DOI: 10.1002/cssc.200800088

Greening the Construction Industry: Enhancing the Performance of Cements by Adding Bioglycerol

Michele Rossi,*[a] Cristina Della Pina,[a] Mario Pagliaro,[b] Rosaria Ciriminna,[b] and Paolo Forni[c]

The addition of glycerol, a by-product of biodiesel manufacturing, to cement eases its grinding and handling while considerably enhancing the strength of the resulting concrete. The benefits of using bioglycerol are significant both for the environment and for the concrete and biodiesel industries. The advantages for industry derive from having a single, readily available material that offers all three major technical improvements required of cement additives, namely enhanced concrete strength, and grinding and handling aids for cement, while the environmental impact is eased by using bioglycerol instead of ethylene glycol and hydroxyamines that are presently used as major components of cement additives.

The single most widely used material in the world, concrete, is produced in quantities of over 2 billion tons per year with a large, global environmental impact.[1] Indeed, the production of concrete currently accounts for 5% of annual anthropogenic global CO_2 production, with China's booming construction industry alone accounting for 3%.[2] The global production is expanding rapidly also in India and other developing countries (Figure 1), and by 2050 the use of concrete is predicted to reach four times the 1990 level.

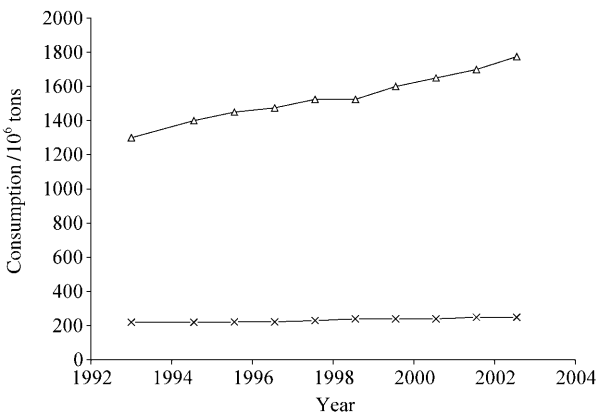

Figure 1. World consumption of cement is rapidly on the rise (△), whereas in Europe it is constant at about 200 million tons per year (×). (Source: Grace Construction Products.)

The most efficient cement kilns (cement is the key ingredient of concrete) produce about 800 kg CO_2 per ton of cement, with around 530 kg of carbon dioxide being released by the decomposition of limestone ($CaCO_3$) into CaO and CO_2 and the rest coming from the consumption of fossil fuels required to reach reaction temperatures of up to 1500 °C.

Hydraulic cements are produced by calcining a mixture of calcareous and argillaceous materials comprising limestone, sand, clay, and iron ore to produce a sintered "clinker". At temperatures approaching 1000 °C, the crude material decomposes and then combines into di- and tricalcium silicate. Finally, the clinker is ground in ball mills along with gypsum and other process additives to a finely divided state with a large surface area to yield the finished cement (Figure 2). The grinding process accounts for 40% of the total cost of production. The heat required for calcination is normally generated by burning petroleum coke, but the mechanical and thermal energy for the cooler is provided by electricity and amounts to around 20% of the overall energy consumption (Table 1). While thermal energy consumption has fallen almost to the technical minimum of 3500 MJ per ton of clinker (Figure 3), the consumption of electricity is on the increase as a result of the growing demand for higher-grade cements.

The development of new concrete additives (admixtures) to produce a stronger, easier-to-handle material is being intensely investigated worldwide.[3] As a common practice, synthetic plasticizers such as polycarboxylate ethers or polyols are added to mixes as dispersants to prevent through steric repulsion the cement particles from combining together. As a result, the mechanical processing of dry cement is eased and less water is required to achieve high-strength concrete, whereas the cement retains good workability.

Cement additives, used in 60% of global cement production, are composed primarily of organic materials (and minor proportions of inorganic ingredients). The organic components are derived from ethylene and other fractions of petroleum distillation. In general, water-soluble polyols, mainly glycols

[a] Prof. M. Rossi, Dr. C. Della Pina
Dipartimento di Chimica Inorganica, Metallorganica e Analitica
Università degli Studi di Milano
via Venezian 21, 20133 Milano MI (Italy)
Fax: (+39) 02-503-14405
E-mail: michele.rossi@unimi.it

[b] Prof. M. Pagliaro, Dr. R. Ciriminna
Istituto per lo Studio dei Materiali Nanostrutturati, CNR
via U. La Malfa 153, 90146 Palermo PA (Italy)

[c] Dr. P. Forni
Grace Construction Products, W. R. Grace Italiana S.p.A.
via Trento 7, 20017 Passirana di Rho MI (Italy)

