Alkali-Activation of Calcined Clays – Past, Present and Future

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Abstract. The combination of a calcined clay with an alkali silicate or hydroxide solution has been identified since the 1920s to yield potentially useful materials. More recently these have become termed 'geopolymers', and have been popularised under that name. This paper briefly summarises some of the earlier history of alkali-calcined clay binders and related materials including synthetic zeolites, exploring some of the reasons underlying the more recent broadening of interest in this research field, and identifying some of the future opportunities that arise through the use of these materials. These cements may particularly be capable of offering very good technical performance and cost-effectiveness in a variety of applications, with an environmental emissions footprint lower than that of competing materials.

1 Introduction

The term 'geopolymer' was introduced by Davidovits in the 1970s to describe binders based on the reaction between calcined clays and a source of alkalinity, most commonly an aqueous alkali metal silicate or hydroxide solution [1–3]. However, this combination of reactants had been described in the technical literature some time prior to the work of Davidovits, in some cases yielding the monolithic alkali aluminosilicate gels which characterise geopolymer materials, but in other cases focused on the synthesis of crystalline zeolites. Some of this work will be reviewed briefly here, and the potential for further future development of alkali-activated binders based on calcined clays will be noted. The details of the chemistry of the alkali aluminosilicate gels which are formed by such processes have been described in detail in the technical literature [4–8]. The scope of this paper is limited to calcium-free binding systems, although lime-pozzolan cements based on calcined clays are certainly both well-known and of significant technological value.

It is also worthwhile to mention that some workers have used the combination of phosphoric acid and calcined clays to produce what they describe as an 'acid geopolymer' [9–11]; although potentially of some technical interest due to their potential for rapid strength gain, the high cost of phosphoric acid limits the use of such cements on a very large scale in construction and they will not be the focus of further discussion in this brief paper.

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2 The First Steps and Further Development

The earliest identified study of the reaction of an alkali silicate with calcined clay (kaolinite, in this instance) was published by the U.S. National Bureau of Standards in 1920 [12], where this combination of materials was included in a set of tests aimed at identifying the preferred cement for use in joining spark plug wires to porcelain insulator bodies. It was reported that "*When brought into contact with a strongly alkaline substance such as sodium silicate, calcined kaolin reacts quite rapidly to form a friable, porous mass*", with "*little strength*" [12]. Fortunately, the development of materials based on similar chemical reaction processes, for this and other applications, did not stop at this rather unpromising beginning. The addition of lard was found to improve the properties of these cement sufficiently to enable their successful use in spark plugs [13], while applications for similar materials in construction were also developed, for example in waterproof structural wallboard [14] and surfacing granules [15].

The longest-running research and development programme related to alkali-activated binder materials is the group in Kiev, Ukraine, which was initiated by V.D. Glukhovsky and is now continued in the institute which bears his name. An early landmark publication from that group was a 1957 book entitled *Gruntosilikaty* (Soil Silicates) [16]. This book describes binder formulations based on combinations of metallurgical slags, clay soils such as loess, brown clay, and loam, and alkaline solutions containing NaOH, silicates, carbonates and/or fluorides. Subsequent work by the same group led to the development of a broad range of alkali-activated binder systems, mainly based on metallurgical slags, but with systems based on calcined clays particularly highlighted as having potential in the immobilisation of radioactive wastes [17].

The reaction of calcined clays with alkaline solutions was also studied in the context of zeolite synthesis, with the work of the group led by Barrer [18–20] being of particular importance in understanding the alkali-hydrothermal reactions of metakaolin. Although the purpose of that work was to produce crystalline zeolites rather than monolithic binder phases, the insight developed into the conditions which lead to the formation of numerous different types of zeolitic crystal has proven essential in understanding the nanostructures of the binders which are formed through analogous reactions under non-hydrothermal conditions [21].

In this context, Davidovits in the early 1970s began to develop alkali-aluminosilicate cements based on metakaolin as an inorganic, fireproof alternative to organic polymers [22], and subsequently introduced 'geopolymer' terminology as a descriptor for this class of materials [1–3]. His work in promoting and popularising geopolymer cements has led to a high degree of international prominence for the materials since the 1980s, and the term geopolymer has become applied to ever broader groups of materials beyond its original definition. Nonetheless, applying the original sense of a geopolymer as a mineral binder based on alkali-aluminosilicate chemistry, with physical characteristics resembling to some degree those of an organic thermoset, research in this area has since led to many valuable products for both cement-like and ceramic-like applications.

3 The Present and the Future; Development Opportunities and Needs

Innovation in the construction materials industry is currently being driven by environmental pressures, specifically the need to reduce sector-wide CO_2 emissions [23]. It has been identified that calcined clays offer probably the greatest scope among all materials to be used on a gigaton per annum scale in place of Portland cement [24]; their incorporation into blends with Portland cement is certainly a key avenue by which these materials will add value in the global built environment, but the production of alkali-activated clay-based cements is certainly of strong technological and societal interest in areas where the necessary resources are available [25]. Significant commercial advances have recently been made in this regard in the UK [26, 27] and elsewhere, but there is a clear need for further advancement in both the design and testing of clay-based alkali-activated binders to enable scale-up and deployment to continue at pace, to exercise the full potential of these materials. This will also feed into ongoing standardisation efforts (e.g. [28]), where the availability of validated testing methods will enable the confident application of performance-based routes to specification.

In terms of materials design, one of the greatest strengths of alkali-activation as a route to cement production is the ability to match activators to precursors in a controlled way, to manipulate and optimise material properties in a very flexible way. The activator that usually gives the best results in conjunction with a calcined clay is an aqueous alkali metal silicate (also called ‘waterglass’), which is a commercial product usually sold for applications in detergent manufacture and other fields where the total mass of material used is orders of magnitude below the demand for construction materials. The ability to produce and/or source activators at reasonable cost and sufficient volume, and with an acceptable ecological footprint to enable the ‘green’ credentials of the material to be attractive, lies at the heart of the quest for industrial uptake of these cements, and there are rapid and ongoing developments in this area worldwide.

In terms of materials testing, it has been identified that the durability tests which give reliable results for materials based on Portland cement are often less representative when applied to non-Portland cement binders. The alkali-activated materials based on calcined clays are among the groups of materials for which improved testing methods are needed; the chemistry of these binders is very different from that of Portland cement (much more so than many other alkali-activated materials which may contain higher levels of calcium), and so many of the durability tests designed to determine the performance of calcium-rich binders may not provide realistic insight into the behaviour of a material that is so different in chemistry. Much ongoing work, including through a RILEM Technical Committee and a European Federation of Corrosion Task Group, is aimed at remedying this mismatch and providing guidance for specifiers and testing laboratories regarding how these materials can realistically be tested to provide an understanding of in-service performance.

4 Concluding Remarks

Alkali-activation of calcined clays has been trialled for almost 100 years as a means of producing cementitious products, for specialty and/or bulk applications. The current drive towards sustainable development in the construction industry has generated significant impetus for the deployment of these materials, and the technical and non-technical hurdles which have historically impeded their uptake are being eroded or removed as field experience is gained, standards and specifications are put in place, and improved methods of designing, producing and utilising these materials are developed.

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