is done. This situation clearly cannot continue if the world is going to survive.

4.2 Geopolymer Cements Energy Needs and CO₂ emissions

This section compares the energy needs and CO₂ emissions for regular Portland cement, Rock-based Geopolymer Cements and Fly ash-based geopolymer cements. The comparison proceeds between Portland cement and geopolymer cements with similar strength, i.e. average 40 MPa at 28 days. There have been several studies published on the subject [23] that may be summarized in the following way:

4.2.1 Rock-based Geopolymer cement manufacture involves:

- 70% by weight geological compounds (calcined at 700°C)
- blast furnace slag
- alkali-silicate solution (industrial chemical, user-friendly).

The presence of blast furnace slag provides room-temperature hardening and increases the mechanical strength.

Energy needs and CO₂ emissions for 1 tonne of Portland cement and Rock-based Geopolymer cement.

Energy needs (MJ/tonne)	Calcination	Crushing	Silicate Sol.	Total	Reduction
Portland Cement	4270	430	0	4700	0
GP-cement, slag by-product	1200	390	375	1965	59%
GP-cement, slag manufacture	1950	390	375	2715	43%
CO ₂ emissions (tonne)					
Portland Cement	1.000	0.020		1.020	0
GP-cement, slag by-product	0.140	0,018	0.050	0.208	80%
GP-cement, slag manufacture	0.240	0.018	0.050	0.308	70%

4.2.1.1 Energy needs

According to the US Portland Cement Association (2006), energy needs for Portland cement is in the range of 4700 MJ/tonne (average). The calculation for Rock-based geopolymer cement is performed with following parameters:

- the blast furnace slag is available as by-product from the steel industry (no additional energy needed);
- or must be manufactured (re-smelting from non granulated slag or from geological resources).

In the most favorable case — slag availability as by-product — there is a reduction of 59% of the energy needs in the manufacture of Rock-based geopolymer-cement in comparison with Portland cement.

In the least favorable case —slag manufacture — the reduction reaches 43%.

4.2.1.2 CO₂ emissions during manufacture

In the most favorable case — slag availability as by-product — there is a reduction of 80% of the CO₂ emission during manufacture of Rock-based geopolymer cement in comparison with Portland cement.

In the least favorable case —slag manufacture — the reduction reaches 70%.

4.2.2 Fly ash-based cements Class F fly ashes

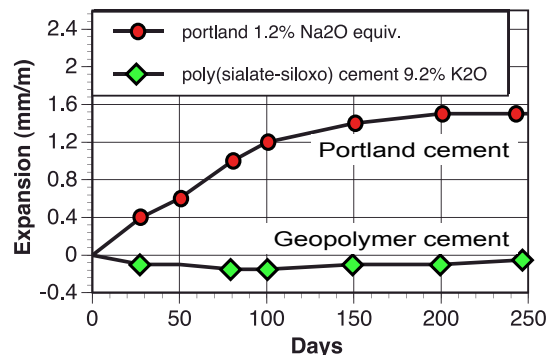
They do not require any further heat treatment. The calculation is therefore easier. One achieves emissions in the range of 0,09 to 0,25 tonnes of CO₂ / 1 tonne of fly ash-based cement, ie. CO₂ emissions that are reduced in the range of 75 to 90%.

5. Properties for Rock-based geopolymer cement (Ca,K)-poly(sialate-disiloxo)

See [24]

- shrinkage during setting: < 0.05 %, not measurable.
- compressive strength (uniaxial): > 90 MPa at 28 days (for high early strength formulation, 20 MPa after 4 hours).
- flexural strength: 10–15 MPa at 28 days (for high early strength 10 MPa after 24 hours).
- Young Modulus: > 2 GPa.
- freeze-thaw: mass loss < 0.1 % (ASTM 4842), strength loss <5 % after 180 cycles.
- wet-dry: mass loss < 0.1 % (ASTM 4843).
- leaching in water, after 180 days: K₂O < 0.015 %.
- water absorption: < 3 %, not related to permeability.
- hydraulic permeability: 10⁻¹⁰ m/s.
- sulfuric acid, 10 %: mass loss 0.1 % per day.
- chlorhydric acid 5 %: mass loss 1 % per day.
- KOH 50 %: mass loss 0.02 % per day.
- ammonia solution: no mass loss.
- sulfate solution: shrinkage 0.02 % at 28 days.
- alkali-aggregate reaction: no expansion after 250 days (-0.01 %), as shown in the graph, comparison with Portland cement (ASTM C227). These results were published as earlier as 1993 [25]. Geopolymer binders and cements even with alkali contents as high as 10 %, do not generate any dangerous Alkali-Aggregate Reaction.

The innocuity towards Alkali-Aggregate Reaction is always confirmed in geopolymer cements. More recently Li et al. [26] used another standard, ASTM C 441-97, by which powdered quartz glass is the reactive fine element. The test duration is 90 days. Portland cement mortars exhibited expansion at 90 days in the range of 0.9– 1.0 % whereas geopolymer cement remained practically unchanged, with a small shrinkage of -0.03 % at 90 days.



6. The need for standards

In June 2012, the institution ASTM International (former American Society for Testing and Materials, ASTM) organized a symposium on Geopolymer Binder Systems. The introduction to the symposium states: *When performance specifications for Portland cement were written, non-portland binders were uncommon...New binders such as*

geopolymers are being increasingly researched, marketed as specialty products, and explored for use in structural concrete. This symposium is intended to provide an opportunity for ASTM to consider whether the existing cement standards provide, on the one hand, an effective framework for further exploration of geopolymer binders and, on the other hand, reliable protection for users of these materials.

The existing Portland cement standards are not adapted to geopolymer cements. They must be created by an *ad hoc* committee. Yet, to do so, requires also the presence of standard geopolymer cements. Presently, every expert is presenting his own recipe based on local raw materials (wastes, by-products or extracted). There is a need for selecting the right geopolymer cement category. The 2012 State of the Geopolymer R&D [27], suggested to select two categories, namely:

- Type 2 slag/fly ash-based geopolymer cement: fly ashes are available in the major emerging countries;

and

- Ferro-sialate-based geopolymer cement: this geological iron rich raw material is present in all countries through out the globe.

and

- the appropriate user-friendly geopolymeric reagent.

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- Geopolymer Institute: <http://www.geopolymer.org/>
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