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Sustainable Cement-Gypsum Composite with Reduced Ettringite Expansion

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ABSTRACT

Construction materials based on either Portland cement or gypsum are amongst the most popular and widely used construction materials. Their applications however may be restricted by the specific properties or economical requirements. Composite incorporating both binders could be a cheap solution for construction industry of good mechanical/physical properties. However, creation of a composite of low shrinkage and preferably small expansion based on ettringite formation may be difficult due to its high aggressiveness. The authors propose that the limitation of ettringite crystals growth may be achieved by introduction of puzzolanic additives in form of microsilica and methylamonic compounds, strongly bonding calcium hydroxide. Application of hexamine may further reduce ettringite expansion.

INTRODUCTION

Construction materials nowadays are expected to comply with requirements reaching far beyond a general-utility market. More and more frequently, the construction industry must respond positively to the growing market for special-purpose materials. (Aitcin, 2000) The occurrence and development of which has been facilitated by advancements in the knowledge of materials technology, accompanied closely by a development of sophisticated means of structural analysis at micro- or even nano-levels. Recently revised codes of practice (e.g. EN206) have also forced a revision of hitherto applied practices. More holistic approach towards design concepts taking into account materials, construction as well as maintenance issues emphasized the importance of durability and environmental sustainability. The latter, being sometimes more important than strength, that can be compensated by an intricate design. It is essential to know the strength, but preservation of the mechanical characteristics over time, especially when exposed to severe environmental conditions, is equally or even more important. (Aitcin, 2000) “Cradle to grave” approach to sustainability integrates design, construction, use and demolition/reuse stages. It implies energy conservation, reduction in emissions and waste generation at all phases of building’s life.

More durable materials must comply with socio-economic requirements for reduced environmental impact. This would include use of salvaged, refurbished, or remanufactured materials. Locally available, reusable or recyclable products including waste products are becoming more and more popular in building materials composites. The ultimate goal is to produce high-technology materials tailored to special requirements/conditions at low economic cost, evaluated in performance terms.

Construction materials based on Portland cement and gypsum are amongst the most popular and widely used construction materials. Their applications however may be restricted by the specific properties or economical requirements. Portland cement can offer relatively high compressive strength, however its production is associated with high-energy consumption and it exhibits a high level of shrinkage preventing from application in certain types of structures. On the other hand a considerable expansion of gypsum during the hydration process making it suitable for filling moulds or for repairing cracks etc. The main disadvantage though is its low resistance to water. Composite incorporating both binders would be cheap solution for construction industry of good mechanical/physical properties.

Since the production of Portland cement is associated with high-energy consumption its partial replacement by synthetic gypsum would significantly reduce the cost of new composite and minimise its environmental impact. Application of synthetic gypsum, produced by flue gas de-sulphurisation (FGD) equipment at coal-fired power stations would additionally address an important waste management issue.

In construction practice, it is commonly accepted that these two binders should not be mixed together because of adverse processes taking place, associated mainly with ettringite expansion, cracking and loss of strength. Unmodified gypsum-cement composites in dry conditions have satisfactory physical and mechanical properties for a variety of applications. However, when exposed to hydrous environments show very little resistance, which manifests in form of linear changes and surface deterioration resulting from creation and growth of ettringite crystals.
Creation of a composite of small shrinkage based on ettringite formation may be difficult due to its high aggressiveness. Although the unwanted effects taking place in cement-gypsum composites are well known (Mather, 1973), (Odler at all 1988), Mehta, 1978), no systematic attempts have been made to limit them. Solution of the problem would allow application of OPC-gypsum composites on commercial scale (Konca, 1999). The aim of the research project was therefore to assess destructive effects of ettringite formation in cement-gypsum composites and to develop mitigating technique.

