Natural Pozzolans

Use of mixtures with NP is much smaller than that without NP for both NSCC and RSCC mixes.

From: Waste and Supplementary Cementitious Materials in Concrete, 2018

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Portland cement concrete

Qiang Yuan, ... Cong Ma, in Civil Engineering Materials, 2021

3.3.5.5 Natural pozzolans

Natural pozzolans can be subdivided into two categories as materials of volcanic origin and materials of sedimentary origin. The first category includes materials formed by the quenching of molten magma when it is projected to the atmosphere upon explosive volcanic eruptions. The explosive eruption has two consequences: (i) The gases, originally dissolved in the magma are released by the sudden decrease of pressure. This causes a microporous structure in the resulting material. (ii) Rapid cooling of the molten magma particles when contacted with the atmosphere results in quenching, which is responsible for the glassy state of the solidified material. Pozzolanic materials of volcanic origin may be found in loose (incoherent) or compacted (coherent) forms in nature. The latter results from the postdepositional processes such as weathering, compaction, cementation, and hardening of the originally loose material. These processes may change the original structure into sharp or zeolitic character. Transformation into sharp structure reduces the pozzolanicity, whereas zeolitization improves it. The second category of natural pozzolans includes clays and diatomaceous earth. Clays have very limited pozzolanic reactivity unless they are thermally treated. Diatomaceous earth, which is a sedimentary rock, consists basically of the fossilized remains of diatoms (a type of algae). It has an amorphous structure for having the main crystalline phases up to 36%, by mass.

The reactive chemical components of natural pozzolans are silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). The sum of these three oxides is required to a minimum value of 70% by mass for a suitable pozzolan. The chemical composition of natural pozzolans vary much from location to location. Similar to the variability in chemical compositions, many different minerals may be present in natural pozzolans. However, the fundamental constituent is always a glassy phase of siliceous nature which can be distinguished by XRD techniques. Glass content of natural pozzolans of volcanic origin generally varies from 50% to 97% and the rest are mostly clay minerals, quartz, and feldspars. Glassy phase in diatomaceous earths may be as low as 25%, and some may be almost totally glassy. The remainder is composed of clay minerals, quartz, and feldspars.

The use of natural pozzolans is now accepted by modern cement and concrete industry as supplementary cementitious materials due to the many advantages they offer apart from the obvious environmental benefit of supplementing clinker or cement which require a lot of energy and emit high quantities of CO_2 during their production. They are responsible for higher compressive strength in later ages of cement hydration which continues to increase for a long period of time; they provide self-healing properties to the concrete and significantly improved durability which is the main reason for their use. Particularly, the use of natural pozzolans demonstrates lower chloride migration and improved sulfate resistance, while in most cases, their addition leads to mitigation of ASR. However, they reduce bleeding and segregation considerably, lower the heat of hydration which is beneficial in large concrete structures, and eliminate microcracking. However, their use can also bring some side effects, such as workability loss, and higher need for SP demands, and higher shrinkage.

It is important to note that each natural pozzolan has different effects on cement and concrete properties and can be used in different ratios in a concrete mix. Overall, the benefits of using pozzolans in concrete are well established in most parts of the world, leading to extensive research and application in construction worldwide.

In summary, SCMs have great effects on the fresh and hardened properties of concrete. Table 3.10 summarize general effects that these materials have on the fresh and hardened properties of concrete. It should be noted that these effects vary considerably between and often within classifications of SCMs. Specified performance should be evaluated for specific mixtures.

Table 3.10 ...

Component	By weight%
...	...

