# Energetically Modified Cement WIKIPEDIA



## Wikipedia Page (August 2020)

# Energetically Modified Cement



An EMC made from volcanic rocks (Luleå, Sweden, 2020)

**Energetically modified cements** (EMCs) are a class of cements made from pozzolans (*e.g.* fly ash, volcanic ash, pozzolana), silica sand, blast furnace slag, or Portland cement (or blends of these ingredients).<sup>1</sup> The term "energetically modified" arises by virtue of the mechano-chemistry process applied to the raw material, more accurately classified as "high energy ball milling" (HEBM). This causes, amongst others, a thermodynamic transformation in the material to increase its chemical reactivity.<sup>2</sup> For EMCs, the HEBM process used is a unique form of specialised vibratory milling discovered in Sweden and applied only to cementitious materials, here called "EMC Activation".<sup>3</sup>

Energetically modified cements have a wide range of uses. For example, EMCs have been used in concretes for large infrastructure projects in the United States, meeting U.S. concrete standards.<sup>4</sup>

## Justification

The term "energetically modified cement" incorporates a simple thermodynamic descriptor to refer to a class of cements produced using a specialised highly-intensive milling process first discovered in 1993 at Luleå University of Technology (LTU) in Sweden.<sup>56</sup>

The transformatory process is initiated entirely mechanically as opposed to heating the materials directly.<sup>678</sup>The mechanisms of mechanochemical transformations are often complex and different

from "traditional" thermal or photochemical mechanisms.<sup>910</sup>

The effects of HEBM-transformation cause a thermodynamic change that resides ultimately in a modified Gibbs Energy.<sup>11</sup>The process increases the binding capacity and chemical reactivity rates of the materials transformed.<sup>3</sup> <sup>12</sup>



Luleå University of Technology (LTU) campus, Sweden

Continuing academic work and research regarding "self-healing" properties of energetically modified cements is ongoing at LTU.<sup>13</sup> For example, EMCs has received awards from the *Elsa*  $\bar{o}$  *Sven Thysells stiftelse för konstruktionsteknisk forskning* (Elsa & Sven Thysell Foundation for Construction Engineering Research) of Sweden.<sup>14</sup>

## Usage of the "EMC" term

The term "energetically modified cement" was first used in 1992 by Vladimir Ronin, introduced in a paper by Ronin et al. dated 1993 and presented at a formal meeting of the academic Nordic Concrete Research group.<sup>15</sup> The process was refined by Ronin and others, including Lennart Elfgren (now Professor Emeritus of LTU).<sup>16</sup>

At the 45th World Exhibition of Invention, Research and Innovation, held in 1996 in Brussels, Belgium, EMC Activation was awarded a Gold Medal with mention by EUREKA, the European inter- governmental (research and development) organisation, for "modification énergique de ciments".<sup>17</sup>

The term "energetically modified" has been used elsewhere — for example as recently as 2017 — although such usage does not denote the method used was EMC Activation as defined here.<sup>18</sup>

## Overview

The claims made include: 4 19 20 21

- An EMC is a fine powder (typical of all cements) whose colour depends on the material processed.
- The purpose of an EMC is to replace the Portland cement requirement in the mortar or

concrete being used.

- EMC Activation is a dry process. EMCs are produced using only a fraction of the energy used in Portland cement production.
- EMCs require no chemicals for their thermodynamic transformation.
- There are several types of EMCs, depending on the raw materials transformed.
- Depending on user-requirements, delivered dry products may comprise also a minority proportion of Portland cement.
- Each type of EMC has its own performance characteristics, including mechanical load and strength development. Concretes cast from EMCs may yield significant "self-healing" capabilities.
- The most frequently used EMCs are made from fly ash and natural pozzolans. These are relatively abundant materials, and the performance characteristics can exceed those of Portland cement.
- EMC products have been extensively tested by independent labs and certified for use by several USDOTs including in Federal Highway Administration projects.

## EMCs as "Low Carbon" cements

Unlike Portland Cement, an EMC's production releases no carbon dioxide whatsoever. This makes EMCs "low carbon cements".<sup>7</sup>

The first cited claims for EMC's CO<sub>2</sub>-reduction capabilities were made in 1999, when worldwide Portland cement production stood at 1.6 billion tonnes per year.<sup>19 22</sup> From 2011 to 2019, worldwide Portland cement production increased from 3.6 to 4.1 billion tonnes per year.<sup>23</sup> Energetically modified cement's potential for contributing to a worldwide reduction of CO<sub>2</sub> has been *externally* recognised since 2002 and has been ongoing.<sup>568 NOTE 1</sup>

In its 2020 article Laying the foundation for zero-carbon cement, McKinsey & Costated:

"Traditional cement may compete with an improved variety-energetically

NOTE1 <u>Two aspects</u>: (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 was estimated that Global Portland cement production would increase to 3.7 billion tonnes (a 100 million tonne increase, year-on-year), when in fact the actual figure for 2012 was 3.8 billion tonnes. (II) 2011 Estimate of Global total CO<sub>2</sub> 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, '10, '11). [As of May 2013.].

modified cement (EMC)—which releases less carbon and requires less energy to produce. EMC has already been used (in combination with traditional cement) for a variety of projects in Texas".<sup>24</sup>

## Production and field-usage

## No noxious emissions or toxic chemicals during production

EMC Activation is purely a mechanical process. As such, it does not involve heating or burning or indeed any chemical treatments.

This means no fumes at all are produced during an EMC's manufacture.<sup>19</sup>

## History of Usage

EMCs have been produced for project usage since 1992 for a wide range of uses.<sup>4</sup> By 2010, the volume of concrete poured containing EMCs was about 4,500,000 cu·yd (3,440,496 m<sup>3</sup>), largely on US DOT projects.<sup>4</sup> To place this into context, that is more than the entire construction of the Hoover Dam, its associated power plants and



Application of EMC on IH-10 (Interstate Highway), Texas, USA.

appurtenant works, where a total of 4,360,000 cu·yds  $(3,333,459 \text{ m}^3)$  of concrete was poured — equivalent to a U.S. standard highway from San Francisco to New York City.<sup>25</sup>

## Early Usage in Sweden

An early project using EMC made from fly ash was the construction of a road bridge in Karungi, Sweden in 1999, with Swedish construction firm Skanska. The Karungi road bridge has withstood Karungi's harsh subarctic climate and divergent annual and diurnal temperature ranges.<sup>19</sup>