It is generally accepted that ettringite expansion in cement-gypsum composites depends mainly on the amount of hemihydrate form of synthetic gypsum and calcium hydroxide (Mehta, 1982). The authors propose that the limitation of ettringite crystals growth may be achieved by introduction of puzzolanic additives in form of microsilica and methyloamonic compounds, strongly bonding calcium hydroxide. Application of hexamine may further reduce ettringite expansion.
The paper presents experimental results and analysis. The main objectives of the presented study involved:

- Assessment of the effect of anhydrous synthetic gypsum on physical and mechanical properties as well as microstructural features of composites;
- Determination of destruction of composites caused by growth of ettringite crystals in air and water environment;
- Limitation of excessive ettringite expansion by application of puzzolanic additives reacting with calcium hydroxide;
- Determination of effect of hexamine on ettringite expansion.

MATERIALS AND MIXES

Assessment of physical-mechanical properties as well as microstructural examinations and analysis were performed in three series (Table 1):

Set 1 - composites with changing proportion of cement and gypsum
Set 2 – composites with constant proportion of cement (60%) and gypsum (40%), changing quantity of amorphous microsilica
Set 3 - composites with constant proportion of cement (60%) and gypsum (40%), changing quantity of hexamine and additional option (D13) 9% microsilica and 0.5% hexamine

Quartz sand of fraction 0-5mm formed about 50% of paste mass. Moisture content of synthetic gypsum was around 3%. Particles size did not exceeded 0.063mm. Amount of gypsum already present in OPC was about 5% in form of $CaSO_4 \cdot 2H_2O$. dry materials were mixed mechanically in a laboratory mixer.

Table 1. Mix compositions (Konca, 1999).

	Option	Portland Cement	Synthetic gypsum	Microsilica	Hexamine
Set 1	D1	100	0	0	0
	D2	80	20	0	0
	D3	60	40	0	0
	D4	40	60	0	0
	D5	20	80	0	0
Set 2	D3	60	40	0	0
	D7	60	40	3	0
	D8	60	40	6	0
	D9	60	40	9	0
Set 3	D3	60	40	0	0
	D10	60	40	0	0.5
	D11	60	40	0	1.0
	D12	60	40	0	1.5
	D13	60	40	9	0.5

All samples have been cured in laboratory conditions (20ºC; RH 60±5%) for 28days followed by curing in water and lab conditions. Experimental tests were performed after 3, 7, 14, 28, 90, 180 and 360 days of hardening.

Experiments involved microstructural analysis - Mercury Intrusion Porosimetry, Scanning Electron Microscopy; physical analysis – Differential Scanning Calorimetry, linear changes during hardening process; mechanical properties – compressive and flexural strength.

RESULTS AND DISCUSSION

As the result of preliminary data analysis of the first set of samples, only one composition has been selected for further modifications, i.e. 60% Portland cement and 40% synthetic gypsum (D3). Samples D3 during the whole process of hardening performed satisfactorily despite a high gypsum content. Mercury intrusion porosimetry technique was employed to determine microstructural variations (total porosity, dominating range of pores) resulting from composite modifications. Figure 1 presents differential distribution curves for composites D1 and D13 after 28 and 365 days of curing.

