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Introductory Chapter: Properties and Applications of Cement-Based Materials

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1. Introduction

Cement-based materials have been used to support human civilizations many decades ago. With the increasing advancement of human activities, these materials were modified to maintain their roles in our lives. The main function of cement is to act as hydraulic binder, which increases the bond between fragmented particles, so it can enable their use in different fields. The resulted material will have different physical and mechanical properties from the initial materials. These changed properties are attributed to the exothermic hydration reactions that are initiated upon mixing the binder with water. The liberated localized heat will lead irreversible rearrangement of water molecules within the framework microstructure [1–3]. Ordinary Portland Cement (OPC) is the most widely used cement. It is prepared by crushing, milling, and mixing calcium, iron, silica, alumina, and sulfate sources with certain amounts. Then, hydraulic cement is passed to the kiln to produce clinker, which is subsequently cooled and pulverized. Portland cement is categorized into eight subgroups according to the ASTM C150, namely normal (type I), moderate sulfate resistance (type II), high early strength (type III), low heat of hydration (type IV), high sulfate resistance (type V), normal, moderate sulfate resistance, and high early resistance with air entraining (types IA, IIA, IIIA), respectively [4]. There are four principal unhydrated phases present in all OPC types, namely tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_5$), and calcium aluminoferrite ($Ca_4Al_nFe_{2-n}O_7$). The formula of each of these minerals can be broken down into the basic calcium, silicon, aluminum, and iron oxides (**Table 1**). Cement chemists use abbreviated nomenclature based on oxides of various elements to indicate chemical formulae of relevant species, that is, C = CaO, S = SiO_2, A = Al_2O_3, and F = Fe_2O_3. Hence, traditional cement nomenclature abbreviates each oxide as shown in **Table 1** [1].

The composition of cement is varied depending on the application. A typical example of cement contains 50–70% C3S, 15–30% C2S, 5–10% C3A, 5–15% C4AF, and 3–8% other additives or minerals (such as oxides of calcium and magnesium). It is the hydration of the calcium silicate, aluminate, and aluminoferrite minerals that cause the hardening, or setting, of cement. The ratio of C3S to C2S helps to determine how fast the cement will set, with faster setting occurring with higher C3S contents. Lower C3A content promotes resistance to sulfates. Higher amounts of ferrite lead to slower hydration. The ferrite phase causes the brownish gray color in cements, so that "white cements" (i.e., those that are low in C4AF) are often used for esthetic purposes. The calcium aluminoferrite (C4AF) forms a continuous phase around the other mineral crystallites, as the iron containing species act as a fluxing agent in the rotary kiln during cement production and are the last to solidify around the others. **Figure 1** shows a typical cement grain.

It is worth noting that a given cement grain will not have the same size or even necessarily contain all the same minerals as the next grain. The heterogeneity exists not only within a given particle, but extends from grain to grain, batch to batch, and plant to plant.

Modifications of cement-based materials are usually carried out by testing the effect of different additives and/or admixtures on certain physicochemical properties that can affect the overall performance of the material [1, 3]. Additives might be classified based on their [3]:

1. Origin—natural igneous, natural sedimentary, industrial waste, or modified soil

2. Particle size—coarse or fine

3. Density—light or heavy

4. Activity—inert, chemically active, physically active, and physically and chemically active

5. Specific surface—low, average, high, ultra, and nano dispersion.

Depending on the amount of used additive to cement ration, cement-based material could be divided into blended cement or modified cement. Blended cement is a class of additive-cement system that contains more than 15% additive. ASTM identified five classes of blended hydraulic cement as follows: Ordinary Portland Cement (OPC)-blast furnace slag (IS type), OPC-Pozzolan (IP and P types), Pozzolan-modified-OPC (I(PM) type), Slag cement (S type), and Slag-modified OPC (SM type) [4]. Modified cement contains less than 15% mineral additives. On the other hand, there are different classifications for the tested/used admixture as follows [2, 3]:

Mineral	Chemical formula	Oxide composition	Abbreviation
Tricalcium silicate (alite)	Ca_3SiO_5	$3CaO.SiO_2$	C3S
Dicalcium silicate (belite)	Ca_2SiO_4	$2CaO.SiO_2$	C2S
Tricalcium aluminate	$Ca_3Al_2O_4$	$3CaO.Al_2O_3$	C3A
Tetracalcium aluminoferrite	$Ca_4Al_nFe_{2-n}O_7$	$4CaO.Al_nFe_{2-n}O_3$	C4AF

Table 1. Chemical formula and cement nomenclature for major unhydrated OPC phases.