## Usage in the United States

In the United States, energetically modified cements have been approved for usage by a number of state transportation agencies, including PennDOT, TxDOT and CalTrans.<sup>21</sup>

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.<sup>4</sup> These projects include

sections of Interstate 10.<sup>4</sup> In these projects, EMC replaced at least 50% of the Portland cement in the concrete poured.<sup>26</sup> This is about 2.5 times more than the typical amount of fly ash in projects where energetic modification is not used.<sup>27</sup> Independent test data showed 28-day strength-development requirements were exceeded in all projects.<sup>26</sup>

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.<sup>4</sup>

## Properties of concretes and mortars made from EMCs

#### Custom design for end-usage

The performance of mortars and concretes made from EMCs can be custom-designed. For example, EMC concretes can range from general application (for strength and durability) through to the production of rapid and ultra-rapid hardening high-strength concretes



(for example, over 70 MPa / 10,150 psi in 24 hours and over 200 MPa / 29,000 psi in 28 days).  $^{20}$ 

This allows energetically modified cements to yield High Performance Concretes.

#### Durability of EMC concretes and mortars

Any cementitious material undergoing EMC Activation will likely marshal improved durability including Portland cement treated with EMC Activation.<sup>20</sup> As regards pozzolanic EMCs, concretes made from pozzolanic EMCs are more durable than concretes made from Portland cement.<sup>29</sup>

Treating Portland cement with EMC activation will yield high-performance concretes (HPCs). These HPCs will be high strength, highly durable, and exhibiting greater strength-development in

**NOTE2** The "Bache method" for testing concrete durability simulates daily temperature variations in brine. Test 1 or Test 2 may be used, or performed sequentially over 48hrs. The method induces saturation by 7.5% salt water (*i.e.*, higher concentration than sea waters), followed by freezing or heating in a 24-hour cycle to simulate high diurnal temperature ranges. The chosen cycle is repeated *ad nausem* to determine the mass-loss. Hence, the Bache method is generally accepted as one of the most severe testing procedures for concrete as an analogue for durability.

contrast to HPCs made from untreated Portland cement.<sup>20</sup> 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.<sup>20 28</sup>

#### Enhanced resistance to salt-water attack

Concrete made from ordinary Portland cement without additives has a relatively impaired resistance to salt waters.<sup>28</sup> In contrast, EMCs exhibit high resistances to chloride and sulphate ion attack, together with low alkali-silica reactivities (ASR).<sup>26</sup> For example, durability tests have been performed according to the "Bache method" (*see diagram*). Samples made of HPC having respective compressive strengths of 180.3 and 128.4 MPa (26,150 and 18,622 psi) after 28 days of curing, were then tested using the Bache method. The samples were made of (a) EMC (comprising Portland cement and silica fume both having undergone EMC Activation); and (b) Portland cement. The resulting mass-loss was plotted in order to determine durability. As a comparison, the test results showed:

- The reference Portland cement concrete had "total destruction after about <u>16 Bache cycles</u>, in line with Bache's own observations for high-strength concrete"; <sup>20 28</sup>
- EMC high performance concrete showed a "consistent high-level durability" throughout the entire testing-period of <u>80 Bache cycles</u>, with for example, "practically no scaling of the concrete has been observed".<sup>20</sup>

In other words, 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.<sup>20</sup>

#### Low leachability of EMC Concretes

Leachability tests were performed by LTU in 2001 in Sweden, on behalf of a Swedish power production company, on concrete made from an EMC made from fly ash. These tests confirmed that the cast concrete "showed a low surface specific leachability" with respect to "all environmentally relevant metals."<sup>30 31</sup>

## EMCs using Pozzolans such as volcanic materials

## Self-healing properties of Pozzolanic EMCs

Natural pozzolanic reactions can cause mortars and concretes containing these materials to "self-heal".<sup>33 34 35</sup> The EMC Activation process can increase the likelihood of the occurrence of these

pozzolanic reactions.<sup>36 37</sup> The same tendency been noted and studied in the various supporting structures of Hagia Sophia built for the Byzantine emperor Justinian (now, Istanbul, Turkey).<sup>38</sup> 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.<sup>39</sup>

EMCs made from pozzolanic materials exhibit "biomimetic" self-healing capabilities that can be photographed as they develop (*see picture insert below*).<sup>32</sup>



Demonstrating an EMC's "self-healing" propensity...



PHOTO B Without intervention, cracks were totally self-filled after 4.5 months <sup>NOTE3</sup>

## **EMCs using California Pozzolans**

EMCs made by replacing at least 50% of the Portland cement with have yielded consistent field results in high-volume applications.<sup>26</sup> This is also the case for EMC made from natural pozzolans (*e.g.*, volcanic ash).<sup>40</sup>

Volcanic ash deposits from Southern California were independently tested; at 50% Portland cement replacement, the resulting concretes exceeded the requirements of the relevant US standard.<sup>41</sup> At 28 days, the compressive strength was 4,180 psi/28.8 MPa (N/mm<sup>2</sup>). The 56-day strength exceeded

NOTE<sup>3</sup> The large photo depicts a concrete test-beam made from an EMC undergoing RILEM 3-point bending at Luleå University of Technology in Sweden (Feb., 2013). This treatment induces cracks to test for "self-healing" propensities. Concrete (total cmt: 350 kg/m<sup>3</sup>) containing 40% Portland cement and 60% EMC made from fly ash was used. **PHOTO A:** Cracks of average width 150-200 µm were induced after circa 3-weeks' water-curing. **PHOTO B:** Without any intervention, the high volume pozzolan concrete exhibited the gradual filling-in of the cracks with newly-synthesized CSH gel (a product of the ongoing pozzolanic reaction). These were completely filled-in after ~4.5 months. During the observation period, continuous strength-development was also recorded by virtue of the ongoing pozzolanic reaction. This, together with the observed "self healing" properties, have a positive impact on concrete durability. *All photos Dr. V. Ronin and The Nordic Concrete Federation*.

the requirements for 4,500 psi (31.1 MPa) concrete, even taking into account the safety margin as recommended by the American Concrete Institute.<sup>42</sup> 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.<sup>41</sup>



Volcanic ash deposits situated in Southern California, USA.

