# Contrasting circulating-bed fly ash and limestone as additions

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## Abstract

Circulating fluidized bed combustion (CFBC) power plants produce as by-product large ash particles with elevated calcium content. They are not commonly accepted as addition for cement although presenting pozzolanic potential. To enhance the activity of this material, the CFBC ash was ground to fineness equal to that of the cement, simulating a joint milling with the clinker. This ground fly ash (GFA) was included in blended cements in ratios of 10%, 20% and 40%. These new cements with GFA surpassed 52.5 MPa at 28 days for even 40% of substitution. Contrasted with limestone addition, the most used in Europe, the cements with GFA presented higher compressive strength, better durability with the only drawback of a slight reduction in workability. This CFBC fly ash could be used as clinker replacement once ground to similar fineness than cement allowing high reductions in clinker consumption and its consequent carbon footprint reduction.

## Keywords chosen from ICE Publishing list

Cement/cementitious materials; Compressive strength; Sustainability

## List of notation (examples below)

| | |
|---|---|
| CFBC | circulating fluidized bed combustion |
| GFA | ground fly ash |

## 1. Introduction

The circulating fluidized-bed power plants burn coal to produce electric power and as side effect they create several by-products such as fly ash, bottom ash, boiler slag, flue gas desulfurization residues, and fluidized bed combustion ash (Sheng et al. 2007). This technology is increasing worldwide due to its advantages: cleaner technology for low quality coal, adaptability to variety of fuel type and load, high combustion efficiency, lower NOx emissions and stable operation. The main advantage of this technology is the ability to burn high $SO_2$ coal and also high quantities of co-firing combustibles. And all this without exceeding the emission limits. The control of the $SO_2$ is achieved thanks to the circulating limestone added in situ during combustion (Sheng et al. 2007). The outcome is that the sulphates are chemically bonded with the calcium oxide and mixed with the fly ash recovered in the electrofilters (Li et al. 2012; Yang et al. 2005). The presence of limestone dust produces higher amount of ash (Redemann et al. 2008). Furthermore, logically this type of ash usually presents high CaO content; so in addition to the pozzolanic activity, it could present self-hardening properties (Ahmaruzzaman 2010). The presence of calcium varies with the plant configuration from 8% (Zheng et al. 2017), to a range of 12 to 20% (Hlaváček et al. 2018) and even to higher CaO contents such as 27% (Jang et al. 2018).

In contrast, the traditional boilers burn pulverized coal and produce mainly fly ash as by-product, this fly ash is usually silicic, altought variable with the composition of the coal (Li et al. 2012). This fly ash usually presents pozzolanic properties so it can be used as addition to the cement, resulting in important economic and ecological benefits (AENOR 2011; Ahmaruzzaman 2010). The cement standards from different countries are strict with the quality of this type of fly ash coming from pulverized coal (ASTM International 2012; AENOR 2011). In this context, the ash that results from boilers with other types of technology is not being used because of the uncertain regulatory framework, scarce experience and lack of research on this type of by-products.

Some authors declare that this fly ash from CFBC boilers is useless as cement addition (Hlaváček et al. 2018), however other authors report suitable properties to produce blended cements (Váchal et al. 2018). There is a need to clarify for each specific fly ash if it could be worth using or not. The combustion in CFBC boiler is different from the usual pulverized coal power plants with a temperature of process of 850-900 ºC, lower than the usual 1500 ºC of pulverized coal boilers (Hlaváček et al. 2018; Zhao et al. 2015). This leads to substantial differences in the produced ashes, where usual boilers produce spherical particles due to sintering at high temperature, the CFBC fly ash presents irregular and porous shape with a larger particle size. This usually leads to higher water demands in mixtures (Zhao et al. 2015; Zheng et al. 2017). The work of González-Fonteboa (Belén González-Fonteboa et al. 2017) studies ground bottom ash from a CFBC power plant. It reported that the effect was negative in compressive strength, however cements with ground bottom ash presented superior strength than those with limestone. On the other hand, it was found that the workability was severely reduced with the use of ground bottom ash.

The large size of the CFBC fly ash could lead to reduced hydraulic and pozzolanic activity. Some authors (Felekoğlu et al. 2009; Kumar et al. 2007; Sadique et al. 2012) who used conventional fly ash with coarse size studied the effect of a grinding process, and reported that the increase in fineness lead to higher activity but also increased water demand. This grinding process consumes energy, however the energetic balance is substantially positive in terms of clinker reduction and the subsequently decrease of carbon emissions (Vargas & Halog 2015).

The regulations of blended cements allow the incorporation of many types of additions directly from the factory (AENOR 2011; ASTM International 2012). The use of this by-products permits to use a lower content of clinker and therefore to reduce carbon emissions and energy consumption. The use of cements with additions has been increasing rapidly since year 2000 and reached a stable market quota of 70% in Europe (The European cement Association 2013). The International Energy Agency (International Energy Agency 2009) encourages this trend with this recommendation "…encourage and facilitate increased clinker substitution". In Spain, for instance, conventional Portland cement without additions represents less than 20% of the market and its use has been decreasing continuously. The most widely used cements in Spain are CEM II/A-V 42.5 R (with 5% to 20% of siliceous fly ash) and secondly CEM II/A-L 42.5 R (with 5% to 20% of limestone) (The European cement Association 2013).

The purpose of this research is to characterize GFA from a CFBC boiler and determine whether it is a suitable addition for the manufacture of blended cements. To achieve this goal, we needed to grind the fly ash from CFBC to produce fineness similar to that of cement to gain acceptable activity. This simulates a simultaneous grinding of the ash with the clinker in the cement mill. The performance of this CFBC fly ash is compared with the most common and used of all additions: the limestone (The European cement Association 2013). One of the major goals is to question if the industry is using profusely certain products –limestone– while others with high potential such as CFBC fly ash are not considered suitable for blended cements production.

## 2. Materials and methods

The fly ash of this research comes from a circulating fluidized bed combustion boiler (CFBC). This power plant burns primarily lignite coal with high sulphate content, hence the necessity of lime in the fluidized bed to control sulphate emissions. It also used a reduced quantity of co-combustion materials. The original fly ash produced was coarse and presented insufficient reactivity, therefore it was necessary to grind it before its use. For this task we used a ball mill for a time sufficient to simulate the grinding process of this type of ash simultaneously with the clinker in the ball mills of a cement factory (Belén González-Fonteboa et al. 2017).

In this research, it is compared the effect of Ground Fly Ash (GFA) with commercial blended cements with limestone addition and also with a standard Portland cement. Table 1 shows the composition of these blended cements.

