Development of calcium sulfate – ggbs – Portland cement binders

Brian O'Rourke [a], Ciaran McNally [bc*], Mark G. Richardson [b]

[a] Department of Civil, Structural and Environmental Engineering, Cork Institute of Technology, Cork, Ireland

[b] School of Architecture, Landscape & Civil Engineering, University College Dublin, Richview, Dublin 4, Ireland

[c] UCD Urban Institute Ireland, University College Dublin, Ireland

Abstract

Binders manufactured using a blend of gypsum, ground granulated blast furnace slag and Portland cements are technically viable and possess considerable environmental and economic advantages when compared to binders manufactured using Portland cement alone. As such, the evaluation of binders made from these materials offers a promising research focus in the quest to produce technically sound, environmental and economical binders for specialist uses as an alternative to traditional concrete binders of higher carbon footprint. The aim of the test programme was to investigate the viability of a series of binders designed to fulfil particular user needs while having significantly decreased carbon footprints.

Two distinct series of binders were designed; the dominant ingredient in the first was calcium sulfate while in the second it was ggbs. Potential applications for both series of binders were considered and the strength development of each binder was analysed. In addition, the effect of water on the gypsum-based binders was analysed, as was the sulfate resistance of the ggbs-based binder.

The results of the laboratory tests carried out were varied. For the calcium sulfate-based binders, those manufactured using anhydrite II as the dominant ingredient were found to achieve highest strengths. However these binders were found to be particularly susceptible to moisture-induced deterioration. For the ggbs-based binders, it was found that the early strength development was improved by the addition of small quantities of anhydrite II and gypsum. The strengths and sulfate resistance at later ages remained unaffected. These binders may have significant potential in situations were early strength development is a requirement.

Keywords: Anhydrite II; CO_2 emissions; ggbs; gypsum; Portland cement

* Corresponding author. Tel.: +353 1716 3202; fax: +353 1716 3297.

Email address: ciaran.mcnally@ucd.ie (Dr. Ciaran McNally).

1. Introduction

The effects of global warming due to the emission of greenhouse gases have been acknowledged as one of the major challenges facing society [1, 2]. The cement industry has been identified as one of the key contributors to this problem, contributing 5% to global anthropogenic CO_2 emissions [3]. These emissions largely arise from the fact that the key ingredient in the production of Portland cement is cement clinker, the manufacture of which results in the release of significant quantities of CO_2. A key reaction in the production of clinker is the calcination of limestone in the presence of silica to produce alite (Ca_3SiO_5), the key active component in cement clinker. This reaction also involves the release of large quantities of CO_2. A simple form of this reaction is shown in (1), with the mass proportions given in italics:

$$\underset{\textit{300}}{3CaCO_3} + \underset{\textit{60}}{SiO_2} \rightarrow \underset{\textit{228}}{Ca_3SiO_5} + \underset{\textit{132}}{3CO_2} \qquad (1)$$

From the equation it can be noted that for each tonne of C_3S produced, 0.58 tonne of CO_2 is liberated, irrespective of the energy consumed by the process [4]. Furthermore, for the kinetics of this reaction to proceed at a commercially viable rate, the material must be heated to a temperature in excess of 1400°C. This heating, coupled with the energy required for subsequent grinding process, results in the emission of approximately 0.95 tonnes of CO_2 per tonne of Portland cement produced [5].

The cement manufacturing industry however has done much to reduce its dependence on oil and improve the efficiency of the production process since the OPEC oil embargo of the mid-1970s. In the two decades since 1973 the industry in North America has reduced its primary physical energy intensity by 30%, from 7.9 GJ/tonne to 5.6 GJ/tonne [6]. With a commitment from the world's largest cement manufacturer to reduce CO_2 emissions by 15% in the period from 1990–2010 [4], the industry is clearly starting from an already high level of energy efficiency. Nevertheless, there are production facilities around the world that operate at energy levels well above the best available technology, providing scope for an overall improvement.

