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Chapter

Characterizations of Cement and Modern Sustainable Concrete Incorporating Different Waste Additives

Mohanad S. Eid and Hosam M. Saleh

Abstract

This chapter provides a brief introduction to cement and concrete, from their first utilization in constructions and monuments in different civilizations to their development and use in modern times. It discusses the modern forms of these materials, their physical and chemical properties, and their various applications. The chapter also examines the sustainability of concrete mixed with different waste additives, which can impart desirable properties to concrete, as a promising way to reduce environmental hazards resulting from the landfilling of these wastes. In addition to environmental benefits, waste utilization has economic benefits as well.

Keywords: cement, sustainable concrete, waste additives

1. Introduction

According to the *Encyclopedia of Science and Technology*, a hydraulic cementing agent (typically Portland cement), aggregate, water, and frequently regulated proportions of entrained air combine to form a flexible engineering material called "concrete." Concrete starts out as a flexible, workable slurry that can be shaped into a variety of forms. The hydration process between cement and water produces strength. The byproducts, which consist mostly of calcium silicates, calcium aluminates, and calcium hydroxide, are relatively insoluble and bond the aggregate in a cemented matrix [1].

Concrete is popular due to three distinguishing characteristics: plasticity, durability, and economy. When wet, concrete may be poured into almost any form, fit into almost any space, fill almost any vacuum, and coat nearly any surface. However, once it has dried and cured, it retains its shape, growing stronger, harder, and more settled over time [2].

Concrete may be waterproof, stormproof, and fireproof if it is built with the appropriate concentration and under the right circumstances. And because of its endurance, it may be expected to survive indefinitely. When all the steel we used to create our planet has rusted through and the wood has rotted into dust a million years from now, only concrete will remain.

Concrete is not a new or recent material. Like many other methods of building and development, it evolved over time. Our human ancestors discovered naturally existing materials that they could utilize to enhance essential components of their infrastructure, including houses, fences, wells, and so on. The generations that came after built on that knowledge, making small improvements until the advent of the Industrial Revolution, which accelerated building development to its current level [3].

The first concrete-like constructions were established in approximately 6500 BC by the Nabataean merchants, or "Bedouins" as they were called, who inhabited and ruled several oases and established a small empire between the north of Jordan and the south of Syria. They eventually discovered the benefits of hydraulic lime or cement that can gain strength and harden under water. Around 800 BC, they used kilns in the production of mortar to construct homes with rubble walls, floors using concrete, and subterranean watertight cisterns.

The Nabataeans knew the need of keeping the mixture in a dry or low-slump condition while creating concrete, as too much water produces cavities and flaws. Their construction methods included tamp down the fresh produced concrete using a special tool. This tamping process creates an additional gel, which is formed by chemical interactions that occur during hydration and bonds together the particles and aggregate [4].

More than 5000 years ago, its believed that the Egyptians used an early form of concrete to build pyramids. The blocks were limestone blocks hauled from quarries nearby. To hold those blocks together, the builders combined straw with mud consisting of crushed limestone, gypsum, and clay [3].

Around the same period, people in the north of China utilized a sort of cement in the construction of boats and the "Great Wall." Testing revealed that glutenous, sticky rice was a significant element in the mortar utilized to construct the Great Wall and many other ancient Chinese monuments. Some of these monuments have survived for a very long time and even recent demolition attempts [3, 5].

The Greeks found a natural pozzolanic mineral having hydraulic characteristics when combined with limestone around 600 BC, but they were not creative in using concrete like the Romans. After about 400 years, the Romans effectively employed concrete in their construction, but it was not the same as the concrete utilize today. It was more like solidified debris rather than a plastic, flowing substance poured into shapes.

The Romans built most of their constructions by piling up stones of varying sizes and filling in the gaps between the stones with mortar by hand. Above the ground, the walls were coated with bricks made of clay on both the interior and exterior, which also functioned as a form of concrete. The brick was structurally insignificant and was used mostly for decoration. Prior to this period, and in most areas at the time, mortars were made of a slowly hardening lime cement as it reacted with carbon dioxide from the air. These mortars were not effective because no obvious chemical hydration occurred [6].

It wasn't until the mid-18th century, when John Smeaton discovered a more contemporary technique of manufacturing hydraulic lime for cement, that technology advanced significantly. He utilized limestone that included clay and was burned until it became what is called a "clinker," which was then crushed into powder. This material was utilized in the reconstruction of the historical Eddystone Lighthouse in Cornwall, England [7].