[TABLE 1]

In this research, we designed six types of cement, mortar and concrete mixes. Table 2 presents the detailed composition of all of them. For the mortar, we established a water to cement ratio of 0.50 (EN 196-1). On the other hand, in the concrete mix we set a water/cement ratio of 0.55, corresponding with the common practice for general use medium quality concrete used in mild aggressiveness environment (AENOR 2008a). The natural aggregates were crushed limestone with sizes 0/4 mm for sand, 6/12 mm fine gravel and 12/20 mm for the gravel). Also, to obtain fluid consistency, the mix required a naphtalene-sulfonate water-reducing admixture. The replacement of Portland clinker with additions reduces cement density (Table 1) increasing slightly the paste volume content in the mix. However, for durability performance, there is a mandatory lower limit of cement content (AENOR 2008a), so the corrections did not vary the cement weight.

[TABLE 2]

The study contains three parts, firstly the study of the GFA as a possible pozzolanic material, so the characterization tests for fly ash were performed: chemical composition and mineralogical components, grain size, specific surface, fineness and SEM images for the particle shape. Secondly, we produced blended cements with the GFA and compared them with the limestone cements and Portland cement; the characterization of these cements included: sulphate and chloride content, pozzolanic activity, setting time, soundness, compressive strength and a box workability test for mortars (B. González-Fonteboa et al. 2017). Lastly, this cement allowed the production of concrete to perform quality and preliminary durability tests that included: slump, compressive strength at 3, 28 and 90 days, splitting strength at 28 days and two durability parameters, water penetration depth and absorption.

## 3. Results and discussion

### *3.1. Ground fly ash results*

#### *3.1.1. Chemical properties*

The chemical composition of the GFA is given in Table 4 and Table 5. The reactive calcium oxide (CaO) and reactive silica contents, as well as the loss on ignition test, fulfilled the requirements established in the European cement standard (EN 197-1 (AENOR 2011)), with the exception of free CaO content which was slightly higher than the limit (2.5%). This value is not attributable to the coal composition; rather it is due to additional limestone added to the fluidized-bed boiler during combustion, the boiler used it to control the sulphate emission level. This excess of calcium can be adjusted in the CFBC process.

[TABLE 4]

Some authors report volume stability problems reported with CFBC ash (Havlica et al. 2004; Zheng et al. 2017), however this issue did not show up in this ash. The soundness of the GFA cements was much lower than the limit specified in the standard (EN 197-1 (AENOR 2011)), so these cements do not show volume instability due to the calcium oxide. The Loss On Ignition (LOI) values were low and similar to those of conventional fly ash (Kiattikomol et al. 2001).

The results of oxide composition, given in Table 5, are similar to those of coarse high calcium fly ash from CFBC, however in CFBC boilers the CaO content could be up to 50 % (Váchal et al. 2018).

[TABLE 5]

In order to study the mineralogy of GFA, X-ray diffraction tests (XRD) were carried out using an X D5000 SIEMENS diffractometer (CuKα radiation, 2.2 kW). Figure presents the XRD pattern of the ground fly ash. The observed crystalline products are: quartz, lime in form of calcium oxide, hematite, sericite (aluminium-silica feldspar), anhydrite gypsum, magnesite and chalcopyrite. The pattern shape indicates also the presence of amorphous phases. The main differences with the usual composition of fly ash, even coarse fly ash, is the presence of anhydrite due to the reaction of calcium oxide and sulphate in the fluidized bed (Sheng et al. 2012; Hlaváček et al. 2018). Additionally, the presence of crystalline calcium oxide is also specific of this type of ash.

[FIGURE 1]

*3.1.2. Physical properties*

GFA presents large particle size. Hence, some authors recommend grinding to increase the activity. Nevertheless, in some cases GFA exhibits a lower degree of activity than conventional fly ash, which could be attributed to its higher degree of crystallization (Felekoğlu et al. 2009). In this study, the grinding process was applied to a group of samples obtained from the conveyor belt in one single batch of 150 kg. The milling was performed in an industrial ball mill reproducing the milling process of the clinker in a cement factory.

Particle size and distribution analyses of original and GFA were conducted using a sieve analysis technique (EN 933-1 (AENOR 2012)) and a Thermo Finnigan SORPTOMATIC 1990 with nitrogen as sorbent gas. The GFA exhibited a specific surface area of 740 $m^2$/kg and the cumulative percentage retained on a 0.045 mm sieve was 13.6% (Table 6). This fineness was consistent with the mill process applied to the Portland cement and over all, comparable with the cement CEM II/A-L with low quantity of addition. With this fineness it is expectable to find appropriate chemical activity (Felekoğlu et al. 2009).

[TABLE 6]

From the point of view of workability, the spherical shape is the most suitable. The fly ash from the CFBC is different than conventional fly ash due to the lower temperature of formation and its lack of sintering in spherical particles (Hlaváček et al. 2018). There are two types of particles, large and elongated particles from 50 to 300 µm and fragmented and disperse smaller particles (Figure 2. top). The fly ash once ground inherits this shape with the addition of the fragments of the crushed larger particles (Figure 2. bottom). This fragmented particles also present angular shape due to the fracture of the milling (Antiohos & Tsimas 2007; Kumar et al. 2007).

[FIGURE 2]

### *3.2. Cement results*

The results refer to six cements, three commercial products and the other three produced for this experiment. This comparison makes it possible to draw conclusions about the suitability of GFA as an addition to cement and compare it with the most used addition: limestone.

The standard cements were: CEMII/A-L 42.5R and CEMII/B-L 32.5N and CEMI 52.5R (EN 197-1 (AENOR 2011)) and the new GFA blended cements were obtained by partially replacing CEMI 52.5R with GFA ash from a fluidized bed boiler in ratios of 10%, 20% and 40% by weight. These new cements were identified as CEMI+GFA10, CEMI +GFA20, CEMI+GFA40 respectively.

#### *3.2.1. Chemical properties*

The results of the chemical composition of the cements show that sulphate content was lower than 4%; and chloride content lower than 0.10%. We also analysed the pozzolanic activity of CEMI+GFA20 and CEMI+GFA40 (Table 7). The positive results obtained indicated that both cements may be classified as pozzolanic (type IV according to the European cement standard EN 197-1 (AENOR 2011)). These results, together with the characterization of the GFA, indicate that all the new cements with GFA from fluidized-bed power plants fulfil the requirements prescribed by European standard EN 197-1 (AENOR 2011).

