

Energetically modified cement

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Energetically modified cements (EMC) are a class of cementitious materials made from pozzolans (e.g. fly ash, volcanic ash, pozzolana), silica sand, blast furnace slag, or Portland cement (or blends of these ingredients).^[1]

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Classification and field-usage potential

The term "energetically modified cement" (abbreviated as "EMC" or "EMC cement") refers to a class of cementitious materials which have been produced using a special activation process.^{[2][3]} This process is entirely mechanical, as opposed to thermal,^{[3][4][5]} and is carried out by finely grinding the materials to increase binding capacity.^{[6][7]}

There are several types of energetically modified cements, depending on the raw materials used; all contain some proportion of conventional Portland cement, which may itself undergo EMC Activation, and many contain alternative (supplemental) cementitious materials. EMCs can be produced with less energy and carbon dioxide production than traditional cements.^{[4][8]}

Each type of energetically modified cement has its own performance characteristics, including mechanical load. The most frequently used EMCs are made from fly ash and natural pozzolans; these are relatively abundant materials, and the performance characteristics are relatively close to those of Portland cement while providing energy and carbon dioxide savings. ^[Note 1] EMC products have been extensively tested by independent labs.^[9]

History

The term "energetically modified cement" was first used in Sweden, where the EMC Activation process was developed in 1992 by Vladimir Ronin at Luleå University of Technology (LTU). The term was introduced in a paper by Ronin et al. in 1993.^[10] The process was refined by Ronin and others, including Lennart Elfgren (now Professor Emeritus of LTU).^[11] Continuing academic work and research "self-healing" properties of energetically modified cements is ongoing at LTU.^[12]

At the 45th World Exhibition of Invention, Research and Innovation, held in Brussels, Belgium, EMC Activation was awarded a Gold Medal with mention by EUREKA, the European inter-governmental (research and development) organisation.^[13]

The research work connected with EMCs has received awards from the *Elsa o Sven Thysells stiftelse för konstruktionsteknisk forskning* (Elsa & Sven Thysell Foundation for Construction Engineering Research) of Sweden.^[14]

Chemistry

Through the use of pozzolans in concrete, porous (reactive) Portlandite can be transformed into hard and impermeable (relatively non-reactive) compounds, rather than the porous and soft relatively reactive calcium carbonate produced using ordinary cement.^[15] Many of the end products of pozzolanic chemistry exhibit a hardness greater than 7.0 on the Mohs scale.

EMC Activation is a process which increases a pozzolan's chemical affinity for pozzolanic reactions.^{[16][17]} This leads to faster and greater strength development of the resulting concrete, at higher replacement ratios, than untreated pozzolans.^{[18][19]} These highly reactive pozzolans can yield further stabilisation benefits upon the pozzolanic reaction-pathways.

In concrete (including concretes with EMCs), Portland cement combines with water to produce a stone-like material through a complex series of chemical reactions, the full mechanics of which are still not fully understood. That chemical process, called mineral hydration, forms two cementing compounds in the concrete: calcium silicate hydrate (C-S-H) and calcium hydroxide (Ca(OH)₂). This reaction can be noted in three ways, as follows:^[20]



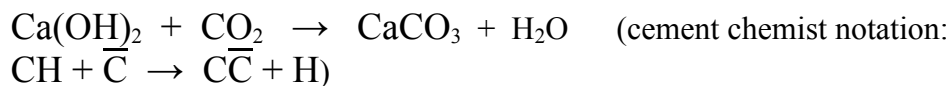
The main campus of Luleå University of Technology (LTU) in Luleå, Sweden

- Standard notation: $\text{Ca}_3\text{SiO}_5 + \text{H}_2\text{O} \rightarrow (\text{CaO}) \cdot (\text{SiO}_2) \cdot (\text{H}_2\text{O})_{(\text{gel})} + \text{Ca}(\text{OH})_2$
- Balanced: $2\text{Ca}_3\text{SiO}_5 + 7\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}_{(\text{gel})} + 3\text{Ca}(\text{OH})_2$
- Cement chemist notation (the hyphenation denotes the variable stoichiometry): $\text{C}_3\text{S} + \text{H} \rightarrow \text{C-S-H} + \text{CH}$

The underlying hydration reaction forms two products:

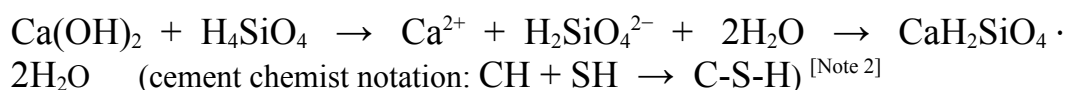
1. Calcium silicate hydrate (C-S-H), which gives concrete its strength and dimensional stability. The crystal structure of C-S-H in cement paste has not been fully resolved yet and there is still ongoing debate over its nanostructure.^[21]
2. Calcium hydroxide ($\text{Ca}(\text{OH})_2$), which in concrete chemistry is known also as Portlandite. In comparison to calcium silicate hydrate, Portlandite is relatively porous, permeable and soft (2 to 3, on Mohs scale).^[22] It is also sectile, with flexible cleavage flakes.^[23] Portlandite is soluble in water, to yield an alkaline solution which can compromise a concrete's resistance to acidic attack.^[24]

Portlandite makes up about 25% of concrete made with Portland cement without pozzolanic cementitious materials.^[15] In this type of concrete, carbon dioxide is slowly absorbed to convert the Portlandite into insoluble calcium carbonate (CaCO_3), in a process called carbonation.^[15]



In mineral form, calcium carbonate can exhibit a wide range of hardness depending on how it is formed. At its softest, calcium carbonate can form in concrete as chalk (of hardness 1.0 on Mohs scale). Like Portlandite, calcium carbonate in mineral form can also be porous, permeable and with a poor resistance to acid attack, which causes it to release carbon dioxide.

Pozzolanic concretes, including EMCs, however, continue to consume the soft and porous Portlandite as the hydration process continues, turning it into additional hardened concrete as calcium silicate hydrate (C-S-H) rather than calcium carbonate.^[15] This results in a denser, less permeable and more durable concrete.^[15] This reaction is an acid-base reaction between Portlandite and silicic acid (H_4SiO_4) that may be represented as follows:^[25]

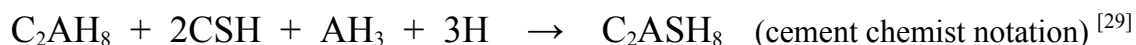


Further, many pozzolans contain aluminate ($\text{Al}(\text{OH})_4^-$) that will react with Portlandite and water to form:

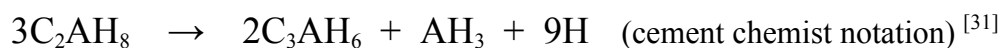
- calcium aluminate hydrates, such as calcium aluminium garnet (hydrogrossular: C_4AH_{13} or C_3AH_6 in cement chemist notation, hardness 7.0 to 7.5 on Mohs scale);^[26] or

- in combination with silica, to form strätlingite ($\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$ or C_2ASH_8 in cement chemist notation), which geologically can form as xenoliths in basalt as metamorphosed limestone.^[27]

Pozzolanic cement chemistry (along with high-aluminate cement chemistry) is complex and per se is not constrained by the foregoing pathways. For example, strätlingite can be formed in a number of ways, including per the following equation which can add to a concrete's strength:^[28]



The role of pozzolans in a concrete's chemistry is not fully understood. For example, strätlingite is metastable, which in a high temperature and water-content environment (that can be generated during the early curing stages of concrete) may of itself yield stable calcium aluminium garnet (see first bullet point above).^[30] This can be represented per the following equation:



Per the first bullet point, although the inclusion of calcium aluminium garnet per se is not problematic, if it is instead produced by foregoing pathway, then micro-cracking and strength-loss can occur in the concrete.^[32] However, adding high-reactivity pozzolans into the concrete mix prevents such a conversion reaction.^[33] In sum, whereas pozzolans provide a number of chemical pathways to form hardened materials, "high-reactivity" pozzolans such as blast furnace slag (GGBFS) can also stabilise certain pathways. In this context, EMCs made from fly ash have been demonstrated to produce concretes that meet the same characteristics as concretes comprising "120 Slag" (i.e., GGBFS) according to U.S. standard ASTM C989.^{[18][34]}

Portlandite, when exposed to low temperatures, moist conditions and condensation, can react with sulphate ions to cause efflorescence; pozzolanic chemistry reduces the amount of Portlandite available, to reduce efflorescence.^[35] }