1. Their effects on setting time and water requirements: ASTM C494, BS 5075, and CAN 3A2662M78 classify admixture according to their role in reducing the amount of water only or reduce the waste and act as retarders or accelerator.

2. Their technological characteristics: used in France, Germany, and Russia where the admixture effect on the setting time, rheology, air content, hardening, workability, cement properties and special properties are used to classify the admixture.

3. Classification is based on the chemical properties of the admixture themselves, that is, soluble and insoluble in water. Under this classification, the admixture is categorized based on their effects.
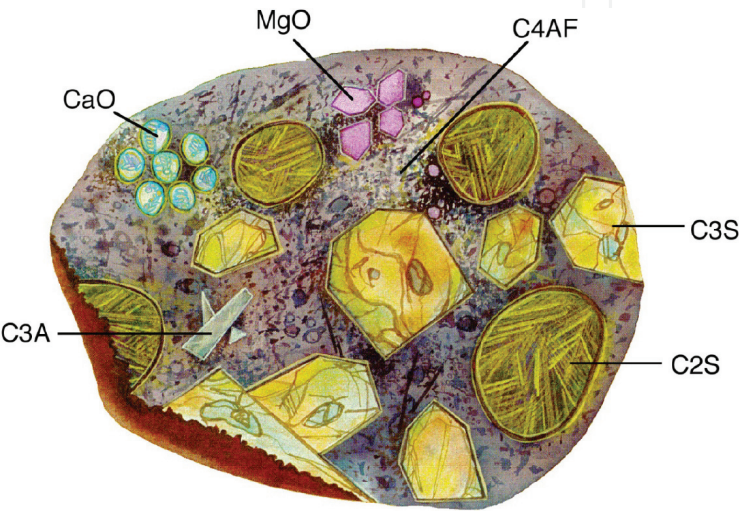

Figure 1. A pictorial representation of a cross section of a cement grain. Adapted from Cement Microscopy, Halliburton Services, Duncan, OK.
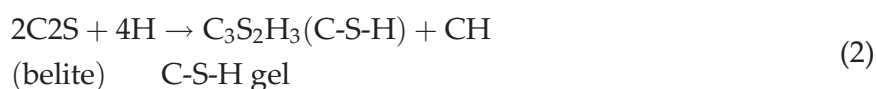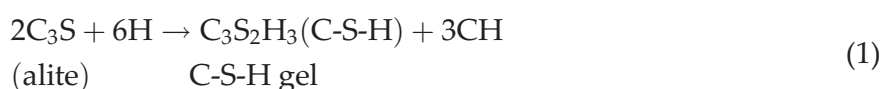
	Aluminates	Phosphate	Sulfoaluminate
Components	Calcium source Limestone Alumina source bauxite, high-alumina slags	Acid-base reactions in the presence of liquid activators containing phosphate anions	Calcium source: lime, Alumina source: bauxite, kaolin Sulfate source: gypsum
CO_2 emission	Low	—	Low
Setting	Fast	Fast	Fast
Strength	High	High adhesive, bending and compressive strength	High early strength
Working condition resistance			
Freeze–thaw	High	—	High
Heat	High	High	—
Chemical	High	High	High in sulfate and magnesium

Table 2. Comparison between different alternative cement and OPC properties.

Almost all the historical applications of cement as hydraulic binders relied on the use of pozzolanic materials with additives, and currently, alternative cements were developed to substitute Ordinary Portland Cement in certain application or to overcome Portland cement drawbacks. These materials include aluminate cements, phosphate cements, sulfoaluminate cements, and alkali-activated cements [3]. The later represent a vast category of subsets of materials that differ based on the alkaline activator of the aluminosilicate system. **Table 2** lists a comparison between the aluminate cements, phosphate cements, sulfoaluminate cements, and OPC [3].

