The sulphate corrosion of mortars containing FBC ash

R. Mróz[1], M. Gawlicki[1], J. Małolepszy[1]
[1]*AGH University of Science and Technology, Kraków, Poland*

Abstract:
One of the potential mixed cements components, which can be used to soil stabilization are by-products coming from fluidized-bed combustion installation. However, the composition of FBC by-products ($CaSO_4$, CaO, $CaCO_3$, methakaolinite) favour thaumasite formation. The comparisons of two - component cements proprieties containing conventional and FBC ash were executed in the article. Mortars and pastes prepared from these cements were exposed to action of SO_4^{2-} rich waters. Composition of sulphate corrosion products, formed from pastes contained different amounts of ashes and stored in different time cycles were examined. For experiments chemical analysis, XRD and SEM/EDS were used. Investigations demonstrated that sulphate corrosion marked more clearly in pastes containing FBC ash.

1. Introduction

In last three decades, there has been a continuous effort made by electric utility companies to reduce sulphur dioxide emissions by coal burning power plants. To achieve the desired concentration of sulphur dioxide in the exhaust gases, they are processed in desulphurisation installation. The most widely used method of removal of sulphur dioxide is the treatment of the flue gases with calcium oxide. During this process, calcium oxide reacts with sulphur dioxide to produce hannebachite and/or gypsum. The by – products from the desulphurisation process also contain the finer fractions of fly ash [1]. If this process is realized in fluidised-bed combustion installation, FBC ash is also produced. Recently, there have been some attempts made to use them as structural filler or some other value – added applications [2-4].
The influence of FBC ash from coal fluidised-bed combustion installation on the sulphate resistance of mortars and pastes will be examined in this paper. The objective of this study is to identify the mechanism of sulfate attack in FBC ash cement and to understand the effect of FBC ash from coal fluidised-bed combustion installation on durability of mortar exposed to sodium sulfate solution. In addition, special attention is focused on the conditions under which thaumasite can be formed in eff ect of sodium sulfate attack at low and ambient temperature.

Until now in literature, there has been a predominant opinion that the destruction of concrete by sulfate ion is connected first of all with expansive ettringite and gypsum formation [5 -7]. The C_3A content in cement is the main parameter limiting the resistance of concrete to chemical corrosion [8]. However, many authors [9-13] indicate that C-S-H also undergoes sulphate corrosion, especially in the presence of CO_2 and at lower temperatures. In this case thaumasite is produced. The formation of thaumasite in contrast to ettringite does not cause high expansion, but it does lead to loss in strength and collapse of the microstructure [13] by the C-S-H transformation into a mush in concretes and mortars.
Results of research show practical limit of the quantity of the FBC ash from coal fluidised-bed combustion installation as a cement additive. Results give a qualification of optimum quantities of FBC ash additive to cement, which will be useful in production of cements compared with properties of cements based on other types of ash.

2. Experimental part

2.1. Cement preparation

Four types of cement were used in the experiment. First one CEM II/B-V 32,5 (CL0) was produced on industrial scale by the Gorazdze Cement plant. The other cements: CEM II/A (CL1), CEM II/B (CL2) and CEM II/B with 5% $CaCO_3$ (CL3) were prepared in laboratory scale by inter-griding of clinker from Gorazdze Cement plant (table 1), FBC ash from coal fluidised-bed combustion installation (table 2) and $CaCO_3$ in a pro-pilot ball mill at the laboratory. The composition and the properties of the cements are given in table 3 and 4.

Table 1. Chemical and mineralogical composition of clinker

Composition	Gorazdze clinker [%]
loss of ignition	0,13
SiO_2	22,57
Al_2O_3	5,69
Fe_2O_3	3,00
CaO	67,37
MgO	1,41
SO_3	0,56
Na_2O	0,15
K_2O	0,92
CaO_f	0,8
C_3S	53,75
β C_2S	22,7
C_3A	9,6
C_4AF	8,9

Table 2. Chemical and mineralogical composition of FBC ash

Composition	Content [%]
loss of ignition	4,00
SiO_2	38,68
Fe_2O_3	3,21
Al_2O_3	16,18
TiO_2	0,51
CaO	21,48
MgO	1,78
SO_3	13,99
S^{2-}	0,16
CaO_f	7,68

SO_3 content as a $CaSO_4$ gives 23,78%. Additionally, considered resistance of cements prepared with addition of FBC ash on thaumasite corrosion it is important to take into account presence of $CaCO_3$ in FBC ash, mainly in form of unreacted sorbent [14-18].

