Advances and Applications in Cements/CBC's, Including Waste Management

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Advanced cements used in the making of very strong or otherwise high performance cementitious materials are discussed. These include CBC (Chemically Bonded Ceramics) which is a generic term describing ceramic-like materials formed by chemical reactions at ordinary temperatures. Innovations in chemistry, as well as processing, are responsible for the major improvements. Recent studies focussed on the synthesis, equilibria, reactions, and bonding mechanisms in chemically bonded ceramics (CBC) in the system $CaO\text{-}Al_2O_3\text{-}P_2O_5\text{-}SiO_2\text{-}H_2O$. MDF and DSP cements are discussed briefly, as are rapid setting belite-sulfoaluminate and related cements. Fundamentals of energy-efficient processing, and utilization of by-products are discussed briefly, as well as applications of certain cements in waste management. These include alkali-activated cements, which generate very high early strength, develop a working strength in about four hours, have relatively low porosity, and consequently have low permeability.

1. INTRODUCTION

Recent years have seen the development of many new advances in cementitious materials(1). These new advances have occurred as a result of manipulating the microstructure and controlling the chemistry or both, of cements. These 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 has been defined as traditional cementitious materials, and the term chemically bonded ceramics (CBCs) has been used to classify these new materials. CBCs are defined(2) as ceramic-like materials formed as the result of chemical reactions occurring at or near ambient temperatures.

These new novel cements or CBCs follow the general rules of behavior of cementitious materials in certain respects: The solidification of cement with water to yield normal hardened cement pastes takes place with little volume change. When high-density cement particles are mixed with low density water, they react to form a solid hydration product consisting of solids of intermediate density and interspersed residual porosity. The strength of hardened cement paste increases as the ratio of water to cement (w/c) is reduced (3). Because the residual porosity, its distribution, and the excess uncombined molecular water are responsible for most of the limitations on the properties of conventional hardened cement paste (4,5), many attempts have been made to reduce the amount of water used in processing. However, there is a practical limit if the mixture is to remain workable. The situation has changed beginning in about 1970, as new approaches have led to the development of more advanced cement matrix composites (1). Major advances have taken place in the following areas: (i)

the formation of specially densified or warm-pressed, ultra-high strength cement pastes that have properties approximating those of fired ceramics (5); (ii) the modification of the chemical composition of the cement (6); (iii) the formation of strong macrodefect-free (MDF) cements prepared by special processing (7, 8); (iv) the development of CBCs with new and different compositions and (v) the design and manufacture of a variety of cement-based composites. In this treatment, we shall limit the latter composite concept to include only the use of fine particle cementitious components. Additional materials mentioned will be (vi) alkali activated cementitious materials and (vii) belite sulfoaluminate cements. The latter type materials have great potential for benign energy-conserving processes. We shall discuss briefly some additional advances in processing of CBC materials, including (viii) microwave processing, and its application to formation of phosphate bonded materials, as well as calcium aluminosilicate CBC's.

Furthermore, such advances have begun to make possible applications in a number of diverse areas, ranging from very specialized exotic materials to bulk concrete for (ix) waste management (both hazardous and nuclear).

2. DENSIFICATION BY PRESSURE AND HEAT

The bonds limiting the strength of cement paste are normally thought to be weak van der Waals forces. However, one might expect materials prepared under conditions involving dissolution and diffusion reactions which result in a dense interlocking microstructure to be somewhat stronger. Before 1970, the potential strength of cement paste at theoretical density (possibly related to Powers "intrinsic strength") (4) had never been approached, because considerable porosity (20 to 30% or more total porosity) always remained after complete hydration of the cement. Following this, research resulted in achieving very high strengths by "warm pressing", strengths an order of magnitude higher than those of normal cement pastes. Compressive strengths (s_C) up to

650 MPa (compared to the more typical 30 MPa) tensile strength (s_T) up to 68 MPa, and values of Young's modulus (E) up to 40 GPa were attained. Highest strengths were attained when the materials which also contained colloidal sized particles. These dense cementitious materials are microcomposites consisting of about 50% residual anhydrous phases surrounded by interstitial hydrous calcium silicates and aluminates of both crystalline and noncrystalline varieties. Enormous increases in strength resulted from the removal of most of the porosity and the generation of very homogeneous, fine, microstructures with porosities as low as about 1.7%. Micrometer-sized flaws were visible occasionally in the microstructure, for example, along residual grain boundaries.

3. MACRODEFECT-FREE CEMENTS

3.1 General

The warm-pressed cements, discussed in the previous section, were successful, but were not easy to produce in large amounts due to the high pressures used. The next step was to develop more easily processed materials. Another innovation was the engineering of a new class of high-strength materials (the so-called macrodefect-free (MDF) cements) originated by Birchall and co-workers at Imperial Chemical Industries and Oxford University (9-14). MDF refers to the absence of relatively large voids or defects which are usually present in conventionally mixed cement pastes because of entrapped air and inadequate dispersion, limiting the strength, by acting as stress concentrators (9-14). In the MDF process, 4 to 7% of one of several water-soluble polymers is added as a rheological aid to permit cement to be mixed with very small amounts of water. Subsequent high-shear mixing produces a plastic, cohesive mixture which can be shaped by extrusion or other forming technique and which sets in times ranging from minutes to hours. The highest strength materials have been prepared with calcium aluminate cements, which harden rapidly, although portland cements have been used less successfully.