2. OPC hydration chemistry

The hydration reactions of cement-based materials are complex, especially when chemically active additives/admixtures are used. However, it is generally accepted that the principal products of hydration of OPC are calcium-silicate-hydrate gel (CSH), which composed of mixture of tobermorite, jennite, and afwillite (60–70%); portlandite (CH) (20–25%); and other minor phases (approximately 5–15%) [1]. The principal reactions involved may be represented by the following two idealized equations:

$$2C_3S + 6H \rightarrow C_3S_2H_3(\text{C-S-H}) + 3CH$$
$$\text{(alite)} \qquad \text{C-S-H gel}$$

(1)

$$2C2S + 4H \rightarrow C_3S_2H_3(\text{C-S-H}) + CH$$
$$\text{(belite)} \qquad \text{C-S-H gel}$$

(2)

The stoichiometry of these reactions clearly shows that the hydration of 1 mol of tricalcium silicate yields 1.5 mol of Ca^{2+} ions (Reaction 1) and the hydration of 1 mol of di-calcium silicate yields 0.5 mol of Ca^{2+} ions (Reaction 2); these ions are released into pore solution with the formation of C-S-H phase. Cement hydration reaction progression occurs at three distinct periods, which are dormant, setting, and hardening. In the first (within few minutes from the reaction initialization) period, aluminate and ferrite phases react with gypsum to form an amorphous gel at the cement grains surface and short ettringite rods. In the second period (hours later), more portlandite and ettringite are formed and C—S—H formation begins. At the last period, the reaction slows down and internal C—S—H continues to grow near alite surface. The hydration rate is dependent on water and/or ion diffusion rate to anhydrous surface, so the timescale for each period and the development of hydrated phases in each time period are dependent on the hydration conditions, cement composition, and the presence of additives [1, 3].

3. Properties of cement-based materials

Cement-based materials are complex systems that have transient physical and mechanical properties. This phenomenon is related to the slow aging process in colloidal hydration

products [2]. In this section, the properties of cement-based material and the factors that affect them are overviewed.

3.1. Hydration heat

Heat is generated as a result of the exothermic hydration reaction, which will subsequently depend on the chemical and physical properties of unhydrated cement system. One of the important physical characteristics is the particle size distribution of the cement. The heat of hydration increases if the ration of fine materials increases, where the average fineness is in the range of 0.3–0.5 m^2/g. This is related to the increased available surface for reaction which subsequently leads to higher early strength [5].The heat of hydration plays a role in determining the setting time, as the release of this heat increases the rate of hardening. It should be noted that aluminates and sulfoaluminate cements have higher heat of hydration than OPC.

3.2. Setting time

Hydration reactions of cement-based materials are characterized by having initial and final setting times. The duration of setting is dependent on the chemical compositions and fineness of the binder and additives and on the ambient temperature. In specific cases, retardates are used to increase the setting time, so extended workability could be achieved. Retardation is applied in hot weather, cementing oil wells, pumping the paste over long distances, and if special finishing is required. It should be noted that in some cases, early strength development is reduced as a result of retarder addition. Free lime, gypsum, and alkali sulfate are used to slow OPC setting time. On the other hand, in some cases, accelerated hydration reaction with small setting time and early age strength development is required. This could be achieved by lowering the water to cement ration via using water reducer, curing at higher temperature or using accelerators [4].

3.3. Strength strain

Strength-strain relationship differs depending on the composition of the cement-based material, and for hardened cement pastes, the relationship is nearly linear, which reflects the brittleness of the material. On the other hand, hardened concretes continue to deform plastically after exceeding maximum load. The development of the strength-strain relationship in the complex heterogeneous system of cement-based material is affected by:

1. The porosity of hardened material, where the increase in porosity reduce the strength.

2. The chemical interaction and mechanical interlocking between the hydraulic binder and the additives.

3. Effect of hydraulic binder composition, that is, calcium, alumina, sulfate, alkali, and silica ration.

4. Effect of curing temperature, as it increases ultimate strength is reduced.

5. Production and testing conditions, including mixing composition, curing, and load humidity

3.4. Soundness

It is the ability of the hardened cement paste to retain its original volume, and the presence of free lime or magnesium oxide can reduce the soundness of the cement-based materials.