Portland cement was developed in 1824 by Joseph Aspdin, who burned finely powdered chalk and clay until the carbon dioxide was eliminated. The cement was named after high-quality construction stones mined from Portland, England [3, 8].

Industrial structures improved greatly in the 19th century. Francois Coignet, who inserted rods made of steel into concrete to prevent the outside walls of construction to spread out, was the first to utilize iron-reinforced Portland cement concrete in houses in France and England.

2. Cementation material

Cement is a fine and dry powdery substance with major ingredients of calcined lime and clay, the former provides calcium oxide, and the later provides silica, alumina, and iron oxide.

When cement is mixed with water, it hardens into a solid mass. Setting and hardening are caused by hydration, which is a chemical reaction that combines the cement compounds with water to produce microscopic-level crystals or a gel-like material (calcium silicate hydrate) with a high specific surface area. The gel has adhesive properties as well as cohesive forces that can bind other solid materials together [9].

3. Cement, mortar, and concrete

The terms cement, concrete, and mortar are often used synonymously even though they are not. Cement, concrete, and mortar are actually three distinct materials [10].

Cement: As mentioned previously, cement turns into a gel-like material when mixed with water, having glue characteristics. Cement is never utilized alone, but it is an essential component of both concrete and mortar, binding their main components together.

Mortar: Mortar is a mixture of cement and fine aggregates (usually sand or other similar components) combined with water. It has the proper consistency to provide a thick, uniform lining that adheres securely to surfaces to bind materials together, for example, bricks, concrete blocks, or stones.

Concrete: Like mortar, concrete is composed of cement and fine aggregates mixed with water, but also coarse aggregates like graves, which makes it stronger and more durable.

Concrete has a lower water-to-cement ratio and thinner consistency than mortar, as well as more strength duo to the presence of the large aggregates.

There are three main types of concrete based on density.

Ordinary concrete: This is the most often utilized kind of concrete. It is employed in building construction where very high tensile strength is not required. It has moderate density around 2200–2500 kg/m³.

Lightweight concrete: The single most essential characteristic of lightweight concrete is its extremely low heat conductivity. It is used for thermal insulation, construction blocks, and to protect steel buildings. It has low density less than 1900 kg/m³ [11].

High-density concrete: This type of concrete is also known as heavy weight concrete. High-density materials are used as fine aggregates, coarse aggregates, or both. It is typically seen in nuclear power reactors and other comparable buildings because it offers excellent protection against all types of radiation. This concrete may have very high density of 3000–4000 kg/m³ [12].

4. Properties and types of cement

4.1 Physical properties

Cement used are characteristic by its physical properties, which can control the quality of the cement. Some parameters of good cement are [13]:



4.1.1 Fineness of the cement

Fineness is defined as the particle size of the cement. It is an important factor influencing the cement's rate of hydration. The reaction between cement and water occurs only at the surface of the solid particles, thus the accumulation of large particles on the surface of unreacted material could hinder the overall reaction.

The required fineness of good cement is achieved during the cement manufacturing process by grinding the clinker, with the most common method used for both controlling the grinding process and testing the finished cement [14].

One method is to measure the surface area per unit weight of cement by determining the rate of passage of air through a bed of cement [15].

4.1.2 Soundness of the cement

Soundness is defined as the immunity of cement to shrinking upon hardening. After the cement has set, it must not undergo any noticeable expansion, which can be caused by the presence of too much hard-burned free lime and magnesia. After setting, a good cement retains its volume without any deferred expansion.

Unsoundness in cement may appear after several years, so tests must be performed to ensure soundness and determine the possibility of this risk occurring [16].

• Le-Chatelier test

This method examines the expansion of cement caused by undesired excess lime. Cement paste is sandwiched between two glass plates and immersed in water for 24 hours at room temperature. It is then removed to measure the distance between the indicators before being returned to the water and boiled for at least an hour. The space between indicator points is measured again after the device has cooled. This distance should not be greater than 10 mm in a good-quality cement [17].