2. Research significance

2.1 The economics of carbon emissions

The advent of the global CO_2 Emissions Trading Scheme under the terms of the Kyoto Protocol is likely to have serious implications for the cement manufacturing industry. On a national level, the second National Allocation Plan (NAP) submitted by Ireland [7] for the years 2008-2012 predicts that CO_2 emissions arising from cement production will increase by approximately 5% per annum to 5.31 million tonnes of CO_2 in 2012. Given that the proposed allocation for this period is 4.21 million tonnes of CO_2, this represents a significant shortfall. The European Commissions subsequent decision concerning the Ireland's NAP for allocation of greenhouse gas emissions will result in a lower allocation than initially proposed. This allocation could result in an allowance shortfall in excess of 1.3 million tonnes by 2012. Given that these emissions are tradable, the Irish government expects that all feasible abatement projects up to a marginal cost of €15/ tonne will be implemented. Similar NAPs were submitted by all EU member states, detailing allowable CO_2 emissions up to the year 2012.

In this light, the economic incentives for reducing the CO_2 emissions associated with cement manufactured are clear. It would seem however that the best opportunity to further decrease these emissions is to alter the materials used in the manufacturing process. In this light the identification of suitable replacement raw materials for the production of cementitious binders with properties similar to that of Portland cement is both desirable and necessary. As the majority of CO_2 emissions associated with cement manufacture arise from the clinker production process, Worrell *et al* [3] suggest the use of a clinker/cement (C/C) ratio as a measure of how energy intensive the process is. For instance a CEM I cement will have a C/C ratio of approximately 0.95; a CEM II/A-L cement replacing 12% of the clinker with limestone will have a C/C ratio of approximately 0.84. In effect, the lower this value of the C/C ratio, the less harmful the binder is likely to be in terms of CO_2 emissions.

2.2 Potential alternative binders

There has been a significant amount of international research carried out into the development of alternative cement binders in recent years. For example Hossain [8] has investigated the development of blended cements using volcanic ash and pumice; Bilodeau and Malhotra [9] have studied the development of high volume fly ash binders; both Konsta-Gdoutos and Shah [10] and Al-Hatry et al [11] have studied the introduction of cement kiln dust to cement binders.

Considerable development of binders such as ground granulated blast furnace slag (ggbs), pulverised fuel ash (pfa) and other pozzolanic materials has been carried out, leading to popular acceptance of their beneficial properties [12]. The production of ggbs leads to emissions of about 60kg of CO_2 / tonne, primarily from the grinding process. As such, the use of materials such as ggbs can lead to significant reductions in CO_2 emissions. Gartner [4] also highlighted the potential of calcium sulfate-based binders. The material, usually supplied as gypsum, does not devolve any CO_2, while the energy intensity of the manufacturing process is also extremely low. The impact of these materials can be seen when a clinker / cement ratio is used. As such, it was considered that a series of binders based on combinations of Portland cement, ggbs and gypsum offer potentially significant environmental advantages should certain mechanical and durability requirements be satisfied. Generally binders manufactured using these constituents can improve performance characteristics and overall economy. Portland cement binders, when set and hardened achieve good strength and water resistance. Gypsum based binders possess properties of rapid hardening and fine surface finish but are often limited in use due to the high solubility of the gypsum when exposed to water [13, 14]. It is well known that the combination of Portland cement and gypsum can lead to the formation of expansive and deleterious compounds such as ettringite and thaumasite. The tendency for such compounds to develop may be reduced however if materials such as ggbs are added to the mix [15].

Combinations of these materials can thus be optimised to produce useful binders with properties of rapid hardening, fine surface finish and adequate resistance to water. Possible specialist applications for these binders are listed in Table 1. It should be noted that gypsum rich cements should not be used with steel reinforcement as the low resultant alkalinity will offer very little corrosion protection. The objective of this study was to investigate the potential for these materials to be used in these specialist applications through determination of strength and stability characteristics.