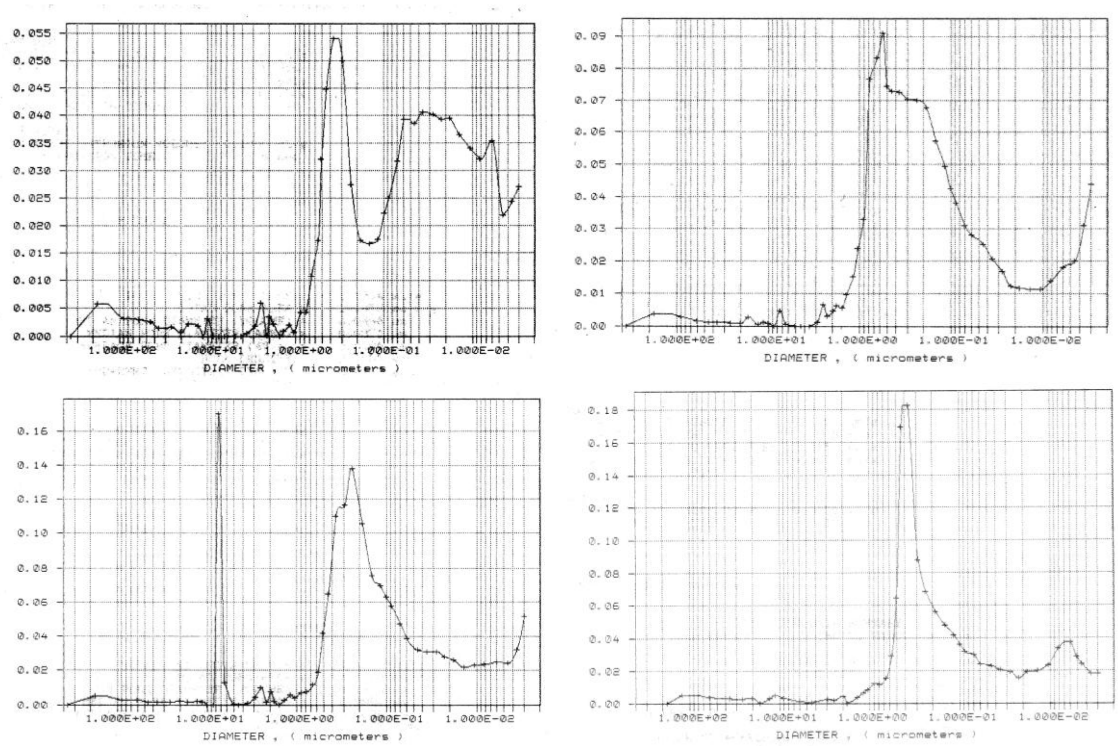

Fig. 1. Differential Distribution curves for D1 (top) after 28 and 365 days and D13 (bottom) after 28 and 365 days.

During 365 days of hydration the total area of pores in composite D1, not containing gypsum, as well as in modified cement-gypsum composites show declining tendencies (Fig. 2.). Differential Distribution curves underwent the most visible changes in composites D1. Addition of microsilica results in increase of pores with diameter around 0.02µm after 28 days of hardening. After 365 days the amount of such pores reduces. During the first month of setting and hardening the dominating range of pores is between 0.1 - 0.3 µm. After a year it moves towards the larger pores 0.2 – 0.7 µm (Fig. 3). Decreasing amount of synthetic gypsum in composites results in decreased density.

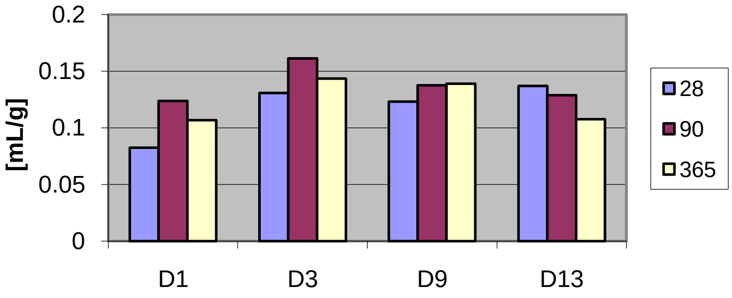

Fig. 2. Total porosity after 28, 90 and 365 days.

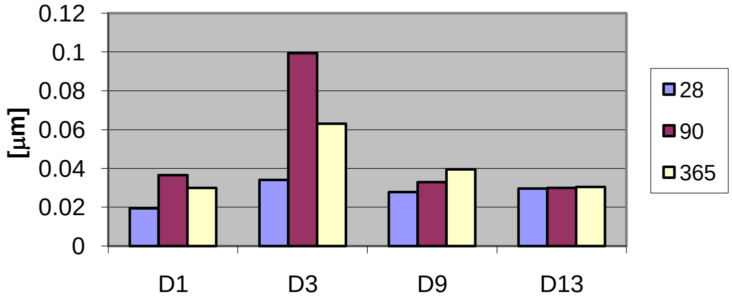

Fig. 3. Average pore diameter after 28, 90 and 365 days.