• Autoclave test

In this test, the cement paste is placed in an autoclave device (high-pressure steam vessel) to be cured. The pressure is slowly brought to about 2 MPa, and the temperature increased to 210°C. The past is then kept in the autoclave for three hours. After bringing the autoclave to room temperature and pressure gradually, the specimen's length change is measured and expressed as a percentage. A maximum



Figure 1. *Le-Chatelier apparatus [18].*

of 0.8 percent autoclave expansion is required for good-quality cement according to the American Society for Testing and Materials (ASTM) (**Figure 1**) [17].

4.1.3 Consistency of cement

Consistence is the minimum amount of water required to complete the chemical reaction between water and the cementation material.

Determining standard consistency of cement is essential because if less water is added than the standard consistency would not complete chemical reaction and more water would increase water-cement ratio in either two cases will result in the reduction in strength. A Vicat apparatus is used to obtain the correct consistency of cement.

Vicat test

The Vicat apparatus is loaded with cement paste and the plunger of the apparatus is lowered until it touches the top surface of the cement. The plunger, which has a length of about 50 mm and a diameter of about 10 mm, will penetrate the cement to a certain depth depending on its consistency. When the needle penetrates 10 mm into a cement, it is said that the cement has a normal consistency.

To obtain a standard or normal consistency of cement, only 25–35% water by weight of cement should be added (**Figure 2**) [19, 20].

4.1.4 Setting time of the cement

When water is added to cement, it hardens and sets. This period can vary according to several factors, including cement fineness, chemical content, cement– water ratio, and admixtures. Setting time could also be used to predict hydration rate. There are two important setting times that can be measured:

Initial setting time is the time it takes for the cement paste to lose its plasticity as soon as the water is added to cement.

Final setting time is the time taken for the cement to harden and completely lose its plasticity and be able to sustain some small loads.

A Vicat test can also be used to measure and test the setting time of the cement according to ASTM guidelines [20].

Sustainability of Concrete with Synthetic and Recycled Aggregates



Figure 2. *Vicat apparatus [18].*

4.1.5 Strength of the cement

Tests measuring the rate at which a cement can develop strength are usually carried out on mortar or concrete. There are numerous factors affecting strength, such as cement–fine aggregate ratio, water–cement ratio, the manner of mixing and molding, size and shape of a specimen, curing conditions, and age and loading conditions.

Before testing strength, it is important to note that cement strengthens over time; thus, a strength test should be performed at a specific time. Most cement strength tests are conducted at 3, 7, and 28 days. However, a one-day strength test may be performed for rapid hardening cement types.

Compressive strength

In a test to determine compressive strength, a cylinder- or cube-shaped test specimen is subjected to a continuous compressive load under a hydraulic presser until failure. The loading sequence should be between 20 seconds and 80 seconds [21].

• Flexural strength

Flexural strength is a measurement of tensile strength in bending. The test is performed on a 40 x 40 x 160 mm rectangular concrete or mortar, which is subjected to a load at its center point until failure, according to ASTM [22].

4.1.6 Hydration heat of the cement

Hydration of cement generates heat, which can affect the cement's quality. When the heat generated is high, it may cause undesired stress, especially in large structures. The heat of hydration is affected mostly by the presence of tricalcium aluminate (C_3A) and tricalcium silicate (C_3S) in cement, in addition to fineness of the cement, water–cement ratio, and curing temperature. The heat of hydration of cement can be calculated according to ASTM [23]. This test method provides the apparatus and procedure for using isothermal conduction calorimetry to determine the total heat of hydration of cementitious materials at test ages up to 7 days.

4.1.7 Loss on ignition of the cement

Loss on ignition is a test used in inorganic analytical chemistry, especially for mineral analysis. It entails strong heating (igniting) of a sample of the material to a specific temperature while letting volatile chemicals escape until the mass of the sample reaches a constant value. In most cement types, water is lost around 100–105°C, organic material is burned at around 550°C, and most carbonates are lost between 800°C and 1000°C, as mentioned in ASTM [24].

4.2 Chemical properties

As mentioned previously, the main raw materials that make up cement are limestone and clay (silica, alumina, and iron oxide), as well as many other components including shells, chalk, and blast furnace slag. Chemical examination of cement raw materials reveals important information about cement's chemical properties [25].

Tricalcium silicate (C_3S), ($3CaO \cdot SiO_2$): This is an important compound that provides early strength of cement paste during hydration (initial sitting).

Dicalcium silicate (C₂**S), (2CaO** \cdot **SiO**₂): In contrast to tricalcium silicate, this compound enhances strength acquired after one week.

