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PAPER

Investigation of glycerol polymerization in the clinker grinding process†‡

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Concrete production is a large scale process that involves high energy consumption. In order to increase the sustainability of this process, the reduction of energy input is necessary. Bio-glycerol was demonstrated to be a highly efficient renewable-based additive in the grinding process for concrete production and helped reduce energy costs and improve the quality of the resulting product. In order to understand its excellent aiding properties, the interaction of glycerol with cement clinkers was investigated; both chemical and physical interactions were taken into account. The results of this investigation points to surface tension modification of the clinker particles as one of the main effects of bio-glycerol addition during the grinding process.

Introduction

Despite the recession that started in 2008, the global production of concrete, which is currently over 2 billion tonnes per year,¹ is expanding rapidly due to China's,² Brazil's and India's booming construction industries. By 2050, concrete use is predicted to reach *four* times the 1990 level. Cement production is also a highly energy intensive process, and particularly, the grinding of the cement clinker accounts for as much as 40% of the total production cost. Therefore, grinding additives are widely used by the cement industry as they can lead to a significant decrease of electrical energy consumption by about 10%.

The development of new concrete additives (admixtures) to produce a stronger, handy material is a topic of intense investigation.³ In general, cement additives are primarily composed of strongly polar and hydrophilic organic molecules, usually derived from non-renewable petroleum feedstocks. They include aliphatic alkali carboxylates³ and nitrogen-containing hydroxyl compounds such as triethanolamine,⁴ which, overall, are used in 60% of the world's cement production. Water-soluble, biomass-derived polyols, mainly glycols and polyglycerols,⁵ sulfonated lignins,⁶ and the acetic acid esters of glycerol,⁷ are also useful cement additives, but are generally more expensive. A combination of more than one component is frequently

employed.⁸ These additives are introduced during the grinding process within the range 150–500 g per ton of cement, and they are considered to be able to adsorb the newly created surface of the particles, changing their electrokinetic potentials and reducing their tendency to re-agglomerate (Table 1).⁹ This reduces the energy needed to grind the clinker. Admixtures actively interact with hydration processes by controlling them in terms of reaction rate, composition, morphology of the hydration products and by reducing pack set inhibition.¹⁰

Recently, some of us reported that crude glycerol obtained as a by-product of biodiesel manufacture (bio-glycerol) is an excellent concrete additive that is capable of enhancing cement performance by (i) improving the compression strength, and (ii) aiding the grinding and handling properties.¹¹ Compression strength is the capability of a manufactured concrete material to withstand pressure. When the ultimate compression strength is reached, fractures are generated at the surface that may cause the material to break. Since a high compression strength is so important, a variety of additives have been developed to improve this property.

The use of bio-glycerol in this application has significant environmental, economic and technical benefits. The environmental benefits can be achieved through better energy efficiency in grinding and handling processes by the use of a renewable resource—bio-glycerol—in place of additives of petrochemical origin. Industry benefits are derived from having a single, readily available material that is capable of offering all three major technical advantages required of cement additives (enhanced concrete strength, grinding and handling aids for cement). Furthermore, bio-glycerol is expected to be an important platform molecule of future bio-refinery schemes and therefore available in high quantities from renewable sources.¹²

The other major advantage of employing crude glycerol as a cement additive is that the use of low levels of raw glycerol gives significant improvements in the morphological and rheological

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Table 1 Advantages impaired by cement additives

Increased cement flowability and reduced pack set	Increased grinding efficiency and mill output	Reduced unit power costs	Reduced handling and pumping costs
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properties of the materials after the milling step of different cement clinkers. These performances are either similar or better compared to the more expensive triethanolamine (TEA) and diethylene glycol (DEG) that are typically used as grinding and handling aids. Moreover, in our original study,¹¹ crude glycerol from a biodiesel plant was found to induce improved mechanical properties with respect to those produced by pure glycerol.

To understand the causes of this particular behaviour, we have tried to investigate whether the beneficial effect of glycerol is just due to physical properties or whether it is due to chemical reactions taking place during the grinding of clinker–bio-glycerol admixtures. Indeed, Ruppert *et al.* recently discovered that colloidal CaO particles, similar to those that might be present in cement, have a very high activity in promoting glycerol etherification (Scheme 1).¹³

In this paper, we report our investigations on the interaction of bio-glycerol and cement clinkers obtained from industry. Both the catalytic properties of the clinkers in glycerol etherification, as well as the physical interactions, were investigated.