3. Materials

The materials used in the experimental tests were a combination of the following materials:

- CEM I: Class 42.5 Portland cement ($C_3A < 7\%$ Bogue)
- Ground granulated blast furnace slag (ggbs)
- Gypsum in the form of commercially available calcium sulfate hemi-hydrate
- Anhydrite II, commercially available
- Hydrated lime, commercially available
- CEN reference sand to EN 196-1

3.1 Formulations

The formulations tested may be considered to comprise two distinct series and are listed in Table 2. The first series (formulations A to E) is dominated by calcium sulfate. Formulations A to D contain 60 to 80% gypsum, while formulation E contains 20% gypsum with 50% anhydrite II. The remaining portion of the binder consists of varying percentages of Portland cement, lime and ggbs. The second series (formulations 1 to 4) contains ggbs as the dominant ingredient. The ggbs content is seen to range from 66% to 70%, with Portland cement contents from 27% to 30% and minor additional constituents of gypsum, anhydrite II and lime. The percentage by mass of each formulation is given in Table 2. In an effort to highlight the low carbon footprint of these binders, the clinker/cement ratio is also included.

The performance of formulations 1 to 4 may be directly compared with the required properties of Portland blast furnace cements, as set down in EN 197-4. The prescribed limits for the constituent materials of these cements are shown below in Table 3. It can be seen that formulations 1, 2 and 3 comply with the requirements of EN 197-4 for a CEM III/B; formulation 4 lies outside of the limits specified as it contains 7% minor additional constituents.

3.2 Testing: calcium-sulfate based cements

3.2.1 Mix design

All tests were carried out on mortar, the composition of which was based on EN 196-1. The mortar consisted of one part cement to three parts CEN Standard sand; water and superplasticiser content were optimised to a standard consistence. Consistence was measured using a flow table and a target value of 175 mm at 5 minutes after mixing was used. For formulations A to D a water / binder ratio of 0.5 or 0.55 was used, with a superplasticiser / binder ratio between 0.1 and 0.135; for formulation E a water / binder ratio of 0.4 and a superplasticiser / binder ratio of 0.07 was used.

3.2.2 Test programmes

A key parameter in the development of any binder is that it possesses adequate compressive and flexural strength. To ascertain this, a series of mortar prisms of dimensions 160 x 40 x 40mm were cast and tested to the procedures outlined in EN 196-1. Due to the nature of calcium sulfate based cements and the high solubility of gypsum, a key concern is the effect of humidity on strength development. Therefore, variable curing conditions were also introduced into the testing programme. Following casting the prisms were covered with a glass plate and cured at 20°C and 65% RH for a period of 6 hours, after which time they were de-moulded for either immediate test or further curing. The prisms were then stored at 20°C and 65% RH for a further 14 days (except for those tested at 7 days), after which they were placed under 3 separate storage conditions, namely:

- at 20°C and at ≥ 65% RH
- at 20°C and ≈ 50% RH
- underwater at 20°C

At the required age the specimens are removed and tested for flexural and compressive strength. Tests are carried out after 6 hours, 24 hours, 7, 14, 28 and 90 days after casting.

To assess the stability of these binders, a series of prisms were cast for testing in accordance with ASTM C 490-93. These prisms were cast with metal studs cast into the ends of the principal axis to allow the taking of comparator measurements. The samples were subjected to the same curing conditions as described above and comparator readings were taken on a monthly basis.

3.3 Testing: ggbs based cements

3.3.1 Mix design

The tests were again carried out on mortar, the composition of which was based on EN 196-1. The mortar consisted of one part cement to three parts CEN Standard sand. In all cases the water binder ratio employed was 0.5; no plasticiser was introduced to the mixes.

3.3.2 Test programmes

Again, a series of mortar prisms with dimensions 160 x 40 x 40 mm were cast to the procedures described in EN 196-1. As no concerns exist with respect to the solubility of ggbs in water, a single curing regime was used. After casting the prisms were covered with a glass plate and cured at 20°C and ≥ 90% RH for 24 hours, after which time they were demoulded and stored under water at 20°C until time of testing. Tests were carried out at 24 hours, 2, 7, 28 and 90 days after casting.