The surface smoothness of pozzolans in the concrete was also increased.<sup>41</sup>

#### **Effect on Pozzolanic reactions**

EMC Activation is a process that increases a pozzolan's chemical affinity for pozzolanic reactions.<sup>36 37</sup> This leads to faster and greater strength development of the resulting concrete, at higher replacement ratios, than untreated pozzolans.<sup>26 40</sup> These transformed (now highly-reactive pozzolans) demonstrate further benefits using known pozzolanic reaction-pathways that typically see as their end- goal a range of hydrated products. An NMR study on EMCs concluded that EMC Activation caused "the formation of thin SiO<sub>2</sub> layers around C3S crystals", which in turn, "accelerates the pozzolanic reaction and promotes growing of more extensive nets of the hydrated products".<sup>43</sup>

In simple terms, by using 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.<sup>44</sup> Many of the end products of pozzolanic chemistry exhibit a hardness greater than 7.0 on the Mohs scale. "Self healing" capabilities may also contribute to enhanced field-application durabilities where mechanical stresses may be present.

In greater detail, the benefits of pozzolanic concrete, starts with an understanding that in concrete (including concretes with EMCs), Portland cement combines with water to produce a stone-like material through a complex series of chemical reactions, whose mechanisms 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)<sub>2</sub>). This reaction can be noted in three ways, as follows:<sup>45</sup>

- Standard notation:  $Ca_3SiO_5 + H_2O \longrightarrow (CaO) \cdot (SiO_2) \cdot (H_2O) + Ca(OH)_2$
- **Balanced:**  $2Ca_3SiO_5 + 7H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 4H_2O + 3Ca(OH)_2$
- **Cement chemist notation** (the hyphenation denotes the variable stoichiometry):

 $C3S + H \longrightarrow C-S-H + CH$ 

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.<sup>46</sup>
- 2. Calcium hydroxide (Ca(OH)<sub>2</sub>), 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).<sup>47</sup> It is also sectile, with flexible cleavage flakes.<sup>48</sup> Portlandite is soluble in water, to yield an alkaline solution which can compromise a concrete's resistance to acidic attack.<sup>29</sup>

Portlandite makes up about 25% of concrete made with Portland cement without pozzolanic cementitious materials.<sup>44</sup> In this type of concrete, carbon dioxide is slowly absorbed to convert the Portlandite into insoluble calcium carbonate (CaCO<sub>3</sub>), in a process called carbonatation:<sup>44</sup>

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

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.<sup>44</sup> This results in a denser, less permeable and more durable concrete.<sup>44</sup> This reaction is an acid-base reaction between Portlandite and silicic acid (H<sub>4</sub>SiO<sub>4</sub>) that may be represented as follows:<sup>49</sup>

$$Ca(OH)_2 + H_4SiO_4 \longrightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \longrightarrow CaH_2SiO_4 \cdot 2H_2O$$

Further, many pozzolans contain aluminate (Al(OH)<sub>4</sub><sup>-</sup>) 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 the Mohs scale);<sup>50</sup> or

 in combination with silica, to form strätlingite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>·8H<sub>2</sub>O), which geologically can form as xenoliths in basalt as metamorphosed limestone.<sup>51</sup>

Pozzolanic cement chemistry (along with high-aluminate cement chemistry) is complex and perse 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:<sup>52</sup>

 $C_2AH_8 + 2CSH + AH_3 + 3H \longrightarrow C_2ASH_8$  (cement chemist notation)<sup>53</sup>

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).<sup>54</sup> This can be represented per the following equation:

 $3C_2AH_8 \longrightarrow 2C_3AH_6 + AH_3 + 9H$  (cement chemist notation)<sup>55</sup>

Per the first bullet point above, 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.<sup>56</sup> However, adding high-reactivity pozzolans into the concrete mix prevents such a conversion reaction.<sup>57</sup>

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.<sup>26 58</sup>

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.<sup>59</sup> NOTE<sup>4</sup>

**NOTE 4** <u>Further notes</u>: (**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 aluminiate reacts with dissolved calcium sulphate to form crystalline hydrates ( $3CaO(Al, Fe)2O_3 \cdot CaSO_4 \cdot nH_2O$ , 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 ( $6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$  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, FHWA/TX-06/0-4085-5, Rev. 06/2006). (**E**) It is thought that pozzolanic chemical pathways utilising Ca<sup>2+</sup> ions cause the AFt route to be relatively suppressed.

## **EMC** Activation

EMC Activation's purpose is to cause a fundamental destruction to the crystalline structure of the material processed, to render it amorphous.<sup>36</sup> Although this change increases the processed material's chemical reactivity, no chemical reaction is caused *during* the EMC Activation process.



Amorphisation: A depiction the moment of impact during HEBM

Mechanochemistry itself can be defined as a branch of chemistry which is concerned with the "chemical and physico-chemical transformation of substances in all states of aggregation produced by the effect of mechanical energy." <sup>61</sup> IUPAC carries no standard definition of the term *mechanochemistry*, instead defining a "mechanochemical *reaction*" as a chemical reaction "induced by the direct absorption of mechanical energy", while noting, "shearing, stretching, and grinding are typical methods for the mechano-chemical generation of reactive sites".<sup>62 63</sup>

More narrowly, "mechanical activation" was a term first defined in 1942 as a process "involving an increase in reaction ability of a substance *which remains chemically unchanged*." <sup>64</sup> Even more narrowly, EMC Activation is a specialised form of mechanical activation limited to the application of high energy ball milling (HEBM) to cementitious materials. More narrowly than that, EMC Activation uses vibratory milling, and even then, only by using its own *grinding media*.<sup>36</sup>

## Thermodynamic Justification

More particularly, HEBM can be described as increasing the chemical reactivity of a material by increasing its chemical potential energy. In EMC Activation, transferred mechanical energy is stored in the material as lattice defects caused by destroying the material's crystalline structure. Hence, the process transforms solid substances into thermodynamically and structurally more unstable states, allowing an explanation for that increased reactivity as an increase in Gibbs energy:<sup>65</sup>

 $\Delta G = G_T^* - G_T$  where, for temperature *T*, the terms  $G_T^*$  and  $G_T$  are the respective Gibbs values in the processed and unprocessed material.

At its simplest, HEBM causes the destruction of crystalline bonds, to increase a material's

reactivity.<sup>66</sup> From the thermodynamic perspective, any subsequent chemical reaction can decrease the excess energy level in the activated-material (*i.e.*, as a reactant) to produce new components comprising both a lower chemical energy and a more stable physical structure. Conversely, to render the pre-processed material into a more reactive physical state, the disordering process during the HEBM process can be justified as being equivalent to a *decrystallisation* (and hence an entropy increase) that in part yields a volume increase (decrease of bulk density).