Experimental conditions

Materials

Three clinker samples originating from plants located in three different countries (France—clinker A, China—clinker B and Germany—clinker C, kindly donated by Grace Construction Products), were used throughout the study. To study interactions, we tested the catalytic activity of the clinkers in (bio-)glycerol etherification, followed by characterization of the clinkers before and after the reaction, and finally we examined the stability of the clinkers in the presence of glycerol solutions.

Raw glycerol was received from a bio-diesel plant with the following composition: 85 wt% glycerol and 15 wt% water solution containing a mixture of inorganic salts, fatty acid salts, methanol and ashes.¹⁴

Catalytic reaction

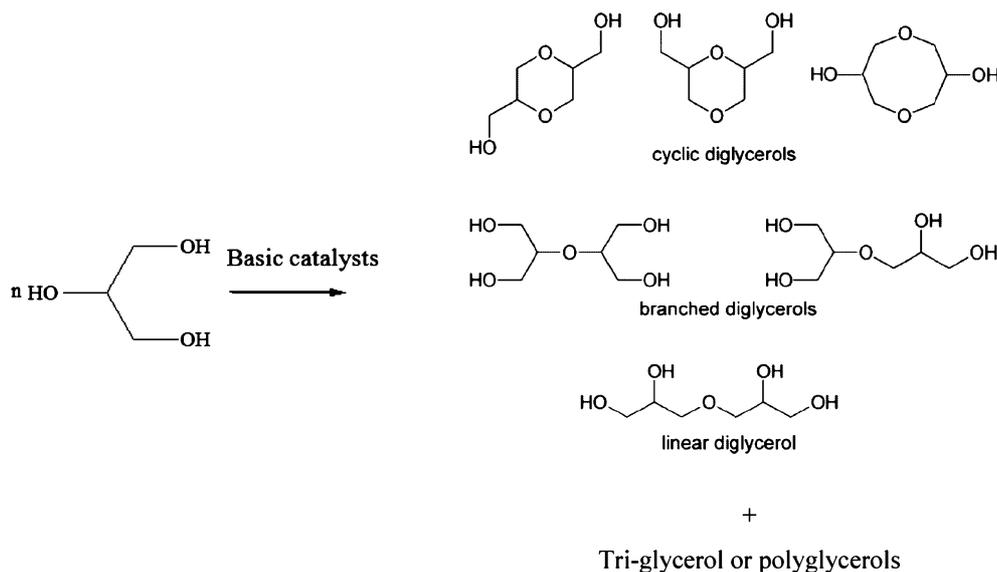
Clinkers powdered before the etherification reaction and Na₂CO₃ (Acros, anhydrous pure) were used as received. The catalytic tests were carried out at temperatures between 120–220 °C, both in a 40 ml Parr autoclave and a three-necked 250 ml flask equipped with a mechanical stirrer (500 rpm) under a flow of argon connected to a Dean–Stark apparatus, with a reflux condenser for removal of water by-product according to the method of Ruppert *et al.*¹³ Typical loadings were 50 g of glycerol substrate and 1 g of clinker catalyst.

Analytical methods

The products were analyzed using a GC 2010 system from Shimadzu with a CP-WAX 57CB (25 m × 0.2 mm × 0.2 μm) column using internal calibration, a GC-MS from Shimadzu with a CP-WAX 57CB column (25 m × 0.2 mm × 0.2 μm) and also by HPLC-MS using an HPLC-ESI-MS from Shimadzu with a Pathfinder PS column (RP-18, 3.5 μm, 4.6 × 150 mm). Details of these methods can be found in the work of Ruppert *et al.*¹³

Catalyst characterization

X-Ray powder diffraction (XRD) was performed using a Bruker-AXS D8 Advance powder X-ray diffractometer equipped with an automatic divergence slit, Vântec-1 detector

**Scheme 1** Glycerol polymerization by basic catalysts.

and cobalt $K\alpha_{1,2}$ ($\lambda = 1.79026 \text{ \AA}$) source. Infrared measurements were recorded on a Perkin-Elmer 2000 FTIR spectrometer with a data point resolution of 4 cm^{-1} using a DTGS detector with an accumulation of 16 scans per spectrum. The samples were diluted prior to measurement with KBr in a 5:95 mixture ratio.

