

Cementing materials from the pharaohs to the 21st century

Hanaa Youssef Ghorab^{1*}

¹ Chemistry Department, Faculty of Science, Helwan University 11795, Cairo, Egypt.

*Corresponding author: Hanaa Youssef Ghorab, E-mail: hanaa.ghorab@gmail.com

DOI: 10.21608/ERURJ.2022.265364

ABSTRACT

Human's ability to live comfortably depends on their housing. Homes must be safe, strong, and environmentally friendly. Construction materials have changed over time in accordance with the conditions. They ranged from stone structures to palm grids and mountain caverns. Bricks that had been burned and treated were also known. Builders were accustomed with using natural resources like animal and plant glue to bond the decorative pieces and increase the workability of mortars. In areas where its color wouldn't be an issue, bitumen was extensively employed as a man-made organic glue. It is the primary part of asphalt pavement nowadays. Natural stones represented strong building elements among these resources. The ancient people mastered their challenging quarrying techniques and used rocks and stones exclusively in their construction.

Keywords: Cementing materials, Ancient Egypt, Portland cement clinker

1. Introduction

Housing is an essential element for the life of the human being. Homes have to be secure, comfortable, durable and sustainable. Over the history, the materials used for construction differed with the environments. They varied from palm grids, mountain caves to stone buildings. Burned and processed bricks were known as well. Natural materials such as animal and plant glue, mostly used with the mortars to improve the workability and to bind the decoration items, were familiar for builders. The bitumen, as a man-made organic adhesive was intensively used in places which would not be disturbed by its color. Nowadays it is the main component of the asphalt pavement. Among these materials, natural stones represented well secured construction

materials. The ancient people relied on rocks and stones in their buildings and mastered their difficult quarrying processes.

Few thousand years before Christ, in undetermined timing from at least 2000 BC, huge stones of around 1600 tons (~4 m width x 4m height) each, were used to construct the temple of Baalbek in Lebanon in a miracle building (Figure 1). In this temple the evacuation of air during the placing of one stone above the other was enough to keep the lining of the wall in perfect conditions without the aids of cementing materials.



Figure 1. Baalbek stone in Lebanon around 1600 tons (~4 m width x 4 m height)
(wikipedia.org)

The dimensions of the stones used in construction diminished with the evolution of cementing binders with time. Stones weighing ~2.5 tons of dimensions 1 m x 2.5 m were used in the pyramids with weak non-hydraulic binders which do not resist water (Figure 2). Gypsum and lime were the most popular materials at that time. They lasted up to the medieval era in the monuments of Islamic architecture (1) (Figure 3).



Figure 2. Pyramids stones in Giza around ~2.5 tons (1 m x 2.5 m)
(wikipedia.org)

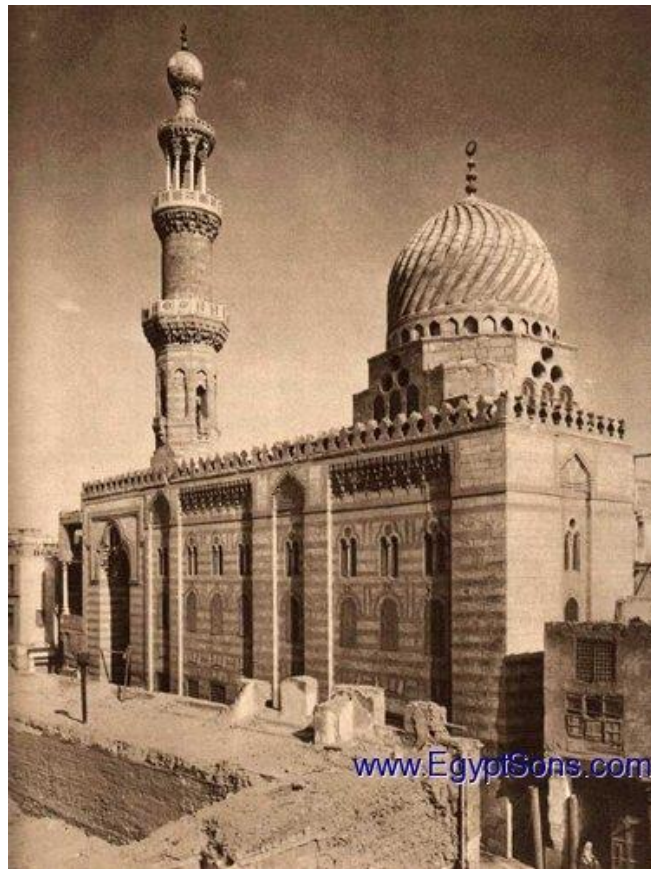


Figure 3. Islamic monuments Pyramids stones in the medieval era
(Egyptsons.com)

The durability concerns of any construction are generally related to the water resistance; i.e. to resist rain, river, ground and salty waters. In the monuments built with natural stones, the major

areas were occupied by the stones and only small areas of the binders were exposed to the environment. The binders were therefore quite protected from external attacks (2).