Besides being a processing aid, the polymer constituent appears to be a significant structural component. Control of the particle size distribution (for optimum particle packing) was also considered important for generating strength. A final processing stage, in which entrapped air is removed by applying modest pressure (~5 MPa), or heating at at 80°C resulted in a paste that is free of large defects with excellent mechanical properties, and easily fits within the category of CBCs. A volume decrease of 9% occurred with heating, which could be the result of the polymer shrinkage, reflecting a collapse of the colloidal porosity. Very low porosities were achieved (<1%) (15) as well as flexural strength of ~ 150 MPa, a compressive strength of ~300 MPa, and a Young's modulus of 50 GPa.

Figure 1 compares the flexural strengths observed (8) in normal portland cement paste, portland cement based MDF and calcium aluminate cement-based MDF as a function of flaw size. Young and co-workers (15) have reported upper limit strengths of approximately 300 MPa for calcium aluminate systems and 150 MPa for portland cement systems. The offset of the curves for the portland MDF, as compared to the ordinary portland cement paste at the same flaw sizes is interesting. This suggests that the higher strengths observed in these systems are not due simply to a reduction in the flaw sizes and that the polymer phase may be contributing significantly to strength development.

The term, macrodefect-free, should not be interpreted as implying pore-free systems. Porosities (by mercury porosimetry) of up to twenty percent are not unusual for MDF materials prepared from portland cements (MDF-PC); however, for MDF materials prepared using calcium aluminates (MDF-CA) much lower porosities (1-5%) are typically observed.

Li et al. (16) contrasted the behavior of an inert filler, corundum (plus lime) with that of cement in preparing MDF materials. They investigated corundum, polyacrylamide, lime and water mixtures and reported flexural

strengths in excess of 80 MPa, only slightly lower than MDF cements prepared in a comparable manner. In contrast, simply replacing portland cement with ground quartz (17) did not produce an MDF cement body with typical MDF cement characteristics.
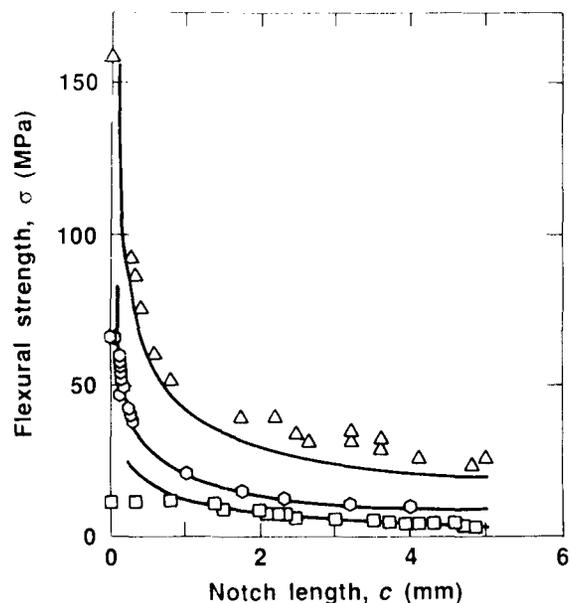

Figure 1. Notched beam test of the flexural strength of cement pastes. Curves are theoretical fits to the data. Bottom curve (squares) normal portland cement paste, middle curve (hexagons), portland MDF; upper curve (triangles), calcium aluminate MDF (8).

3.2 Influence of Moisture

The problem of the detrimental influence of moisture on MDF cement is now well established, and has been reported in several studies (9-20). The importance of the final drying step at 80°C in calcium aluminate MDF cements is to remove all traces of moisture and provide high strength. When an MDF material is exposed to moisture, the polymer phase, which may constitute up to 30% on a volume basis, swells and softens. Uchiyama (9) investigated the effect of repeated wet-dry cycling on the flexural strengths of MDF-PC, observing that the wet strengths increased with repeated cycling while the dry strengths remained more or less constant. Park et al. (20)

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investigated the effect of acetone-water mixtures on the flexural strengths observed in MDF-PC, finding that when even a small amount of moisture was present in the mixtures, the strengths were drastically reduced and that the loss in strength was accompanied by an expansion in the MDF-PC.

Others have examined the hydration of the cementitious portions of MDF materials. Rodger et al. (22) used infrared spectroscopy to examine the molecular interactions in MDF materials, suggesting that a calcium acetate forms as the result of the interactions between PVA and Secar 71. Maes (23) examined the Raman spectra of polyacrylamide gels containing Na or Ca hydroxide and concluded that Ca^{2+} formed real cross-links while Na^+ forms no permanent cross-links or chain entanglements; differences in the viscoelastic behavior of the gels that were observed were dependent on the cross-linking ion (23).

Approaches to improving the moisture resistance of MDF materials have included developing water-resistant MDF cement (24) by incorporating an isocyanate compound to cross-link the PVA molecules through urethane bonding. Russell et al. (18) have generated improvement in water resistance of MDF (PVA-CA) cements by silane treatment, while boric acid and Quilon L were less successful in promoting enhanced cross-linking. Park et al. (20b) have recently examined the effects of certain inorganic additives on the structure change and cross-linking, showing that even monovalent cations enhance reaction, (Figure 2) and appear to promote reaction and cross-linking. Accompanying IR absorption spectral studies have been made to follow structure change.

Dielectric properties of MDF cements have been investigated by a number of authors (25, 26, 15) with a view of applications for electronic substrates. Dielectric constants as low as 5.3 (14) were achieved in CA/PVA MDF cements filled with silica, while use of hollow microspheres in sintered CA/PVA composites resulted in a dielectric constant below 3 (25).