A reverse process, sometimes called "relaxation", can be almost immediate (10<sup>-7</sup> to 10<sup>-3</sup> seconds) or take much longer (*e.g.*, 10<sup>6</sup> seconds).<sup>67</sup> Ultimately, any overall *retained* thermodynamic effect can be justified on the basis that any such reverse process is incapable of reaching an ideal thermodynamic end-state of its own accord. As a result, in the course of the mechanical activation of minerals, reverse "relaxation" processes cannot completely decrease the Gibbs free energy that has been created. Hence, energy remains in the material, which is stored in the crystal-lattice *defects* created.<sup>68 69</sup>

#### Net Thermodynamic Effect of HEBM

Overall, HEBM renders a net thermodynamic effect: 70 71 72

— The structural disordering implies an increase of both entropy and enthalpy and thus stimulates the crystal properties according to the thermodynamic modifications. Only a small fraction (approximately 10%) of the excess enthalpy of the activated product may be accounted-for as surface-area enlargement.

—Instead, the main part of the excess enthalpy and modified properties can mostly be assigned to the development of thermodynamically unstable states in the material's lattice (and not as a reduction of particle size). Since the activated system is unstable, the process of activation is reversible—resulting in deactivation, re-crystallization, entropy loss and energy output of system. That reverse ("relaxation") process continues to a thermodynamic equilibrium, but ultimately can never reach an ideal structure (*i.e.*, one free of defects).

—A more complete description of such an "activation" process factors-in enthalpy also, by which according to the *Gibbs-Hemholtz equation*, the Gibbs free energy between activated and non-activated solid state can be represented:

 $\Delta G = \Delta H - T \Delta S$ 

where,  $\Delta H$  is the change in enthalpy and  $\Delta S$  the change in entropy.

#### **Resulting Crystalline Disorder**

Where the crystal disordering is low,  $\Delta S$  is very small (if not negligible). In contrast, in highly deformed and disordered crystals, the values of  $\Delta S$  can have a significant impact on rendered the Gibbs free energy. Leaving aside the heat generated during the process on account of friction etc. occasioned during the activation process, the excess Gibbs free energy retained in the activated material can be justified as being due to two changes, namely an increase in (I) specific surface area; and (II) defect structure.<sup>73 74</sup> In successful HEBM processes such as EMC Activation:<sup>75 76</sup>

- as to (I), only about 10% of the excess energy of such an activated product may be accounted-for as a change in surface area.
- as to (II), almost all the imparted energy is contained in the actual structural defects in the material processed.

#### An approximation for EMC Activation

The relatively low value of (I) as against the high value of aspect (II) serves to further distinguish HEBM from general grinding or "milling" (where instead the only aim there is to increase the surface area of the materials processed), thereby accounting for an explanation for the change in entropy of the rendered material in the form of elastic energy (stored in lattice defects that can take years to "relax" ) that is the "source of excess Gibbs energy and enthalpy".<sup>73</sup> As for enthalpy, four descriptors can be derived to provide an overview as to the total change during such an activation process: <sup>75 77 78</sup>

$$\Delta H_T = \Delta H_d + \Delta H_S + \Delta H_A + \Delta H_p \quad \text{where:}$$

- $\Delta H_d$  is a measure of the *dislocation density*;
- $\Delta H_p$  is a measure of new phases (polymorphic transformation);
- $\Delta H_A$  is a measure of the formation of amorphous material;
- $\Delta H_S$  is a measure of specific surface area.

Because the majority of the work exacted during the EMC Activation process goes to aspect (II) above,  $\Delta H_S$  is trivial. Hence the major functions for the change in enthalpy approximate to:

$$\Delta H_{EMC} \cong \Delta H_d + \Delta H_A + \Delta H_p$$

In EMC Activation, the foregoing terms  $\Delta H_d$  and  $\Delta H_A$  are seen as being particularly prominent because of the nature of the changes in the physical structure observed.<sup>36</sup> Hence, the change in

enthalpy H occasioned during EMC Activation can be approximated to: 77 78

$$\Delta H_{EMC} \approx \Delta H_d + \Delta H_A$$
  
*i.e.*, 
$$\Delta H_{EMC} \approx (\rho M_V) \frac{b^2 \mu_s}{4\pi} \ln\left(\frac{2(\rho)^{1/2}}{b}\right) + C_A E_A$$

where:

- $M_V, b, \mu_s$  and  $\rho$  correspond respectively to the molar volume of the material, Burgers vector, shear modulus and dislocation density;<sup>7778</sup>
- $C_A$  and  $E_A$  are respectively the concentration of the amorphous phase and molar amorphisation energy.<sup>77 78</sup>

#### Low Temperature Reactivity

From the above thermodynamic construct, EMC Activation results in a highly *amorphous* phase that can be justified as a large  $\Delta H_A$  and also a large  $\Delta H_d$  increase.<sup>36 77 78</sup>

The benefits of the EMC Activation being large in H means that an EMC's reactivity is less temperature dependant. In terms of any reaction's thermodynamic impetus, a reactant's overall His not T dependent, meaning that a material having undergone HEBM with a corresponding elevation of H can react at a lower temperature (as the "activated" reactant is rendered less reliant on the temperature-dependant function  $T\Delta S$  for its onward progression). Further, an EMC's reaction can exhibit physical mechanisms at extremely small scales "with the formation of thin SiO<sub>2</sub> layers" to aid a reaction's pathway—with the suggestion that EMC Activation increases the ratio of favourable reaction sites.<sup>43</sup>

Studies elsewhere have determined that HEBM can significantly lower the temperature required for a subsequent reaction to proceed (up to a three-fold reduction), whereby a major component of the overall reaction-dynamics is initiated at a "nanocrystalline or amorphous phase" to exhibit "unusually low or even negative values of the apparent activation energy" required to cause a chemical reaction to occur.<sup>79</sup>

Overall, EMCs are likely less temperature dependent for a chemical pathway's onward progression (see previous major section on Pozzolanic reactions), which may explain why EMCs provide *self-healing* benefits even at low arctic temperatures.<sup>80 81</sup>

#### **Physical Justification (Amorphisation)**

Large changes in terms  $\Delta G$ , more particularly in the resultant values of  $\Delta H_A$  and  $\Delta H_d$  provide an insight into EMC Activation's efficacy. The amorphisation of crystalline material at high-pressure conditions "is a rather unusual phenomenon" for the simple reason that "most materials actually experience the reverse transformation from amorphous to crystalline at high-pressure conditions".<sup>82</sup> Amorphisation represents a highly distorted "periodicity" of a material's lattice element, comprising a relatively high Gibbs free energy.<sup>68 70</sup> Indeed, amorphisation may be compared to a *quasi-molten state*.<sup>69 71</sup>