[TABLE 7]

### *3.2.2. Physical properties*

Table 8 shows the results of setting time and soundness (EN 196-3 (AENOR 2008b)). As can be observed, all the cements fulfilled the requirements prescribed by European standard EN 197-1 (AENOR 2011). It should be noted that, in spite of the high free CaO content of GFA, the results of cement soundness were close to zero.

[TABLE 8]

### *3.2.3. Consistency and mechanical properties*

Figure 3 & Table 9 exhibit the mechanical properties of the six cements. The flexural and compressive strength after 2, 7, 28 and 90 days were measured using prismatic mortar specimens (40x40x160 mm) according to EN 196-1 (AENOR 2005). Additionally, using a box test we measured the consistency of the fresh mortars. The result of this test is the number of hits needed for the fresh mortar to reach the end of the mould. The lower the number of hits, the more fluidity of the mortar. For further details, there is a detailed description in the work of González-Fonteboa .

[FIGURE 3]

[TABLE 9]

The cements that included GFA from a CFBC boiler presented in all substitution rates a greater number of hits to reach the end of the mould than any of the reference cements, also higher water demand for the standard paste in setting times (Table 8). Both effects increased with the percentage of GFA, and this indicates that workability of concrete would decrease significantly with the use of GFA. This is not the usual effect of conventional spherical fly ash from pulverized coal (Corinaldesi & Moriconi 2011). This outcome of loss in workability is in keeping with the results reported by other authors who used ground fly ash (Kiattikomol et al. 2001; Felekoğlu et al. 2009) and also with authors that used CFBC fly ash without grinding (Zheng et al. 2017). In this case, the negative effect of the irregular shape of the fly ash from CFBC boilers adds to the reduction of workability produced by the grinding process.

All cements fulfilled the mechanical specifications of European standard cements (EN 197-1 (AENOR 2011)). The higher performance is exhibited by CEMI+GFA20 that fulfilled the requirements of the highest quality of standard cement “52,5 R” (fc > 20 MPa after 2 days and fc > 52.5 MPa after 28 days (AENOR 2011)), CEMI+GFA10 and CEMI+GFA40 could be classified as “42,5 N” (fc >10 MPa after 2 days and fc >42.5 MPa after 28 days).

As seen in Figure 3, the pattern of the compressive strength curves of the GFA mortars is different from that of the reference cements. The rates of strength development are higher in the mortars with GFA cement, according to the results presented by other authors who used ground fly ash (Kiattikomol et al. 2001; Felekoğlu et al. 2009).

If one compares the behaviour of the GFA blended cements to that of the reference ones GFA cements showed similar long-term strength than the commercial CEM I, however at early age they produced lower compressive strength. This evolution can be attributed clearly to the pozzolanic activity of the GFA from the CFBC boiler. In any case, the effect of the GFA on mechanical properties is much better than that obtained by commercial cements with limestone. It is remarkable that CEMI+GFA20 showed equivalent compressive strength to a commercial CEM I 52,5 R.

If we compare the cements with GFA in terms of compressive strength with CEM II/A-L or CEMII/B-L, the results with GFA from the CFBC power plant are substantially superior.

### *3.3. Concrete properties*

Six concrete mixes were designed using the GFA and the reference cements. In all mixes, the fixed amount of cement was 350 kg/m$^3$ and a water/cement ratio of 0.55 was used (Table 2). The analysis performed included, for each type of concrete: consistency, density, compressive strength and splitting tensile strength. Additionally, water penetration depth and water absorption to study the durability provided by the GFA cements.

### *3.3.1. Consistency, density and mechanical properties*

The test performed started after mixing with the slump value (EN 12350-2 (AENOR 2009a)). Once the concrete hardened, we tested compressive strength after 3, 28 and 90 days using 100 mm cubic specimens (EN 12390-3 (AENOR 2009b)) and also splitting tensile strength after 28 days using ϕ150x300 mm cylindrical specimens (EN 12390-6 (AENOR 2009c)). Table 9 summarizes these results.

All concrete mixes with GFA cements presented slump values substantially worse than those of the control concrete mixes. This trend agrees with the results of the non-standard test carried out with mortars (Table 9). This could be attributed partially to the irregular particle shape of GFA from the CFBC boiler and also to the grinding process; both negative effects collaborate to reduce the workability (Kiattikomol et al. 2001; Kim & Lee 2011; Zheng et al. 2017).

The trend of the strength development curves (Figure 4) is similar to the ones observed in mortars (Figure 3). The strength at early ages is lower in the case of cements with GFA from the CFBC boiler in comparison with CEM I (Portland cement without addition), however the mortars with GFA developed their strength from 3 to 28 days. Finally at 90 days, the concretes with GFA cements present compressive strength values equal to the CEM I reference cement, and higher than the cements with limestone CEM II/A-L and CEM II/B-L.

[FIGURE 4]

The compressive strength of the mixes with GFA cements was 12 to 36 % lower than that of the CEMI mix after 3 days. Although compared with CEM II/A-L they perform with resistance values 19% and 11% higher in the cases of 10 and 20% of clinker replacements, in the case with 40% of replacement, the values were 14% inferior. When we studied the compressive strength after 28 days, the difference with CEM I was only 0.1% and 7% lower for substitutions of 10 and 40 % and 1% higher for 20 % of GFA from the CBFC process. Contrasted with CEM II/A-L, the use of GFA as substitution of clinker produces strength values 21%, 23% and 14% higher (substitutions of 10%, 20% and 40% respectively). Finally, the CEM II/B-L cement produces concretes with lower compressive strength at all ages and this trend is more pronounced at 28 and 90 days.

The hardened density of the resulting concrete mixes is shown in Table 9, where all mixes show similar values of density in the range 2.27 to 2.31 t/m3 with no significant effect of the GFA addition.

### *3.3.2. Water absorption capacity and water penetration depth*

The research included two parameter related to durability: water penetration depth at 1 day using 100 mm cubes (EN 12390-8 (AENOR 2009e)) and water absorption capacity after 28 days using $\phi$150x300 mm cylindrical specimens (EN 12390-7 (AENOR 2009d)). Figure 5 shows the results.

[FIGURE 5]

There are references of a relation between the porosity and permeability of mortar and concrete (Basheer et al. 2001; Kearsley & Wainwright 2001). The permeability of concrete gives an indication of the ease with which fluids, gases and vapours move through it and it is therefore an indicator of durability (Chia & Zhang 2002; Basheer et al. 2001).