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Supplementary cementing materials

Damian A. Panesar, in Developments in the Formulation and Reinforcement of Concrete (Second Edition), 2019

3.1.4 Metakaolin

Metakaolin is an amorphous aluminosilicate that is a highly reactive natural pozzolan produced by the calcination and dehydroxilation of kaolinitic clay at temperatures between 500°C and 900°C. Metakaolin is a porous, angular shaped, platy particle with a mean size that can range from 1 to 20 μm (Al-Akhras, 2006; Ambroise et al, 1994; Tafraoui et al, 2016). The specific gravity of metakaolin can fall between 2.20 and 2.60 (Nadeem-Aghabaghlu et al, 2014; Ramezanianpour & Jovein, 2012; Siddique & Klaus, 2009). As shown in Table 3.1, although the major constituents of metakaolin are silicon dioxide and alumina oxide, its composition varies with different sources of kaolin. Other components are ferric oxide, calcium oxide, magnesium oxide, and potassium oxide. In order for metakaolin to be classified as a Class N (raw or calcined natural pozzolan) in accordance with ASTM C618 (ASTM-C618-17, 2017), the combined requirements that need to be met are (SiO_2+Al_2O_3+Fe_2O_3)≥70.0%, SO_3≤4.0%, moisture content ≤3.0%, and LOI content ≤10%.

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Methods to control efflorescence in alkali-activated cement-based materials

A. Allahverdi, ... M. Lachemi, in Handbook of Alkali-Activated Cements, Mortars and Concretes, 2015

17.2.2 A brief literature survey

In research work on the possibility of utilizing a pumice-type natural pozzolan in the aluminosilicate source material in the production of alkali-activated or geopolymer cement, Allahverdi et al. (2008) considered the extent of efflorescence formation as a soundness determining parameter. To evaluate the extent of efflorescence formation, they placed 28-day cured cubic paste specimens 2 cm³ in size in 50 ml water individually and kept them in open-air atmosphere at 25 °C until the water was evaporated completely. Based on a qualitative comparison, they showed that the extent of efflorescence formation is a function of not only the Na_2O concentration of alkali activator, but also the silica modulus of alkali activator and the water-to-binder ratio. The effect of Na_2O concentration of the alkali activator was found to be much more pronounced than that other two factors. Comparing the results of the 28-day cured cubic paste specimens, they concluded that a relatively high compressive strength attainable at relatively higher Na_2O concentration does not necessarily imply soundness and durability.

In their works on material and structural characterization of alkali-activated low-calcium brown coal fly ash and the influence of the temperature ranging from 20 to 1000 °C on properties of aluminosilicate polymer or alkali-activated binder based on brown coal fly ash, Škvára et al. (2008, 2009b) elaborated the susceptibility of alkali-activated binders to exhibit efflorescence formation. Based on results obtained from ²³Na NMR MAS spectra, they claimed that alkali metals are rather bonded to Al in Si-O-Al chain structure in the range of 200–250 °C, thereas on Na⁺. The bond of alkali metals in the form of Na₂O·xSiO₂ complex is weaker than the direct bond of Na⁺. This model of bonding of the Na atom helps to explain the ease in leaching of alkali metals out of the alkali-activated binders (regardless of whether prepared from fly ash or metakaolin) and efflorescence formation. They showed that the tendency for efflorescence formation decreases substantially by firing the material at temperatures higher than 400 °C. Such a high temperature treatment eliminates the H₂O content of the structure and results in the transformation of alkali metal bonds. They reported the presence of hydrates of the type Na₂CO₃·xH₂O and Na₂SO₄·2(SO₄)·10H₂O·nH₂O in typical efflorescence observed in their studies.

Temuujin et al. (2009) investigated the influence of CaO and Ca(OH)₂ on mechanical properties of geopolymer pastes developed from fly ash. Considering two different curing temperatures including 20 °C (ambient temperature) and 70 °C, they reported that all the samples cured at ambient temperatures exhibited efflorescence formation. They neglected that at ambient temperatures the production rates are low and result in the presence of residual excess alkaline solution in the material. Analytical studies performed on some fragments of efflorescence by SEM-EDS and XRD clarified the nature of the efflorescence as sodium phosphate hydrate (Na₃PO₄·12H₂O) instead of sodium carbonate hydrate (Na₂CO₃·2H₂O). The authors attributed the formation of sodium phosphate hydrate to the presence of 1.3 wt.% P₂O₅ in the fly ash and explained that a strong alkaline medium could really dissolve the phosphate content of the material and enable it to recrystallize as sodium phosphate efflorescence. This observation, however, is contrary to Nasvik's suggestion (Davidovits, 2008) that phosphates are able to form geopolymer structures such as poly(alate-siloxo)/phosphate or phospho-siloxonate geopolymers.