1.1 Portland cement

With the discovery of the famous hydraulic binder: the Portland cement, at the end of the 18th century, and with the invention of the reinforced concrete in the middle of the 19th century, the construction of the high buildings (Figure 4), bridges and highways were introduced and intensified (3). In the 20th century, the dependence on the strength of the cement binder increased and the natural stones were crushed to sizes as small as 2 cm in the concrete aggregates (4) (Figure 5):



Figure 4. Skyline constructed with reinforced concrete structure
(wikipedia.org)

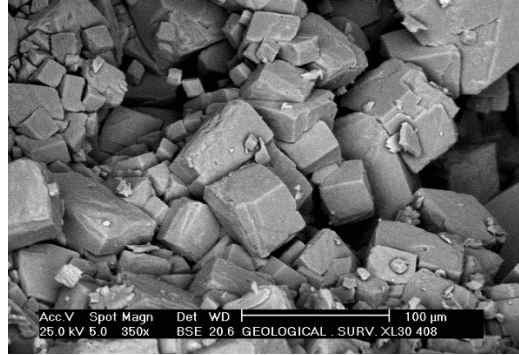


Figure 5. Crushed stone aggregate for concrete ~2 cm in size
(concretenetwork.com)

The ancient builders knew burning temperatures as high as 900°C for the calcination of limestone and the production of fat lime. Portland cement, as the heaviest industry known presently, needs temperatures up to 1450°C (5).

The advantage of Portland cement lays in the components of the clinker produced from burning limestone and clays at this high temperature. It is composed of four main phases: two calcium silicates, a calcium aluminate and the calcium aluminoferrite. The size of the particles forming these phases is in the range of several ten of microns (6) (Figure 6). The calcium silicates are depicted in the figure as dark particles, the aluminates and aluminoferrite are found in the bright background. These components are unstable and tend to react with water to produce more stable phases (7). The hardening and strength development of Portland cement is due to the calcium silicate hydrate fibers with dimensions of ~ 7 nm (Figure 7). One can imagine the fineness of these fibers when compared with the thickness of one human hair which attains 70 nm (8) (Figure 8).-These fibers are responsible for the early strength which can be achieved only with Portland cement. They are the main reason for the evolution of buildings and constructions in the civil engineering domain.

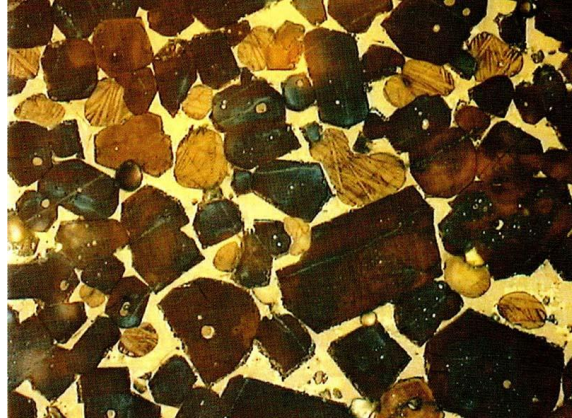


Figure 6. Particles of Portland cement clinker few tens of microns in size (concretenetwork.com)

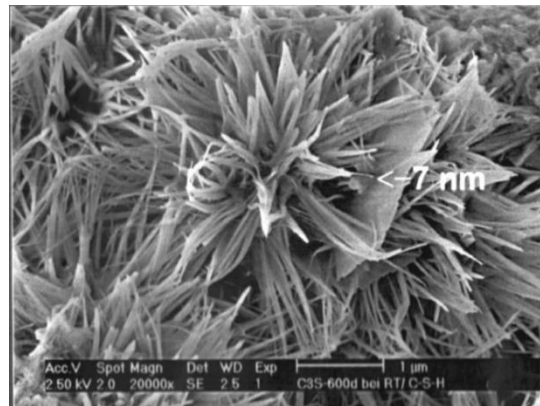


Figure 7. Calcium silicate hydrate fibers around 7 nm in size (F.A.Finger Institut Weimar, Germany)

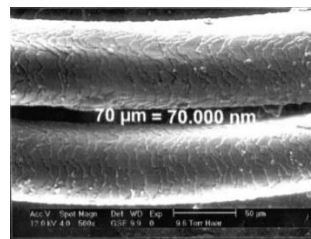


Figure 8. A human hair around 70 microns in size (F.A.Finger Institut Weimar, Germany)

The role of Portland cement in concrete is to bind sand and gravel or crushed stones aggregates to form a hard matrix. Restrictions are put to avoid any volume change after hardening. The area of the cement binder in concrete structures exposed to external environment is significantly large

because of the small aggregate size and has to be protected. Attacks of sulfate, chloride, carbonates and alkalis may destroy the concrete structures (9).