The results obtained (Figure 5) show that the water absorption of concrete mixes with GFA were similar to those of CEM I mixtures, and lower than the ones which included limestone filler (CEMII/A-L & CEMII/B-L). There is a slight rising tendency in the water absorption with the percentage of GFA. Some authors indicate that that porosity decreases with the incorporation of fly ash (Termkhajornkit et al. 2009). This agrees with the results of Sinsiri et al. (Sinsiri et al. 2010) in the case of fly ash from pulverized coal, however when studying CFBC fly ash, this author observed an increase in porosity with the use of this type of ash. It seems that the trend varies with the type of ash depending on its shape, specific surface, chemical composition, etc.

The results of water penetration depth are similar for all concretes. However, the mixes with GFA showed marginally lower values lower than those of CEM II/B-L. On the contrary, the reference cements CEM I and CEM II/A-L presented slightly lower water penetration than in concretes with GFA.

### *3.4. Contrasting the production and performance of GFA and limestone filler for lower clinker cements*

The use of fluidized-bed boilers have increased in number in recent years due to several environmental and economic advantages, principally the reduction of NOx and SO2 emissions (Chi 2016; Li et al. 2012; Redemann et al. 2008). With this technology, and thanks to the use of limestone in the combustion chamber, it is possible to burn coal and other co-combustion materials with higher contents of sulphates (Redemann et al. 2008; Chi 2016; Yang et al. 2005).

In this context, there is a social, environmental and legislative pressure that leads the cement market to the maximum use of available additions with the resulting reduction of clinker content (Comission 2015). As result of the application of this philosophy, the most used cements nowadays in Europe (The European cement Association 2013) (more than 50% in major countries, and more than 70% in Spain) are those blended with limestone and fly ash.

The use of ash from different origins and the use of different types of processing is not clearly defined in the legislation. This means that some types of ashes from different origins than traditional pulverized coal combustion are not supported to serve as additions in the cement industry. In the context of global climate change, regulations should be updated to allow the inclusion of any type of ash that could “with sufficient security” be included in blended cements. This would represent a severe reduction of clinker use and subsequently of CO2 emissions. It would also reduce the landfill of large quantities of perfectly usable fly ashes.

The references used in the research were commercial cements CEM II/A-L with 11% of limestone, CEM II/B-L with 26 % of limestone and Portland cement CEM I. The production of the cement with limestone addition includes the grinding of the limestone simultaneously with the clinker. In this case, to ensure appropriate pozzolanic activity for the CFBC fly ash, it was ground to achieve fineness equivalent to that of the cement. Therefore, to produce cement with CFBC fly ash it would be necessary to grind this ash in the ball mill (the same operation needed with limestone).

The use of GFA allows reductions of clinker content up to 40%, obtaining compressive strength at 28 days equivalent to that of 52.5 MPa class cement, of the highest quality commercially available. However, at early age, the GFA cements perform worse than CEM I although they allow a greater clinker reduction than with CEM II/A-L. If early strength is a key factor, that would allow only a 20% of reduction instead of a 40%. Additionally, this type of ash might allow higher reductions of clinker up to 55% (the legal maximum of CEM IV/B). This high substitution rate will produce substantial loss of consistency, so it might not be recommended for general use.

The major drawbacks of this type of ash are the need of grinding and the reduction in workability. If there were fly ash from pulverized coal available, the GFA would be a secondary option. However, in many places it is not locally available and there is fly ash from CFBC. Unfortunately, this type of ash is not generally accepted as commercial addition due to its origin and production process. However, within the scope of this research and with this specific fly ash, GFA performed as a high-quality addition for blended cements and significantly superior than limestone filler.

## 4. Conclusions

This study analyses the potential use of ground fly ash (GFA) obtained from a circulating fluidized-bed combustion (CFBC) power plant as an addition to cement and compares its performance with that of the usual limestone addition. These are the main conclusions of this research work:

- The fly ash from this type of plants presented large and irregular particles so it was necessary to grind it to increase its activity.
- The GFA from CFBC presented adequate composition within EN 197-1 cement standard, and it could be classified as silicocalcareous fly ash. There was a slight excess in free CaO content, that could be adjusted in the fluidized-bed production.

- Three blended cements were produced with GFA replacements of 10%, 20% and 40%. They exhibited high mechanical strength at 28 and 90 days, equivalent to that of 52,5 class cement (highest).
- The use of GFA as addition permits higher reductions of clinker use than limestone, even replacements up to 40 % exhibit at 28 days compressive strenght equivalent to that of Portland cement without additions.
- The incorporation of GFA produced a negative effect in workability when compared with the standard cements. This reduction could be excessive for the 40% of GFA replacement, so it might prevent the use of this replacement for general use.
- Two durability parameters were checked: water absorption and water penetration depth. The incorporation of GFA even in percentages of 40% did not produce significant changes in porosity and water permeability. In contrast, the performance of the addition of limestone was worse.

The fly ash from CFBC is produced in large amounts and is presently rarely used. It only needs to be ground, operation that can be made simultaneously with the clinker milling. Limestone is widely used, and it requires also grinding. If we include this type of ash in blended cements the amount of clinker consumption and subsequently CO2 emissions could drop significantly. The limits to the use are principally the undefined standard specifications and the limited scientific background.

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**Figure captions (images as individual files separate to your MS Word text file).**

Figure 1. X-ray diffractogram of the GFA

Figure 2. SEM photography of the GFA. Top: Original CFBC fly ash. Bottom: Ground CFBC fly ash.

Figure 3. Mortar: compressive strength development

Figure 4. Concrete: compressive strength development (100 mm cubic specimens)

Figure 5. Concrete: water absorption capacity and water penetration depth

*Table 1. Cement composition (by weight)*

| Cement code | Portland cement (%) | Limestone filler (%)[(1)] | Ground Fly Ash (GFA) (%) | Cement density kg/l |
|---|---|---|---|---|
| CEM I | 100 | – | – | 3.14 |
| CEM II/A-L | 89 | 11 | – | 3.09 |
| CEM II/B-L | 74 | 26 | – | 3.03 |
| CEM I + GFA10 | 90 | – | 10 | 3.03 |
| CEM I + GFA20 | 80 | – | 20 | 2.91 |
| CEM I + GFA40 | 60 | – | 40 | 2.69 |

(1) *Data provided by the manufacturer of the commercial cements*

*Table 2. Mortar and concrete composition*

| Material | Weight (kg) for 1 $m^3$ Concrete | Weight (g) EN 196-1 Mortar | Density (kg/l) |
|---|---|---|---|
| Water | 192.5 | 225 | 1.00 |
| Cement | 350.0 | 450 | 2.69 - 3.14 |
| Sand 0/4 (1) | 855.2 | 1350 | 2.58 |
| Fine gravel 4/12 | 738.6 | | 2.72 |
| Gravel 12/20 | 322.2 | | 2.73 |
| Superplasticizer | 6.0 | | 1.15 |