3.3 Summary

It is clear that the role of the polymer phase in MDF materials is not simply that of a rheological aid, but the polymer phases interact with the cementitious phases by a variety of means. It seems that many of the properties and characteristics of MDF materials are heavily influenced by the metal cross-linked polymer gels. It seems reasonable that the inorganic portion of these composites forms a semi-rigid network around which the metal cross-linked polymer gel forms. Thus, the final composite shares many of the properties and characteristics of metal cross-linked organic polymer systems and inorganic cementitious systems in a single material (27). Advances in controlling hygroscopicity have been achieved, but much work remains to be done. Nevertheless, the risks attendant in developing applications for these novel materials are rapidly diminishing. The next few years should see a further gradual introduction of components made from MDF cements into the market place.
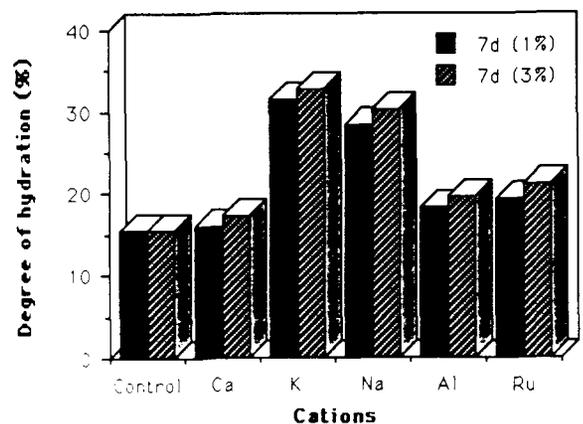
Figure 2.   Degree of hydration of portland cement in MDF cements as a function of cation (oxide) additions. Al is from Alum; Ru is sodium silicate.

4. DSP AND OTHER DENSELY-PACKED SYSTEMS

4.1 General

An important class of new materials termed DSP (Densified Systems containing homogeneously arranged, ultra-fine Particles) was first elucidated in detail by Bache (28), following earlier studies mostly in Scandinavia. (15, 29-32). The "new" class of materials is defined as materials with a matrix comprising, or formed from, 1) densely packed particles of a size ranging from 0.5 to 100μm, usually cement, and 2) homogeneously arranged, ultra-fine particles ranging in size from about 50Å to 0.5μm, usually silica fume, arranged in the spaces between the larger particles. The shaping of the fresh material is typically performed from a viscous mass in a low stress field achieved by reducing the surface forces between adjacent particles by means of dispersing agents. The combination of densely packed cement and silica fume was found to be fortuitous for a combination of reasons (28):

1) The silica particles are smaller than even the finest cement produced by grinding, and therefore, pack more easily into the spaces between the cement particles.

2) The silica particles are spherical in shape.

3) The particles are chemically less reactive than cement, which eliminates the problem of too rapid hardening encountered with very fine cement.

4) Finally, with added dispersing agents, a low water requirement may be achieved.

Numerous investigators have contributed to the understanding of the effects of fine particles in densely-packed cementitious materials, including (15, 16, 31-34). Cohen et al. (16) calculated that for a 15% silica fume replacement of cement there are approximately 2,000,000 particles of silica fume for each grain of portland cement in a concrete mixture. Concretes containing 5 to 15% silica fume have high compressive strengths (up to and above 100 MPa), flexural strengths (up to 12 MPa), and Young's moduli (up to 34 GPa), and also have very low permeabilities to water (10^{-9} μm^2). The microstructure of the critical interfacial zone between cement paste and the aggregates in concrete is more dense and uniform than when conventional pastes are used, and the bond between paste and other embedded materials such as aggregates and fibers appears to be improved.

The most striking results, however, have been found with silica fume-substituted pastes, and DSP systems. Compressive strengths of up to 270 MPa or higher with Young's moduli up to 80 GPa were achieved in preparations with up to 20 to 25% silica fume at a water to solids (w/s) ratio of 0.12 to 0.22 through mechanical compaction. A dense but fairly fluid paste is formed by the combination and chemical dispersion of particles that have dissimilar size ranges. No major air voids remain in products that are processed properly, as hydration proceeds, and only a few small "capillary" pores exist. Such materials are used to resist severe mechanical erosion in impeller screws for moving coal and fly ash and in flooring to industrial area. Another version is commercially available as a tooling and molding material in applications where vacuum tightness or mirror finishes are required. The latter material (Table 1, last column) retains a compressive strength of ~300 MPa up to about 500°C and ~200 MPa at about 700°C.

4.2 Silica Fume Hydration Reactions

Properly dispersed silica fume particles when used in proportions to replace up to 10% of cement significantly reduces bleeding and segregation of the mixtures, and may be used in higher proportions. Although aqueous slurries of silica fume may be prepared without superplasticizing admixtures, the resulting cementitious mixtures usually require higher w/c ratios. Because of their very high surface

area, early reaction of the fume takes place with the alkaline cement pore solution.

Silica fume contains particles as fine as 0.1 μm or less which partially dissolve in saturated $Ca(OH)_2$ solution in a time as early as 5 to 15 minutes, and a SiO_2-rich hydrate is deposited in layers or films on the silica fume particles. This lower C/S ratio tends to be confirmed in reports of Taylor (42). Diamond (43), Glasser (44) and Roy (45) have described the changing composition of pore solutions with longer time periods, which reflect the hydration processes occurring beyond the early ages. Despite the early rapid reaction, however, much silica fume remains for later slow reaction. For example, Li et al. (46) showed from selective dissolution experiments that, while much SF is reacted in a SF-OPC mixture at 7 days, considerable unreacted SF remains. The early heat of hydration of silica fume-containing mixtures is frequently equivalent to that of high-early-strength cement, although the rate at which heat is liberated depends upon the proportions, and the w/c ratio.