Due to the high ggbs content in this series of formulations, a key potential application may be for use in precast concrete pipes; as such resistance to sulfate attack is a parameter of particular interest. The test method was again based on ASTM C 490 – 93, whereby a series of concrete prisms of dimension 25 x 25 x 285 mm are used to determine length change. The samples were cured underwater at 20°C for 27 days after de-moulding before being transferred to a 16 g / litre sodium sulfate solution at 20°C. Comparator readings were taken at 1 month intervals and expansion subsequently determined.

4. Results & discussion

4.1 Calcium sulfate-based cements

4.1.1 Strength tests

The results for tests to determine compressive strength are shown in Figure 1. It can be seen that formulations A and B gain strength quite quickly, producing a compressive strength of over 4 MPa after 6 hours; all other samples failed to display any strength before 24 hours. From 7 days on, it is clear that the formulation producing the highest strength is formulation E, containing 50% anhydrite II. Similar trends were observed in the tests for flexural strength.

The effects of the various curing conditions are shown in Figure 2. It is notable that for the majority of cases, a drop in strength is associated with an increase in the amount of water available to the samples. Once more the highest strengths are associated with binder formulation E, but these drop significantly as the moisture supply increases. For formulations A and E, the effect of storage in moisture is a 35% drop in strength relative to being stored at 50% RH. For formulations B, C and D the drop ranges from 41 to 50%, indicating that the binders do have issues with respect to being stored in damp environment. It is speculated that this is most likely due to dissolution of gypsum into the available water.

4.1.2 Dimensional stability tests

All of the formulations displayed good stability when maintained at 20°C and either 50 or 65% RH. After 6 months a number of very small expansions or shrinkages were observed, none of which may be considered significant. This however was not the case for the prisms stored in water at 20°C from age 14 days, as shown in Figure 3. It can be seen that all prisms expanded considerably, with the highest expansions associated with the formulations that all produced the highest strengths. In all cases the prisms displayed considerable cracking and were severely damaged, once more highlighting the effect of prolonged exposure to moisture on the gypsum.

4.2 Ggbs-based cements

4.2.1 Strength tests

The requirements of EN 197-4 for compressive strengths for Portland blastfurnace cements are shown in Table 4. The results of the compressive strength tests on these formulations are shown in Figure 4 and indicate that after 7 and 28 days they complied with the requirements for a CEM III/B 32.5L. The continued gain in compressive strength beyond 28 days can be attributed to the slower rate of hydration of ggbs.

Of particular interest was the two-day strength of these formulations. Using Formulation 1 as a reference, the effect of the inclusion of additional minor constituents was observed. Formulation 2 involved maintaining a Portland cement / ggbs ratio of 0.43 while adding 0.5% gypsum and 2.5% anhydrite II. The effect was significant, increasing the two-day compressive strength from 4.3 to 10.2 MPa. Similar effects were observed for Formulations 3 and 4, also leading to improvements in two-day strengths, although the effect was not as pronounced as that observed for Formulation 2. In addition to conforming to EN 197-4, Formulation 2 also complied with the requirements of EN 197-1, where a minimum value of 10 MPa at two days is stipulated for CEM III/B 32.5R, indicating that it was suitable for use where early strength is a requirement.

The resistance of the formulations to sulfate attack from the formation of gypsum or ettringite was also tested. Each formulations displayed some initial expansion in the first month, but after this no further signs were observed that expansive or disruptive compounds had formed after six-months' storage in the solution. The expansions ranged from 0.27% to 0.56% as shown in Table 5. Again using Formulation 1 as a reference, the effect of adjustments to the formulations and the inclusion of minor additional constituents did result in slightly increased expansions, but these were not considered significant.

6. Conclusions

The essential properties of cementitious binders containing combinations of gypsum, ground granulated blastfurnace slag and another mineral admixtures were reliably assessed. The results of the laboratory tests show that binders manufactured using calcium sulfate as the dominant ingredient develop adequate strengths, but are only suitable for use in dry environments.