Figure 9. Concrete deteriorated from external sulfate attack
(theconstructor.org)

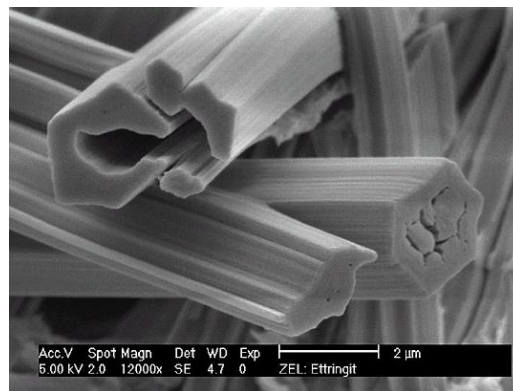


Figure 10. The ettringite salt formed from the external sulfate attack in concrete (F.A.Finger
Institut Weimar, Germany)

Figure 9 illustrates a concrete deteriorated from a sulfate attack, due to the formation of the ettringite salt which dimension is ~2 microns (Figure 10). Figure 11 shows a concrete structure deteriorated as a result of alkali silicate reactions; the expansive alkali silicate gel is illustrated in Figure 12. Figure 13 presents a concrete crack formed as a result of corrosion of steel reinforcement due to chloride or carbonation attack.



Figure 11. Concrete deteriorated from alkali silica reactions
(theconstructor.org)

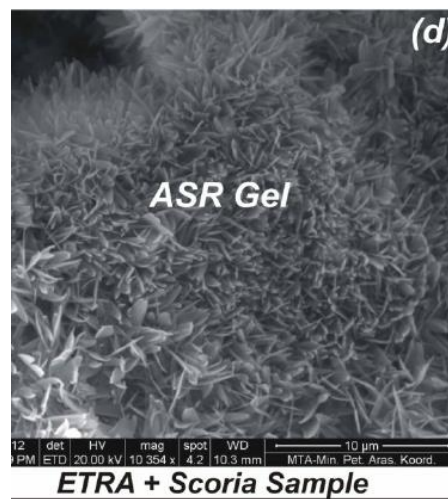


Figure 12. The gel formed from the alkali silica reactions in concrete
(theconstructor.org)



Figure 13. Concrete deteriorated from corrosion of the steel reinforcement
(theconstructor.org)

1.2 Other cements

Worth to note that the mentioned inorganic binders are composed mainly of calcium oxide either in its free state exemplified in the air hardening lime used by the ancient builders, or as a basic constituent combined with other acidic oxides in Portland cement. Other cements of acid resistant properties as the sodium silicate and geopolymers do not contain lime. A less abundant cement based on magnesium is the Sorel cement applied mainly as a flooring material (10).

The air hardening fat lime is not suitable for long term unprotected uses because of its high solubility in water around ~ 1.3 g/liter and can be easily leached upon exposure to water. Its least exposure to the environment in the ancient buildings was therefore necessary (11).

Only the quarries of the clay- free limestone produce fat lime upon calcination. These quarries are quite limited and most limestones quarries contain a certain amount of clay varying between ~ 6 to 25%. The calcination process of the clay-bearing limestone splits off the water of the clay at temperatures well below 900°C (~550-850°C) and produce reactive acidic oxides; the silica, alumina and ferric oxide (12). These oxides react with lime during the calcination process and produce low grade cementing materials leaving a significant amount of lime free. This is called hydraulic lime which resists water more than fat lime because of its weak hydraulic properties. It is mostly used in the restoration of the monuments. The Portland cement discovery was related to the burning of marl limestone which had enough clay to react with most of the lime upon calcination and leaves only a small amount free. Marl is present in Aswan Egypt and the cement factory there do not need to have an extra quarry for clay (13).