Internal microstructure of materials can be seen on images obtained from scanning electron microscopy. Figure 4 below shows scanning electron micrographs of cement-gypsum composites taken at the magnification of 3000x and 20000x. All composites had well developed CSH phase with portlandite and ettringite crystals.

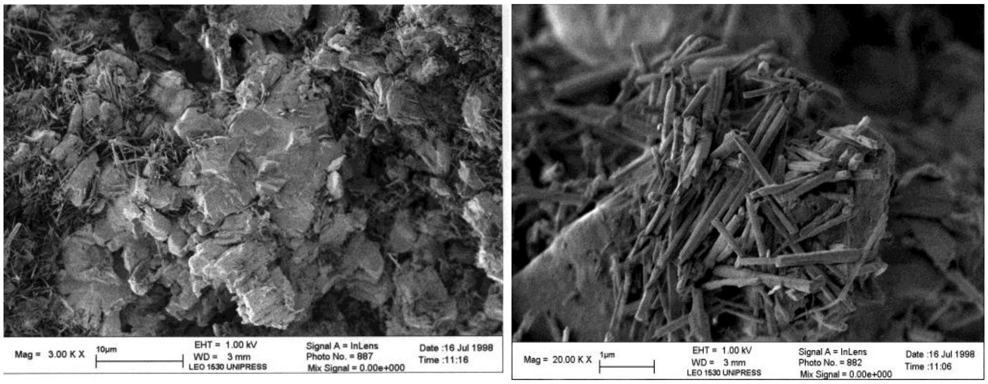

Fig. 4. Scanning electron micrographs of cement-gypsum composites (3000x and 20000x).

In some micro-regions it was possible to observe the process of dissolving of portlandite crystals, which most probably react in a liquid phase with alumina ions forming ettringite (Ogawa, 1982). After a long period of hydration microstructure becomes much denser. It is possible to distinguish fine crystalline forms of $Ca(OH)_2$ well dispersed in gel. Microscopic analysis showed also ettringite crystallising in gel, with clearly defined needle-like crystals.
Ettringite crystals sometimes crystallise in direct vicinity of un-hydrated particles of clinker. In the composite D1 (40% gypsum, 60% cement) CSH phase is very similar to the material containing only cement however in smaller quantity. Samples containing large amount of gypsum (without microsilica) and stored in water contain large amount of well crystallised ettringite.

Linear changes observed in samples not containing gypsum (D1) were restricted to linear shrinkage reaching 1mm/m after 28 days and 1.8mm/m after 365 days. Addition of gypsum leads to swelling of samples during the first 10 days and a subsequent shrinkage. The most pronounced changes were observed in samples D2 containing 20% of synthetic gypsum. During the first 5 days of hydration swelling was very severe reaching its maximum of 0.4 mm/m followed by shrinkage of 2.2 mm/m after 365 day of hardening. With the exception of samples D2, all cement-gypsum composites show smaller shrinkage than pure cement composites, with smaller changes in higher gypsum content samples.

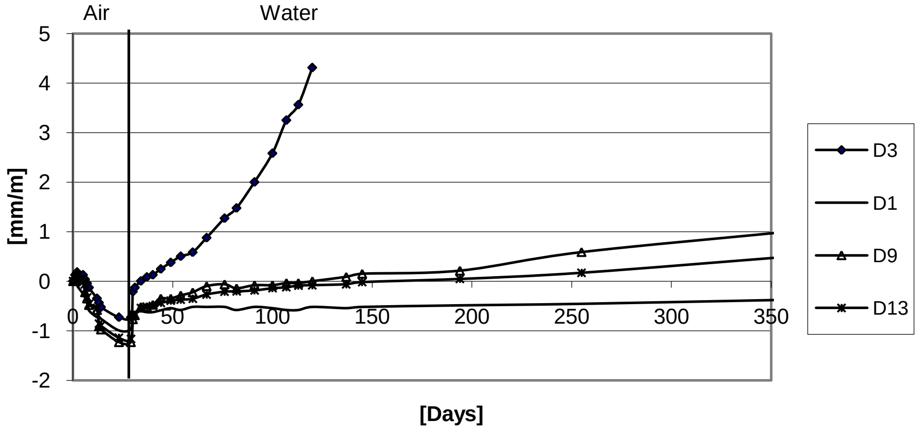

Fig. 5. Linear changes in composites during water curing.