Table 3. Chemical characteristic of cement CEM II/B-V 32,5

Composition	Content %
loss of ignition	3,27
SiO_2	26,37
Fe_2O_3	3,79
Al_2O_3	10,82
Na_2O	0,43
K_2O	1,42
CaO	47,87
MgO	1,67
SO_3	2,21

Table 4. Composition and properties of cements

Sample code/cement type		Cement composition			Specific surface	Density
		Gorazdze clinker	FBC ash	$CaCO_3$		
		wt. %			cm^2/g	g/cm^3
CL1	CEM II/A	85	15	-	3570	3,07
CL2	CEM II/B	78	22	-	3510	3,03
CL3	CEM II/B	73	22	5	3590	3,01

The aim of 5% $CaCO_3$ addition to CL3 was to estimate how additional calcium and carbonate ions influence on corrosion resistance of these types of cements [14-17,19,20].
Cement mortar prisms (20x20x160 mm) for linear changes tests and mortar prisms (40x40x160 mm) for compressive and flexural strength tests were made with prepared cements. Both series were kept initially for 28 days in water.

2.2. Curing conditions

After 28 days of curing period the mortars were divided into two groups, each stored in different temperature ranges:

- range I: 5 ± 1ºC
- range II: 20 ± 2ºC.

Samples of mortars were soaked in 5% Na_2SO_4 solution. Simultaneously comparative samples were kept in distilled water. Samples were cured in horizontal position, dipped in 10 mm under the surface of solution. The salt solution was changed for 28 days during all period of investigation. The compressive and flexural strength tests, linear changes tests, XRD and SEM-EDS studies were carried out. The tests were made in terms according to accepted procedures.

3. Results

3.1. Results of linear changes

The linear changes tests of prism were carried out after 4, 8, 12, 16, 20, 28, 40, 52, 70, 87 and 104 weeks of maturing of samples in solutions. The results of measurements of linear changes tests are presented in Fig. 1-4.

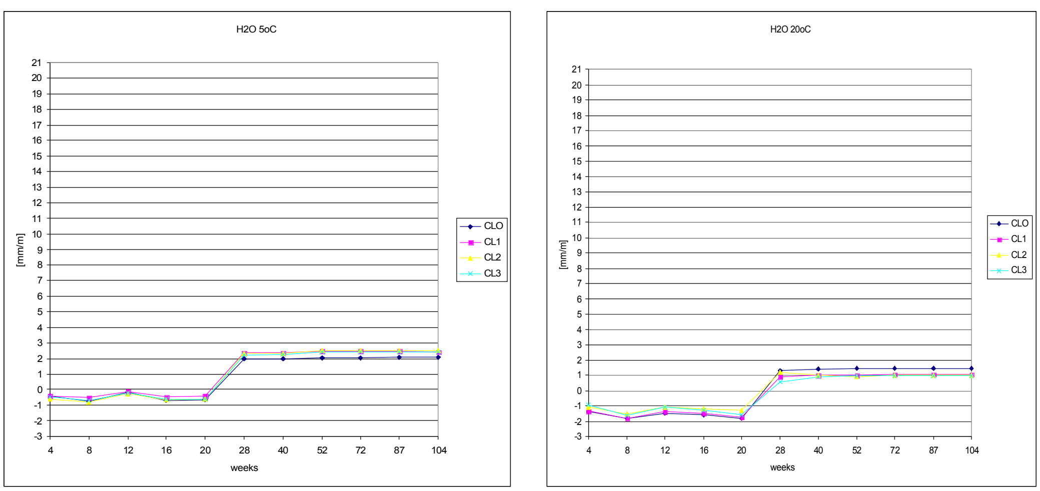

Fig. 1-2. The linear changes of cement mortars stored at 5 and 20°C in water.