The heat of hydration, measured by isothermal calorimetry is shown to increase relative to pure cement by addition of silica fume when rationalized with respect to the amount of cement. See Figure 3. Using selective dissolution procedures, Li and Roy (46) have found in cement-SF mixtures that half of the silica fume (with 10% SF-90% cement) was hydrated in one day, and two-thirds during the first three days, although thereafter the hydration proceeded slowly. Between 28 and 90 days, additional hydration took place.

The fume particles also play an important role in various composites, when they surround each cement grain, densifying the matrix, filling the voids with strong hydration products, and improve the bonding with aggregates, and reinforcing materials such as glass fiber. Silica fume by reacting with alkali also affords a protection against the alkali-aggregate type reaction occurring between a cement pore solution and glass fiber.

4.3 Particle Packing in Concrete

Elsewhere (28, 48-51) the same principles of particle packing have been applied to other types of materials. The Toufar/Aim (49-51) model of dry particle packing has been verified as adequately modeling the dry packing of mixtures of powder, each with a different size distribution. Typically, in the model, materials with three different size distributions may be mixed. Furthermore, the characterization of the size distribution can be modeled by a commonly used procedure described by Rosin-Rammler (51).
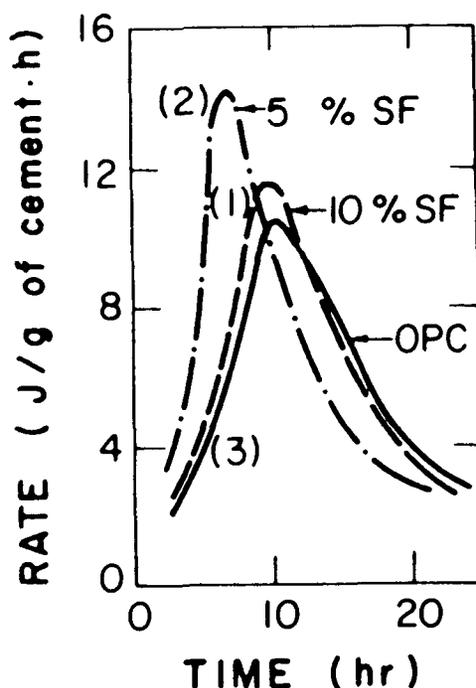

Figure 3. Heat evolution during hydration of cement with 0 and 10% silica fume, and 5% ultra-fine aerosil (46 b.)

Table 1.   Comparison of mechanical properties of cement particle composites; MDF, Warm-pressed, and Several DSP Type Materials.

Cement particle composite	σ_T (MPa)	σ_F (MPa)	E (GPa)	σ_c^* (MPa)
1. Ordinary cement	~5	6	15	40
2. MDF cement		40-150	35-50	100-300
3. Warm-pressed dense-fume mortar	68		27-41	300-650
4. Slag mortar 81-20[i]			48	180
5. Steam cured 82-11[ii]			50	250
6. Steel aggregate steam-cured mortar[.]	28		49	250-350
7. Chopped steel, fiber high temp. steam-cured DSP/CBC	75			500

* Compressive strength.   [i] See (36); [ii] See (37); [.] See (38) and * See (39 and 40)

Input to this PC-based algorithm consists of the experimentally determined tap density of each component and the characteristic diameter of the distribution as described by D' in the Rosin-Rammler fitting equation. The results of applying this algorithm to concrete systems have provided the mathematical basis for formulating concrete mixtures which were developed through field experience in the practice of concrete placement. Its applications should prove useful in monitoring the quality of concretes in the design stages and to adjust the components of the formulation to maximize performance.

4.4 Discussion and Summary

The particle packing and hydration reactions in DSP cement pastes are responsible for the fine microstructural development. These complex reactions involve phase solubility, accelerating and retarding effects of a multiphase, multi-particle size distribution material, and surface effects at the solid-liquid interface. This particle packing combined with

chemical reaction is extremely important for developing strength. The initial degree of dispersion of cement and fume in the paste strongly influences the development of the final hardened paste microstructure. The ultra-fine particles can fill the intergranular interstices and produce a denser paste structure, reflected in a very high strength. Superplasticizers should be used to minimize the water demand and adequately disperse the fine particles, resulting in dense products with fine pore size (52, 54), very low permeability (52, 53), and low ionic diffusivity. Despite the rapid early hydration, much silica fume remains unreacted until a later stage (46, 47).

Physical and chemical characteristics together influence the hydration kinetics. Silica fume ordinarily accelerates the early portland cement hydration, largely because of its very high surface area, increasing the heat development and resembling a high early strength cement. Fume also disperses the hydration product, provides for deposition of

The mechanical properties of some high-strength DSP-type materials have been summarized earlier in Table 1 (numbers 4-7) where they are compared with normal cement paste, MDF cement paste, and warm-pressed materials.

5. ALKALI-ACTIVATED CBC/CEMENTITIOUS MATERIALS

5.1 General

Blended cements have not always been popular in applications where rapid setting times and early strength development are required, due to their relatively slow rates of reaction. One possible remedy is the use of alkali additions, for many years applied to activate the latent capabilities of certain pozzolanic materials. The F-cements of Finland (55a) and related (56) cements are the result of this technique being employed, to produce materials typically requiring approximately 30% less water than conventional cements, resulting in lower total porosities. The CaO/SiO_2 (C/S) ratio is adjusted such that there is no free calcium hydroxide remaining in the hydrated material. Two main disadvantages are longer mixing times and smaller batch sizes, due to stickiness and special handling requirements because of the highly alkaline nature of the activators.