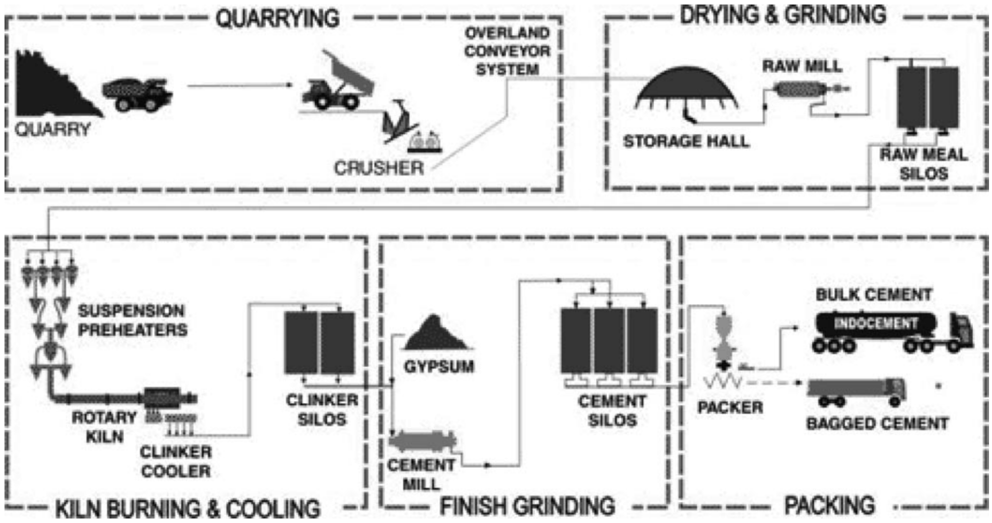

Figure 2. Typical dry process for cement manufacture (source: Indocement).

process in the range of 150–500 g per ton of cement and result in 1) increased cement flowability and reduced pack set; 2) increased grinding efficiency and mill output; 3) reduced unit power costs; and 4) reduced handling and pumping costs.

All the chemicals that are able to improve the grinding process are strongly polar in nature. The grinding aids are adsorbed on the newly created surface of the cement particles, neutralizing electrical charges and reducing their tendency to reagglomerate (Figure 4). As a result, the cement grains become easier to grind into smaller particles.

Table 1. Electrical energy represents about 20% of the overall energy input for cement manufacture, with typical values in the range of 90–130 kWh per ton.

Process	E [kWh ton^{-1}]
Crushing	1–3
Grinding of crude mixture	8–30
Homogenization of crude mixture	1–2
Cooking	16–18
Grinding finished cement	30–80

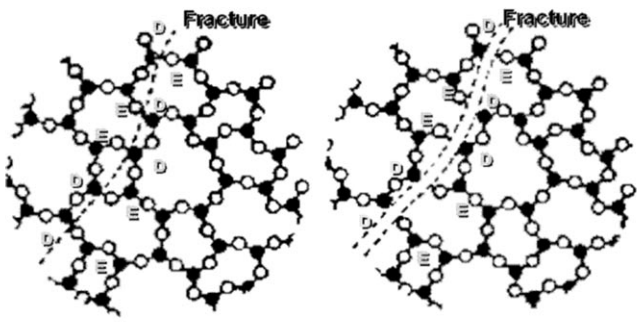

Figure 4. Crystal structure of silica. D and E refer to oxygen-deficient (positive) and oxygen-rich (E = excess; negative) sites, respectively.

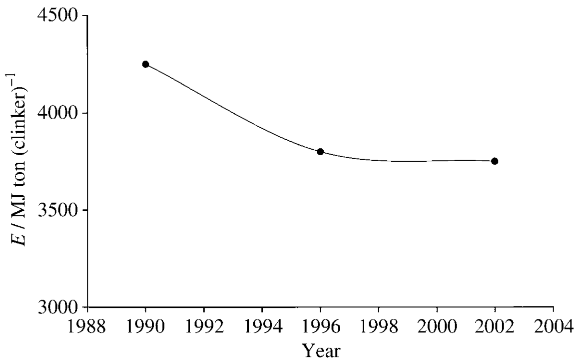

Figure 3. Evolution of specific thermal energy consumption for the production of each ton of clinker in Italy. Similar trends are common in Germany and other leading industrialized countries (source: Grace Construction Products).

and polyglycerols,[4] and the acetate esters of glycerol[5] are useful cement additives which act as grinding aids and reduce pack set.[6] Grinding aids (admixtures) reduce the cost of cement manufacture by decreasing the attractive forces between the cement particles that cause agglomeration. Furthermore, such admixtures actively affect the hydration processes by controlling not only these processes in terms of reaction rate but also the composition and morphology of hydration products. They are added to the cement during the grinding

Apart from polyols, other types of additives may be used, including water-soluble aliphatic alkali carboxylates,[3] nitrogen-containing hydroxy compounds such as triethanolamine,[7] and sulfonated lignins.[8] A combination of more than one component is frequently employed.[9] Herein, we report that crude glycerol obtained as a by-product of biodiesel manufacturing can be used as an excellent quality additive for cement by enhancing its compression strength[10] and aiding its grinding and handling properties.