The lime needed to produce Portland cement obtained from the limestone quarries is irreplaceable by wastes of similar function and equivalent abundance. Lime can react with industrial wastes of latent hydraulic or pozzolanic materials to form the same products of Portland cement; but with slower rate. The combination of lime in the latent hydraulic or pozzolanic materials takes place in around a month time and produces only late strengths (13).

The Portland cement hydration products are not insoluble in water as clay or sand and their solubility in water lays is in the range of 10^{-40} which explains their water- resistant properties. In spite of this low solubility, it is still attackable and the surface of concrete has to be protected to reduce the porosity and the permeability of the surface (14).

Because the production of the clinker consumes energy, it is responsible for the greenhouse effect and the emission of ~6% from the CO₂ to the atmosphere, an important trend was adapted

in the 20th century to reduce the clinker factor. Materials with latent hydraulic and pozzolanic properties were used to replace up to ~60% of the clinker in different types of cements (15).

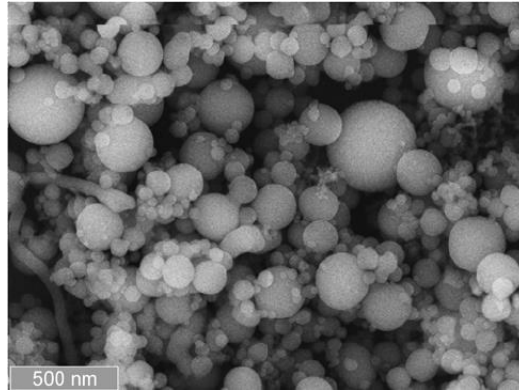


Figure 14. Silica fumes as cement replacement material
(microsilica-fume.com)

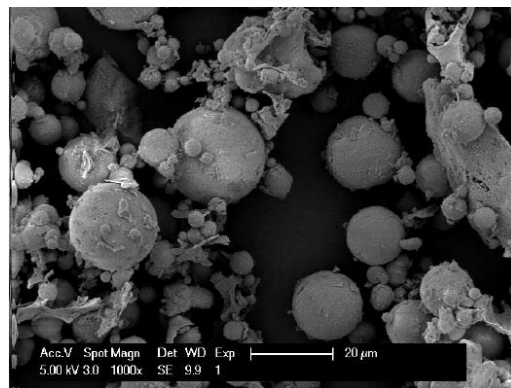


Figure 15. Fly ashes as cement replacement material
(microsilica-fume.com)

The well-known cement replacement materials are industrial wastes such as silica fumes (Figure 14), fly ashes (Figure 15) and granulated blast furnace slag (Figure 16). Natural and artificial pozzolana are obtained from volcanic ashes (Figure 17), calcined clays (Figure 18) and agricultural ashes such as rice husk ash (Figure 19, 20). Limestone powder can replace part of the clinker and acts mainly as filler because of its inertness.

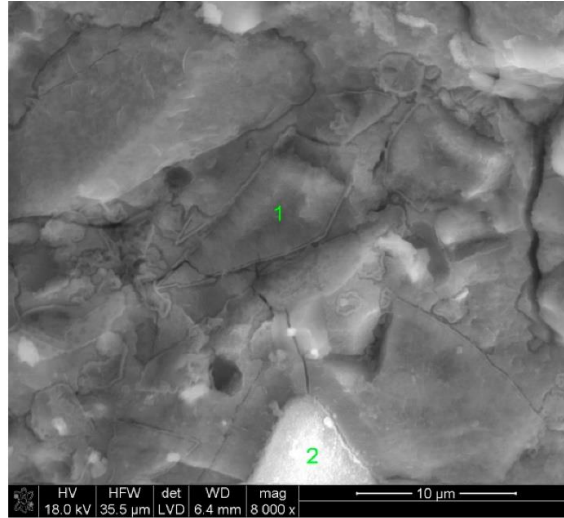


Figure 16. Granulated blast furnace slag as cement replacement material
(microsilica-fume.com)



Figure 17. Volcanic tuffs as cement replacement material
(microsilica-fume.com)