Results and discussion

Calcination of a mixture of calcareous and argillaceous materials comprising limestone, sand, clay and iron ore at a temperature of about $1400\text{--}1500 \text{ }^\circ\text{C}$ produces a sintered nodular material called “clinker”, whose major components are tricalcium silicate (typically about 65% of the total), dicalcium silicate (about 15% of the total), tricalcium aluminate (typically about 7% of the total) and tetracalcium aluminoferrite (typically about 8% of the total).¹⁵ Overall, these phases constitute about 90% of the material composition, whereas the mineralogical structure differs of course from clinker to clinker. No calcium sulfate was present in the clinker samples analyzed in this work as CaSO_4 is used as a cement constituent added during the grinding process and is not considered an additive.

Due to the above mentioned complex chemical composition, it is very difficult to distinguish between the clinker components by FT-IR or Raman spectroscopy. Fig. 1a, for example, shows the FT-IR spectra of the three clinker samples. All three samples present a strong band at 927 cm^{-1} , with additional peaks at 1100 cm^{-1} , which most probably correspond to the stretching vibration of the T–O–T groups (where T is either Si or Al) and the Si–O–Ca bond.¹⁶ Additional bands are observed in the region $400\text{--}600 \text{ cm}^{-1}$ that can be attributed to the tetrahedral alumina stretching band at 532 cm^{-1} and to silica at 453 cm^{-1} . A small broad band with a maxima at 3400 cm^{-1} is also observed that corresponds to water (–OH) stretching vibrations. Furthermore, as the spectra are very similar, the FT-IR measurements indicate that all three clinker samples contain the same major structural components.

In order to investigate the influence of bio-glycerol mixing with the clinker, samples were prepared and analyzed by FT-IR spectroscopy. The simple physical mixing of the clinkers with bio-glycerol does not induce any important chemical transformations in the structure of the cement precursor, as indicated for clinker B (Fig. 1b). Similar results were observed for the other two clinkers (spectra not shown).

The FT-IR spectra of the fresh clinker sample (B), mixed with 10 wt% bio-glycerol and of bio-glycerol alone are presented and compared in Fig. 1b. The main characteristic bands of the clinker material in the region $400\text{--}1000 \text{ cm}^{-1}$ are present in the mixed material (Fig. 1b, B and C). The new bands that appear in the IR spectrum are due to bio-glycerol (Fig. 1b, A and C). The strong broad band with a maxima at 3400 cm^{-1} is due to water and glycerol O–H stretching vibrations, where the band at 1600 cm^{-1} corresponds to adsorbed water molecules.

The bands at 2932 and 2861 cm^{-1} correspond to the asymmetric stretching vibration of $-\text{CH}_2-$ and the symmetric stretching vibration of $-\text{CH}_2-$ groups of the glycerol molecule, as well of the other organic impurities (fatty acids or fatty esters are normally present in bio-glycerol mixtures). The presence of alkyl groups is further evidenced by the bands in the 1409--