Application of microsilica resulted in comparable alterations. Application of hexamine led to the reduced shrinkage when compared with samples D3.

Situation has changed completely when composites were cured in water. Samples with no gypsum did not undergo any linear changes and scaling of surface even after a year. Presence of gypsum, in the other composites led to a very severe swelling. The higher gypsum content the more pronounced changes. All these samples suffered from surface damage during the first three months of water curing. Introduction of microsilica resulted in significant reduction of swelling. Addition of 3 and 6% of microsilica reduced expansion but not completely eliminated it. Samples with 3% microsilica suffered from scaling after 7 months in water while samples with

6% showed first signs of cracking after one year. However samples containing 9% of microsilica did not undergo any surface deterioration and only very limited swelling. Application of only hexamine limited to some extend sulphate expansion but not protected against damage during the first months in water environment. The most optimal solution was introduction of both microsilica and hexamine. It could be attributed to simultaneous action of pozzolan and chemically active compound binding calcium hydroxide. It is worth to mention that the application of increasing amount of gypsum in composites increased capillary action in composites. Addition of microsilica reduced the capillary action while hexamine did not have an effect the final result. It changed slightly the process, most probably due to the alterations of microstructure resulting from the additions.

Figures 6-8 presents results of compressive strength for composites in three sets. Samples have been tested in a laboratory conditions after 3, 7, 14, 28, 90, 190 and 365 days.

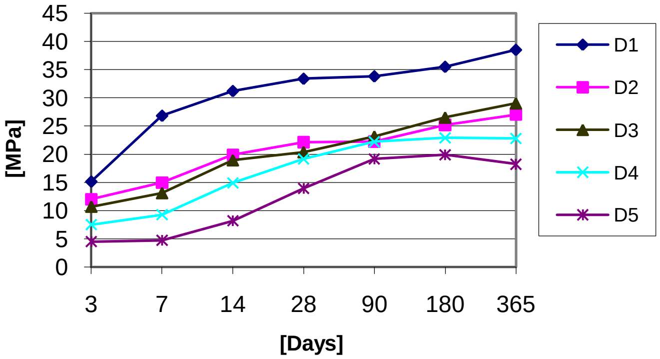

Fig. 6. Compressive strength development in Set 1.

In the first set of composites, without modifying admixtures, the highest values of compressive strength were obtained for samples without gypsum D1. Strength was almost twice as high as for other samples. Samples D2 and D3 with 20% and 40% of gypsum had similar strength still higher then remaining samples. During the first 90 days it is possible to distinguish direct relation between gypsum content and compressive strength. Figures 7-8 show strength development in sets 2 and 3 during 365 days of curing.

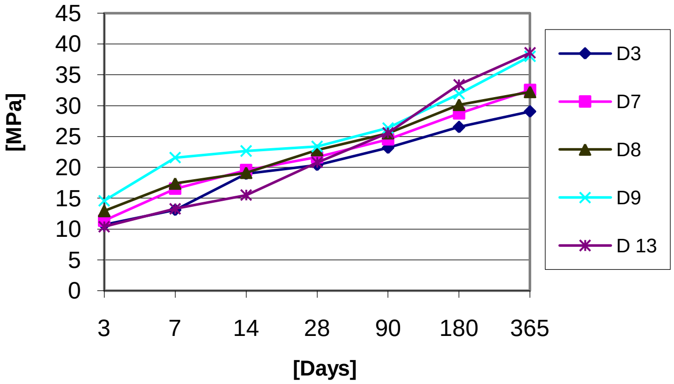

Fig. 7. Compressive strength development in Set 2.