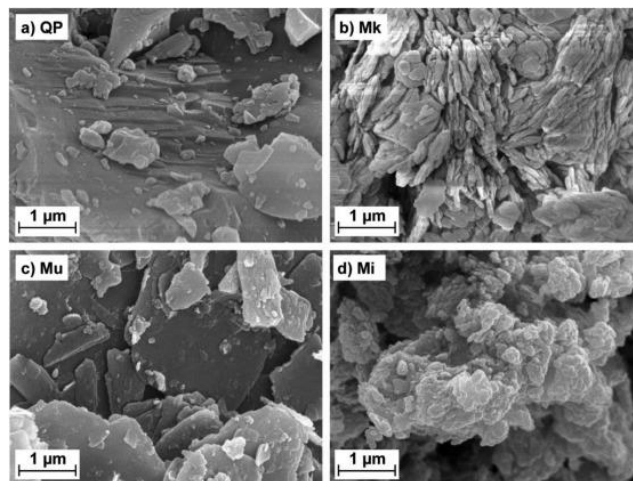


Figure 18. Activated clays as cement replacement material



Figure 19. Rice husk

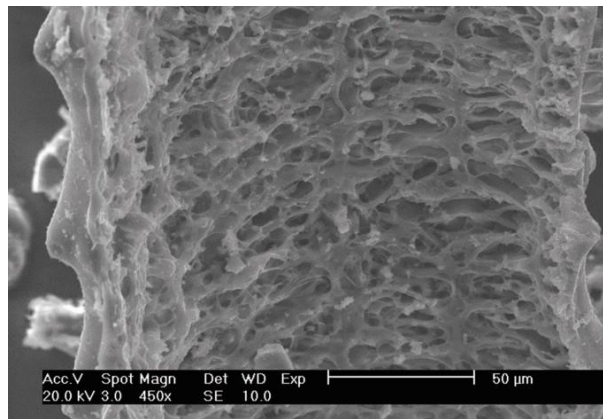


Figure 20. Rice husk ashes as cement replacement material

2. Conclusion

The role played by the binders in construction increased over time. Portland cement clinker is an important material and shall last for long time with no similar material. Because of environmental reasons, of the power of the clinker and the presence of suitable partial replacement materials, the future cements will contain the minimum amount of clinker and other latent hydraulic materials and the same level of performance and quality can be achieved.

3. References

1. Hemeda S, Sonbol A. Sustainability problems of the Giza pyramids. *Herit Sci.* 2020;8(1).
2. Chabas A, Jeannette D. Weathering of marbles and granites in marine environment: Petrophysical properties and special role of atmospheric salts. *Environ Geol.* 2001;40(3).
3. Vossen P, Caselli T, Cybulska A. How Concrete Do We Get Telling Stories? *Top Cogn Sci.* 2018;10(3).
4. Chindapasirt P, Hatanaka S, Mishima N, Yuasa Y, Chareerat T. Effects of binder strength and aggregate size on the compressive strength and void ratio of porous concrete. *Int J Miner Metall Mater.* 2009;16(6).

5. Forster AM, Válek J, Hughes JJ, Pilcher N. Lime binders for the repair of historic buildings: Considerations for CO₂ abatement. Vol. 252, *Journal of Cleaner Production*. 2020.
6. Dunuweera SP, Rajapakse RMG. Cement Types, Composition, Uses and Advantages of Nanocement, Environmental Impact on Cement Production, and Possible Solutions. Vol. 2018, *Advances in Materials Science and Engineering*. 2018.
7. Wesselsky A, Jensen OM. Synthesis of pure Portland cement phases. *Cem Concr Res*. 2009;39(11).
8. Nontananandh S, Yoobanpot N, Chaysuwan D, Thongdaeng K. Influence of fineness of cement produced from industrial wastes on strength of mortar. *Kasetsart J - Nat Sci*. 2011;45(4).
9. Lv SH. High-performance superplasticizer based on chitosan. In: *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials*. 2016.
10. Shahzadi P, Shahnaz A, Khan MS, Rana BB, Chaudry MY, Yasmeen S. A Short Study to Test the Compliance of Various Pakistani Ordinary Portland Cements with ASTM Composition Standards. *Pakistan J Chem*. 2013;3(4).
11. Argo WR, Biernbaum JA. Effect of Lime, Irrigation Water Quality, and Water-soluble Fertilizer on pH and Macronutrient Management of Peat-based Root Media. *HortScience*. 2019;30(4).
12. Pliya P, Cree D. Limestone derived eggshell powder as a replacement in Portland cement mortar. *Constr Build Mater*. 2015;95.
13. Serry MA. Assessment of the Egyptian clay deposits for ceramic industries: A review paper. Vol. 28, *Industrial Ceramics*. 2008.
14. Tosun K, Felekoğlu B, Baradan B, Akin Altun I. Effects of limestone replacement ratio on the sulfate resistance of Portland limestone cement mortars exposed to extraordinary high sulfate concentrations. *Constr Build Mater*. 2009;23(7).
15. Antunes M, Santos RL, Pereira J, Rocha P, Horta RB, Colaço R. Alternative clinker technologies for reducing carbon emissions in cement industry: A critical review. Vol. 15, *Materials*. 2022.