The early strength development of CEM III/B Portland blastfurnace cements was significantly improved by the addition of small quantities of anhydrite II and gypsum. This did not affect the sulfate resistance of these binders. These binders have significant potential in situations were early strength development is a requirement

References

[1] Hoffert M, Caldeira K, Benford G, Criswell DR, Green C, Herzog H, Jain AK, Kheshgi H.S., Lackner KS, Lewis JS, Lightfoot HD, Manheimer W, Mankins JC, Mauel ME, Perkins LJ, Schlesinger ME, Volk T, Wigley TML. Advanced technology paths to global climate stability: energy for a greenhouse planet. Science, 2002, November 1, Vol. 298, No. 5595, pp. 981-987.

[2] Root TL, Price JT, Hall KR, Schneider SH, Rosenzweig C, Pounds JA. Fingerprints of global warming on wild animals and plants. Nature, 2003, January 2, Vol. 421, No. 6918, pp. 57-60.

[3] Worrell E, Price L, Martin N, Hendriks C, Meida LO. Carbon dioxide emissions from the global cement industry. Annual Review of Energy and the Environment, 2001, Vol. 26, pp. 303-329.

[4] Gartner E. Industrially interesting approaches to “low-CO_2” cements. Cement and Concrete Research, 2004, Vol. 34, No. 9, pp. 1489-1498.

[5] Van Oss HG, Padovani AC. Cement manufacture and the environment: Part II Environmental challenges and opportunities. Journal of Industrial Ecology, 2003, Vol. 7, No. 1, pp. 93-126.

[6] Worrell E, Martin N, Price L. Potentials for energy efficiency improvement in the US cement industry. Energy, 2000, Vol. 25, No. 12, pp. 1189-1214.

[7] Environmental Protection Agency. Irelands National Allocation Plan 2008-2012: As Notified to the EU Commission July 2006. 2006, available at www.epa.ie.

[8] Hossain KMA. Blended cement using volcanic ash and pumice. Cement and Concrete Research, 2003, Vol. 33, No. 10, pp. 1601-1605.

[9] Bilodeau A. Malhotra VM. High volume fly ash system: concrete solution for sustainable development. ACI Materials Journal, 2000, Vol. 99, No. 1, pp. 41-48.

[10] Konsta-Gdoutos MS Shah SP. Hydration and properties of novel blended cements based on cement kiln dust and blast furnace slag. Cement and Concrete Research, 2003, Vol. 33, No. 8, pp. 1269-1276.

[11] Al-Harthy AS Taha R Al-Maamary F. Effect of cement-kiln dust on mortar and concrete mixtures. Construction and Building Materials, 2003, Vol. 17, No. 5, pp. 353-360.

[12] Neville A. The Properties of Concrete. 5th Edition, John Wiley & Sons, 2002.

[13] Kovler K. Setting and hardening of gypsum-Portland cement-silica fume blends, Part 1: temperature and setting expansion. Cement and Concrete Research, 1998, Vol. 28, No. 3, pp. 423-437.

[14] Kovler K. Setting and hardening of gypsum-Portland cement -silica fume blends, Part 2: early strength, DTA, XRD and SEM observations. Cement and Concrete Research, 1998, Vol. 28, No. 4, pp. 523-531.

[15] Colak A. The long term durability performance of gypsum-Portland cement-natural pozzolan blends. Cement and Concrete Research, 2002, Vol. 32, No. 1, pp. 109-115.

Table 1. Potential applications for proposed binders.

Product	**Key technical requirements**
Painting-quality masonry blocks	• Smooth surface finish • Early strength at low binder content
Precast concrete pipes	• Sulfate resistance • Smooth surface finish • High early strength
Composite precast wall panels	• Smooth surface finish • High early strength
Non-structural precast concrete products (e.g. kerbs, flags etc)	• Durability • Smooth surface finish • High early strength • Colour
Float-ready plaster	• Durability in external environments • Smooth surface finish • Colour

Table 2. Formulations selected for testing.