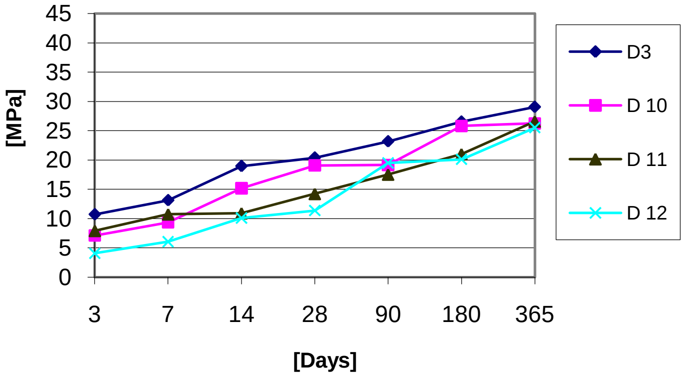

Fig. 8. Compressive strength development in Set 3.

In the second set sample D3 was modified with microsilica with sample D13 containing also small amount of hexamine. Addition of microsilica improved significantly compressive strength values. Sample D13, although during the first 28 days of hardening had the lowest values, reached one of the highest compressive strength. The results of compressive strength for samples from the third set clearly show an adverse effect of hexamine.

Summarising, the difference in compressive strength between samples D3 and D1 (with no gypsum) was in the range of 10MPa after 365 days and in flexural strength 2MPa (Fig. 9.). Application of 9% of microsilica affected positively mechanical properties of composites. Compressive strength of samples D9 (60% cement, 40% gypsum, 9% microsilica) and D13 (60% cement, 40% gypsum, 9% microsilica, 0.5% hexamine) after a year of curing was almost identical to samples not containing gypsum.

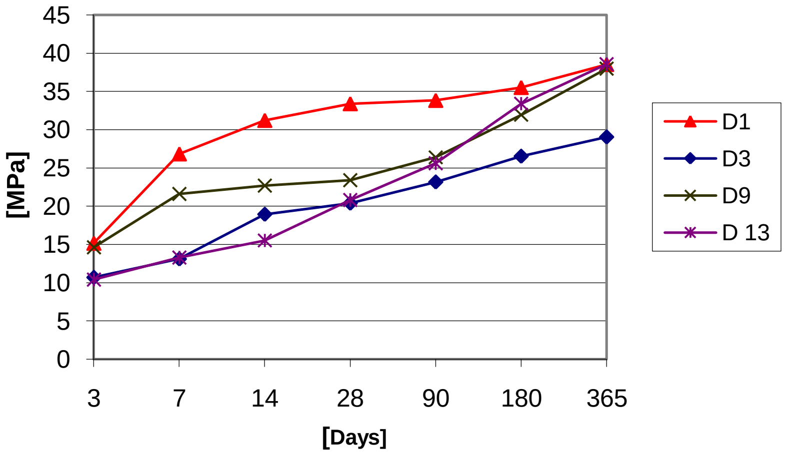

Fig. 9. Compressive strength of samples cured in laboratory conditions.

Although in samples D1 an increase in compressive strength during the first 28 days was significantly higher, final strength after 365 days was similar. Addition of hexamine reduced compressive strength particularly during the first 28 days. Only application of both 9% microsilica and 0.5% hexamine gave satisfactory results.

After one year of curing in water only samples D1, D9 and D13 were suitable for compressive strength testing due to undamaged surfaces subjected to crushing (Fig. 10.)

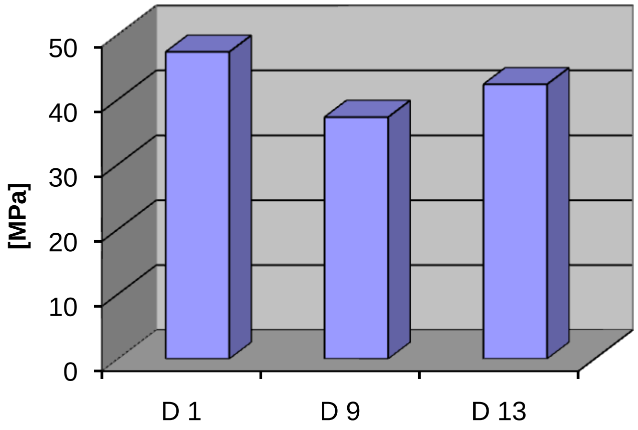

Fig. 10. Compressive strength of composites after 365 days of water curing.