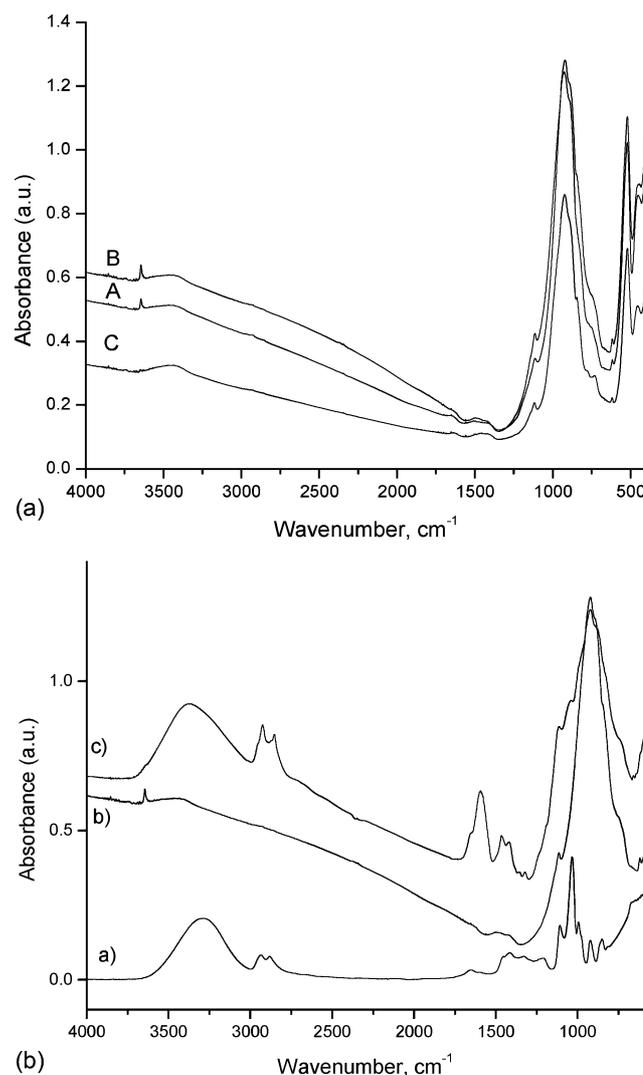


Fig. 1 (a) FT-IR spectra of the three clinker samples: (A) is clinker A, (B) is clinker B and (C) is clinker C; (b) FT-IR spectra of a: bio-glycerol, b: clinker B and c: clinker B + 10 wt% bio-glycerol. The compounds were physically mixed.

1463 cm^{-1} region, which correspond to the asymmetric bending of $-\text{CH}_2-$.¹⁶

In the spectrum of bio-glycerol alone (Fig. 1b, C), the bands at $1000\text{--}1200 \text{ cm}^{-1}$ correspond to the C–O symmetric stretching vibration, whereas the presence of some small fatty acid residues is suggested by a small shoulder at 1705 cm^{-1} , which corresponds to the C=O stretching vibrations of carboxyl groups.

XRD measurements confirm that the clinker–bio-glycerol admixtures have no effect on the chemical structure of the clinkers, even after heating the mixtures at $800 \text{ }^\circ\text{C}$ for 1 h. Fig. 2a, comprising the XRD patterns of the three clinkers, shows that their composition is very similar; the only differences being in the ratio of the different crystalline phases. The positions of the main diffraction lines of the three main components of the clinker mixtures (dicalcium silicate, tricalcium silicate and calcium aluminate) are indicated in Fig. 2a.

Clearly, the thermal treatment at $800 \text{ }^\circ\text{C}$ of the physical mixture of clinker and bio-glycerol has no effect on the XRD

Table 2 Catalytic results of the etherification of glycerol

Entry	Catalyst	Substrate	Time (h)	<i>T</i> (°C)	Conversion (%)	Selectivity for di-glycerol (%)	Others (%)
1.	Na ₂ CO ₃ ^a	Glycerol	20	220	75	60	35 ^b
2.	Clinker B ^a	Glycerol	23	220	15	69	31
3.	Clinker A ^a	Glycerol	17	220	20	68	32
4.	Clinker C ^a	Glycerol	20	220	13	68	32
5.	Na ₂ CO ₃	Glycerol	3	120	none	none	—
6.	Clinker B	Glycerol	3	120	none	none	—
7.	Clinker B	Bio-glycerol	2	120	2	100	0
8.	Clinker B	Di-glycerol	2	120	n.d. ^c	—	—

^a Reactions performed in a round-bottomed flask under an Ar flow: 1 g clinker, 50 g glycerol. Other reactions were performed in an autoclave: 6 g catalyst, 18 g glycerol. ^b Tri-glycerol is the main byproduct (35%). ^c Conversion < 1%, tri-glycerol was formed.