Three classes of activators are used (56): 1) caustic alkalis; 2) non-silicate salts of weak acids; and 3) silicate salts; and more recently other, perhaps less alkaline, materials such as high alumina cements and aluminum sulfates (57) have been investigated as activators for slags. The hydration of the slag generally requires the breaking of bonds and dissolution of the three-dimensional network structure of the glass, requiring dosages (56) in the range of 3-10% of NaOH, as Na_2O The network contains interlinked SiO_4 and AlO_4 tetrahedra and AlO_6 octahedra which are attacked by the OH-ion in a high pH environment. When the pH of the liquid phase is kept at approximately 12 and sulfate ions coexist, a well-crystalized calcium sulfo-aluminate can be produced (38) or zeolitic hydro-aluminosilicates that have the general formula:

$$R_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot nH_2O \qquad (1)$$

With normal short-term curing, x will be approximately 2, while with longer curing times or steam curing, x will be in the range of 2 $\leq$ x $\leq$ 3 and with long-term steam curing x will approach 4. Under normal curing conditions, the reaction products will be mostly noncrystalline; however, they increase crystallinity with long curing times, especially at elevated temperatures. Combinations of conventional hydraulic cements with one or more of the class of latent hydraulic materials (i.e., fly ash, blast furnace slag, silica fume, etc.) plus a small amount of activator can lead to materials with high early strength and enhanced durability and/or strength.

New hydraulic compositions have been developed recently, utilizing many of these features in combination to make a new type of cement. One type of composition is commercially available, the outgrowth of work on alkali-activated aluminosilicate materials originally inspired by studies of ancient building materials (57). The new formulations are very early high strength cements which combine rapid strength development with relatively high later strength. Silica fume, in common with its role in DSP cements, has been found to be particularly useful in formulations we have studied (55b, 58, 59).

5.2 Reactivity and Strength Development

The accelerated hydration of alkali activated cements is illustrated in Figure 4, while an illustration of typical strength development is shown in Table 2 (55b). We and others have developed dense, low water/cement ratio formulations, employing alkali activation to shorten the setting times and increase the rate of strength development.

Table 2. Compressive strengths (MPa) for three alkali-activated cements and portland cement cured at 25°C, at W/C = 0.25 (standard deviation in paranetheses); normally cast.

Time	Portland Type III	Alkali-activated		
		Commercial	P-14	P-15
5 hours	not set	23.4 (0.4)	23.3 (0.4)	29.1 (0.6)
1 day	83.5 (2.8)	47.0 (0.9)	64.7 (2.9)	63.9 (1.0)
3 days	91.0 (8.7)	59.1 (1.6)	60.1 (1.2)	---
7 days	109.9 (8.3)	69.5 (0.6)	77.3 (9.9)	---
14 days	122.4 (4.6)	78.6 (1.4)	92.4 (5.5)	---
21 days	118.3 (13.1)	82.5 (3.3)	93.0 (1.6)	71.0 (10)
28 days	107.1 (10.1)	84.6 (2.0)	75.2 (4.9)	92.3 (0.8)

Characterization of these materials has been made, using hydration calorimetry, SEM, x-ray diffraction, and mechanical property techniques; the results show that the properties developed early do not deteriorate, but continue to be enhanced with time. These materials have been prepared employing both normal and high-shear mixing MDF processing techniques.

Various activators such as sodium sulfate, potassium aluminum sulfate and alkalis were used in recent studies of more normal blended cement compositions (60). Other additives investigated include superplasticizers (SP), aluminate, or high alumina cement (HAC) (61). The results of these studies confirmed that each of these activators or additives increases the reactivity, under proper conditions, and synergetic effects may be shown due to the combination of additives, increasing early age compressive strength and shortening the setting time.

A typical rate of adiabatic temperature rise during curing of a concrete containing an alkali-activated cement is shown in Figure 4. More recently studies have determined the effects of alkali-activation on individual components of the cements (59b). Figure 5 shows the effects of KOH activation on the pH change of solutions in contact with Class C and Class F fly ashes, granulated blast-furnace slag, and silica fume. As expected, the ultra-fine silica fume is the most reactive. The

microstructure of Figure 6a compares class C fly ash "activated" for only one hour in water, with that in KOH (6b) [1.2 wt % Na_2O equivalent]. Both show the beginning stages of reaction which is not surprising since there are sufficiently soluble alkaline and sulfate phases present in Class C fly ash to induce early reactivity. A greater contrast is seen with Class F fly ash, however, (Figure 7) in which the effect of the KOH solution (7b) is much more pronounced than in water (7a).
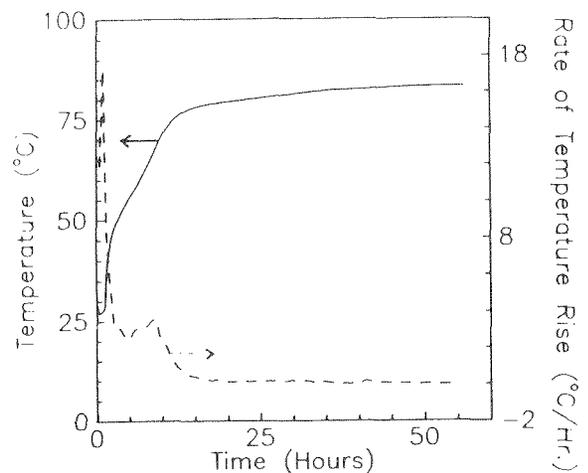