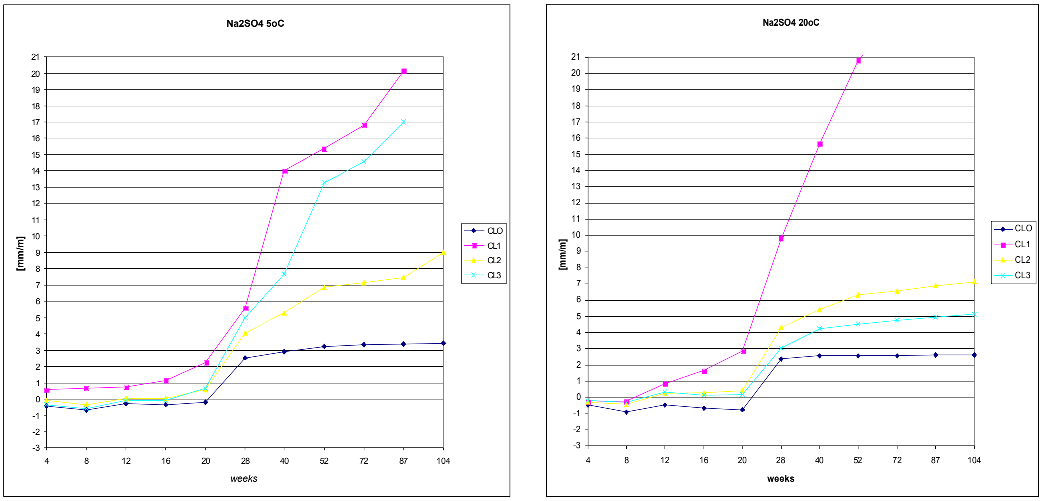

Fig. 3-4. The linear changes of cement mortars stored at 5 and 20°C in Na_2SO_4 solution.

Analysis of results (fig. 1-2) showed that, there are no significant differences in behaviour of cement mortars depending of storage temperature in case of samples stored in distilled water . In case of experiment with sodium sulphate we can observe different effects (fig. 3 and 4). In this case evident expansion of samples is seen. The intensity of changes depends of cement type. The highest expansion was observed for mortar samples CL1 made with cement with 15% addition of FBC ash, independently of the storage temperature. The expansion is so high, that in some cases it leads to formation of cracks in samples after 16-20 weeks of storage in corrosion solution (fig. 5). Obtained results suggested, that 15% addition of FBC ash to clinker does not cause the reduction of clinker compliance on sulphate corrosion. It happens with regard on insufficient quantity of puzzolana addition (FBC ash), which makes impossible sufficient packing of cement matrix.

Fig. 5. The cracks visible in CL1 cement mortars prism stored in sulphate solution after 20 weeks.

However, more interesting results were obtained for cements CL2 and CL3. If we take into consideration differences in behaviour of CL2 and CL3 cements (22% of addition of FBC ash), we can note that these mortars demonstrate more expansion at low temperature. Additionally the 5% $CaCO_3$ addition visible accelerated expansion of mortars CL3 stored in sodium sulphate at low temperature. This phenomena could be explained by crystallization of some series of solid solutions between ettringite and thaumasite, in opposite to mortars stored at room temperature, in which the expansion is caused probably only by ettringite formation. The formation of ettringite-thaumasite solid solutions can be explained by presence of free CaO, $CaCO_3$ and $CaSO_4$ in CL2 and CL3 cements. The source of CaO, $CaCO_3$ and $CaSO_4$ is the addition of 22% of FBC ash (in both cements) and additionally 5% $CaCO_3$ addition to cement CL3.

3.2. Results of compressive and flexural strength

The compressive and flexural strength tests of cements mortars were made at the following terms: 28, 90, 180, 270, 360 and 720 days. The results are presented in fig. 6-13.