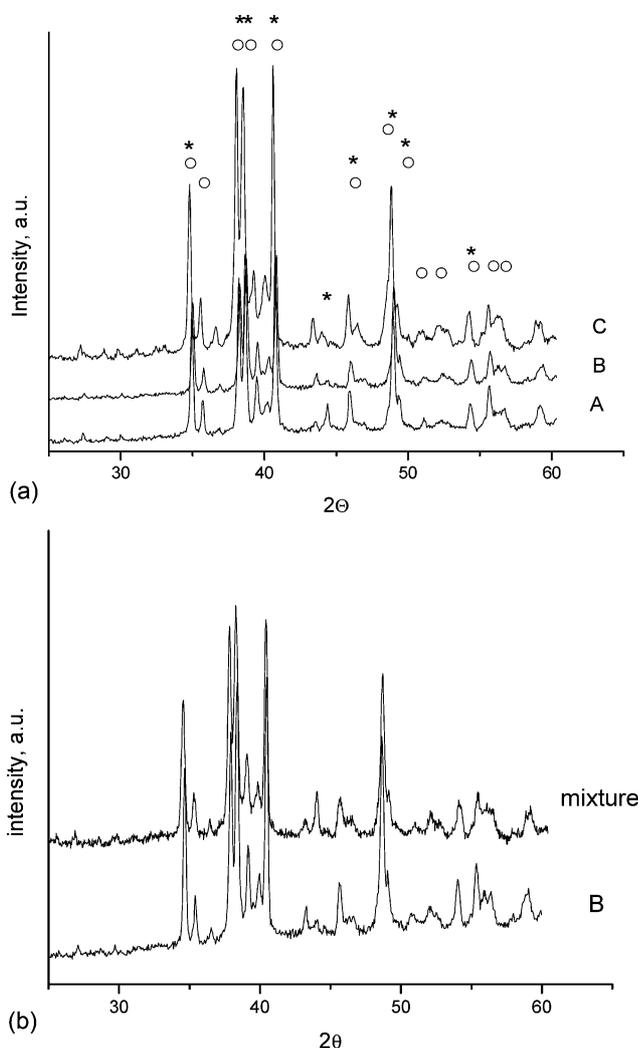


Fig. 2 (a) XRD patterns of the clinkers: A—clinker A, B—clinker B and C—clinker C; * = Ca₂SiO₄, O = Ca₃SiO₅ (according to the Powder Diffraction file from the International Centre for Diffraction Data, 2000). (b) Samples a—clinker A and b—clinker A mixed with 10 wt% of bio-glycerol and heated to 800 °C for 1 h.

pattern of clinker B (Fig. 2b), and the same result was obtained for the other two clinker–bio-glycerol admixtures.

In conclusion, as both the FT-IR and XRD analyses of the clinker–bio-glycerol admixtures indicate that no chemical transformation occurs in the structure of the clinker in the

presence of the polyol, we decided to investigate if indeed the positive effect of bio-glycerol addition during clinker grinding originates from its catalytic activity.

Clinkers' catalytic activity in glycerol etherification

Temperatures in ball mills or grinders are generally up to 120 °C, and normally range from 80 to 120 °C. Under these conditions, water tends to evaporate; but in the real system, both water and glycerol will be constantly adsorbed and desorbed from the surface of the solid material. In the production process, crude glycerol addition is continuous, namely the additive is constantly added to the fresh feed of the mill and exits the mill adsorbed onto the surface of the finished cement. Depending on the specific mill system, the time spent inside the mill by the clinker along with the added glycerol varies from 15 to 60 min. In this sense, the conditions employed by us during the catalytic tests can be considered extreme, since temperatures of up to 220 °C were used, as well as an excess of glycerol.

Table 2 presents the main results of the catalytic etherification of glycerol conducted in the presence of the three clinker samples, as well as of sodium carbonate (a standard catalyst for glycerol etherification). A reaction temperature of 220 °C was previously found to be optimum for a high glycerol etherification yield.¹³

Indeed, in agreement with previous results,^{13a} glycerol conversion after 20 h of reaction with Na₂CO₃ was 75%, mainly yielding di-glycerol (60% selectivity) and tri-glycerol (35% selectivity) (Table 2, entry 1). At 220 °C, all three clinkers showed catalytic activity, but the conversions of glycerol were in each case lower compared to Na₂CO₃ alone (Table 2, entries 2–4). Hence, clinker B after 23 h caused a glycerol conversion in 15% yield, whereas clinker A gave 20% yield after 17 h. Clinker C gave only 13% conversion after 20 h. For all three clinkers, di-glycerol was obtained with selectivities close to 70% in a mixture of both linear and cyclic isomers. No tri-glycerol formation was observed, and the by-products were mainly composed of a mixture of dehydrated products and their corresponding oligomers.