Compressive strength of composites D9 and D13 after water curing is only slightly smaller than for samples containing only cement.

Macroscopic examinations of samples cured in laboratory conditions did not show signs of internal ettringite expansion. Samples of gypsum-cement composites cured in water underwent significant deterioration of similar nature. Figure 11 shows images of samples exposed to hydrous conditions.

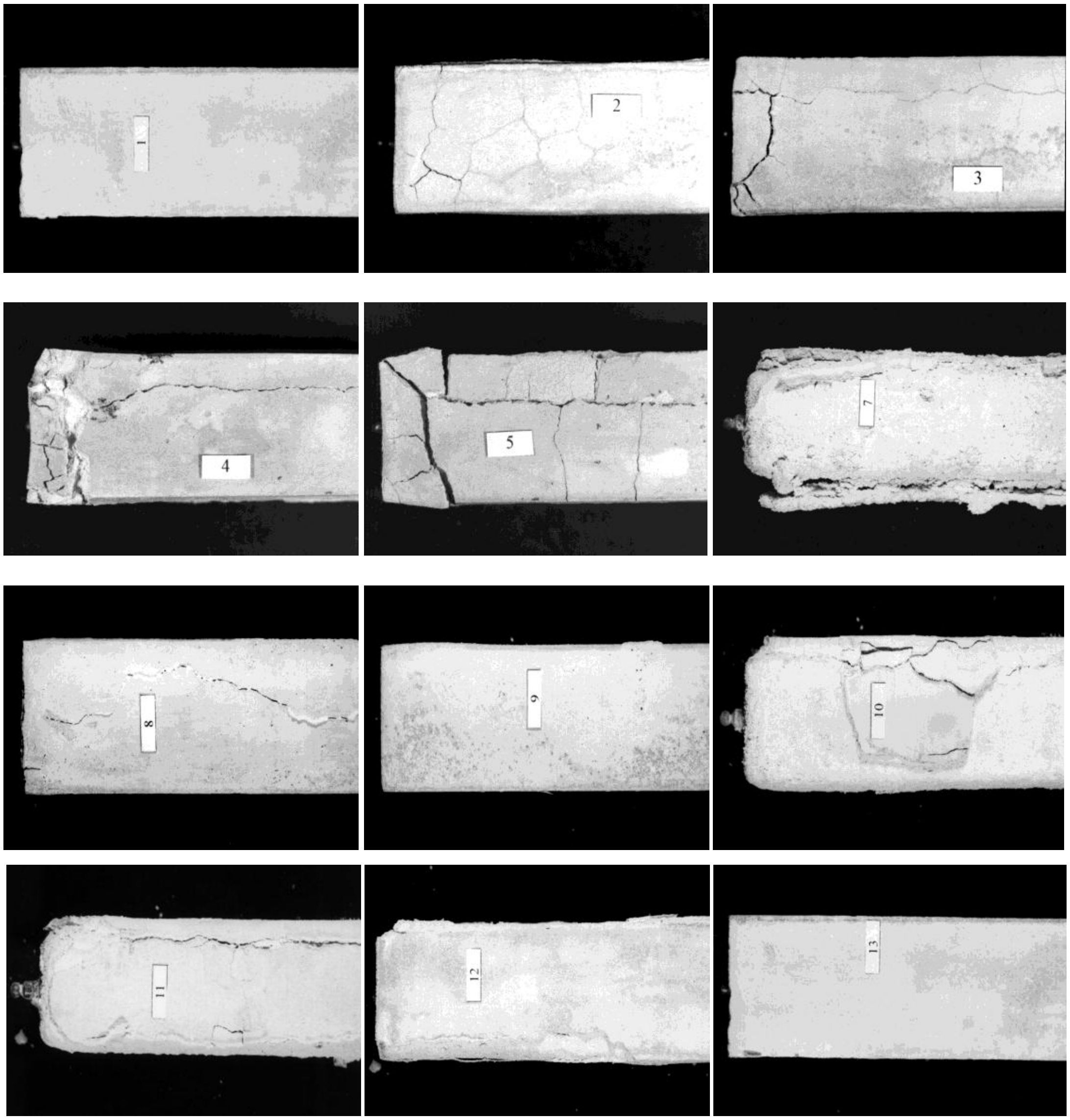

Fig. 11. Images of samples cured in water for 365 days.

Ettringite expansion was also visible on samples containing 3 and 6% of microsilica and hexamine. Again only samples with 9% microsilica and 0.5% hexamine did not reveal signs of expansion.

SUMMARY AND CONCLUSIONS

Based on experimental investigations, the following can be summarised:
Destructive expansion in cement-gypsum composites of high percentage of gypsum is caused by the growth of hydrophilic crystals of anhydrous phase of ettringite. During the initial phase of

setting and hardening chemically unbound water is quickly absorbed by hydrating phases and consequently there is no sufficient water for full growth of needle like crystals of ettringite. In the laboratory conditions air humidity is insufficient to initiate destructive expansive processes. Growth of ettringite crystals is possible only after supplying large quantities of water from outside. Destructive processes are initiated at surfaces and then progress inside material.

Very fine particles and developed surfaces of particles of amorphous microsilica results in high puzzolanic properties. Microsilica reacts easily with calcium hydroxide (CaOH) released during hydration, thus increasing amount of hydrous silicates – CSH. Good effects can be obtained by incorporating microsilica and hexamine (hexamethylenetetramine), which combine calcium hydroxide, protecting cement-gypsum composite against ettringite corrosion.
Samples containing large quantities of synthetic gypsum in laboratory conditions show chemical shrinkage, the smaller the higher is gypsum content. Increase of gypsum content leads to increase of ettringite and swelling of sample, reaching 6mm/m, particularly in aqueous conditions.