All told, in common with other HEBM processes, EMC Activation causes crystalline destruction because of extremely violent and disruptive factors that are occasioned at the nanoscale of the material being processed.<sup>83</sup>

Although over in short duration and highly focal, the processes are repeated at a high frequency: hence those factors are thought to mimic pressures and temperatures found deep inside the Earth to cause the required phase change.<sup>2</sup> For example, Peter Thiessen developed the *magma-plasma model* that assumes localised temperatures—higher than 10<sup>3</sup> Kelvin—can be generated at the various impact points to induce a momentary excited plasma state in the material, characterized by the ejection of electrons and photons together with the formation of excited fragments (*see "Amorphisation" diagram above*).<sup>84</sup>

Experimental data gathered from localised crack-generation, itself an important component of EMC Activation, has confirmed temperatures in this region as long ago as 1975.<sup>85</sup>

#### Vibratory Ball Mills (VBMs)

For EMC activation, the HEBM method used is a vibratory ball mill (VBM).<sup>36</sup> A VBM uses a vertical eccentric drive-mechanism to vibrate an enclosed chamber up to many hundreds of cycles per minute. The chamber is filled with the material being processed together with specialised objects called *grinding media*. In their most simple format, such media can be simple balls made from specialised ceramics.

In practical terms, EMC Activation deploys a range of grinding media of different sizes, shapes and composites to achieve the required mechanochemical transformation.<sup>4</sup>

It has been suggested that a VBM will grind at 20 to 30 times the rate of a rotary ball mill, reflecting that a VBM's mechanism is especially rapacious.<sup>86</sup>

#### **VBM Kinetics**

In simple terms, the compressive force acting between two identical colliding balls in a VBM can be expressed: <sup>87</sup>

$$F = \left[ \left(\frac{5m}{8} \right)^{3/5} \left(\frac{2r}{9\pi^2 k^2} \right)^{1/5} \right] v^{6/5} \quad \text{where, } k = \frac{1 - v^2}{\pi E}$$

*Where,* m is the mass of both balls, r the radius, v the absolute velocity of impact and E the Young's modulus of the balls' material.<sup>87</sup>

As can be seen, an increase in velocity of impact increases F. The size and mass of the grinding media also contribute. F's denominator term k incorporates E meaning that the nature of the material used for the grinding media is an important factor (k is ultimately squared in F, so its negative value is of no consequence). More fundamentally, due to the rapid vibration a high acceleration is imparted to the grinding media, whereupon the continuous, short, sharp impacts on the load result in rapid particle-size reduction.<sup>86</sup> In addition, high pressures and shear stresses facilitate the required phase transition to an amorphous state both at the point of impact and also during the transmission of shock-waves that can yield even greater pressures than the impact itself.<sup>83</sup>

For example, the contact time of a two-ball collision can be as short as 20µs, generating a pressure of 3.3 GPa upwards and with an associated ambient temperature increase of 20 Kelvin.<sup>83</sup> Because of the short duration of the impact, the change in momentum is significant—generating a shock wave of duration only 1-100µs but with an associated pressure of up to 10 GPa upwards and a highly localised and focal temperature (*i.e.*, at the nanoscale) up to several thousands of degrees Kelvin.<sup>83</sup> To place this into context, a pressure of 10GPa is equivalent to about 1,000 kilometers of sea water. As a further example, the impact of two identical steel balls of 2.5 cm diameter of velocity 1 m/s will generate a collision energy density of over 109 joules/m<sup>2</sup>, with alumina balls of the same 2.5 cm diameter and velocity of 1 m/s generating an even greater energy density.<sup>87</sup> The collisions occur in a very short timescale and hence the "rate of energy release over the relatively small contact area can be very high".<sup>87</sup>

## References

- Mark Anthony Benvenuto (2015). Industrial Chemistry: For Advanced Students. De Gruyter. pp. 134. ISBN 978-3-11-035170-5.
- Tole, Ilda; Habermehl-Cwirzen, Karin; Cwirzen, Andrzej (1 August 2019). "Mechanochemical activation of natural clay minerals: an alternative to produce sustainable cementitious binders – review". Mineralogy and Petrology. Springer. 113 (4): 449–462.
- 3. Jean-Pierre Bournazel; Yves Malier (1998). PRO 4: International RILEM Conference on Concrete: From Material to Structure RILEM Publications. pp. 101. ISBN 978-2-912143-04-4.
- Ronin, V; Elfgren, L (2010). "An Industrially Proven Solution for Sustainable Pavements of High-Volume Pozzolan Concrete – Using Energetically Modified Cement, EMC". Washington DC, United States: Transportation Research Board of the National Academies.
- 5. Humpreys, K.; Mahasenan, M. (2002). "Toward a Sustainable Cement Industry Substudy 8: Climate Change". Geneva, Swtizerland: World Business Council for Sustainable Development (WBCSD).
- 6. Harvey, D (2013). Energy and the New Reality 1 Energy Efficiency and the Demand for Energy Services. Taylor & Francis. ISBN 9781136542718.
- Kumar, R; Kumar, S; Mehrotra, S (2007). "Towards sustainable solutions for fly ash through mechanical Activation". Resources Conservation and Recycling. London: Elsevier Ltd. 52 (2): 157– 179. ISSN 0921-3449.
- Hasanbeigi, A; Price, L; Lin, E; Lawrence Berkeley National Laboratory, LBNL Paper LBNL-5434E (2013). "Emerging Energy-efficiency and CO2 Emission-reduction Technologies for Cement and Concrete Production". Renewable and Sustainable Energy Reviews. London: Elsevier Ltd. 16 (8): 6220–6238. ISSN 1364-0321.
- Hickenboth, Charles R.; Moore, Jeffrey S.; White, Scott R.; Sottos, Nancy R.; Baudry1, Jerome; Wilson, Scott R. (2007). "Biasing Reaction Pathways with Mechanical Force". Nature. 446 (7134): 423–427.
- 10. Carlier L. & al., "Greener pharmacy using solvent-free synthesis: investigation of the mechanism in the case of dibenzophenazine". Powder Technol. 2013, 240, 41-47.
- Živanović, D; Andrić, L; Sekulić, Ž; Milošević, S (1999). "Mechanical Activation of Mica". In Stojanović, B.D.; Skorokhod, V.V.; Nikolić, M.V. (eds.). Advanced Science and Technology of Sintering. Springer. pp. 211–217. ISBN 978-1-4613-4661-6.