Figure 4. Rate of temperature rise and temperature attained in a commercial akali-activated cement concrete (59).
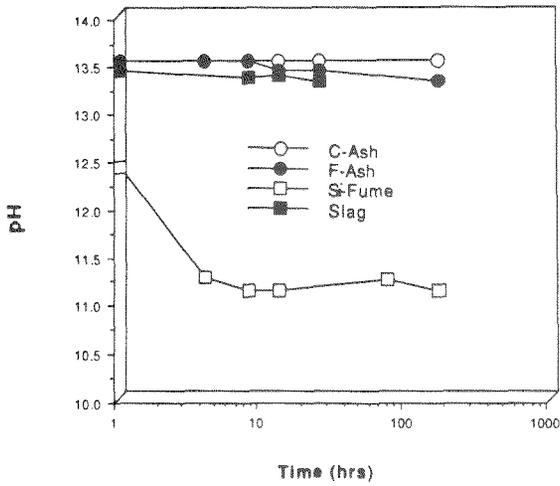
Figure 5. Change of pH with time in KOH solutions in contact with fly ashes, silica fume, and glassy slag.

5.3 Discussion

Overall, the results of the above studies describe a very promising new class of materials. They show that it is possible to combine the advantages of rapid strength development by alkali activation with high ultimate strength, by control of particle packing and chemistry in a single formulation of blended cements containing fly ash, slag and silica fume. More research will be required to fully optimize and characterize the long-term behavior of these materials. One unknown aspect is the effect of the somewhat higher alkali levels on the long-term behavior.

6.0 BELITE CEMENTS AND BELITE-SULFOALUMINATE CEMENTS

OPC (ordinary portland cement) consists mainly of four clinker minerals $C_3S(Ca_3SiO_5)$, $C_2S(Ca_2SiO4)$, $C_3A(Ca_3Al_2O_6)$, and C_4AF $(Ca_4Al_2Fe_2O_{10})$, which are compatible in the four-component system $CaO-Al_2O_3-Fe_2O_3-SiO_2$.
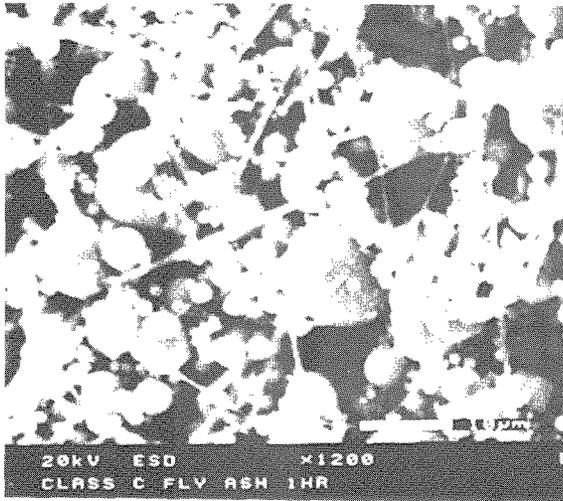
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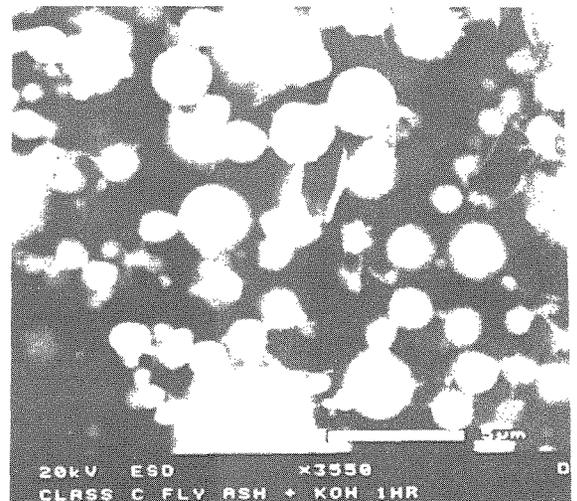
b

Figure 6. SEM of class C fly ash hydrated 1 hour in a) de-ionized water, b) KOH (1.2 wt % Na_2O equivalent).

a

b

Figure 7. SEM of class F fly ash hydrated
2 hours in a) de-ionized water, b)
KOH (1.2 wt % Na_2O equivalent).

The major mineral component C_3S in particular consumes much energy in its production because of the high calcium content (high $CaCO_3$ content of the usual source material) and the high temperature required in processing. In belite cements reactive alpha C_2S takes the place of alite C_3S (in portland cement) as the main source of strength development. The alpha belite forms as the result of thermal quenching of the clinker materials or via the incorporation of either alkalis or sulfates into the C_2S. These materials offer the potential for reduced energy consumption during the production of cement by lowering the maximum clinkering temperature required. Reduction of NO_x emissions is also likely.

On the other hand, the compound $C_4A_3\bar{S}$, ($4Ca_3Al_2O_3 \cdot SO_3$) similar in structure to the natural mineral hauyne, is known to be hydraulic and may be produced at lower temperatures, as may C_2S. Cements which are predominantly a mixture of these two compounds may be produced from alternate raw materials such as blast-furnace slag (with the addition of limestone and gypsum + bauxite).

Sulfoaluminate belite (SAB) clinkers contain phases that are inherently sulfates ($C_4A_3\bar{S}$, $C\dot{S}$), so ashes high in sulfate content may be a valuable source material for their production. Development of cements containing the sulfoaluminate phase began in the middle 1970s (62-64) and there is now extensive literature in this field.