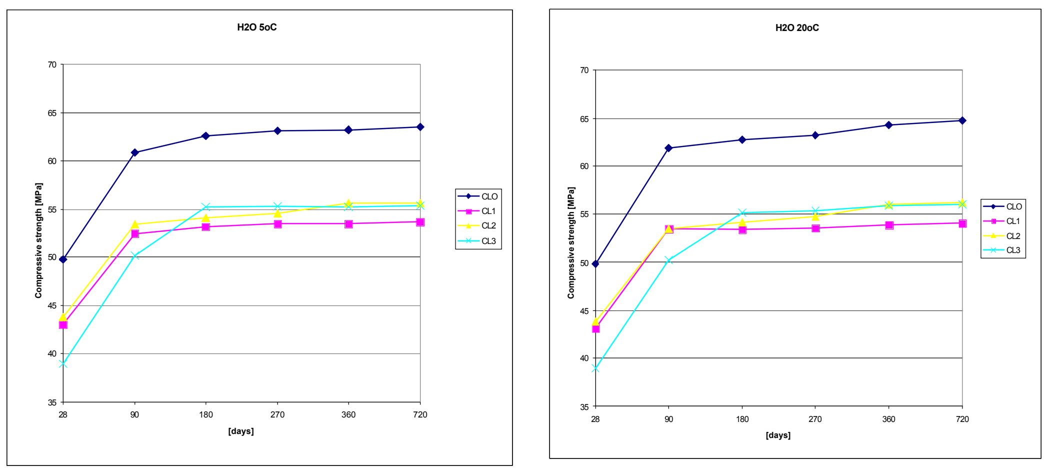

Fig. 6-7. The compressive strength of cement mortars stored at 5 and 20°C in water.

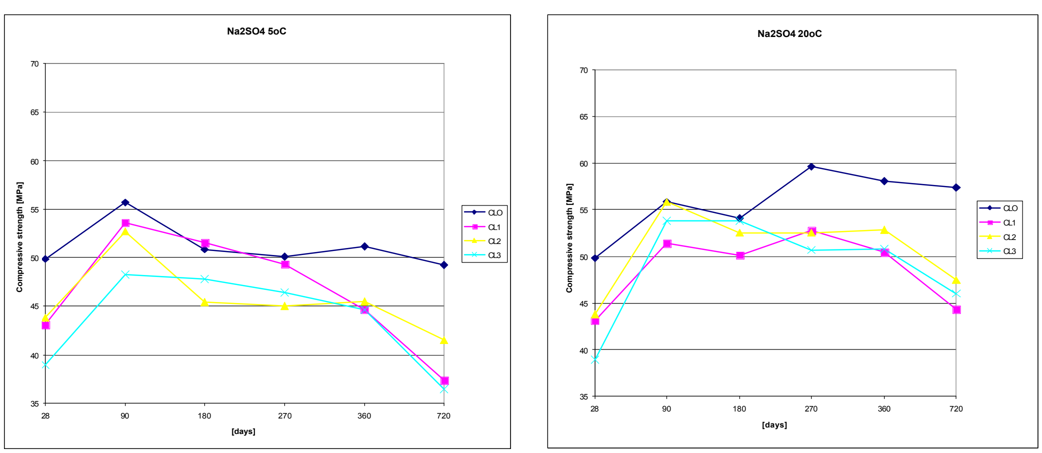

Fig. 8-9. The compressive strength of cement mortars stored at 5 and 20°C in Na_2SO_4 solution.

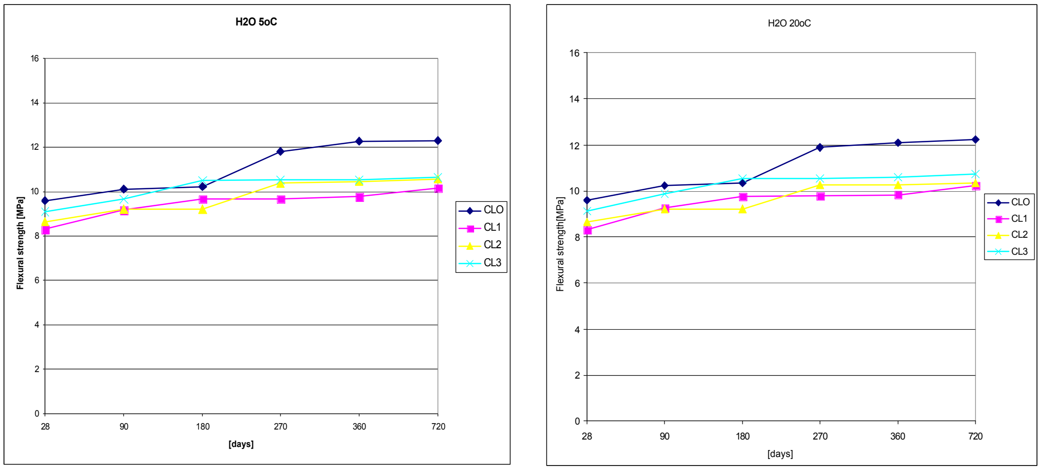

Fig. 10-11. The flexural strength of cement mortars stored at 5 and 20°C in water.