(1) *The sand used in mortar complies with EN 196-1 specifications*

*Table 4. Chemical composition of the GFA (EN 197-1)*

| Parameter | Standard | Ground fly ash (%) | Limit (%) (EN 197-1) |
|---|---|---|---|
| Free CaO % | EN 451-1 | 2.9 | > 1 y < 2.5(1) |
| Reactive CaO % (2) | EN 196-2 | 10.9 | 10-15 |
| Reactive $SiO_2$ % | EN 196-2 | 25.2 | > 25 |
| Loss on ignition (LOI) | EN 196-2 | 4.1 | < 5 |

(1) *This value is suitable if the Le Chatelier's expansion values of a cement (30% of ash and 70% of CEM I) are lower than 10 mm.*

(2) *The sulphate and $CO_2$ bonded calcium was not taken into account.*

*Table 5. Oxide composition of the GFA (XRF).*

| Oxide (FRX) | $SiO_2$ | $Al_2O_3$ | CaO | $Fe_2O_3$ | $K_2O$ | $SO_3$ | MgO | $TiO_2$ | $Na_2O$ | $P_2O_3$ | BaO | MnO | $CO_2$(1) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GFA (%) | 37.8 | 22.0 | 16.9 | 6.3 | 3.4 | 6.3 | 1.2 | 0.9 | 0.1 | 0.5 | 0.1 | 0.05 | 4.1 |

(1) *This parameter was obtained from Loss on Ignition.*

*Table 6. Particle size of the GFA and reference cements*

| Material | Cumulative passing in the 32 µm sieve (%) | Cumulative passing in the 45 µm sieve (%) |
|---|---|---|
| Ground fly ash (GFA) | – | 13.6 |
| CEM I 52,5 R | 3.4 | 10.2 |
| CEM II/A-L | 4.9 | 13.5 |

| Material | Cumulative passing in the 32 µm sieve (%) | Cumulative passing in the 45 µm sieve (%) |
|---|---|---|
| CEM II/B-L | 8.3 | 18.1 |

*Table 7. Cement: chemical properties and pozzolanicity*

| Cement type | Sulphate content (%) (EN 196-2) | Chloride content (%) (EN 196-2) | Pozzolanicity test at 8 and 14 days (EN 196-5) | |
|---|---|---|---|---|
| | | | $OH^-$ concentration (mmol/l) | Result |
| Limit (EN 197-1) | ≤ 4.00 | ≤ 0.10 | | Positive at 8 or 14 days |
| CEM I | 2.81 | 0.02 | | – |
| CEM II/A-L | 3.09 | 0.02 | | – |
| CEM II/B-L | 2.99 | 0.02 | | – |
| CEM I + GFA10 | 2.73 | 0.02 | | – |
| CEM I + GFA20 | 2.10 | 0.01 | 62.5 | Positive (14 days) |
| CEM I + GFA40 | 2.48 | 0.01 | 57.8 | Positive (8 days) |

*Table 8. Setting time and soundness*

| Cement | SETTING TIME | | | Le Chatelier's expansion value (mm) |
|---|---|---|---|---|
| | Initial setting time (min) | Final setting time (min) | Standard consistency water requirement (%) | |
| EN 197-1 Requirement | ≥ 75[(1)] | -- | -- | ≤ 10.0 mm |
| CEM I | 135 | 175 | 32.0 | <0.5 |
| CEM II/A-L | 120 | 160 | 29.6 | <0.5 |
| CEM II/B-L | 155 | 195 | 29.6 | <0.5 |
| CEM I + GFA10 | 140 | 180 | 32.0 | <0.5 |
| CEM I + GFA20 | 140 | 175 | 32.6 | <0.5 |
| CEM I + GFA40 | 175 | 210 | 34.4 | <0.5 |

(1) The most restrictive value of the EN 197-1.

*Table 9. Mortar: Consistency and flexural strength. Concrete: Slump, splitting tensile strength and density*

| Cement type | Mortars | | Concrete | | |
|---|---|---|---|---|---|
| | Number of hits | $f_{ct,fl}$ flexural strength (MPa) | Slump value (EN 12390-2) (cm) | Tensile splitting strength (EN 12390-6) (MPa) | Hardened density EN 12390-7 (kg/l) |

| Age (days) | | 2 | 7 | 28 | 90 | | 28 | |
|---|---|---|---|---|---|---|---|---|
| CEM I | 15 | 5.2 | 6.2 | 6.5 | 6.5 | 14 | 3.12 | 2.30 |
| CEM II/A-L | 14 | 4.1 | 5.3 | 6.5 | 6.6 | 19 | 3.90 | 2.24 |
| CEM II/B-L | 13 | 2.5 | 3.8 | 4.8 | 5.3 | 14 | 3.34 | 2.25 |
| CEM I + GFA10 | 13 | 4.9 | 5.6 | 7.1 | 7.0 | 11 | 3.29 | 2.31 |
| CEM I + GFA20 | 27 | 4.8 | 5.6 | 6.4 | 7.5 | 9 | 4.43 | 2.30 |
| CEM I + GFA40 | 43 | 3.7 | 4.8 | 6.6 | 7.3 | 5 | 4.44 | 2.27 |

