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Alkali-activated cements
Opportunities and challenges

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Abstract

Alkali-activated cements as discussed here are those with compositions falling in the Me_2O-MeO-Me_2O_3-SiO_2-H_2O system. This paper reviews their history of development and discusses their present status. Currently, there are major opportunities for such cements based upon (a) substantial knowledge of properties and mechanisms; (b) good track record of field performance in various applications and; (c) future orientation as environmentally friendly materials in accord with making use of substantial amounts of by-product and waste materials, thereby consuming less energy and generating less waste. The equivalent performance to Portland cement materials is one target for these cements, but, in many cases, the properties of alkali-activated cements actually are superior. It is important for assuring long-term durability to characterize more fully the complex solid phases, including determining the combined state of alkali in the solid hydration products, and of the residual soluble species in the pore fluids as a function of time. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali activated cements; Acceleration; Pozzolan; Reaction; Durability

Building from a history starting in the 1940s, there have been many recent developments in alkali-activated cements [1–33]. But the use of alkaline activators to stimulate the latent pozzolanic properties of materials has an even longer history; in fact, the initial use dates from at least the time of Nebuchadnezzar. Bricks in the city of Ur of the Chaldees have been found to have produced from a mixture of lime and ashes. Studies of the alkali activation of glassy blast-furnace slag have a long history in the former Soviet Union, Scandinavia, and Eastern Europe [1]. The Trief cements and F-cements from the Scandinavian countries [2,3] and alkali-activated blended cements (sold under the trade name Pyrament) are more recent examples [4–6]. In recent years, particular emphasis has been placed on the utilization of industrial by-products in chemically bonded ceramics [4,7].

In addition, the annual output of fly ashes from power plants and other by-product materials is so enormous that there is a constant need to find new uses for them [8,9]. Approximately 49% of the utility wastes are simply land filled, 41% are contained in surface impoundments, and about 10% are disposed of by discharging into old quarry operations. Increasingly, storage is conducted “on site” due to reduced costs to the utilities. This is to say nothing of the need to utilize SO_3-rich by-products. Although much of the development of alkali-activated or alkaline cements has been based on activated slags [34–37], as will be seen there is great potential for utilization of these other by-products.

At the other end of the spectrum, there is considerable interest in utilizing such by-product materials in the synthesis and processing of high-performance cementitious materials. Recent advances have led to the development of new families of high-performance cementitious materials, including very high strength (for cements) materials. Some of these materials cross the boundaries of what have been defined as traditional cementitious materials, and the term chemically bonded ceramics has been used to classify these new materials. Chemically bonded ceramics are defined as ceramic-like materials formed as the result of chemical reactions occurring at or near ambient temperatures [7]. Additionally, these cements may be more durable than hydrated Portland cement.

1. General background and status of alkali-activated/alkaline cements

In this treatment, we will discuss both alkali-activated systems and materials for which the “activator” becomes a more essential component of the product. The discussion is organized as follows, with a major emphasis on the history/background leading to the current state of knowledge and need for future developments: history/background, status of

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current knowledge, systems/materials, mechanisms, characterization, properties, new methods of study, applications, needed knowledge, and future directions.

The last century has focused quite properly its technology on Portland cements, those cementitious materials based on compositions in the MeO-Me_2O_3-SiO_2 system, concentrating on the development of binding systems consisting of the high calcium content minerals, C_3S, C_2S, C_3A, and C_4AF. These systems have served well, but not without some drawbacks: synthesis of high CaO minerals involves large fuel and energy consumption. Because Portland cement and concrete derived from it constitute the largest volume manufactured material in the world, it is a significant source of carbon dioxide. This is the result of decarbonation of limestone in the kiln during manufacturing

$$5CaCO_3 + 2SiO_2 \rightarrow 3CaO \cdot SiO_2 + 2CaO \cdot SiO_2 + 5CO_2$$

and the use of fossil fuel in the kiln. The production of 1 ton of Portland cement accounts for 1 ton of CO_2. Furthermore, there are certain limitations regarding the durability of the concrete products. Therefore, it is appropriate that now more attention should be given to more conservative systems.

2. History and development

2.1. Earliest history

Table 1 chronogically summarizes some important references outlining steps in the development of alkali-activated and alkaline cements [2,3,5,10–33]. The formative works of Feret [10], Purdon [11], and Glukhovsky [12,13] have already been mentioned briefly as those that provide the earliest groundwork. Glukhovsky, in particular, emphasized the difference between the composition of traditional Portland cements and the basic rock-forming minerals of the earth's crust. The major hydration in products of the former are, of course, calcium silicate hydrate (C-S-H) and portlandite ($Ca(OH)_2$), whereas the latter are more represented by zeolitic materials, containing alkalis. The formation of the latter should give rise to the probability of enhanced durability. This is aside from the role of alkali-activated cements in helping protect the environment through a) their utilization of by-product materials in their manufacture and b) end applications in waste management [16,23,38–41].

