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Ancient and Modern Pozzolanic Materials as Admixtures of Lime and Cement Composites: A Brief Review

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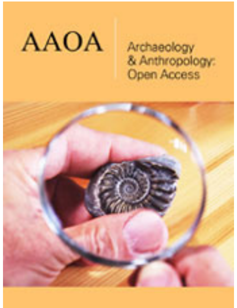

Abstract

This lecture provides an overview of ancient and modern pozzolanic materials used as admixtures mainly in lime and cement composites. It presents the methods for characterising these admixtures that enhance the properties and durability of composite materials. The study highlights the historical significance of ancient pozzolanic materials and compares them with their contemporary counterparts, evaluating their effectiveness and benefits in modern construction. The findings contribute to a deeper understanding of how these admixtures were specifically used for the development of new materials, considering sustainable development, as well as economic and environmental aspects.

Keywords: Pozzolans; Characterisation; Pozzolanic activity; Waste materials

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Introduction

Mortar is considered the oldest manufactured building material. The Egyptians first used a mixture of burnt gypsum, sandy silt from the Nile, and crushed limestone. The use of mineral admixtures has its historical and practical justification [1]. The colossal artificial harbour at Caesarea in 22-10BC was one of the most ambitious engineering feats of the ancient world. It was built of the so-called Roman concrete, which consisted of quicklime and volcanic ash. However, it is believed that knowledge of these binders and engineering skills originated with the Greeks or even with the ancient Egyptians and Persians with a slight influence of oriental culture through Mesopotamia and Mediterranean civilisations. In the Roman period, mortars of various compositions were widely used in the construction of buildings, harbours, bridges, aqueducts, roads, sewers, etc. Analysis of the surviving foundations, walls, and dams revealed very advanced technology and concrete composed of hydraulic lime, or air lime, and volcanic ash from Mount Vesuvius mined in the Pozzuoli region near Naples. Vitruvius recommended the ratio of one part lime to two parts fly ash in his work De Architectural libri decem, written around 27BC [2].

The state of practical knowledge and the views on lime and hydraulic mortars can be derived from the publications of Bélidor [3]. The use of blast furnace slag to produce binder was patented as early as 1728 by the Englishman John Payne. In the middle of the 19th century, slag cement began to be produced. John Smeaton in 1756, comparing various properties properties of limestone by chemical analysis, found that the most suitable for hydraulic binder production are limestones polluted with clays [4]. So, he prepared a concrete that hardened excellently under water and built a lighthouse out of it at Eddystone near Plymouth on the Cornish coast. This artificial stone, based on “Roman cement”, in colour resembled the building stone from the vicinity of Portland, which was considered to be of the finest quality. Here the silicate cement was later given the nickname ‘Portland cement.’ The tradition of using pozzolanic admixtures was considered a trade secret of the building families. The benefits of pozzolanic materials were rediscovered during the Industrial Revolution during the 18th and 19th centuries. Engineers and scientists began to systematically study and apply industrial by-products such as fly ash and slag, recognising their pozzolanic properties [5-8]. As we can see from the analyses of the preserved mortars as pozzolanic admixtures in this period, ceramic tiles and bricks were also crushed [9-11], burnt clays [12], or natural zeolites [13].

The widespread industrial use of pozzolanic materials surged, driven by the need for durable and sustainable construction materials in the 20th century. Advances in material science allowed for a better understanding of the chemical reactions and benefits provided by these admixtures. Modern pozzolanic admixtures continue to play a crucial role in enhancing the properties of cementitious materials. These materials are widely used in construction to improve the durability, strength, and environmental sustainability of concrete and mortars [14]. This also led to the development of High-Performance Concrete (HPC) in the 1960s and 1970s [15,16]. In the 1980s, pozzolans were incorporated as Supplementary Cementitious Materials (SCMs) to composite materials [17] and Ultra-High-Performance Concrete (UHPC) was proposed [18]. High-performance concretes are characterised by high strengths, resistance to water and salt penetration, frost resistance, etc. [19]. In this period of time, industrial by-products such as silica fume from silicon metal or ferrosilicon alloy production [20], fly ashes from coal combustion in power plants [21], Ground Granulated Blast Furnace Slag (GGBFS) a by-product of iron production in blast furnaces [22], or metakaolin derived from calcined kaolinite clay [23-25], rice husk ash [26], and of course natural pozzolans (volcanic ash, pumice, and certain sedimentary rocks [27,28]) were widely used.