Allahverdi et al (2010) investigated the influence of sodium oxide concentration of alkali activator on the compressive strength and efflorescence formation of alkali-activated blast furnace slag. They considered mix designs of the same silica modulus (M_s = 0.6) and different sodium oxide concentrations ranging from 1 to 8% by weight of slag. The tendency of the mix designs for efflorescence formation was studied qualitatively in a similar way as explained in their earlier work (Škvára et al, 2009a). They reported that, based on observations, mixes with 1 and 2 wt.% sodium oxide concentration showed a relatively slight tendency for efflorescence formation, mixes containing 3 wt.% sodium oxide exhibited a relatively moderate tendency for efflorescence formation, and mixes containing higher concentrations of sodium oxide (4, 5 and 6 wt.%) displayed a relatively severe tendency for efflorescence formation.

Pacheco-Torgal and Jalali (2010) considered the tendency for efflorescence formation as a criterion of structural stability for alkali-activated binder based on calcined tungsten mine waste mud. While alkali-activated binder produced from alkali mine waste mud calcined at different temperatures did not suffer from efflorescence formation, alkali-activated binder based on mine waste mud calcined with sodium carbonate exhibiting relatively high early compressive strength showed a relatively severe tendency for efflorescence formation. This indicates that even a relatively high early compressive strength does not always imply efflorescence formation.

Allahverdi et al (2011) investigated the influence of blast furnace slag on basic engineering properties and efflorescence formation of natural pozzolan-based geopolymer cement. They studied different mix designs of the same silica modulus (M_s = 0.6) and different sodium oxide concentrations ranging from 5 to 8% by weight of binder. The water-to-dry binder ratio (w/c) ranged from 0.26, 0.28, 0.30 and 0.32 and blast furnace slag was used in four different replacement levels of 0, 5, 15 and 25% by weight of binder. They obtained results showed that incorporation of blast furnace slag did not provide any improvement in strength behavior of the studied natural pozzolan-based geopolymer cement, but an improvement of which was beneficial in reducing the efflorescence formation. They also obtained mixes with blast furnace slag content higher than 15% suffered from relatively high early age strength of 8 MPa at 7 days, and a relatively high initial tendency for efflorescence formation of about 9.8 MPa with the least tendency for efflorescence formation. They reasoned the tendency of the mixes with blast furnace slag content for efflorescence formation by lower concentrations of alkali metals required for geopolymerization process of blast furnace slag.

Najafi Kani et al. (2012) focused their work on controlling efflorescence formation in a geopolymer binder based on a pumice-type natural pozzolan. They showed that efflorescence formation can be reduced and controlled either by the addition of alumino-silica admixtures or by a hydrothermal curing. Both of these techniques provide benefits to the binder structuring by enhancing the binder structure formation process. Škvára et al (2012) reviewed the existing models for Na(X) bonds in Na₂X–K-S-H and pointed out that Na⁺ will be insufficiently leached out with significant consequences for efflorescence in alkali-activated or geopolymer cements. They also obtained interesting results in their studies supported by a series of long-term leaching experiments as discussed in detail with the compressive strength measurements, studies by SEM/EDS etc, ²³Na and ²⁷Al, ²⁹Si, and ³⁵P NMR, and also modelling the leaching phenomenon; they compared the leaching and concluded that phosphate admixtures can slow down the rate of leaching as it decreases the rate of alkali leaching. They figured out the process of alkali activation is to create a medium that leaching process, but without the use of phosphate admixtures to modify the process of the binder structure formation.