Enhanced Compression Strength

Compression strength is the capability of a manufactured concrete article to withstand pressure. When the ultimate compression strength is reached, fractures are generated at the surface which may cause the article to break. As high compression strength is so important, a variety of additives have been developed to improve this property. These additives are preferably added during the clinker milling step. Pure glycerol gives good results in improving compression strength, but its

Table 2. Compression strength of three cement clinkers with addition of pure or crude glycerol.[a]

Cement and additive	Blaine [$cm^2 g^{-1}$][b]	Particle size [μm][c] R32	R45	R63	R90	Compressive strength [MPa] 1 day	2 days	7 days	28 days
Belgium	3230	21.9	10.5	3.2	0.1	n.d.	25.9	45.0	58.2
Belgium + pure glycerol	3290	24.7	12.5	4.1	0.4	n.d.	26.7	45.0	58.8
Belgium + crude glycerol	3160	26.5	14.2	5.2	0.7	n.d.	28.3	46.9	60.8
Greece	3570	18.8	8.7	2.6	0.2	16.1	n.d.	41.6	53.0
Greece + pure glycerol	3550	22.1	10.8	3.4	0.3	20.1	n.d.	41.6	53.8
Greece + crude glycerol	3590	21.5	10.7	3.6	0.5	18.1	n.d.	43.8	56.6

[a] Standard procedures such as those described in the European standard EN 196 were used to evaluate the properties of the clinkers herein. Analytical data for crude glycerol (density = 1.29 kg L^{-1}) are as follows (wt %): glycerol 92 %; water 1.5 %; NaCl 5 %; non-glycerol organic matter 0.8 %. [b] Blaine: test for determining the fineness of cement on the basis of its permeability to air. The value increases as the fineness increases. [c] Laser post-source decay: granulometry distribution (%) of particles with diameters greater than 32, 45, 63, and 90 μm.

industrial usage has traditionally been impeded by the high cost of the pure material.

Table 2 lists the results of industrial tests carried out on two types of commercial clinker. The performance of crude glycerol produced by a biodiesel plant is compared with that of a commercial, high-purity-grade glycerol. The cement precursor was blended with gypsum and milled for a given time in order to produce cements with a similar fineness (Belgium, Greece, and Italy are arbitrary names of different types of cement) in the presence of crude or pure glycerol, which was added as 50 % solutions in water in amounts comparable to those used with current commercial additives such that the final concentration was 400 ppm. Compressive strength tests were carried out according to international standards (EN 196). In all cases, crude glycerol (containing 5 % NaCl and with an amber-brown color owing to the presence of natural dyes) was found to give improved mechanical properties with respect to those produced by pure glycerol. This result is surprising and points to a synergy between glycerol and the inorganic salts present in the crude sample and retained in the final concrete. We propose that glycerol could be polymerized to give di- and triglycerol in an etherification reaction mediated by CaO and further assisted by homogeneous Na_2CO_3 formed upon the addition of NaCl-doped crude (and hydrated) glycerol. Indeed, it was recently reported that colloidal CaO particles of about 50–100 nm, such as those present in cement, display a very high activity in promoting the etherification of glycerol.[11]

Grinding and Handling Aid

Glycerol also has an effect on the solids; for example, it will fragment CaO (formation of colloidal particles) and its related solids and therefore improve the "mixing" of compounds in the concrete. Accordingly, a second major benefit of crude glycerol as a cement additive comes from its use in grinding and handling technologies. Indeed, a common practice in the cement industry is to add small amounts of grinding additives during milling to lower the friction between particles. In general, these additives are composed of hydrophilic molecules which, adsorbed on the surface of solid cement particles, change their electrokinetic potentials resulting in a reduction of the energy needed to grind the clinker to the required particle size.

In the production of cement, the energetic balance is dominated by thermal heating of the furnace and electrical energy required by the mill. As mentioned above, these factors account for as much as 40 % of total production costs (fuel: 3500 MJ per ton of clinker; electricity: 90–120 kWh per ton of cement). The benefit of grinding additives is to decrease the consumption of electrical energy by about 10 %, which is a remarkable result.