Tricalcium aluminate (C3A), (3CaO · Al₂O₃): This compound is characteristic for its fast reacting with water, which causes an immediate stiffness of the cement paste. In addition, small amounts of C3A make cement resistant to sulfate.

Magnesia (MgO): A large amount of magnesia in cement can make it unsound and expand, but a small amount can make it stronger. CO_2 emissions are also minimized while MgO-based cement is produced. The MgO percentage of all cement is capped at 6% [26].

Tetracalcium aluminoferrite (C4AF), (4CaO · Al₂O₃Fe₂O₃): Ferrite is a fluxing agent that lowers the raw material melting temperature in a kiln from around 1650–1420°C. Even though it hydrates quickly, it does not make a significant contribution to the hydration process [27].

Sulfur trioxide and free lime: Just like magnesia, excessive amounts can cause expansion and the cement to become unsound.

Alkalis: The alkali content of cement is determined by the quantities of potassium oxide (K₂O) and sodium oxide (Na₂O). Too much alkali in cement might make it difficult to control the cement's setting time. When used with calcium chloride in concrete, low-alkali cement can induce discoloration [28].

Alumina: Because alumina is chemical-resistant, cement with a high alumina content may tolerate frigid temperatures. It also speeds up the setting time but weakens the cement [29].

Silica fume: This is used to increase a range of qualities in cement, including compressive strength, abrasion resistance, and bond strength. Although the use of silica fume extends setting time, it can provide extremely high strength. As a result, cement with a silica fume content of 5–20% is typically used in high-strength cement projects [30].

5. Different types of cement

Cements with different chemical compositions may have various properties. As a result, it should be possible to select a mixture of raw materials to produce a cement with desired properties.

In general, cement is divided into two kinds based on the method of hardening and setting:

- **Hydraulic cement**: Cements that harden when exposed to water, also produce water-resistant products. The main raw materials used to synthesize hydraulic cement are limestone, clay, and gypsum. Hydraulic cement is made by burning this raw material at a very high temperature, according to ASTM.
- Non-hydraulic cement: Water is not required for the hardening of non-hydraulic cement because it absorbs carbon dioxide (CO₂) from the atmosphere. To harden, this sort of cement requires dry circumstances. Non-hydraulic cement involves lime, gypsum plasters, and oxychloride as basic materials.

5.1 Portland cement

Portland cement is the most common, low-cost, and widely used type of cement worldwide because its basic ingredients are inexpensive and readily available. It consists of four major components: tricalcium silicate, tricalcium aluminate, dicalcium silicate, and tetracalcium aluminoferrite.

For specialized objectives, such as durability and high early strength, several kinds of Portland cement are produced to fit distinct physical and chemical characteristics [31, 32].

- Ordinary Portland cement (Type I): This all-purpose cement may be used in any situation where specific characteristics are not required.
- **Modified Portland cement (Type II):** This is a cement that is commonly utilized in situations with abnormal sulphate concentrations in groundwater and soils. It is also used when a cement with a moderate heat of hydration is required. The concentration of the C3A shall not exceed 8%.
- **Rapid hardening cement (Type III):** This cement attains high strength in several days. The chemical makeup of this cement is the same as that of Type I Portland cement, but it has greater C3S content with finer ground. Its strength after 24 hours is approximately comparable to that of conventional Portland cement after 3 days with the same water ratio. The use of this cement results in significant time and cost savings.
- Low-heat cement (Type IV): This cement is used when the level and rate of heat generation must be kept to a minimum. The percentages of C2S and C4AF are quite high, whereas the percentages of C3S and C3A are comparatively low. A small bit of tricalcium aluminate (usually less than 7%) causes the concrete to have a low heat of hydration. This type of cement is ideal for mass concrete structures such as dams.
- Sulphate resisting cement (Type V): This is a cement that is commonly used in concrete subjected to severe sulphate conditions in harsh environments, particularly when soils or groundwaters have a high sulphate concentration. Type V cement builds strength slower than Type I cement does, due to high silicate content with low C3A and C4AF concentrations.
- Air-entraining cement (Type IA, Type IIA, and Type IIIA): These cement types have the same properties as Type I, Type II, and Type III cements. Grinding a tiny quantity, approximately 0.05%, of animal and vegetable fats,

oil, and another acid with a wetting agent such as aluminum powder, hydrogen peroxide, and so on results in the entrainment of extremely fine air bubbles in the concrete, which improves workability with a lower water-cement ratio, as well as improves frost-resistant characteristics.