Self-healing properties

Natural pozzolanic reactions can cause mortars and concretes containing these materials to "self-heal".^{[36][37][38]} The EMC Activation process can at times increase the likelihood of the occurrence of these pozzolanic reactions.^{[16][17]} The same tendency been noted and studied in the various supporting structures of Hagia Sophia built for the Byzantine emperor Justinian (now, Istanbul, Turkey).^[39] There, in common with most Roman cements, mortars comprising high amounts of pozzolana were used — in order to give what was thought to be an increased resistance to the stress-effects caused by earthquakes.^[40]

Range of characteristics

Concretes made from energetically modified cements can be designed to exhibit superior strength and durability or to exhibit rapid and ultra-rapid hardening.^[41] This depends upon the "pozzolanic" characteristics of the raw material that is employed to make it. For example, fly ash in its natural state is typically, but not always, more "pozzolanic" than volcanic ash.

An important consideration in choosing a concrete material is its strength-development within a specified time period, which must match or exceed a project's specifications. According to Ronin, the current upper-limit for using EMC made from natural pozzolans is 60% for practical large-scale usage.

No noxious emissions and low leachability of EMCs

The EMC activation of fly ash is a mechanical process, and does not involve heating or burning.^[8] Leachability tests were performed by LTU in 2001 in Sweden on behalf of a Swedish power production company. These tests confirmed that EMC made from fly ash "showed a low surface specific leachability" with respect to "all environmentally relevant metals."^{[42][43]}

EMCs using California volcanic ash

Energetically modified cements have been used in large infrastructure projects in the United States.> EMCs made by replacing at least 50% of the Portland cement with have yielded consistent field results in high-volume applications.^[18] This is also the case for EMC made from natural pozzolans (e.g., volcanic ash).^[19]

Volcanic ash deposits from Southern California were independently tested; at 50% Portland cement replacement, the resulting concretes exceeded requirements.^[44] At 28 days, the compressive strength was 4,180 psi / 28.8 MPa (N/mm²). The 56-day strength exceeded the requirements for 4,500 psi (31.1 MPa) concrete, even taking into account the safety margin as recommended by the American Concrete Institute.^[45] The concrete made in this way was workable and sufficiently strong, exceeding the 75% standard of pozzolanic activity at both 7 days and 28 days.^[44] The surface smoothness of pozzolans in the concrete was also increased.^[44]



Natural Pozzolan (volcanic ash) deposits situated in Southern California in the United States.

Durability of concretes produced and high-performance concretes (HPCs)

Treating Portland cement with EMC activation will yield high-performance concretes. These HPCs will be high strength, highly durable, and exhibiting greater strength-development in contrast to HPCs made from untreated Portland cement. Concrete made from ordinary Portland cement without additives has a

relatively impaired resistance to salt waters.^[46] Treating Portland cement with the EMC activation process may increase the strength development by nearly 50% and also significantly improve the durability, as measured according to generally accepted methods.^[46]

Energetically modified cements also exhibit high resistances to chloride and sulphate ion attack, together with low alkali-silica reactivities (ASR).^[18] Like all concretes comprising pozzolans, they are more durable than concretes made from Portland cement.^[24]

Projects using EMC

An early project using EMC made from fly ash was the construction of a road bridge in Karungi, Sweden, with Swedish construction firm Skanska. The Karungi road bridge has withstood Karungi's harsh subarctic climate and divergent annual and diurnal temperature ranges.^[8]

In the United States, energetically modified cements have been approved for usage by a number of state transportation agencies, including PennDOT, TxDOT and CalTrans.^[9]

In the United States, highway bridges and hundreds of miles of highway paving have been constructed using concretes made from EMC derived from fly ash. These projects include sections of Interstate 10. In these projects, EMC replaced at least 50% of the Portland cement in the concrete poured.^[18] This is about 2.5 times more than the typical amount of fly ash in projects where energetic modification is not used.^[47] Independent text data showed acceptable 28-day strength requirements in all projects.

[18]



Application of EMC on IH-10 (Interstate Highway), Texas, United States

Another project was the extension of the passenger terminals at the Port of Houston, Texas, where energetically modified cement's ability to yield concretes that exhibit high resistances to chloride- and sulphate-ion permeability (i.e., increased resistance to sea waters) was a factor.