4. Cement composites

Different materials are used as additive to cement to improve the cement characterizations. The mechanical properties of the newly formulated composites were improved. Cement-waste fiber composite was produced due to the incorporation of waste fibers in cementitious materials and used in radioactive waste immobilization [6–9]. Polymers also were impregnated with cement to increase the durability and reduce the porosity of cement, producing favorable composite suitable for many applications and resistive to various aggressive conditions [10–15]. Natural additives such as clay were mixed progressively with cement to treat the retardation property of organic solvent with cement [16, 17].

5. Applications of cement-based materials

5.1. Construction

The application of OPC and its blends is widely applied in construction engineering. **Table 3** illustrates the use of different OPC and OPC blend types in constructions. Aluminate cement concrete is applied in the construction of industrial floors and refractory castables, where the floor must resist chemical, heat, and corrosion [4]. Moreover, decorative tiles, building bricks, and light concrete were performed [18]. Sulfate cement is used in repairing pavement and concrete structures and for places where aggressive chemicals exist.

Purpose	OPC	OPC blend	Applications
General use	I	IS, IP, I(PM), I(SP), S, P	For all uses including pavements, floors, reinforced concrete buildings, bridges, pipe, precast concrete products
Resist sulfate attack	II	IS, IP, P, I(PM), I(SM)	Where moderate sulfate concentration exists, that is, drainage structure, sea structures, and soil structure should be used at low water to cement ration
	V	—	High sulfate concentration media
Early strength	III	—	Used in cold weather to shorten the curing period
Hydration heat	IV	p	Low heat of hydration is required in massive concrete structures, such as large gravity dams
	II	IS, IP, I(PM), I(SM)	Moderate heat of hydration is required, in large structure in warm places, that is, large piers, large foundations, and thick retaining walls

Table 3. OPC and OPC-blend applications in construction [1, 3, 4].

5.2. Environmental aspects

The application of cement-based material in environmental protection and restoration is increasing, and they are used in radiation shielding in nuclear industry, cutoff walls in remediation activities, stabilization of contaminated soil, engineering barriers in disposal facilities, and waste immobilization matrices [19–34]. This wide range of applications is supported by their technical properties, where they have low diffusion coefficients and have available sorption sites; their alkaline environments reduce the mobility of different contaminants and flexibility of modification. In nuclear and radioactive waste industries, they are used as shield due to their good self-shielding performance, and they are suitable to solidify different radioactive waste streams, that is, sludge, emulsified organic liquid, fragmented solids, and exhausted ion exchangers, due to their chemical, radiological, thermal, mechanical, and physical stability. The economic value of these materials plays an important role in their widespread applications, as they are inexpensive and readily available, and has reduced operational cost (which is related to the simplicity of operation and operation at ambient temperature) [20–30]. To ensure the sustainability of these materials for the intended use, they need to be tested to evaluate their strength, radiation, biological and thermal stabilities, free water content, porosity, permeability, corrosion, leaching, dissolution rates, and release mechanisms.

6. Conclusion

The continuous widespread applications of cement-based materials to support human civilization is attributed to their simple modification ability. Different types of hydraulic binder were modified to address the needs to have functional constructions in different environments. With the continuous need to protect the environment from the effect of contaminated sites, either water or soil, cement-based materials were applied in different areas. There is still a need to enhance the performance of these materials in different applications, and this could be achieved by:

1. Testing the effect of industrial wastes as additives on OPC and alternate cements to increase the productive use of these wastes.

2. A quantitative assessment of the effect of additive on the microstructure of the produced material.

3. Developing models that could be used to predict the long-term behavior of the materials, either physical models or mathematical models.

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