• Hydrophobic cement: Hydrophobic cement is made from regular Portland cement clinker by grinding it with specific water repellent components such as oleic acid, stearic acid, or naphthenic acid. A water-resistant coating is formed over each cement particle, preventing water or moisture from the air from being absorbed by the cement. This film is broken during the regular hydration process and behaves just like ordinary Portland cement.

This cement has excellent resistance during transportation and long-term storage in severely moist climatic conditions.

• **Quick-setting cement:** This is cement that has the property of setting very quickly. This feature is obtained by decreasing the gypsum content during the clinker grinding process.

Quick-setting cement is used for concreting in static or flowing water, underwater construction, and rainy and cold weather conditions, or when work must be finished in a short period of time, like in places with higher temperatures where water evaporates easily.

The distinction between rapid hardening and quick-setting cement is that quick-setting cement sets faster. Simultaneously, the rate of strength growth is comparable to that of ordinary Portland cement, but quick hardening cement builds strength rapidly.

5.2 Pozzolanic cement

Pozzolanic cements are blends of Portland cement with pozzolanic material, which might be natural or synthetic. Natural pozzolanas are mostly volcanic in origin like diatomaceous earth. Fly ash, burnt clays, and shales are examples of materials utilized in synthetic pozzolanic.

Pozzolanas are materials (natural or synthetic) that have no cementitious properties, but they contain reactive silica (and alumina). When divided into fine form, they are capable of combining with lime (calcium hydroxide) in the presence of water to create compounds having cementitious characteristics [2, 32].

This cement is widely utilized because it has a strong resistance to different chemical attacks when compared to regular Portland cement.

5.3 High alumina cement

High alumina cement is a rapid hardening cement produced by fusing a combination of bauxite (aluminum ore) and limestone in a reverberatory or electric furnace or rotary kiln at 1500–1600°C.

The cement consists of about 30–40% lime, 45–50% alumina, up to 10% iron oxides, and preferably no more than 6% silica. Calcium aluminate (CaO \cdot Al₂O₃) is the main cementing ingredient.

High alumina cement has a high early strength, as it can reach ultimate strength within 24 hours, a high heat of hydration, and a very high durability against high temperatures, frost, and chemical attacks [2, 33].

5.4 Slag cements

Slag is the glass-like byproduct left over after separating a desired metal from its raw ore, and it is generally generated via a blast furnace–oxygen converter method or electric arc furnace. The primary components of these slags are calcium, iron, silicon, magnesium, and aluminum oxides, with lower quantities of phosphorus, manganese, and others depending on the raw materials utilized [2, 34].

- Blast-furnace slag cement: This is a mixture obtained by adding Portland cement or grinding the clinkers with about 65% granulated slag. It can be utilized for projects when economic considerations are important.
- Super-sulphated cement: This is a slag-containing cement with less than 6% sulfuric anhydride (SO₃), at least 8% granular slag, 10–20% hardburned gypsum or anhydrite (natural anhydrous calcium sulphate), and a few percentages of Portland cement. This cement is used in severe situations such as maritime construction, mass concrete projects to withstand the aggression of strong seas, and chemical works exposed to high concentrations of sulphates.

6. Sustainable concrete

Mortar and concrete can have various properties and applications according to the type of cement used and the other components of fine and large aggregates.

The future of concrete research and engineering is trending towards employing waste materials. These wastes, which can be hazardous and difficult to dispose of, may be present in large quantities in the environment [35].

Employing waste in concrete can be achieved by adding it or using it to replace one of the other components, which can achieve or even improve desired properties.

7. Metallic waste additives

The amount of industrial metallic waste is huge and can be challenging to recycle. These metals, however, can be added to concrete and mortar to improve their properties. In this context, Małek et al. utilized metal chip waste generated by lathes and CNC machines as an additive to concrete. Results show that adding metal waste can improve the physical and mechanical properties of concrete [36].

Norambuena-Contreras et al. utilized two kinds of steel industrial wastes, steel shavings and steel wool fibers, to manufacture mortar. They concluded that there were small variations in flexural and compressive strength, but an overall improvement of the mortar due to adding the steel [37].