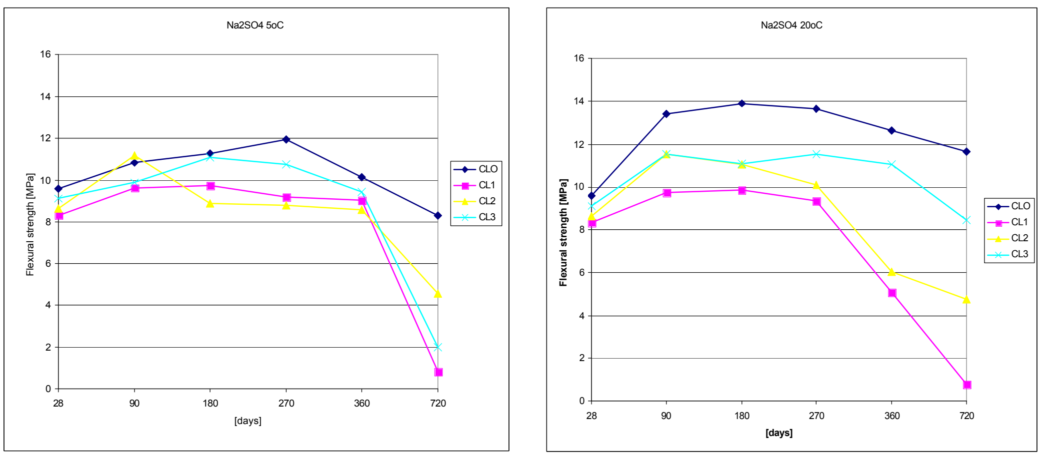

Fig. 12-13. The flexural strength of cement mortars stored at 5 and 20°C in Na_2SO_4 solution.

The results of compressive and flexural strength tests of mortars prepared with reference cement and with cements with addition of FBC ash in acceptable amount for CEM II/A and CEM II/B cements stored in water showed insignificant initial grown of strength with time (after 90 days of curing in normal conditions), what is characteristic for cements with addition of puzzolana materials. Also all cement stored in sulphate solution in initial period of time showed the grown of strength, as well as compressive and flexural strength. After about 90 days mortars started marked the differences of their strength characteristic. The results of strength tests of samples stored in sulphate solution showed also differences in behaviour of mortars depending on curing temperature in longer periods of time. Cement mortar samples with 22% addition of FBC ash (CL2 and CL3) stored at 20°C temperature showed a bit lower

compressive strengths, compared to reference cement and cement with 15% addition of FBC ash (CL1). The results of compressive strength tests did not find confirmation in flexural strength of mortars in short periods of time. The CL2 and CL3 cements showed a bit better results then CL1 cement. Decrease of CL2 and CL3 cements compressive strength with time could be interpreted in appearance by the bigger amount of ettringite in this cements, regard to high amount of $CaSO_4$ put in to these cements with addition of FBC ash. Ettringite formed in cement matrix in place of different more durable phases could decrease compressive strength of mortars. However, from the other hand, needle forms of ettringite crystals can positively influence on flexural strength of these cements.
Large decrease in compressive strength of comparable samples stored at low temperature could be explain ed by the thaumasite and some solid solution between ettringite and thaumasite occurrence in cement mortars after about 180 days, especially for CL3 samples (with 5% $CaCO_3$). It is in accordance with literature data. Some authors inform that thaumasite crystallization occurs in cement mortars not earlier then 0,5-1,0 year period of sulphate solutions action at lower temperatures [5,9,10,21]. The additional factor confirming thesis relating to thaumasite role is decrease of compressive strength (after 720 days) of CL2 and CL3 cements, which are richer in CaO, $CaCO_3$ and $CaSO_4$ regard to addition of FBC ash, refer to CL1 cement.
Differences between strength characteristic and linear changes tests in case of sulphate resistance investigations result from the sample preparation method. Samples for strength tests have bigger dimensions (40x40x160 mm) and they are characterized by higher mortar density (better compacted), what is the result of preparation requirements. It decreases the porosity of material, what causes the lower permeability for corrosion solutions. Dimensions and more dense structure of samples prepared for strength tests result in the fact, that the cores of the samples stored in corrosion solution stay unchanged for a longer period of time (270 days).