Acrolein formation is known to take place in glycerol etherification, particularly at high temperature. Here, the formation of acrolein was evidenced by the formation of cyclic products with glycerol and the formation of coke on the clinker catalysts (the formation of a black deposit was observed at the end of the reaction). Another, important dehydration product found was hydroxyacetone. The formation of this product, as well as of the oligomeric products that lead to coke formation, is

particularly interesting since it indicates that some Lewis acidity is present in the clinker samples, along with the basicity of the Ca components. Comparing the catalytic activity of the clinkers with that reported by Ruppert *et al.*¹³ for CaO catalysts under similar conditions, the one obtained here is considerably lower, as shown by the 20% conversion value compared to 80% by Ruppert *et al.*

Yet, as mentioned above, 220 °C is a very high temperature compared to the conditions present in a ball mill. At 120 °C (a more realistic temperature), no reaction with pure glycerol was observed either with Na₂CO₃ or with the clinkers, and this was independent of the reaction setup used (Parr reactor or round-bottomed flask) (Table 2, entries 5–6). At this low temperature, traces of di-glycerol were observed only when bio-glycerol was used as a substrate (Table 2 entry 7). Yet, when 50 wt% water solutions of glycerol or bio-glycerol were used (as in a ball-mill process), no di-glycerol was found. Etherification of di-glycerol was attempted, and some higher glycerol ethers were observed in trace amounts (Table 2, entry 8).

It is important to mention that in these reactions, a glycerol : clinker ratio of between 5 and 50 was used. Although, we observed di-glycerol formation with clinkers at high temperatures above 200 °C and reaction times of 24 h, at 120 °C (which is theoretically the maximum temperature obtained in a ball mill), only traces of di-glycerol were observed; this after relatively long reaction times. However, we cannot totally exclude the formation of di-glycerol in the grinding process since very small amounts of glycerol are used in the real production process (which makes the ratio between the catalytic species and the substrate very high) and localised overheating may occur in the ball mill.

The spent clinker catalysts recovered from reactions at 220 °C were covered by an insoluble black deposit, indicating coke formation. The FT-IR spectrum of the spent clinker catalyst (Fig. 3a) presents a band at 1483 cm⁻¹ corresponding to the -CH₃

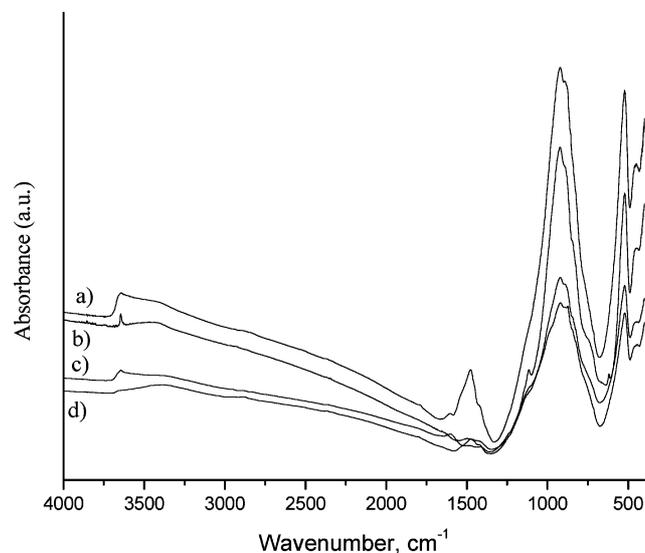


Fig. 3 FT-IR spectra before and after the glycerol etherification reaction: (a) etherification of glycerol with clinker B at 220 °C, (b) clinker B, (c) etherification of bio-glycerol with clinker B at 120 °C and (d) etherification of a 85 wt% water solution of glycerol with clinker B at 120 °C. After the reaction, the solid was washed with water and dried at 120 °C overnight.

asymmetric bending vibration, and some small bands at 2932 and 2861 cm⁻¹ corresponding to the antisymmetric stretching vibration of -CH₃ and the symmetric stretching vibration of -CH₂-. This coke is decomposed at temperatures up to 500 °C, as indicated by the TG analysis (not shown), which may suggest that it is a rather “soft” type of coke.

On the other hand, the FT-IR spectra of the spent clinker samples obtained after reactions at 120 °C are unvaried, no whether or not bio-glycerol or pure glycerol was used.

The XRD analyses of the spent clinkers (not shown) indicate that the composition of the materials is preserved during the reaction.