Production

EMCs have been in production since 1992. As of 2010 the volume of concrete produced containing a least partially energetically modified cement was about 4,500,000 cu yd (3,440,496 m³). This represents approximately 0.13% of the yearly worldwide concrete production.^[48]

See also

Background science to EMC Activation:

- Archard equation
- Asperity
- Contact mechanics

- Crystallinity
- Crystal structure
- Fretting
- Frictional contact mechanics
- Galling
- Hardness
- Lattice constant
- Material mechanics
- Materials science
- Microstructure
- Nanotribology
- Peter Adolf Thiessen
- Surface engineering
- Surface metrology
- Tribology
- X-ray crystallography
- X-ray fluorescence (XRF)

Academic:

- Luleå University of Technology

Notes

1. Two aspects: **(I)** 2011 Global Portland cement production was approximately 3.6 billion tonnes per United States Geological Survey (USGS) (2013) data, and is binding as a reasonably accurate assimilation, rather than an estimate per se. Note also, that by the same report, for 2012 it is estimated that Global Portland cement production increased to 3.7 billion tonnes (a 100 million tonne increase, year-on-year). **(II)** 2011 Estimate of Global total CO₂ production: 33.376 billion tonnes (without international transport). Source: E.U. European Commission, Joint Research Centre (JRC)/PBL Netherlands Environmental Assessment Agency. Emission Database for Global Atmospheric Research (EDGAR), release version 4.2. The 2009–2011 trends were estimated for energy-related sectors based on fossil fuel consumption for 2009–2011 from the BP Review of World Energy 2011 (BP, 2012), for cement production based on preliminary data from USGS (2012), except for China for which use was made of National Bureau of Statistics of China (NBS) (2009, 2010, 2011). [As of May 2013. See, EDGAR, external link section].
2. Further notes on pozzolanic chemistry: **(A)** The ratio Ca/Si (or C/S) and the number of water molecules can vary, to vary C-S-H stoichiometry. **(B)** Often, crystalline hydrates are formed for example when tricalcium aluminate reacts with dissolved calcium sulphate to form crystalline hydrates (3CaO·(Al,Fe)₂O₃·CaSO₄·nH₂O, general simplified formula). This is called an **AFm** ("alumina, ferric oxide, monosulphate") phase. **(C)** The **AFm** phase *per se* is not exclusive. On the one hand while sulphates, together with other anions such as carbonates or chlorides can add to the **AFm** phase, they can also cause an **AFt** phase where ettringite is formed (6CaO·Al₂O₃·3SO₃·32H₂O or C₆S₃H₃₂). **(D)** Generally, the **AFm** phase is important in the further hydration process, whereas the **AFt** phase can be the cause of concrete failure known as DEF. DEF can be a particular problem in non-pozzolanic concretes (see, for ex., Folliard, K., et al., Preventing ASR/DEF in New Concrete: Final Report (http://www.utexas.edu/research/ctr/pdf_reports/0_4085_5.pdf), TXDOT & U.S. FHWA:Doc. FHWA/TX-06/0-4085-5, Rev. 06/2006). **(E)** It is thought that pozzolanic chemical pathways utilising Ca²⁺ ions cause the **AFt** route to be relatively suppressed.

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External links

- Official website for EMC Cement (<http://www.emccement.com>), Sweden – at EMCcement.com
- Luleå University of Technology (<http://www.ltu.se/?l=en>), Sweden – at LTU.se
- Future Infrastructure Forum (<http://www-fif.construction.cam.ac.uk/>), University of Cambridge, United Kingdom – at Fif.construction.cam.ac.uk
- U.S. Geological Survey (USGS) Cement Statistics and Information (<http://minerals.usgs.gov/minerals/pubs/commodity/cement/>) – at Minerals.usgs.gov
- U.S. Environmental Protection Agency (EPA), Rule Information for Portland Cement Industry (<http://www.epa.gov/ttn/atw/pcem/pcempg.html>) – at EPA.gov
- American Concrete Institute (<http://www.concrete.org/general/home.asp>) – at Concrete.org
- EDGAR – Emission Database for Global Atmospheric Research (<http://edgar.jrc.ec.europa.eu/overview.php?v=CO2ts1990-2011>) – at Edgar.jrc.ec.europa.eu
- Vitruvius: *The Ten Books on Architecture* (<http://penelope.uchicago.edu/Thayer/E/Roman/Texts/Vitruvius/home.html>) online: cross-linked Latin text and English translation
- WBCSD Cement Sustainability Initiative (<http://www.wbcscement.org/>) – at Wbcscement.org

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