Formulation No.	**Mix Constituents (%)**					
	Portland Cement	**Gypsum**	**Lime**	**GGBS**	**Anhydrite II**	**C/C ratio**
A	20	80				0.19
B	5	80	5	10		0.05
C	7	70	5	18		0.08
D	10	60	5	25		0.11
E	7	20	5	18	50	0.08
1	30			70		0.33
2	29	0.5		68	2.5	0.32
3	28.5	0.6		67.5	3.4	0.31
4	27	0.6	3	66	3.4	0.30

Table 3. The 3 products in the family of low early strength blast furnace cements.

Main Type	**Notation of the 3 products (types of low early strength blast furnace cement)**		**Composition (proportion by mass, %)**		
			Main constituents		**Minor additional constituents**
			Clinker	**Slag**	
CEM III	Blast furnace cement	CEM III/A	35 - 64	36 - 65	0 - 5
		CEM III/B	20 - 34	66 - 80	0 - 5
		CEM III/C	5 - 19	81 - 95	0 - 5

Table 4. Compressive strength requirements of EN 197-4.

Strength class	**Compressive strength (MPa)**			
	Early strength		Standard strength	
	2 days	7 days	28 days	
32.5 L	-	≥ 12.0	≥ 32.5	≤ 52.5
42.5 L	-	≥ 16.0	≥ 42.5	≤ 62.5
52.5 L	≥ 10.0	-	≥ 52.5	-

Table 5. Sulfate resistance of ggbs-based cements

Age (month)	**Expansion (%)**			
	Formulation 1	**Formulation 2**	**Formulation 3**	**Formulation 4**
1	0.030	0.034	0.052	0.039
2	0.026	0.040	0.056	0.042
4	0.026	0.038	0.049	0.034
6	0.027	0.040	0.049	0.035

Figure 1. Compressive strength development of calcium sulfate-based formulations

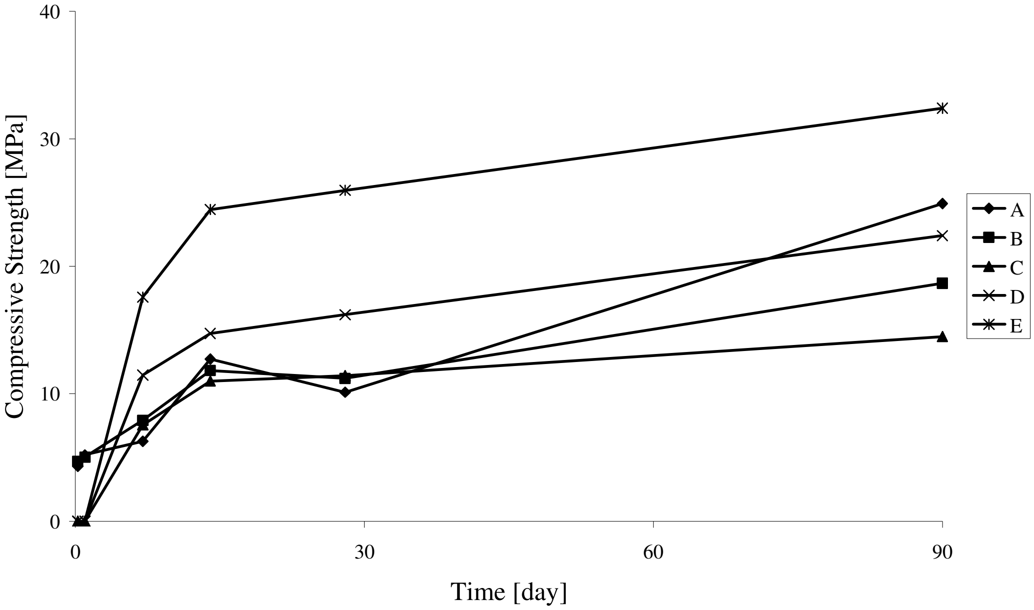

Figure 2. Effect of curing conditions on calcium-sulfate based cements.