3.3. Additional analysis

To confirm the thaumasite formation or evidence of some series of partial ettringite - thaumasite solid solution in discussed cement mortars SEM-EDS and XRD analysis were carried out on the samples stored at low and room temperature in sodium sulfate solution. Samples for SEM-EDS were chosen based on macroscopic observations (fig. 14).

Fig. 14. The samples of CL2 cement mortar (sulphate solution, 5^{o}C, 720 days).

The SEM-EDS observations showed the presence of thaumasite and ettringite in samples CL2 and CL3 stored in sulfate solution at 5^{o}C [21,22] (fig. 15). In the same samples stored at room temperature (20^{o}C) only ettringite was observed (fig. 16).

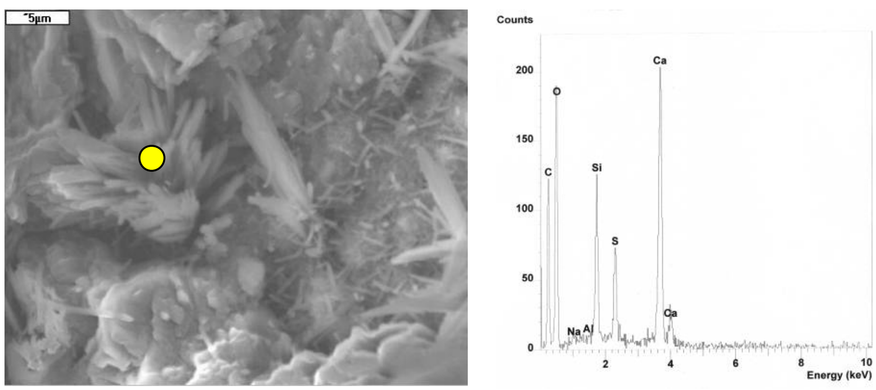

Fig. 15. SEM-EDS CL2 mortars (sulphate solution, 5^{o}C, 720 days).

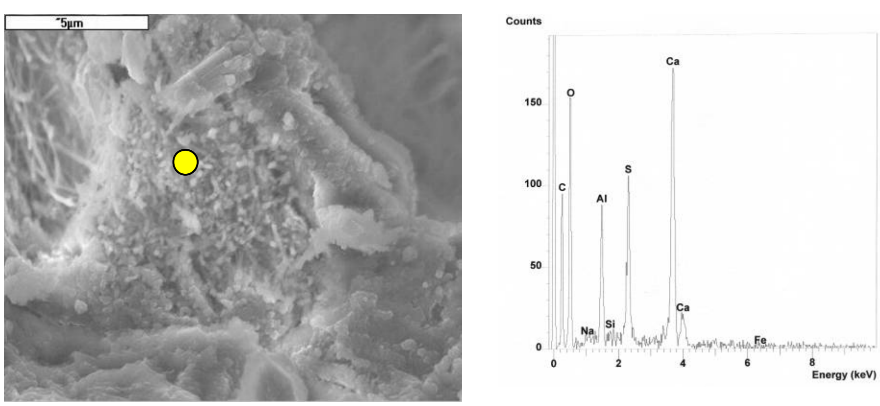

Fig. 16. SEM-EDS CL2 mortars (sulphate solution, 20^{o}C, 720 days).

The highest agglomerations of ettringite – thaumasite solid solutions were observed in CL2 and CL3 samples after 720 days of storage in sulphate solutions.
The results of XRD analysis fully confirm the occurrence of ettringite – thaumasite solid solution in mortars made from CL2 and CL3 cements stored at 5^{o}C in sulphate solutions after 720 days (fig. 17).