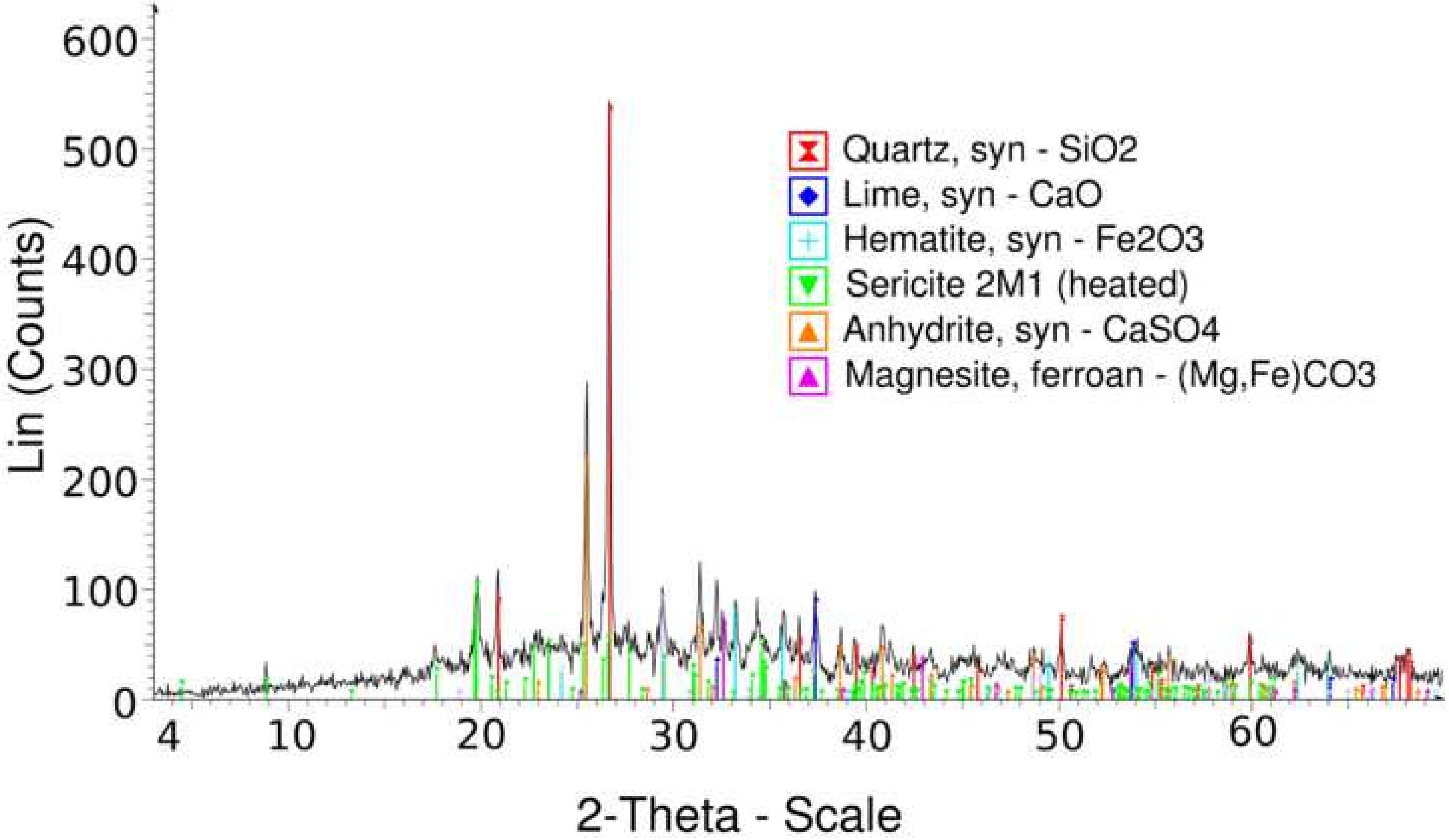
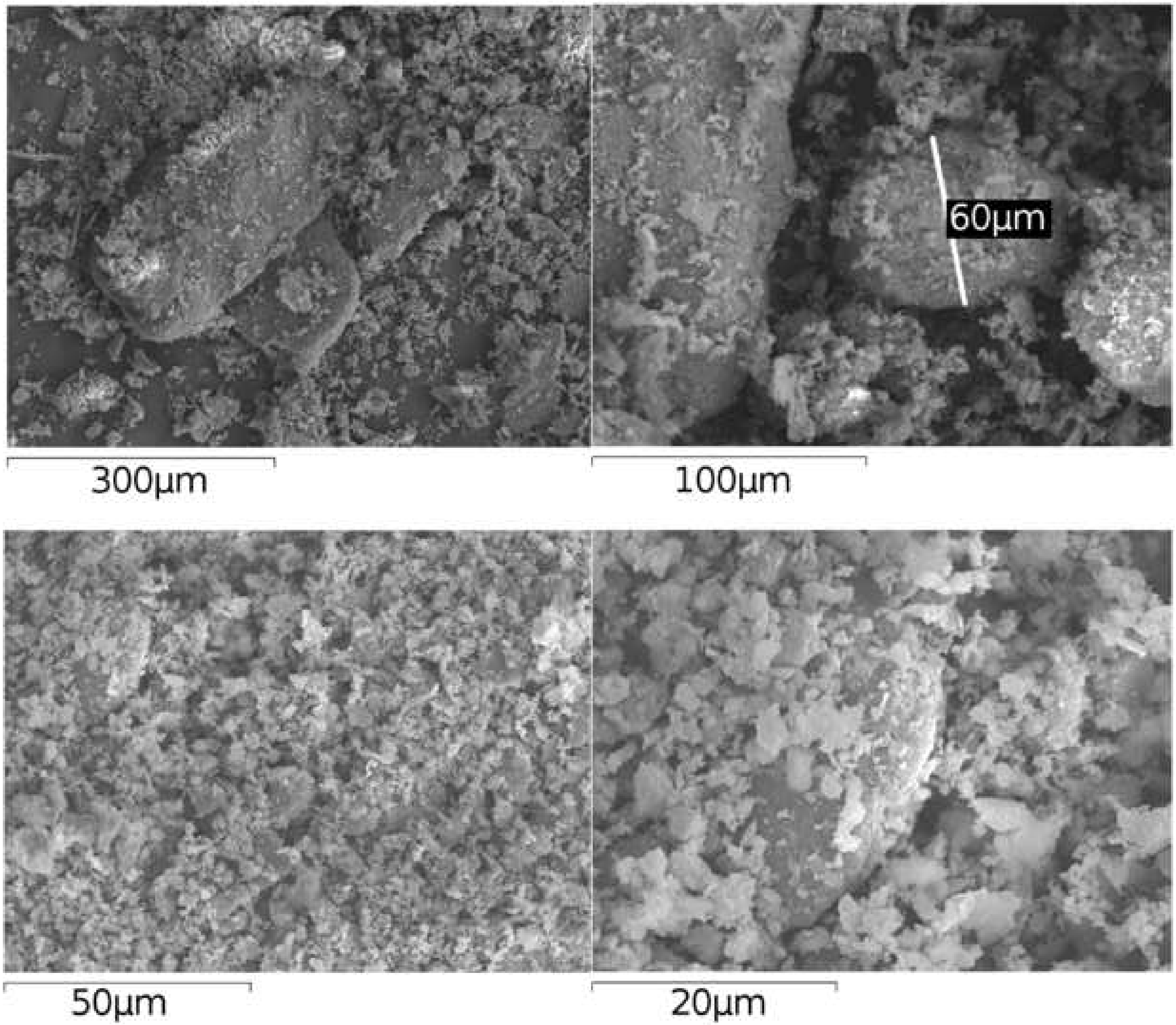