2.2. Earth materials/"soil cements"

Emphasizing the "earth materials" association, Davidovits [14] developed and patented [5,18] analogous alkaline cements in which sintering products of kaolinite and limestone or dolomite were used as the aluminosilicate constituent. These cements were called "geopolymers" and have been put into practice under the trademark Pyrament and others. The "F-cement" in Finland of Forss [2] and "geocements" in the Ukraine of Krivenko [32,34] fall within this category, and the latter, especially, underline the presence within their hydration products of analogues to natural minerals. The interest in alkaline aluminate, Port-

Table 1
Bibliographic history of alkali-activated and alkaline cements: Alkali-activated cement systems and alkaline cements (including geocements/ancient analogs)

Author(s)	Year	Significance	Ref. no.
Feret	1939	Slags used for cement	10
Purdon	1940	Alkali-slag combinations	11
Glukhovsky	1959	Theoretical basis and development of alkaline cements	12
Glukhovsky	1965	First called "alkaline cements" because natural substances used as components	13
Davidovits	1979	"Geopolymer" term—emphasizes greater polymerization	14
Malinowski	1979	Ancient aqueducts characterized	15
Forss	1983	F-cement (slag-alkali-superplasticizer)	2
Langton and Roy	1984	Ancient building materials characterized (Roman, Greek, Cyprus)	16
Davidovits and Sawyer	1985	Patent leading to "Pyrament"	18
Krivenko	1986	D.Sc. Thesis, R_2O-RO-R_2O_3-SiO_2-H_2O	17
Malolepsy and Petri	1986	Activation of synthetic melilite slags	19
Malek et al.	1986	Slag cement-low level radioactive waste forms	20
Davidovits	1987	Ancient and modern concretes compared	21
Deja and Malolepsy	1989	Resistance to chlorides shown	22
Kaushal et al.	1989	Adiabatic cured nuclear waste forms from alkaline mixtures including zeolite formation	23
Roy and Langton	1989	Ancient concrete analogs	24
Majumdar et al.	1989	$C_{12}A_7$ - slag activation	25
Talling and Brandstetr	1989	Alkali-activated slag	3
Wu et al.	1990	Activation of slag cement	26
Roy et al.	1991	Rapid setting alkali-activated cements	27
Roy and Silsbee	1992	Alkali-activated cements: overview	28
Palomo and Glasser	1992	CBC with metakaolin	29
Roy and Malek	1993	Slag cement	30
Glukhovsky	1994	Ancient, modern and future concretes	31
Krivenko	1994	Alkaline cements	32
Wang and Scrivener	1985	Slag and alkali-activated slag microstructure	33

land cements, and their varieties [32] in which alkalis act as activators and structure-forming elements has grown steadily for the last 10–15 years.

2.3. Basic compositions

Krivenko [17,32,34] prefers to separate the binding systems into two main categories: Me_2O-Me_2O_3-SiO_2-H_2O and Me_2O-MeO-Me_2O_3-SiO_2-H_2O), although the composition fields no doubt overlap. The alkaline zeolitic type minerals are the potential end-products of the former, whereas mixed alkali-alkaline earth zeolites and calcium hydrosilicates and carbonates are end-products of the latter. Iron and/or magnesium, of course, may be contained in both, to varying extents. Use of gypsum-free Portland cement clinker is recommended when blending with other alkaline cement components is desired (see also Yudenfreund et al. [42]). Krivenko [17,32] has done much to both advance and integrate an understanding of such materials.

2.4. Ancient cements

Malinowsky [15], Langton and Roy [16], and Roy and Langton [24] observed the durability of ancient constructions in Italy, Greece, Cyprus, and Egypt. When repaired by modern concrete, it has been shown that ancient mortars and concrete have remained unaffected by severely corrosive conditions, such as flowing water and salt-ladenair for 2,000 years, whereas a modern Portland cement concrete used in their repair may turn out to be essentially destroyed after the vicinity of only 10 years [15].

Langton and Roy [16] and Roy and Langton [24] also found analcime in pozzolanic Roman cement mortars and concretes. The presence of zeolites in different ancient cements suggests that zeolites are a final stable phase of long-term conversion of the primary phases to zeolite-like materials, predicting the increased durability of cements of somewhat similar composition.