- 12. Danny Harvey (2010). Energy and the New Reality 1: Energy Efficiency and the Demand for Energy Services. Routledge. pp. 385–. ISBN 978-1-136-54272-5.
- Eflgren, L.; Future Infrastructure Forum, Cambridge University (28 March 2013). "Future Infrastructure Forum: Scandinavian Points of View".
- 14. "Stipendieutdelning" (in Swedish). Luleå tekniska universitet. Retrieved 24 March 2014.
- Ronin, V.; Jonasson, J.E. (1993). "New concrete technology with the use of energetically modified cement (EMC)". Proceedings: Nordic Concrete Research Meeting, Göteborg, Sweden. Oslo, Norway: Norsk Betongforening (Nordic concrete research): 53–55.
- 16. LTU website. "Professor Lennart Elfgren". At ltu.se.
- 17. EUREKA. "EUREKA Gold Award for EMC Cement" (from EMC Website).
- Krishnaraj, L; Reddy, YBS; Madhusudhan, N; Ravichandran, PT (2017). "Effect of energetically modified Fly Ash on the durability properties of cement mortar". Rasayan Journal of Chemistry. 10 (2): 423–428.
- Hedlund, H; Ronin, V; Jonasson, J-E; Elfgren, L (1999). "Grönare Betong" [Green Cement]. 91 (7). Stockholm, Sweden: Förlags AB Bygg & teknik: 12–13.
- 20. Elfgren, L; Justnes, H; Ronin, V (2004). "High Performance Concretes With Energetically Modified Cement (EMC)". Kassel, Germany: Kassel University Press GmbH. pp. 93–102.
- United States Federal Highway Administration (FHWA). "EMC Cement Presentation January 18, 2011". Washington, DC.
- 22. "Cement Data Sheet". U.S. Geological Survey. USGS. 2001.
- 23. "Cement Data Sheet". U.S. Geological Survey. USGS. 2020.
- Czigler, T; Reiter, S; Somers, K (May 2020). "Laying the foundation for zero-carbon cement". McKinsey & Co.
- 25. "Hoover Dam Frequently Asked Questions and Answers". U.S. Bureau of Reclamation.
- 26. "Summary of CemPozz® (Fly Ash) Performance in Concrete." EMC Cement BV (2012).
- 27. Schneider, M.; Romer M., Tschudin M. Bolio C.; Tschudin, M.; Bolio, H. (2011). "Sustainable cement production present and future". Cement and Concrete Research. 41 (7): 642–650.
- Bache, M (1983). "Densified cement/ultra fine particle-based materials". Proceedings of the Second International Conference on Superplasticizers in Concrete.
- 29. Chappex, T.; Scrivener K. (2012). "Alkali fixation of C-S-H in blended cement pastes and its relation

to alkali silica reaction". Cement and Concrete Research. 42(8): 1049-1054.

- 30. Private study, Luleå University of Technology (2001). "Diffusionstest för cementstabiliserad flygaska", LTU Rapport AT0134:01, 2001-09-03
- Ronin, V; Jonasson, J-E; Hedlund, H (1999). "Ecologically effective performance Portland cementbased binders", proceedings in Sandefjord, Norway 20–24 June 1999. Norway: Norsk Betongforening. pp. 1144–1153.
- Ronin, V; Emborg, M; Elfgren, L (2014). "Self-Healing Performance and Microstructure Aspects of Concrete Using Energetically Modified Cement with a High Volume of Pozzolans". Nordic Concrete Research. 51: 129–142.
- Yang, Y; Lepech, M. D.; Yang, E.; Li, V. C. (2009). "Autogenous healing of engineered cementitious composites under wet-dry cycles". Cement and Concrete Research. 39 (5): 382–390. ISSN 0008-8846.
- Li, V., C.; Herbert, E. (2012). "Robust Self-Healing Concrete for Sustainable Infrastructure". Journal of Advanced Concrete Technology. Japan Concrete Institute. 10 (6): 207–218.
- Van Tittelboom, K.; De Belie, N. (2013). "Self-Healing in Cementitious Materials A Review" Materials. 6 (6): 2182–2217
- Justnes, H; Elfgren, L; Ronin, V (2005). "Mechanism for performance of energetically modified cement versus corresponding blended cement". Cement and Concrete Research. Elsevier (London) and Pergamon Press (Oxford). 35 (2): 315–323. ISSN 0008-8846.
- Patent abstract for granted patent "Process for Producing Blended Cements with Reduced Carbon Dioxide Emissions" (Pub. No.:WO/2004/041746; Pub. Date: 21.05.2004).
- 38. Moropoulou, A.; Cakmak, A.; Labropoulos, K.C.; Van Grieken, R.; Torfs, K. (January 2004). "Accelerated microstructural evolution of a calcium-silicate-hydrate (C-S-H) phase in pozzolanic pastes using fine siliceous sources: Comparison with historic pozzolanic mortars". Cement and Concrete Research. 34 (1): 1–6.
- Moropoulou, A; Cakmak, A., S., Biscontin, G., Bakolas, A., Zendri, E.; Biscontin, G.; Bakolas, A.; Zendri, E. (December 2002). "Advanced Byzantine cement based composites resisting earthquake stresses: the crushed brick/lime mortars of Justinian's Hagia Sophia". Construction and Building Materials. 16 (8): 543.
- 40. "Summary of CemPozz® (Natural Pozzolan) Performance in Concrete". (2012). EMC Cement BV.
- 41. Stein, B (2012). "A Summary of Technical Evaluations & Analytical Studies of Cempozz® Derived from Californian Natural Pozzolans". San Francisco, United States: Construction Materials

Technology Research Associates, LLC.