Increase of synthetic gypsum in paste results in decrease of mechanical properties particularly during the first 28 days of hydration. After a year differences between composites with 80% of gypsum and without gypsum at all are almost twofold.

Deterioration of composite materials containing large quantities of gypsum is taking place mainly in hydrous environment, which confirms that needle like crystals of ettringite require chemically unbound water for their growth.

Hexamine (hexamethylenetetramine) adversely affects mechanical properties, particularly during the first weeks of setting and hardening. However it reduces amount of ettringite by binding calcium hydroxide. Application of hexamine in quantities substantially affecting hydration process delays and reduces ettringite expansion however it does not protect against destruction and swelling, in excess of 4mm/m after seven months of curing in hydrous conditions.

Application of puzzolanic materials allows creation of cement-gypsum paste, which after one year of setting and hardening has mechanical properties comparable to cement paste.
Microsilica reduces growth of ettringite in composites and improves physical and mechanical properties after longer period of time. Amorphous microsilica reduces or completely eliminates swelling of material in air and water environment (for 9% of microsilica after one year of curing in water linear changes do not exceed 1mm/m)

The most beneficial modification of cement-gypsum composite was achieved with 9% of microsilica and 0.5% of hexamine. Such composite characterised with high compressive strength, reaching 40MPa and small linear changes within 0.5mm/m, even after curing in water.

Based on the study presented above the following preliminary conclusions can be drawn:
Destructive expansion in cement-gypsum composites takes place in hydrous conditions and is caused by the growth of hydrophilic crystals of anhydrous phase of ettringite. Hexamine adversely affects mechanical properties of composites however it effectively reduces amount of

ettringite by binding CaOH. Amorphous microsilica reduces growth of ettringite in composites and improves physical and mechanical properties after longer period of time.

It should be noted that that further investigations are required in order to verify the results and formulate final, comprehensive conclusions.

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