2.5. Slag-based cements

Much of the work on alkaline cements has been that of the activation of granulated blast-furnace slags by alkalis [2,3,19,20,22,25–28,30,33,35,37]. Such slags with the addition of a source of alkali fall within the system Me_2O-MeO-Me_2O_3-SiO_2-H_2O and appear to be hybrid materials between “alkali-activated” and “alkaline” cements. The term “alkali-activated” is used by those who believe that R^+ (alkali) ions in such materials play a catalytic role in the early stages, then at a later stage they are combined into the structure to form zeolite-like phases. Common reaction products of alkali-activated slag cements are mainly varieties of C-S-H, $(C,M)_4AH_{13}$, or hydrotalcite and minor amounts of C_2ASH_8 (strätlingite).

2.6. Other compositions

Glukhovski [1,31] and Krivenko [32] investigated compositions broadly categorized as a combination of alkalies with aluminosilicates of natural and waste product origin. These studies prove that alkalies and alkali metal salts, as well as silicates, aluminates, and aluminosilicates, exhibit reaction in alkaline aqueous medium when the alkali concentration is sufficient. Such interaction takes place with clay minerals, with aluminosilicate glasses of natural and artificial origin, in which calcium is absent, as well as with calcium binding systems under natural conditions, and form a water-resistant hardened product of alkali or alkali-alkaline-earth hydroaluminosilicates, analogous to natural zeolites and micas. Wu et al. [26], Roy et al. [27], and Roy and Silsbee [28] investigated systems composed of a variety of activators with reactants [43,44] including fly ashes and silica fume [45–48], in addition to slag [46,47]. Malek and Roy [48,49] emphasized metakaolin and low-calcium fly ash as major constituents, showing that the hydration products possessed resistance to transport of certain soluble ions.

Palomo and Glasser [29] and DeSilva and Glasser [50] also investigated the use of metakaolin. Majumdar et al. [25] again changed the chemistry, showing that calcium aluminates are effective activators of slags, or that slags provide stabilization of calcium aluminate cements.

2.7. Characterization of hydration products

The characterization of reaction products of alkali-activated or alkaline cements, as in the case of Portland cements, is not trivial, as much of the product of hydration under normal ambient is amorphous to X-ray [35]. Wang and Scrivener [33], among others, have attempted to decipher the products of NaOH or waterglass-activated slag, finding CSH(I), hydrotalcite, and C_4AH_{13}, whether the materials were hydrated 14 days at 80°C or 15 months at room temperature. They did not find evidence of zeolitic or micaceous minerals. Richardson et al. [51] characterized alkali (K) activated blast-furnace slag pastes cured up to 8 years at room temperature, especially with respect to the C-S-H content, by nuclear magnetic resonance (NMR), electron energy loss spectroscopy (EELS), transmission electron microscopy, and scanning electron microscopy. They showed that Al substitutes for Si in the bridging tetrahedra of the dreierketten; the C-S-H also appears more crystalline than in Portland cement. The C-S-H was found to be intermixed on an intimate scale with an Mg/Al-rich phase, presumably hydrotalcite. In an Si-NMR investigation of slag activated with KOH, Jiang et al. [35] achieved results consistent with those of Richardson et al. [51]. Malek and Roy [49] found evidence in the Si-NMR spectra of K-activated metakaolin blends hydrated 14 days at 38°C, consistent with the formation of some zeolitic structure.

2.8. Alkali-activated cements in waste management

Alkali aluminosilicate reactions appear to have a major role in waste disposal. When used as barriers or for encapsulation, they both may reduce permeabilility of the matrix and fix certain ions in the structures of the phases formed

[39]. The compounds that form in low-temperature clay-alkali reactions (zeolites and cancrinites) are large cage-like crystals that can sequester ions or molecules of waste material. Caustic radioactive wastes can be reacted with clays such as bentonite, kaolinite, halloysite, and dickite and generate a durable monolithic solid. The soluble salts fill the cage-like forms, but these "caged" substances are not specifically part of the crystal structure.

Many of the potentially useful silica/alumina-rich solids are available as glassy, fine-grained by-products that do not require grinding. For example, fly ash or treated clays and kiln dust are common ingredients. Often in the solidification of a radioactive or hazardous waste stream, the waste itself is highly alkaline and serves as activator.

Where alkali wastes (containing sodium or potassium hydroxide) are not available components, sodium or potassium salts can be mixed with alkaline-earth hydroxides (for example, lime) to form hydroxides of alkali metals. The most useful akali salts are generally the least soluble; for example, sodium carbonate is a better activator component than sodium chloride. Common products of Savannah River Plant alkaline wastes solidified in fly ash-slag mixtures include, in addition to C-S-H, zeolite-like nosean, hydrotalcite, and C_4AH_{13} [20,23]. Glasser [52], who has written extensively on cements in radioactive waste management, has made the point that some of the most durable forms use supplementary cementing materials.