- 42. ACI 318 "Building Code Requirements for Structural Concrete and Commentary".
- 43. Johansson, K; Larrson, C; Antzutkin, O; Forsling, W; Rao, KH; Ronin, V (1999). "Kinetics of the hydration reactions in the cement paste with mechanochemically modified cement 29Si magic-angle-spinning NMR study". Cement and Concrete Research. Pergamon. 29 (10): 1575–81.
- 44. Baroghel Bouny, V (1996). Bournazel, J. P.; Malier, Y. (eds.). "Texture and Moisture Properties of Ordinary and High-Performance Cementitious Materials" (in PRO 4: Concrete: From Material to Structure). 144 at 156: RILEM. p. 360. ISBN 2-912143-04-7.
- 45. "Cement hydration" (understanding-cement.com/hydration.html). Understanding Cement.
- 46. *See, for ex.*, Thomas, Jeffrey J.; Jennings, Hamlin M. (January 2006). "A colloidal interpretation of chemical aging of the C-S-H gel and its effects on the properties of cement paste". Cement and Concrete Research. Elsevier. 36 (1): 30–38.
- 47. Portlandite at Webmineral (http://www.webmineral.com/data/Portlandite.shtml)
- 48. Handbook of Mineralogy (http://rruff.geo.arizona.edu/doclib/hom/portlandite.pdf)
- 49. Mertens, G.; Snellings, R.; Van Balen, K.; Bicer-Simsir, B.; Verlooy, P.; Elsen, J. (March 2009).
  "Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity". Cement and Concrete Research. 39 (3): 233–240.
- 50.  $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ , with hydroxide (OH) partially replacing silica (SiO<sub>4</sub>).
- Webmineral.com. "Stratlingite Mineral Data". See, also, Ding, Jian; Fu, Yan; Beaudoin, J.J. (August 1995). "Strätlingite formation in high alumina cement – silica fume systems: Significance of sodium ions". Cement and Concrete Research. 25 (6): 1311–1319.
- 52. Midgley, H.G.; Bhaskara Rao, P. (March 1978). "Formation of stratlingite, 2CaO.SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub>.8H<sub>2</sub>O, in relation to the hydration of high alumina cement". Cement and Concrete Research. 8 (2): 169–172. ISSN 0008-8846. *See, also,* Midgley, H.G. (March 1976). "Quantitative determination of phases in high alumina cement clinkers by X-ray diffraction". Cement and Concrete Research. 6 (2): 217–223. ISSN 0008-8846.
- 53. Heikal, M.; Radwan, M M; Morsy, M S (2004). "Influence of curing temperature on the Physicomechanical, Characteristics of Calcium Aluminate Cement with air cooled Slag or water-cooled Slag". Ceramics-Silikáty. 48 (4): 185–196. *See, also,* Abd-El.Aziz, M.A.; Abd.El.Aleem, S.; Heikal, Mohamed (2012). "Physico-chemical and mechanical characteristics of pozzolanic cement pastes and mortars hydrated at different curing temperatures". Construction and Building Materials. 26 (1): 310–316. ISSN 0950-0618.

- Mostafa, Nasser Y.; Zaki, Z.I.; Abd Elkader, Omar H. (2012). "Chemical activation of calcium aluminate cement composites cured at elevated temperature". Cement and Concrete Composites. 34 (10): 1187–1193. ISSN 0958-9465.
- 55. Taylor, HFW, (1990) Cement chemistry. London: Academic Press, pp.319-23.
- 56. Matusinović, T; Šipušić, J; Vrbos, N (2003). "Porosity-strength relation in calcium aluminate cement pastes". Cement and Concrete Research. 33 (11): 1801–1806. ISSN 0008-8846.
- 57. *See, for ex.*, Majumdar, A.J.; Singh, B. (November 1992). "Properties of some blended high-alumina cements". Cement and Concrete Research. 22 (6):1101–1114. ISSN 0008-8846
- ASTM International (2010). "ASTM C989: Standard Specification for Slag Cement for Use in Concrete and Mortars". Book of Standards Volume. 4 (2).
- 59. Nhar, H.; Watanabe, T.; Hashimoto, C. & Nagao, S. (2007). "Efflorescence of Concrete Products for Interlocking Block Pavements" (Ninth CANMET/ACI International Conference on Recent Advances in Concrete Technology: Editor, Malhotra, V., M., 1st ed.). Farmington Hills, Mich.: American Concrete Institute. pp. 19–34. ISBN 9780870312359.
- 60. Boldyrev, V.V.; Pavlov, S.V.; Goldberg, E.L. (March 1996). "Interrelation between fine grinding and mechanical activation". International Journal of Mineral Processing. 44-45: 181–185.
- Heinicke, G.; Hennig, H.-P.; Linke, E.; Steinike, U.; Thiessen, K.-P.; Meyer, K. (1984).
  "TRIBOCHEMISTRY: In Co-Operation with H.P. Hennig, et al" [and with a preface by Peter-Adolf Thiessen]. Berlin: Akademie-Verlag: 495.
- 62. "IUPAC-Mechano-chemical reaction (MT07141)" (goldbook.iupac.org/terms/view/MT0714).
- 63. Baláž, P; Achimovičová, M; Baláž, M; Billik, P; Cherkezova-Zheleva, Z; Criado, JM; Delogu, F; Dutková, E; Gaffet, E; Gotor, FJ; Kumar, R; Mitov, I; Rojac, T; Senna, M; Streletskii, A; Wieczorek-Ciurowa, Kr (2013). "Hallmarks of mechanochemistry: from nanoparticles to technology". Chemical Society Reviews. Royal Society Publishing. 42 (18): 7571.
- Smekal, A. (April 1942). "Ritzvorgang und molekulare Festigkeit". Die Naturwissenschaften. 30 (14–15):224–225.
- 65. Hüttig, Gustav F. (1943). "Zwischenzustände bei Reaktionen im festen Zustand und ihre Bedeutung für die Katalyse". Heterogene Katalyse III: 318–577. ISBN: 978-3-642-52046-4.
- Zelikman, AN; Voldman, GM; Beljajevskaja, LV (1975). Theory of hydrometallurgical processes. Metallurgija (In Russian).
- 67. Meyer, K (1968). Physikalisch-chemische Kristallographie. VEB Deutscher Verlag für

Grundstoffindustrie. p. 337. ASIN B0000BSNEK.