By "SAB clinkers" is meant primarily those containing the phases C_2S, C_4AF, $C_4A_3\bar{S}$, and $C\bar{S}$ (65). In addition to utilizing sulfates in such clinkers, the C_4AF phase makes possible the consumption of iron-containing byproducts from the environment. They offer the great advantage of low burning temperature, approximately in the range of 1200°-1300°C, rather than the 1450°C range of portland cement clinkers.
SAB clinker cements are a special variation of belite cements which have been used as repair materials or in grouting applications (67). In contrast to cements relying on belite alone these cements show early strengths superior to those observed in conventional materials. Such cements, among others have

alone these cements show early strengths superior to those observed in conventional materials. Such cements, among others have the potential for better resource utilization. These cements have great potential for both their energy and resource conservation because they may utilize by-product or waste materials in their production (63, 65, 66, 70, 71). For example, the fly ash from fluidized bed combustion is normally not suitable as a raw material for cement manufacture, because of high sulfur content. Calcium sulfoaluminate belite cement clinkers may provide a way to make this fly ash usable as a cement raw material. A well-known computational technique can be used to identify mixture/phase composition relationships for the raw materials (71).

Table 3 lists some compositions of by-product materials which may be combined to illustrate the potential for using phase change diagrams to calculate potential cement compositions, while Figure 8 illustrates the use of calculated phase composition diagrams (using a Modified Bogue calculation method). This method identifies combinations of five compatible phases in the five-component system. The range of approximately 37-45 wt% of TVO_5 ash would be the best proportions for a SAB clinker (71).

Other recent studies have demonstrated the potential of hydrothermal processing in the utilization of fly ash and FBC ash (72, 73).

7.0 PHOSPHATE CBC's

7.1 General: Microwave Processing

Recent studies in this Laboratory have also focused on the synthesis, equilibria, reactions, and bonding mechanisms in phosphates within the system CaO-ZnO-Al_2O_3-P_2O_5-SiO_2-H_2O (1b, 74-76). These include studies of means of achieving accelerated reaction and densification or bonding in ceramic materials. Microwave energy used to process a variety of materials is still in the early stage of research and development. In the microwave process, heat is generated internally within the

material instead of originating from external heating sources as in the conventional heating. This offers many possibilities for heating shapes very rapidly and uniformly; to efficiently remove volatile constituents (binders, moisture, etc.) from thick sections; and to reduce thermal stresses that cause cracking during processing. Microwave processing can be used as an attractive and economic alternative for sintering of ceramics.

7.2 Hydroxyapatite Ceramics

Hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2$, HAp] ceramics have been investigated for years for biomedical application and are very promising, but microwave sintering of HAp ceramics has only recently been achieved (74, 75). Deliberately porous hydroxyapatite ceramics have been fabricated with porosity up to 73% by microwave processing at 1150 to 1200°C for 1 to 5 minutes. Various porosities in these ceramics have been obtained by using starting
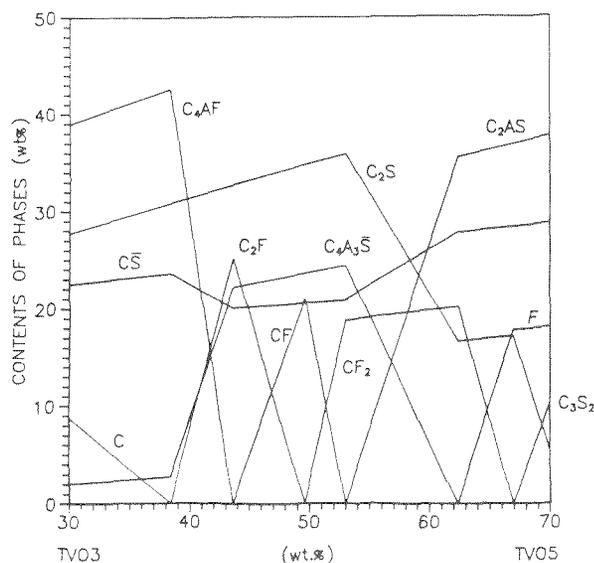
Figure 8.   Change in the mineralogical composition of clinkers for the TVO_3-TVO_5 (see Table 3) raw mix, depending on the raw mix composition (71).

materials with different morphology, adjusting green density, and changing sintering time and

Dense sintered hydroxapatite ceramics have been successfully fabricated by microwave sintering in a 600W microwave oven. A temperature as high as 1415°C was reached and the ceramics were highly sintered with relative density of 93% (74).

Studies have also been made of the acceleration of reactions in the synthesis of hydroxapatite by means of ultrasonication (76).

Other recent efforts have addressed the effect of composition and processing conditions on the microstructure of zinc phosphate-based CBC's in the system $ZnO-MgO-CaO-P_2O_5-SiO_2-H_2O$ (77).

8.0 CEMENTS FOR WASTE MANAGEMENT

8.1 General

The role of cementitious materials in nuclear and hazardous waste management has been summarized in recent review papers (78, 79). Several factors stand out in serious attempts to predict their performance. The durability of cementitious materials in waste disposal applications (encapsulants, sealants) is most directly affected by the transport of fluids to and from the cementitious matrices. The design of a durable cementitious material in the broadest sense must control two major aspects; the physical behavior of the material and the chemical behavior of the hydrating matrices. In practice, neither can be totally isolated from the other. The physical properties of cementitious materials are determined by control of particulate size distributions of the components, and the placement and processing variables. The hydration behavior and chemical durability are a result of selection of components based upon their chemistry and reactivity, and also reflect interaction with the environment where it will be used. Synergistic effects are common between the chemical and physical aspects and can often be used to enhance the performance of the material.