Recent research has shown that effective radioactive and hazardous waste forms may be based on a nontraditional cementitious system that relies upon the alkali activation of aluminosilicate materials, where the components may be metakaolin, fly ash, or slag [52–55]. A number of the aluminosilicate compositions may develop zeolitic products through the reaction of alkaline waste stream with aluminosilicate materials such as metakaolin [41]. The cementitious waste form not only has characteristics of low leachability, but certain controlled compositions have the optional feature of being vitrifiable should that choice be desired [40,53,55].

3. Discussion and summary

It is evident that there has been extensive research on, and experience with, alkali-activated or alkaline cements beginning about 1940 or earlier. The extensive research of workers in the Ukraine, Russia, and Eastern Europe has contributed a great deal of this knowledge. In attempting to distill the current knowledge, it is inevitable to turn to these sources. The classification of alkali-activated cements by Krivenko [34] has been quite useful. He summarized five categories: (1) geocements, (2) slag-alkaline cements, (3) fly ash alkaline, (4) alkaline-Portland cements, and (5) alkaline aluminate cements. These appear to cover many of the major categories of alkali-activated cements, although not all. For example, silica fume, metakaolin, and a variety of fly ash materials are important alkali-activated cement components and may become increasingly important in the future.

Table 2, modified from Krivenko [34], summarizes the numerous applications of alkali-activated cements up to the present. Alkali-activated cements have found a variety of applications, particularly since the 1970s, such as agricultural, industrial, residential, transportation (e.g., railway ties), mining, various high-volume applications, oil well cements, and water stop or sealing applications. There appears to be much evidence for including alkali-activated cements among those used to generate high performance. As discussed, one of the major newer applications expected to play an increasingly important role is in waste management, including nuclear waste management and immobilization of toxic metals.

There are major opportunities for such cements based upon: (1) substantial knowledge of properties and mechanisms, (2) generally good track record of field performance in various applications, and (3) a sense that these are future-oriented environmentally friendly materials in accord with future expectations that our society must involve in its technological use of substantial amounts of by-product and waste materials, thereby consuming less energy and generating less waste, greenhouse gases, and other undesirable products.

It would be inappropriate to close without saying something about the remaining unknowns, current research needs, limitations, and, indeed, research imperatives relative to the use of these materials:

1. Standards: Considerable effort will be needed to gain more widespread development of the use of these materials through the evolution of more performance-based standards and not necessarily those directly derived from current Portland cement standards. Although Portland cement performance equivalence is one target to aim at, it is recognized that even Portland cements are not "perfect" and that, in many

Table 2
Applications to the present

	Roads	Agriculture	Industrial	Residential	Mining	Hydraulic
Construction	Heavy-duty pavements cast in situ and pre-cast; reinforced	Cast in situ and pre-cast concrete; storage	Acid-resistant buildings garages; floor slabs; foundations	Pre-cast and in situ concrete buildings; slabs; foundations	Oil well grouts; ties; sealing; prevent water penetrations	Irrigation systems; break waters
Nonconstruction	Waste immobilization		Bodies of machine tools	Dies; molds		Linings

cases, the properties of alkali-activated cements, especially durability, are superior.

2. Development of data base: Greater confidence will be gained in the manufacture and use of alkali-activated cements as a more extensive data base is available to enhance the predictability of performance. This is particularly true because of some of the variability in natural or by-product/waste source materials.
3. Reactivity and reaction mechanisms: Greater understanding of the reactivity and reaction mechanisms is required, e.g., there is substantial evidence that slag glasses with Al in 4-coordination are more reactive than those glasses having Al in 6-coordination. Is this universal, or compositionally dependent? It is necessary to define better the activation effectiveness of different types of alkalis (the comparative mechanisms of reaction of different alkali systems, e.g., K vs. Na are not yet fully understood).
4. Characterization: Especially because of the variability in composition of many of the alkali-activated cements, continuation in the search for, and application of, new characterization methods is needed. Although some of the newer methods, such as magic angle spinning nuclear magnetic resonance (MAS-NMR) are useful, in complex systems it is not always possible to separate out the effect of a single phase; it is necessary to resolve what are the effects of minor components, either in "solid solution," as phase-separated structures, or as minor crystalline phases. It is important from the stance of long-term durability to characterize more fully the complex solid phases, including determining the combined state of alkali in the solid hydration products and of the residual soluble species in the pore fluids as a function of time.
5. Processing of raw materials: Additional studies are needed to determine the effect of differences in the processing parameters of raw materials, e.g., granulation process of slags, beneficiation of fly ashes or other by-product or earth materials. Further emphasis is needed to determine the effects of processing parameters during hydration, such as temperature, curing ambient, and other factors.

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