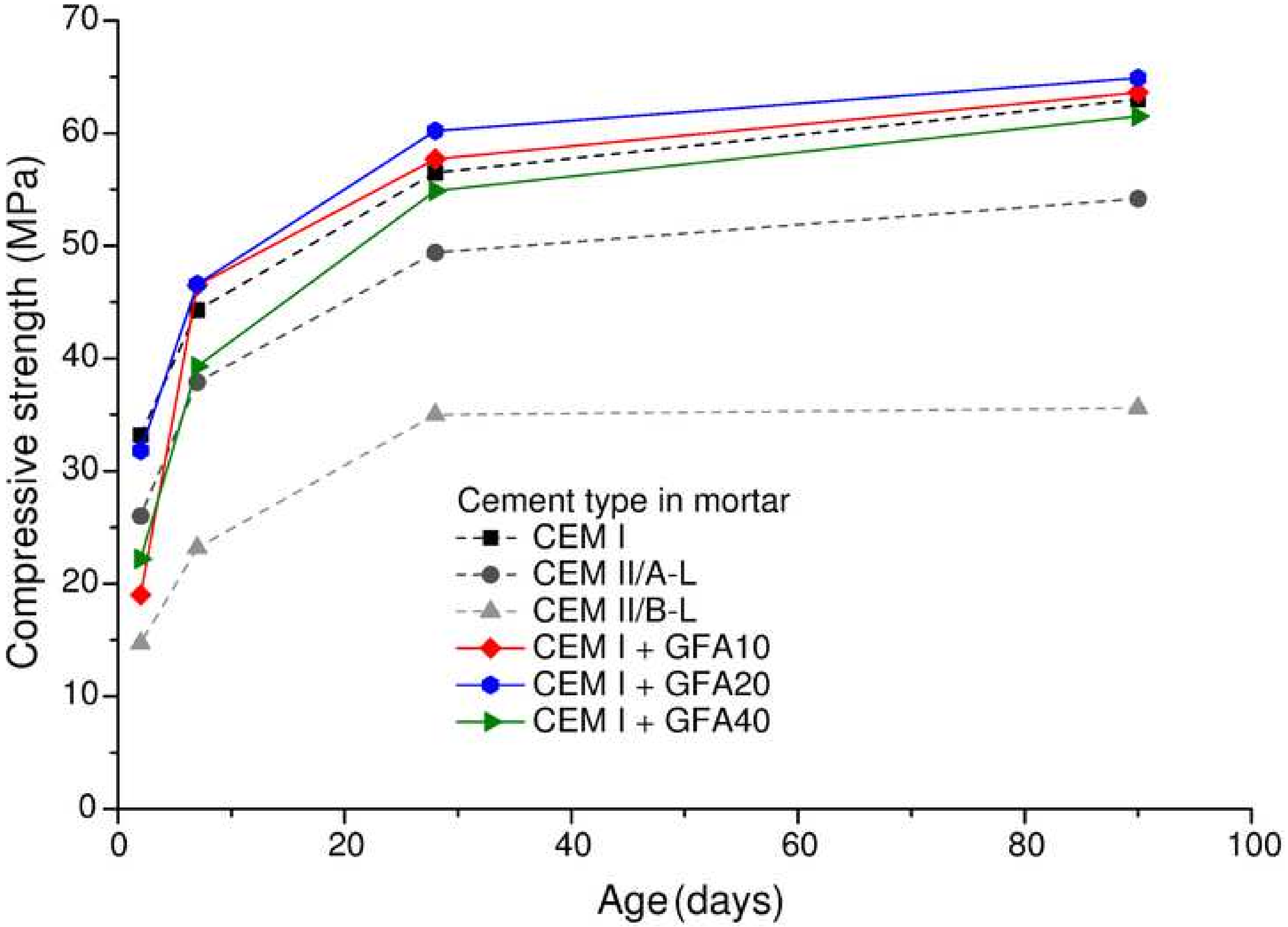
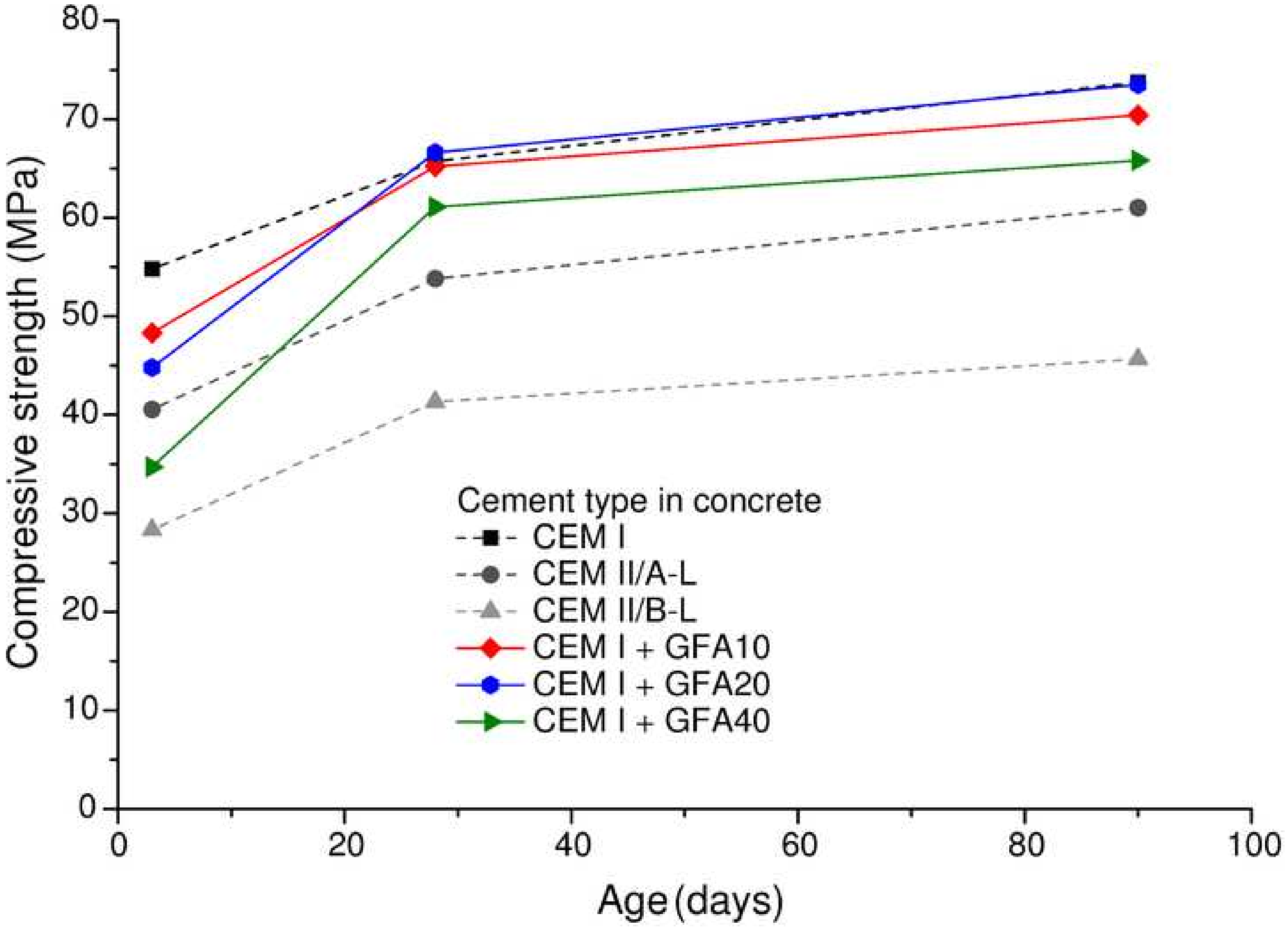