Permeability and leaching characteristics are major properties of the matrix which control the rate of degradation. Low permeability can be associated with either or both low porosity or more importantly a pore size distribution fine enough to minimize the transport of fluids. Further, low permeability can be controlled by the distribution of sizes of the constituent components of the cement, rate of the hydraulic reaction, interactions with other components of the cementitious system, and processing methods as well as the use of processing aids. Insolubility of the matrix combined with low permeability prevents or retards the release of hazardous radionuclides or hazardous species to the leachate.

8.2 Bulk Chemistry Effects

To ensure maximal durability of a cementitious object, the matrix must be designed to exhibit minimal solubility. For

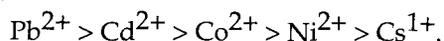Table 3.   Composition of Selected By-Product Materials

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O
TVO3	45.1	3.2	2.7	4.8	6.5	0.6	0.3	0.3
TVO5	22.6	15.3	15.0	18.9	17.3	0.5	1.9	0.3

cementitious systems, based on portland cement and cured at ambient conditions, this objective is achieved by controlling the Ca/Si ratio of the anhydrous cement phases and the reactive mineral admixtures. Work conducted by Barnes et al. (80) has demonstrated that a minimum in leachability exists for a Ca/Si ratio of 1.0, increasing as the ratio is changed in either direction.

Simulated wasteforms have been developed based on numerous studies in which the host matrix was chemically modified by the additions of reactive silica. The principal chemical effect introduced is minimization of the formation of portlandite $(Ca(OH)_2)$ as a hydration of product of alite (Ca_3SiO_5) and belite (Ca_2SiO_4), and the enhancement of the C-S-H gel formation.

This type of modification also can exert a minimal control over pH of the pore fluids. Table 4 summarizes some leach rate data for an OPC waste form contrasting the chemical effect of adjustment to the results with OPC. Typical pH control amounts to lowering by about one half of a pH unit. Dramatic reductions of leach rates for hazardous ions can be achieved as demonstrated by the approximately 20-fold reduction for Cs^+ leaching found in this study. Certain materials, either added to the cementitious matrix or formed during hydration, have the effect of exchanging ions between the phase itself and the pore fluids, usually reducing solubility. Data reported by Komarneni et al. (81) have shown that tobermorite phases formed with maximal aluminum substitution are extremely efficient in exchanging both radioactive and hazardous cations. They report the ranked order of selectivity as being:

$$Pb^{2+} > Cd^{2+} > Co^{2+} > Ni^{2+} > Cs^{1+}.$$

8.3 Summary

The success of cement-based waste forms in retaining radioactive and hazardous ions species can be attributed to the porosity of the wasteform combined with the solubility of the species concerned. Through these avenues transport from the interior to the surface is the most probable and it is also through this structure that aggressive external fluids can penetrate deeply into the cementitious matrix. Therefore control over the effect of exchanging ions between the phase porosity and size distribution of this porosity will impact the behavior of the waste form. Tailoring the bulk chemistry and phase chemistry (as well as minimum solubility) of the cementitious matrix to achieve optimum porosity can be achieved. This utilizes a knowledgeable selection of reactive mineral and chemical admixtures based both upon the chemical and physical properties of the admixture. Further, the synergistic effects among properties of the waste forms must be understood and accounted for if the waste forms are to perform as anticipated.

9. CONCLUSIONS

Major advances have been made in several properties of advanced cement/chemically bonded ceramics (CBC) materials of widely ranging compositions having much potential in modern technology. After a general discussion of progressive developments, in this paper, we have focused on high performance, strong, high density

Table 4. Effects of chemically adjusting the cementitous matrix with added silica on pH and leaching rate. OPC = ordinary portland cement, ADJ = adjusted.

Adjusting	OPC	ADJ
Lowers pH	11.3	10.8
Lowers A1 leaching*	3	0.7
Lowers Cs leaching*	5.8	0.24

materials of the pressed, MDF, DSP, alkali-activated, advanced energy or resource conserving varieties. The latter include belite cements and belite-sulfoaluminate cements. Other phosphate CBC's are also included.

A number of key properties have been investigated, and very high strengths have been attained. Certain of these materials are already being used in novel applications, which include, but are not limited to, those depending on chemical properties. Examples of potential applications are given below in Table 5.

The future of CBC's faces the challenge to better understand the mechanisms involved in generating strength and toughness, the effects of compositional and microstructural modifications, and the range of methods and parameters which control the properties of such composites. Major future challenges include the dual focus on high performance cementitious materials, along with the development of more environmentally benign cements, the effective utilization of various types of mineral by-products in cementitious materials, and the applications of the above to solve waste management problems. A third focus must be emphasis on the prediction of long-term durability. Such knowledge will open further horizons in the field of synthesis of new cementitious materials.

ACKNOWLEDGMENTS

Table 5.   Potential Applications of CBCs and Their Composites

- Acoustics
- Biomaterials
- Cryogenics
- Tooling, molding materials, machine beds
- Armor/impact resistance
- Electro-magnetic radiation screening
- Electronic packaging
- Fire-resistant application
- Erosion-resistant materials/stilling basin
- Rapid repair materials; road overlays
- Boards, panels, claddings; machinable components; permanent forms
- Nuclear and hazardous waste management
- By-product utilization; resource conservation

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