8. Polymeric waste additives

Polymers have been increasingly used over the last 50 years in almost every industry as well as in human daily life. However, these products are hazardous to the environment and almost impossible to recycle. Therefore, finding a useful way to reuse these products is a focus of research. One potential way to reuse polymers is to add them to concrete or mortar.

Daud et al. utilized thermoplastic polyethylene terephthalate (PET) waste obtained from recycling bottles to replace the graves in lightweight concrete used for insulation walls in building construction faces [38].

Plastic pollution is exacerbated by the constant manufacture and disposal of plastic. Jain et al. successively employed non-metallic polymeric plastic waste with flay ash in concrete and concluded that the addition of non-metalized waste plastic bag fibers together with fly ash in concrete greatly improved properties like split tensile strength, resistance to abrasion, flexural strength, impact, and drying shrinkage [39].

Another type of sustainable concrete incorporates waste rubber as an additive. Rubber is one of the hardest materials to recycle, thus the utilization and reuse of leftover waste rubber in concrete can minimize raw material consumption, resulting in economic efficiency and long-term development of the building sector. Yang et al. utilized waste tire rubber as a replacement for fine aggregates (sand) by reducing its size. The disposal of leftover waste tires has become a major environmental concern worldwide [40].

Concrete containing waste polymeric material can be utilized to reduce the contamination of radioactive material in the environment. Saleh et al. incorporated recycled PET waste with cement into making container-like material for reducing the activity of radioactive borate waste obtained from pressurized water reactor (PWR). They provided a characterization for these samples and concluded that the combination of cement with PET is an acceptable product for immobilization of radioactive borate [41].

9. Biowaste additives

Biomass and agriculture waste can be great additives or even replacements to cement in concrete and mortar. Because cement is a key building material that accounts for 8–10% of total CO₂, there is a critical need to replace cement in order to reduce greenhouse gases (GHGs) such as CO₂, which are responsible for global warming [42].

The research of agricultural wastes as extra ingredients in mortar and concrete, as well as replacements for aggregates, resulted from the quest for alternative materials for cement. Agricultural wastes are readily available, inexpensive, and have high reactivity in concrete, which has increased researchers' interest in these materials. The effective use of these elements in concrete will result in a green manner of disposing of enormous amounts of trash that might otherwise have caused environmental harm.

Bassam et al. provide an excellent review on previous studies that use rice husk waste as a replacement for cement. The influence of rice husk on concrete characteristics such as workability, flexural strength, splitting tensile strength, density, compressive strength, modulus of elasticity, durability abilities, and sustainability is reported [43].

Not only the biomaterial itself but also its byproduct ashes can be used for making a sustainable cementitious material.

Blessen et al. provide a comprehensive review based on previous research and current developments in concrete using biomass ashes from agricultural farming wastes, ashes from bamboo leaves, date palm, rice straw, olive waste, elephant leaves, banana leaf and plantain peels, rice straw, wheat straw, olive waste, and corn cob as pozzolanic materials in cement concrete [44].

Some plants can be harmful and dangerous to the environment like the aquatic plant *Myriophyllum spicatum*, which is an invasive and noxious. Saleh, et al.

incorporated this plant into cement for safe immobilization of radioactive isotopes and other hazardous waste. Results show the cementation of dry solid waste generated during phyto-remediation was effective in immobilizing these wastes [45].

10. Glass waste additives

Waste glass is another readily accessible resource that may be utilized in place of cement. Only a portion of waste glass is reused in the production of new glass, and the remainder is discarded owing to impurities, color, or cost.

Glasses are categorized into 32 different kinds, although the most common are soda-lime, vitreous silica, borosilicate, lead, aluminosilicate, alkali silicates, barium, and aluminosilicate glasses [46].

Crushed waste glass has a variety of characteristics, including a high concentration of silicon and calcium and an amorphous structure. As a result, waste glass possesses pozzolanic or cementitious characteristics and can be utilized as a partial substitute for cement.

Ankur et al. published a review of studies that employed silica fume and waste glass into concrete as replacements for cement and provided results on physical and mechanical properties [47].

Author details

Mohanad S. Eid¹ and Hosam M. Saleh²*

1 Faculty of Science, Physics Department, Tanta University, Tanta, Egypt

2 Nuclear Research Center, Radioisotope Department, Egyptian Atomic Energy Authority (EAEA), Egypt

*Address all correspondence to: hosamsaleh70@yahoo.com

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