- 68. Pourghahramani, P; Forssberg, E (2007). "Effects of mechanical activation on the reduction behavior of hematite concentrate". International Journal of Mineral Processing. 82 (2): 96–105.
- 69. Pourghahramani, P; Forssberg, E (2007). "Reduction kinetics of mechanically activated hematite concentrate with hydrogen gas using nonisothermal methods". Thermochimica Acta. 454 (2):69–77.
- Pourghahramani, P; Forssberg, E (2006). "Comparative study of microstructural characteristics and stored energy of mechanically activated hematite in different grinding environments". International Journal of Mineral Processing. 79 (2): 120–139.
- Pourghahramani, P; Forssberg, E (2006). "Microstructure characterization of mechanically activated hematite using XRD line broadening". International Journal of Mineral Processing. 79 (2): 106–119.
- 72. Pourghahramani, P; Forssberg, E (2007). "Changes in the structure of hematite by extended dry grinding in relation to imposed stress energy". Powder Technology. 178 (1): 30–39.
- 73. Pourghahramani, P (2007). "Mechanical Activation of Hematite Using Different Grinding Methods with Special Focus on Structural Changes and Reactivity". Luleå University: 242. ISSN 1402-1544.
- 74. Pourghahramani, P; Forssberg, E (2007). "Changes in the structure of hematite by extended dry grinding in relation to imposed stress energy". Powder Technology. 178 (1): 30–39.
- Tkáčová, K.; Baláž, P.; Mišura, B.; Vigdergauz, V.E.; Chanturiya, V.A. (1993). "Selective leaching of zinc from mechanically activated complex Cu-Pb-Zn concentrate". Hydrometallurgy. 33 (3): 291– 300.
- Baláž, P (2000). Extractive metallurgy of activated minerals. Amsterdam: Elsevier Science B.V. p. 292. ISBN 9780080531533.
- 77. Tkáčová, K. (1989). Mechanical activation of minerals. Amsterdam: Elsevier. p. 170. ISBN 978-0444988287.
- Tromans, D.; Meech, J.A. (November 2001). "Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation". Minerals Engineering. 14 (11): 1359–1377.
- 79. Nepapushev, A. A.; Kirakosyan, K. G.; Moskovskikh, D. O.; Kharatyan, S. L.; Rogachev, A. S.; Mukasyan, A. S. (2015). "Influence of high-energy ball milling on reaction kinetics in the Ni-Al system: An electrothermorgaphic study". International Journal of Self-Propagating High-Temperature Synthesis. 24 (1): 21–28.
- 80. Ronin, V; Jonasson, JE (1994). Investigation of the effective winter concreting with the usage of

energetically modified cement (EMC) - material science aspects, Report 1994:03, 24 pp (in Swedish). Luleå University (LTU), Div. of Struct Eng.

- 81. Ronin, V; Jonasson, JE (1995). High strength and high peformance concrete with use of EMC hardening at cold climate conditions. Proceedings of International Conference on Concrete under Severe Conditions, Sapporo, Japan, Luleå University (LTU), Div. of Struct Eng.
- 82. Handle, Philip H.; Loerting, Thomas (2015). "Temperature-induced amorphisation of hexagonal ice". Physical Chemistry Chemical Physics. 17 (7): 5403–5412.
- Sobolev, K (2005). "Mechano-chemical modification of cement with high volumes of blast furnace slag". Cement and Concrete Composites. 27 (7–8): 848–853.
- 84. Weichert, R.; Schönert, K. (1974). "On the temperature rise at the tip of a fast running crack<sup>+</sup>". Journal of the Mechanics and Physics of Solids. 22 (2): 127–133.
- Fuller, K. N. G.; Fox, P. G.; Field, J. E. (1975). "The Temperature Rise at the Tip of Fast-Moving Cracks in Glassy Polymers". Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences. 341 (1627): 537–557. ISSN 0080-4630.
- Krycer, I; Hersey, JA (1980). "A comparative study of comminution in rotary and vibratory ball mills". Powder Technology. 27 (2): 137–141.
- 87. Venkataraman, K.S.; Narayanan, K.S. (1998). "Energetics of collision between grinding media in ball mills and mechanochemical effects". Powder Technology. 96 (3): 190–201.

Produced 2020-08

All Rights Reserved.

Copyright ©2020 EMC Cement BV.

This document is for internal evaluation use only. Copying or transmission of this document whole or in part, for purposes beyond those as set out in the previous sentence is strictly prohibited, except with our express prior consent.

The entire contents of this document are under copyright protection. The contents may not be copied other than as expressly permitted above without the express written consent of EMC Cement BV.

CemPozz and the three-leaf device whether not appearing in large print or with a "tm" or "®" trademark symbol, are trademarks of EMC Cement BV. The use or misuse of these trademarks or any other materials, except as may be permitted by us in writing, is hereby expressly prohibited and may be in violation of applicable law.

References to CemPozz products and services do not per se imply that EMC Cement BV (or any of its subsidiaries) is bound to offer or provide such products and services in every country throughout the World. Product specifications upon deliver may vary according to ultimate options chosen. Specifications of products are a matter of continual evaluation and evolution. We reserve the absolute right to amend vary modify our products in any manner as we deem fit without any obligation of prior notice.

Other company, product and service names may be trademarks or service marks of others.

Please be advised that EMC Cement BV aggressively enforces its intellectual property rights to the fullest extent permitted by law. For further information please feel free to contact us.

#### ΕN

EMC Cement B.V. Alvägen 33 SE - 97 332 Luleå Sweden

Tel: +46 705 498 892 E-mail: emcdev@telia.com

See: www.lowcarboncement.com

IMPORTANT NOTICE THIS IS NOT AN OFFERING MEMORANDUM. NOTHING HEREIN SHALL BE CONSTRUED AS AN OFFER TO SELL OR THE SOLICITATION OF AN OFFER TO BUY ANY SECURITIES OR OTHER INTERESTS IN OR THE SERVICES OF ANY AFFILIATE OF EMC OR TO IMPLY ANY TYPE OF FIDUCIARY RELATIONSHIP. ALL INFORMATION HEREIN IS PROVIDED STRICTLY ON AN EX-GRATIA AND "AS IS" BASIS ONLY. BASED UPON ACTUAL OPERATING EXPERIENCE AND INFORMATION AS MAY BE PRESENTLY AVAILABLE TOGETHER WITH OUR OWN EVALUATIONS, INTERPRETATIONS, EXTRAPOLATIONS, ANALYSES, CALCULATIONS AS MAY BE PERFORMED FROM TIME TO TIME IN OUR ABSOLUTE DISCRETION. ALTHOUGH REASONABLE CARE HAS BEEN TAKEN TO ENSURE THE ACCURACY OF THE CONTENTS OF THIS DOCUMENT. NO WARRANTIES OF ANY TYPE WHATSOEVER ARE GIVEN OR IMPLIED AS TO ITS ACCURACY.

SOURCE:

https://en.wikipedia.org/wiki/Energetically\_modified\_cement