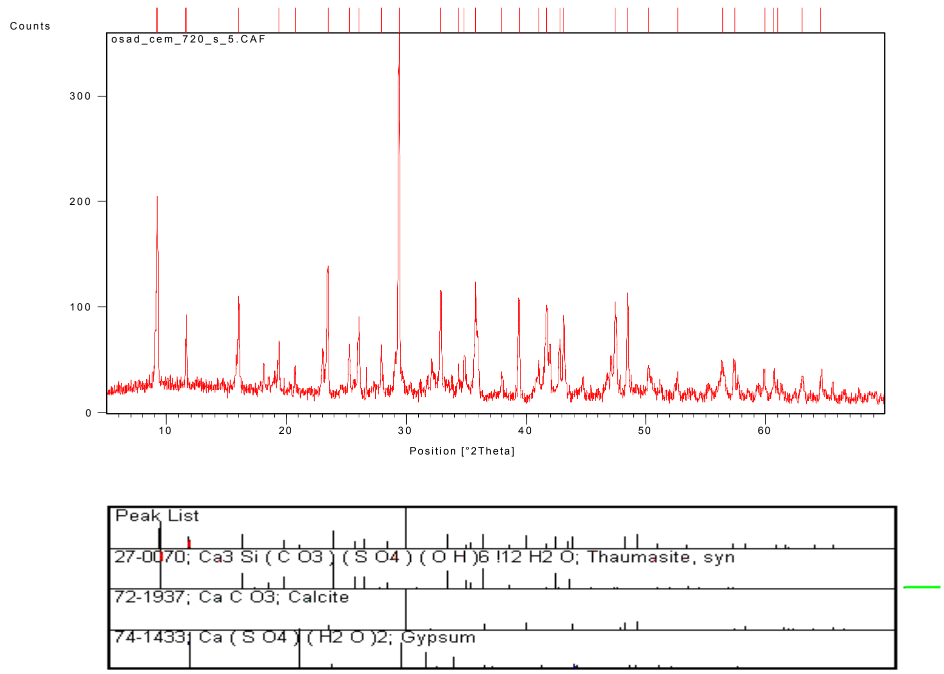

Fig. 17. The results of XRD analysis of CL2 mortar (sulphate solution, 5^{o}C, 720 days).

4. Summary

Fluidized ash (bottom or fly) has particularly different physical and chemical properties in reference to traditional fly ash. Fluidised ash contains in its phase composition amorphous phases formed from dehydration of clay minerals and also unreacted sorbent in form of $CaCO_3$, free calcium and anhydrite [4,20].
The results of investigation showed unambiguously, that amount of ash-addition used in cements determine sulphate resistance of these cements.
A significant benefit of application of FBC ash in cement is elimination of gypsum added as a setting time regulator. In case of investigated cements, FBC ash from desulphurization process plays the role of setting time regulator.
From the chemical resistance point of view, the presence of sulphate ions in this material is very significant. The sulphate ions react with aluminates ions what can lead to delayed ettringite formation. The presence of the other mineral phases in cement matrix can lead to thaumasite formation. It

could be direct reason of deterioration of concrete made with these types of cements. The usage of FBC ash from fluidized combustion as a cement additive should be realized with the focus on CaO, $CaCO_3$ and $CaSO_4$ content in ash, which limited its usefulness.

It seems to be possible to use the FBC ash as cement additive together with the conventional fly ash. The amount of fluidized ash should be limited by maximum CaO and $CaSO_4$ content in cement. The adequate proportion of both ashes could increase the sulphate resistance of these cements.

The results obtained for reference cement confirmed opinion about sulphate resistance of fly ash cements. Presence of fly ash in reference cement considerable increase sulphate resistance of mortars stored at 5 and 20°C according to cement with FBC ash addition.

Acknowledgements

The financial support from the Polish State Committee for Scientific Research KBN in 2005 – 2008 years (grant No. 4 T07E 005 29) is fully acknowledged.