Zhang et al (2014) focused their work on the effects of the addition of alkali admixtures in creating a denser binder structure for discolouration of glass phases from precursor materials and the process whereby the rate of leaching alkali metals out of the gel formation, alkali remain in the nanostructure of C-S-H & C-S-H gel weakly as secondary base leaving remnants from enhancing solution. Only based on the formed binder structure, this explained the nanostructure of potassiumbased polymeric chains consisting conditions of solution based on the form of Na(H₂O)ₓ⁺ or Al₂Oₓ(H₂O)ₙ model after which can compensate the negative charge (Glass et al., 1997). The presence of other cations (Fe³⁺, K⁺, and Ca²⁺) in the precursor can also balance the negative charge on Al³⁺.

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Studies on Ugandan Volcanic ash and Tuff

S.O. Ekolu, ... M.D.A. Thomas, in Proceedings from the International Conference on Advances in Engineering and Technology, 2006

1.0 INTRODUCTION

The use of natural pozzolans results in a reduction of CO_2 emissions associated with Portland cement production. A 50% Portland cement replacement by a natural pozzolan would mean a reduction of such greenhouse gas emissions in cement production by one half, which could have enormous positive consequences for the environment. Secondly, depending on the grindability (if necessary) and fineness to the construction site, natural pozzolans can significantly reduce the cost of concrete production, dam construction or production of mass housing units. As found with ancient concrete structures (Malinowski, 1981), natural pozzolans used in normal proportions typically improve concrete performance and durability. Whereas the benefits of most pozzolans used for strength their disadvantages, it is imperative that a thorough study of any particular geological source of natural pozzolan is conducted to understand its performance characteristics. This also helps to define discretionary use of materials where applicable. In this investigation, tuff and volcanic ash quarried from the mountainous regions of Elgon and Rwenzori in Uganda were studied to determine their properties for potential use as pozzolans, appropriate blending proportions for incorporation in cement and concrete, and evaluation of their pozzolanic activities. Earlier extensive studies by Hobbs and Ekolu (2006) and Taylavo (2006) found the volcanic ash properties to be satisfactory for use in making lime-pozzolan cements.

The pozzolan materials were blended with ordinary Portland cement in proportions ranging from 15 to 30% and performance related parameters were measured and compared in accordance with ASTM C-311 procedures. The techniques employed include differential thermal analysis (DTA), scanning electron microscopy (SEM) and ...

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Low clinker cement as a sustainable construction material

L. Black, in Sustainability of Construction Materials (Second Edition), 2016

17.6.5 Emissions associated with metakaolin

Metakaolin, an amorphous pozzolan, differs from the other SCMs mentioned in this chapter by not being an industrial by-product. Consequently, its environmental footprint is greater than that of the others. The principle source of carbon emissions associated with metakaolin production is the heating of kaolin to about 700°C. A recent study by Heath et al. (2014) reported a value of 0.423 tonne CO_2/tonne, while quoting values from other studies of 0.330 and 0.370 tonne CO_2/tonne.

In addition, the replacement of cement with metakaolin does not greatly reduce clinker depletion. Indeed, Heath et al. (2014) quoted that 1.16 tonnes of kaolin are required to yield 1 tonne of metakaolin compared to 1.6 tonnes of limestone and clay to produce Portland cement. Furthermore, kaolin mining in the United Kingdom produces large quantities of waste just as cement production does. As with silica fume, additional environmental benefits may be derived from the use of metakaolin in terms of increased durability and improved strength (albeit greater than for silica fume in the former case and less in the latter). Again, these effects are project-specific, so generalizations cannot be made here.

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Crucial insights on the mix design of alkali-activated cement-based binders

J. García-Lodeiro, ... A. Fernández-Jiménez, in Handbook of Alkali-Activated Cements, Mortars and Concretes, 2015

3.2.4 Other aluminosilicate materials

Volcanic ash and other natural pozzolans

Volcanic ash, the origin of natural pozzolans, was initially used by the Romans to make concrete. This ash consists of small particles of pulverized volcanic rock and glass. As a result of rapid post-eruption cooling, volcanic ash exhibits high chemical reactivity. That, together with its large proportion of vitreous phases and high silica and alumina content make it a promising raw material for alkaline activation (Provis and van Deventer, 2014; Leonelli et al., 2007; Kamseu et al., 2009).