A common problem in the handling of cementlike materials lies in the packaging of the powdered material. After grinding, most cements become semirigid when vibrated and compacted, thus hardly flowing under a consistent mechanical effort. To lower the "pack-set tendency", that is, the energy required to initiate flow, is of paramount importance while unloading cement powder from storage silos and trucks.

The use of low levels of glycerol, either in pure or crude form as a by-product of biodiesel, leads to significant improvements in the morphologic and rheologic properties after the milling step of different cement clinkers. In fact, a similar or better performance is obtained in blaine and pack-set determinations when using glycerol as compared to the more expensive triethanolamine and diethylene glycol typically used as grinding and handling aid. Table 3 shows that the number of mill revolutions required for producing similar fineness (blaine value 3510–3590 $cm^2 g^{-1}$) is lower when crude glycerol is used. This result is associated with good flowability of the resultant cement as shown by the fairly good value of the pack-set values.

In summary, these findings will have significant environmental, economic, and technical benefits. Environmental benefits can be achieved through a better energy efficiency in grinding and handling processes by the use of a renewable resource—bioglycerol—in place of additives of petrochemical origin. The benefits to industry derive from having a single, readily available material that can offer all three major technical advantages required of cement additives: enhanced concrete strength, and enhanced grinding and handling aids for cement. Finally, from a broader economic viewpoint, the low cost of crude glycerol along with the diffuse distribution of biodiesel production sites, which are generally not far away from the large number of cement production sites in all continents, provides both biodiesel and cement manufacturers with a large market to exchange an abundant by-product that is currently pro-

Table 3. Properties of clinkers with added crude glycerol (GLY), triethanolamine (TEA), or diethylene glycol (DEG).

Cement and additive	Particle size [μm][a] R32	R45	R63	R90	Blaine [$cm^2 g^{-1}$][b]	NMR [s][c]	Pack set [s][d]
Italy	71.2	82.4	91.7	97.8	3580	2200	41
Italy + TEA	73.8	85.3	93.8	98.6	3510	2250	29
Italy + DEG	74.1	84.8	93.3	98.5	3590	2200	28
Italy + GLY	79.9	89.8	96.3	99.5	3590	2050	32
Greece	80.0	89.7	96.3	99.5	3610	2350	68
Greece + TEA	77.5	88.1	95.4	99.3	3510	2400	21
Greece + DEG	78.5	89.0	96.0	99.4	3620	2200	38
Greece + GLY	77.3	88.1	95.5	99.3	3530	2400	32

[a] See footnote [b] in Table 2. [b] See footnote [c] in Table 2. [c] Total number of mill revolutions. [d] Time required to break cement agglomeration under a standard test.

duced in large surplus by the burgeoning biodiesel industry,[12] although in the biorefinery concept[13] glycerol will also be produced by other ways. The positive aspects of applying crude glycerol to concrete manufacture have been underpinned by a growing commercial application in Europe and the United States in the last two years.

Keywords: cement · glycerol · industrial chemistry · organic–inorganic hybrid composites

[1] J. M. Crow, *Chem. World* **2008**, *5*, 62.
[2] J. S. Damtoft, J. Lukasik, D. Herfort, D. Sorrentino, E. M. Gartnerb, *Cem. Concr. Res.* **2008**, *38*, 115.
[3] K. L. Scrivener, R. J. Kirkpatrick, *Cem. Concr. Res.* **2008**, *38*, 128.
[4] H. H. Moorer, C. M. Anderegg, US 4204877, **1980**.
[5] I. C. Bechtold, US 2225146, **1940**.
[6] L. A. Jardine, J. H. Cheung, W. M. Freitas, US 6641661, **2003**.
[7] G. R. Tucker, C. W. Tucker, H. L. Kennedy, M. S. Renner, US 2031621, **1936**.
[8] J. G. Mark, US 2141570, **1938**.
[9] H. H. Moorer, C. M. Anderegg, US 3615785, **1971**.
[10] M. Rossi, M. Pagliaro, R. Ciriminna, C. Della Pina, W. Kesber, P. Forni, WO2006051574, **2006**.
[11] A. M. Ruppert, J. D. Meeldijk, B. W. M. Kuipers, B. H. Erné, B. M. Weckhuysen, *Chem. Eur. J.* **2008**, *14*, 2016.
[12] M. Pagliaro, M. Rossi, *The Future of Glycerol: New Usages for a Versatile Raw Material*, RSC Publishing, Cambridge: UK, **2008**.
[13] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484.

Received: April 22, 2008
Revised: June 10, 2008
Published online on September 4, 2008