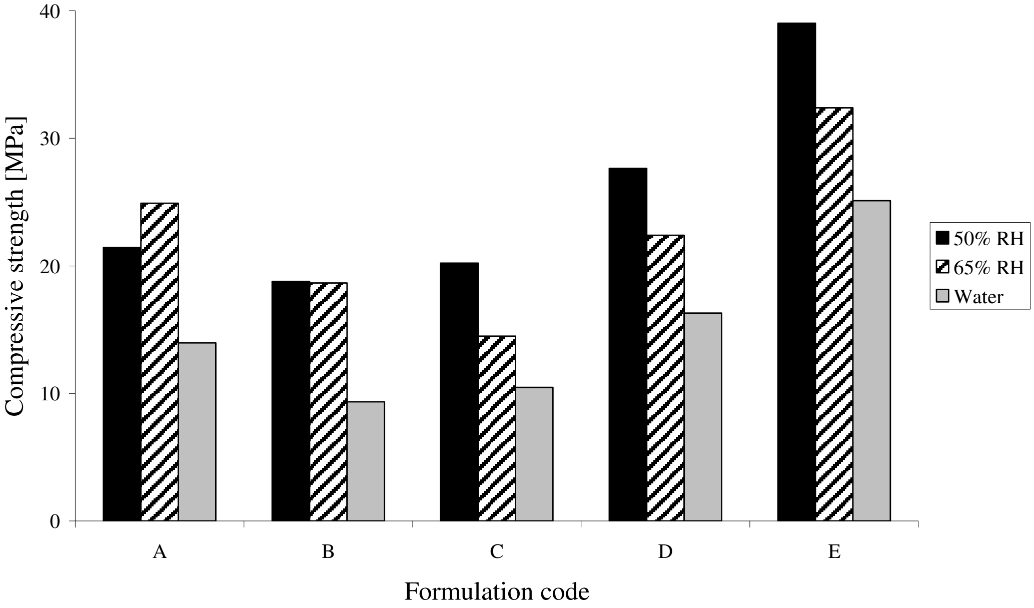

Figure 3. Stability of mortar prisms using calcium-sulfate based cements, when stored underwater.

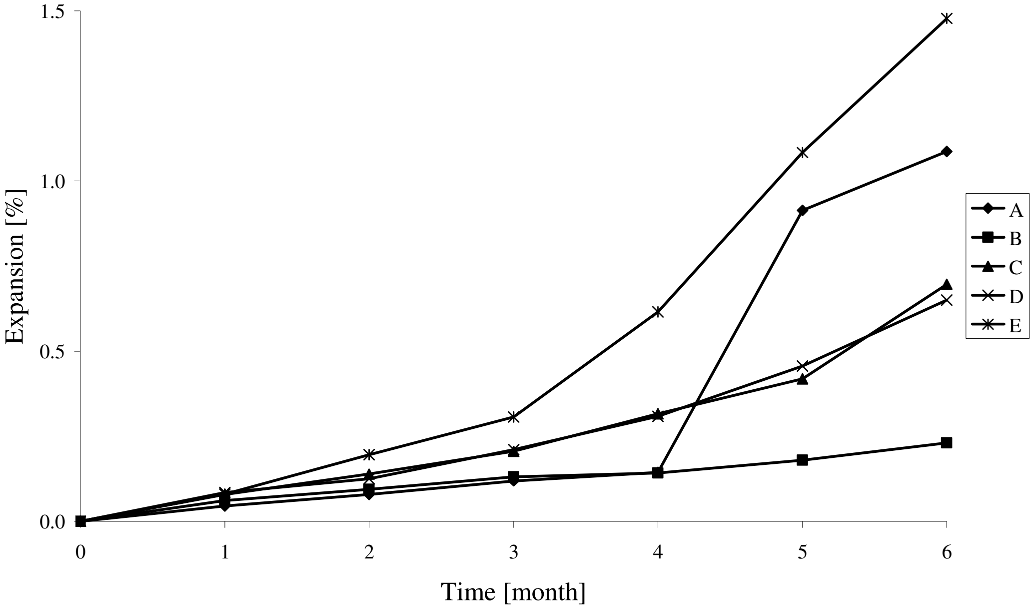

Figure 4. Compressive strength development of ggbs-based formulations