References

[1] M. Schneider, S. Puntke, M.M. Sylla, K. Lipus, " The influence of cement on the sulfate resistance of mortar and concrete", Cement International 1, 2002, p. 131-148

[2] S. Sahu, S.A. Brown, R.J. Lee, „Thaumasite formation in stabilized coal combustion by-products", Cement & Concrete Composites 24, 2002, p. 385-391

[3] W. Brylicki, J. Małolepszy, "The Hydraulic and Pozzolanic Properties of Waste Products from Fluidizes Black Coal Combustion in Circulation Atmospheric Boiler Furnace", 14th Int. Baustofftagung IBAUSIL. Weimar 2000. Proceedings. p. 2043 - 2051.

[4] W. Brylicki, J. Małolepszy, „Properties of cement containing waste materials from coal fluidized combustion installation ", Polish Ceramic Bulletin. CERAMICS Vol. 66/1. Kraków 2001, p. 307-377 in Polish.

[5] J. Bensted, „Scientific background to thaumasite formation in concrete", World Cement Research 11, 1998, p. 102-105

[6] M. Santhanam, M.D. Cohen, J. Olek, „Mechanism of sulfate attack: A fresh look. Part 1: Summary of experimental results", Cement and Concrete Research 32, 2002 p. 915-921

[7] M. Santhanam, M.D. Cohen, J. Olek, „Mechanism of sulfate attack: A fresh look. Part 2: Proposed mechanisms", Cement and Concrete Research 33, 2003, p. 341-346,

[8] O.S. Baghabra Al.-Amoudi, „Attack on plain and blended cements exposed to aggressive sulfate environments", Cement & Concrete Composites 24, 2002, p. 305-316

[9] J. Bensted, S. P. Varma, „Studies of thaumasite, part II", Sil. Ind. T 39, 1974
[10] J. Bensted, S. P. Varma, „Studies of Thaumasite", Sil. Ind. T 2, 1973
[11] K. Lipus, H.M. Sylla, "Investigations in Germany of the thaumasite form of sulphate attack", Proceedings of the First International Conference on Thaumasite in Cementitious Materials, BRE, Garston, Great Britain, June 2002
[12] P. Nobst, J. Stark, Investigations on the influence of cement type on the thaumasite formation", Proceedings of the First International Conference on Thaumasite in Cementitious Materials, BRE, Garston, Great Britain, June 2002
[13] P.W. Brown, „Thaumasite formation and other forms of sulfate attack", Cement & Concrete Composites 24, 2002, p. 301-303
[14] I. Soroka, N. Stern, „Effect of calcareous fillers on sulphate resistance of Portland cement", Bull. Am. Ceram. Soc. 55(6), 1976, p. 594-595
[15] J. Małolepszy, R. Mróz, „Sulphate corrosion of cement mortars containing bottom ash from coal fluidized combustion installation", Proceedings "Concrete Days – Tradition and Modernity" Conference, Wisła 11-13 October 2004.
[16] M.A. Gonzalez, E.F. Irassar, „Effect of limestone filler on the sulphate resistance of low C_3A Portland cement", Cement and Concrete Research 28, 1998, p. 1655-1667
[17] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, „Thaumasite formation in Portland-limestone cement pastes", Cement and Concrete Research 29, 1999, p.1331-1340
[18] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, „The Thaumasite form of sulphate attack in Portland-limestone cement mortars stored in magnesium sulphate solution", Cement & Concrete Composites 24, 2002, p.351-359
[19] P. Brown, R.D. Hooton, "Ettringite and thaumasite formation in laboratory concretes prepared using sulphate-resisting cements", Cement & Concrete Composites 24, 2002, p. 361-370
[20] Z. Pytel, "Influence of curing conditions on the sulphate resistance of cement mortars with bottom ash from coal fluidized combustion installation", IV Conference Problems in Civil Engineering MATBUD'2003 PK, Kraków, 25 - 27 June 2003
[21] J. Małolepszy, R. Mróz, "The condition of thaumasite formation and its role in concrete", Proceedings of 11th International Congress on the Chemistry of Cement, Durban, South Africa, 2003, p. 1487-1496
[22] S. Barnett, "Study of thaumasite and ettringite phases formed in sulfate/blast furnace slag slurries using XRD full pattern fitting", Cement & Concrete Composites 24, 2002, p. 339-346