Lin (Counts)
600
500
400
300
200
100
0
4
10
20
30
40
50
60
2-Theta - Scale
Quartz, syn - SiO2
Lime, syn - CaO
Hematite, syn - Fe2O3
Sericite 2M1 (heated)
Anhydrite, syn - CaSO4
Magnesite, ferroan - (Mg,Fe)CO3

Figure 2

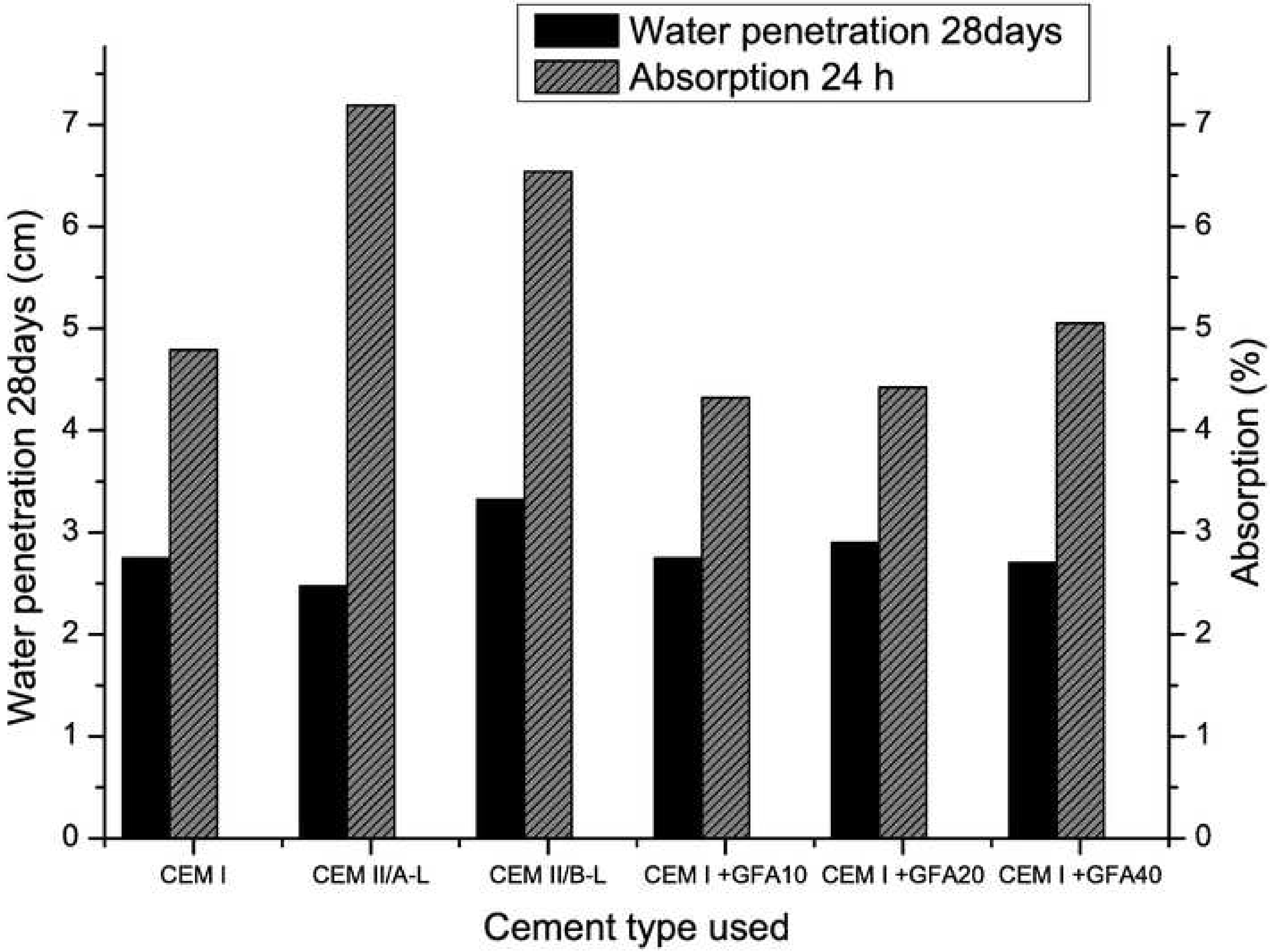




Compressive strength (MPa)
0
10
20
30
40
50
60
70
Age (days)
0
20
40
60
80
100
Cement type in mortar
CEM I
CEM II/A-L
CEM II/B-L
CEM I + GFA10
CEM I + GFA20
CEM I + GFA40



Compressive strength (MPa)
0
10
20
30
40
50
60
70
80
Age (days)
0
20
40
60
80
100
Cement type in concrete
CEM I
CEM II/A-L
CEM II/B-L
CEM I + GFA10
CEM I + GFA20
CEM I + GFA40


Water penetration 28days
Absorption 24 h
Water penetration 28days (cm)
Absorption (%)
0
1
2
3
4
5
6
7
CEM I
CEM II/A-L
CEM II/B-L
CEM I +GFA10
CEM I +GFA20
CEM I +GFA40
Cement type used