Volcanic ash is normally characterized by high SiO_2, Al_2O_3, Fe_2O_3 and CaO contents, along with smaller proportions of other oxides including MgO, Na_2O, K_2O and TiO_2, as well as traces of many other elements. In addition to a high vitreous phase content, it contains mineral phases such as plagioclases, olivines and pyroxenes (Provis and van Deventer, 2014).

Natural pozzolans have proven to be another low-cement alternative to Portland cement (Malinowski et al., 2006; Najafi Kani and Allahverdi, 2009; Bondar et al., 2011a). In natural pozzolans a low lime content and pozzolanic nature with calcium-rich zeolites and a high soluble silica content, the optimal SiO_2/Al_2O_3 molar ratio is less than in other higher-Ca (lower in CaO-rich or pre-calcined pozzolans (Bondar et al., 2011a). High temperature curing has also been shown to improve the mechanical strength of these materials considerably (Najafi Kani and Allahverdi, 2009; Bondar et al., 2011b; Najafi Kani et al., 2012) and lower the risk of efflorescence (Najafi Kani and Allahverdi, 2009).

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Assessing the environmental impact of conventional and 'green' cement production

G. Habert, in Eco-Efficient Construction and Building Materials, 2014

Main non-renewable mineral SCMs

Among SCMs with a natural origin, we can distinguish natural pozzolans which do not need to be treated to react with calcium hydroxide, and those which need an activation to react with calcium hydroxide and thus are called calcined pozzolans. The so-called natural pozzolans, used as SCMs in the production of pozzolanic cements, are pyroclastic rocks rich in siliceous or siliceous and aluminous volcanic glass. The origin of the pozzolanic activity lies in this high content of reactive silica (Massazza, 1993). Common volcanic minerals are feldspars, mica, hornblende, pyroxene and quartz or olivine depending on the volcanic rock's chemical composition, but most of these minerals are easily alterable and the high porosity and specific surface area of pyroclastic rock enhance the alteration rate. Therefore, it is very common to find secondary minerals resulting from alteration of primary minerals and devitrification of the volcanic glass. Clays, zeolites, calcite and various amorphous silica-based minerals. The effect of these secondary minerals on the pozzolanic activity of the natural pozzolan is still controversial (Tchernikov and Tankut, 2002; Shi and Day, 2001; Pentsak et al., 2001; He et al., 1995a). It is mainly accepted that a good pozzolanic material must be a combination of reactive volcanic glass with clays and zeolites (Habert et al., 2008). Several techniques have been used to assess the enhance the reactivity of pozzolanic materials (and remove unreactive ones, which include calcination (Costa and Massazza, 1977), acid treatment (Alexander, 1955) and finally grinding (Aboudebra, 1967).

Among artificial pozzolans, we can distinguish volcanic rocks which generate certain pozzolanic activity due to their thermal history (Habert et al., 2008) and clays submitted to calcination process (Habert et al., 2009). The pozzolanic activity of calcined clays is much dependent on the loss of structural water which favours the creation of an amorphous structure (Ambroise et al., 1987). Numerous studies have shown that there exists a specific optimal activation temperature for each clay mineral (Ambroise et al., 1987; He et al., 1995a, 1995b, 1996, 2000; Murat, 1983; Sabir et al., 2001; Bich, 2005). Our results confirm the existence of an optimum for each mineral around 700 °C for kaolinite, 750 °C for palygorskite, 800 °C for montmorillonite and 900 °C for illite (Habert et al., 2009). Measurements of phase changes show...

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Progress in the Adoption of Geopolymer Cement?