Finally, the stability of the clinkers during (bio)-glycerol etherification was investigated. All of the clinkers partially dissolved in the glycerol solutions. In Fig. 4, the FT-IR spectra of the recovered materials from the reaction of bio-glycerol and glycerol are presented and compared with the FT-IR spectra of pure clinker B. Unmodified clinker solids were obtained by evaporating the reaction solution, from which the catalyst was

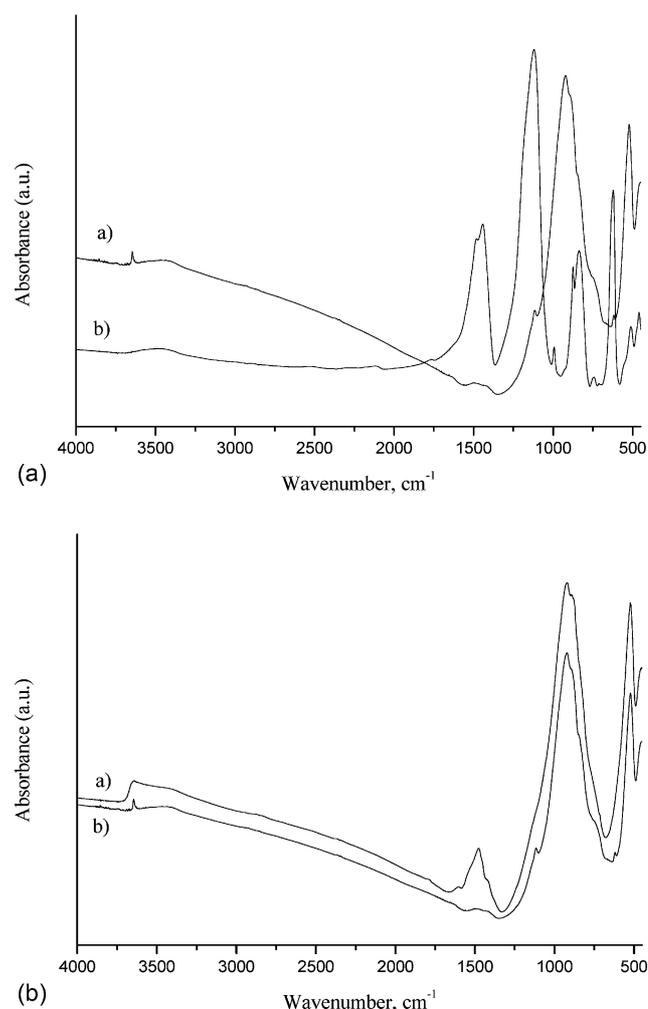


Fig. 4 The FT-IR spectrum of the solid recovered from the solution after reactions of glycerol and bio-glycerol with clinker B; the liquid was centrifuged, filtered (0.45 micron) and heated at 800 °C for 6 h: (A-a) clinker B before the reaction, (A-b) recovered material from the reaction of clinker B with bio-glycerol, (B-a) clinker B before the reaction and (B-b) recovered material from the reaction of clinker B with glycerol.

previously filtered and centrifuged, at temperatures up to 800 °C (Fig. 4B).

The solid material recovered from the reaction with bio-glycerol presents bands similar to the ones of the pure clinker, plus additional bands most probably due to the inorganic compounds found in the bio-glycerol mixture (Fig. 4A). This experiment is a proof that glycerol helps break down the clinker particle agglomerates during the ball milling process by modification of their surface tension. Similarly, in the etherification of glycerol in the presence of CaO,¹³ it is clearly observed that glycerol can extract the calcium from the catalyst, helping to dissolve the calcium ions.

Conclusions

In order to understand the excellent aiding properties of biodiesel-derived glycerol (bio-glycerol) as an additive in the grinding process for cement production, we studied the interaction of glycerol with cement clinkers; both chemical and physical interactions were taken into account. The results of these investigations point to surface tension modification of the clinker particles as the main effect of bio-glycerol during the grinding process. No significant change in the composition of the clinker in the presence of the additive was observed, even if high loadings of additive were used, as suggested by FT-IR and XRD analyses. On the other hand, glycerol also has a physical effect on the solids as it helps fragment the colloidal solid particles and therefore improves the mixing of compounds in the grinding process. The formation of polyglycerols or dehydrated/oligomeric species, which in principle can take place due to local overheating in ball mills, is not significant and therefore is not responsible for the significant enhancement of the milling process due to bio-glycerol.

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