Today, the exploration of pozzolanic admixtures involves extensive research and development to optimise their use in various applications. This includes mainly characterisation of natural and artificial pozzolans, performance testing, and sustainability studies. In the 21st century, the construction industry is confronted with the environmental and economic impacts of cement production. For this reason, it is essential to design hydraulic binders using secondary raw materials. Fly ash from biomass combustion [29-31], municipal waste [32,33], treated sewage sludge [34,35], and waste coal gangue [36,37] appear to be very promising. Additionally, these secondary waste materials may contain heavy metals and other dangerous chemicals that could be released into the environment by only landfilling. Therefore, its use in the form of active admixtures is highly desirable and contributes to the sustainable development of the construction industry.

Discussion

The term pozzolanic activity covers all the reactions that take place between the active components of the pozzolan, lime, or calcium hydroxide, and water and practically defines the maximum amount of lime that the pozzolan can react with and the rate at which it does so. The activity of pozzolans has many variables, all depending on the nature of the pozzolan used, its quality, the amount of active ingredients contained, the ratio in the mixture, the specific surface, the water content, but also the chemical composition, the grain size, and of course the ambient conditions of the reaction, especially temperature, humidity, and partial pressure [38-40]. In recent years, researchers have proposed many methods for evaluating pozzolanic activity. Many countries have also selected different test methods and standardised them to provide the industry with a basis for assessing the activity of pozzolanic materials. The methods used for the determination of pozzolanic activity can be divided into two categories: direct and indirect. Direct methods monitor the presence of calcium hydroxide and its subsequent reduction during the pozzolanic reaction using analytical methods such as X-ray diffraction, thermogravimetric analysis, or classical chemical titration. Indirect methods include the measurement of physical properties such as the determination of the strength characteristics of the test specimens, electrical conductivity, or thermal conduction [41,42].

At first, it is necessary to characterise the material, which means determining the chemical composition, particle size distribution, and specific surface area. The values of these parameters can indicate whether a given material will be pozzolana active or how much. Subsequently, several methods can be used individually or in combination. Physical test methods, including the strength activity index method, electrical conductivity test, isothermal calorimetry test, thermal analysis method and bound water ratio method, indirectly reflect activity by measuring the conductivity of the solution, the strength of the mortar, heat release, or other factors [43,44]. These methods are defined by standards, specifically ASTM C331 [45], ASTM C1702 [46], and ASTM D8329 [47]. The chemical testing procedure quantitatively identifies the amount of $Ca(OH)_2$ consumed or the content of SiO_2 and $Al2O_3$ in the material according to the nature of the pozzolanic reaction to precisely assess the activity, including the Frattini test [48], the lime absorption method, the Chappell test [49] and the acid/alkali dissolution method. Other methods include the determination of pozzolanic activity by microstructure analysis (degree of polymerisation) or the kinetic model method [50]. All these methods have their own advantages and disadvantages and will find their own specific applications. The appropriateness of using methods has been the subject of much research. In summary, chemical methods are more intuitive and precise than physical methods, which are more likely to be interfered with by the external environment.

From the point of view of practical use, it is essential to perform tests on concrete properties such as strength, durability, and environmental resistance. When designing new composite materials using pozzolans, it is crucial to determine the optimum amount of a given admixture. It can vary depending on several factors, including the type of pozzolan used, the specific application, and the desired properties of the composite material. It also depends on whether the pozzolan is added as a substitute or is added as a binder. For example, typically 15-30 % replacement of Portland cement is common. Silica fume is usually added at 5%-15% by weight of cement, and GGBFS is often used at replacement levels of 30-50% of the cement content. In some cases, up to 70% can be used for specific performance requirements. Typically, metakaolin is used as a replacement for cement and lime at 5-20%. It provides significant improvements in strength and durability.

Conclusion

The use of ancient pozzolanic admixtures revolutionised construction in antiquity, enabling the creation of enduring structures that still stand today. Understanding these materials offers valuable information on sustainable and durable construction practices that can guide the use of modern pozzolanic materials in contemporary engineering. Although general guidelines exist for the optimal amount of pozzolanic admixture in lime and cement composites, the specific requirements of each project should dictate the final proportions. Performance tests and consideration of environmental factors are crucial steps in determining the ideal mix design. Modern pozzolanic admixtures are integral to the advancement of concrete technology, providing solutions that address both performance and environmental challenges. By utilising these materials, the construction industry can produce more durable, sustainable, and cost-effective concrete structures. Substituting a portion of Portland cement with pozzolanic materials can lower the overall cost of concrete production while improving performance.

Conflict of Interest

I can declare that there is no conflict of interest.

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