J.S.J. Van Deventer, in Handbook of Low Carbon Concrete, 2017

Abstract

If formulated correctly, geopolymer cement made from fly ash, metallurgical slags and natural pozzolans could reduce the CO_2 emissions associated with the manufacturing of cement by at least 80%. However, almost all standards and design codes governing concrete are based on the use of Portland cement. The 150+ year track record of in-service applications of Portland cement is used extensively to validate the protracted case for acceptance of concrete durability. Moreover, the entire supply chain associated with cement is geared up around the use of Portland cement. In the geopolymerization of calcium-aluminosilicates constitutes a radical change in chemistry in comparison with the cement-based reactions compared with the calcium silicate hydrate chemistry that underpins Portland cement. Regulatory, supply chain, product confidence, and technical barriers that must be overcome before the widespread adoption of geopolymer concrete is possible. The use of geopolymer concrete in Australia is highlighted to provide regulatory, asset management, liability, and industry-stakeholder engagement process required to commercialize geopolymer cement. While the scale-up from the laboratory to the full commercial application of geopolymer cement presents challenge, its broad-based acceptance is hampered more by non-technical or regulatory, than technical, constraints. Business processes such as innovation in other markets. In the absence of in-service track record, comparison between fundamentals, engineering, regulatory and commercial considerations are needed to validate the performance of geopolymer concrete. Australia, although adoption of newer, engineered cement chemistry is understandably conservative as there is a lack of standards or design codes to validate the long-term performance, the relative novelty of geopolymer technology and improved business processes require a shift in mindset. Nevertheless, the historical adoption of concrete technologies, and geopolymer technology in establishing the relationship between mechanical, microstructural, and durability characteristics for general engineering practice.

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Special considerations for high strength materials

J.H. Bungey, ... Bing-Lin Lai, in Design of Steel Reinforced Composite Structures using High Performance, 2011

7.3.3 Supplementary cementitious materials

Using supplementary cementitious materials (SCMs) such as silica fume, fly ash, and natural pozzolans has become common practice in the concrete and construction fields, and offers several technical advantages. One such advantage is that SCMs can significantly reduce the permeability of hardened concrete, thereby reducing its susceptibility to attack by aggressive chemicals. SCMs also improve the durability of UHPC. Owing to the refinement of the pore structure through the reaction of SCMs, which do not compromise the mechanical properties of UHPC.

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Porous concrete pavement containing nanosilica from black rice husk ash

Ramesh Chandra Jaya, in New Materials in Civil Engineering, 2020

14.5.7.3 Compressive strength activity index

As prescribed in Ref. [65], the strength activity index is used to determine whether the natural pozzolans results in acceptable levels of strength development when used with hydraulic cement in concrete. The calculation was adapted for making a test specimen of the different strength values in the diametral proportions of both control and blended cements using the hydraulic cement values of replacement percentages of the blended cement mix. The strength activity index was calculated using Eq (14.2):

$$\text{Strength activity index} = \frac{A}{B}(100) \qquad (14.2)$$

where A is the compressive strength of the test mixture cube (MPa) and B is the compressive strength of the control mix cube (MPa). The strength activity index of the compressive strength results for all mixes corresponding to different levels of nanosilica from black rice husk ash replacement of cement at various proportions in the blended cement was measured. According to ASTM C618-12a, the strength activity index of binders containing nanosilica should be equal to or exceed the minimum value of 75% either at 7 days or 28 days, as required to be an SCM. The strength activity index results for the replacement percentages at different periods are tabulated. From the results obtained, all mixtures met the minimum strength activity index in all ages belonging to specimens of nanosilica from black rice husk ash and exceeded the minimum value of 75% at 7, 14, 28, 56, and 90 days, respectively. This may be due to the increased reactivity of the nanosilica which is very fine. Based on this, the compressive strength results of this study show that the strength requirements required to confirm with the blended cement for the hydration process, consider the required strength. Also, consider a deficiency in strength as it requires part of the cementitious content to be replaced by the nanosilica, thus requiring the strength which were at least more than 75% for the 28 days age.

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