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Resistance of Concrete with Fine-Ground Granulated Slag Admixture to Sulphates and Acidic Aggressive Media

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Summary

Blast-furnace slag granules may be used not only in mixed Portland cement making but it is also suitable as a partial substitution of Portland cement in concrete. Substitution of 20 – 50 % Portland cement by fine-ground blast-furnace slag granules increases concrete resistance to aggressive media in comparison with concrete made of mere Portland cement (CEM I). In the given case, concrete resistance to sulphates (concentration SO_4^{2-} *- 10 000 mg/l) and to acidic aggressive media (pH = 3) was monitored.*

KEYWORDS: Concrete resistance, sulphates, acid(ic) aggressive medium, blast-furnace slag.

1. INTRODUCTION

Utilization of process waste in making of building materials is a permanent trend. Among others, blast-furnace slag granules have been often used in this process. Most frequently, blast-furnace slag has been used in making of mixed cements based on Portland clinker. Lately however, blast-furnace slag also has been utilized as concrete admixture. The paper deals with results of monitored resistance related to concretes, in which Portland cement (CEM I) was partially substituted by fine-ground blast-furnace slag granules. 10 –50 % of cement were substituted by blast-furnace slag. Resistance of those concretes to sulphates (concentration SO_4^{2-} - 10 000 mg/l) and aggressive acidic media (pH = 3) was monitored, whereas the concretes have been exposed to aggressive medium for 12 months. Concrete containing 100 % of cement based on Portland clinker served as comparative specimen. The resistance was assessed in conformity with standard demands of ČSN 73 1340.

ISSN 1582-3024

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2. DEGRADATION MECHANISM OF AGGRESSIVE MEDIA

2.1. Degradation of Cement Composite by Sulphates

Sulphate corrosion of concrete caused by weather effects or by industrial waste water with higher ionic SO_4^{2-} concentration has been studied by many a prime experts. Statements based on such research say that, dependent on preconditions, degradation produced by sulphates may have a form of gypsum corrosion. Preconditions for sulphicoaluminate corrosion are created with concentrations containing more than 250 $mg.l^{-1}$ sulphates in 1 litre of dilution. $Ca(OH)_2$ reacting with SO_4^{2-} produces gypsum. This process may be expressed by equation (1):

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \Rightarrow CaSO_4.2H_2O + 2NaOH \quad (1)$$

The produced gypsum further reacts with high alkali calcium hydro aluminates, producing ettringite. This process may be expressed by equation (2):

$$3CaO.Al_2O_3.6H_2O + 3(CaSO_4.2H_2O) + 19H_2O \Rightarrow 3CaO.Al_2O_3.3CaSO_4.31H_2O \quad (2)$$

The emerging, insufficiently dissoluble ettringite, substantially swells and pressing against porous walls and capillaries it causes disruption and formation of cracks. In viewpoint of a possibility to eliminate negative affects of sulphates on concrete, resp. on polymer cement mortar, there is a very significant fact that formation of ettringite conditioned by a $Ca(OH)_2$ concentration value of ca 0.46 $mg.l^{-1}$ (conversion to CaO) as a minimum, i.e. ettringite only arises, when cement stone contains aluminates with high percent of CaO. In case of poor concentration, no reaction between SO_4^{2-} and $Ca(OH)_2$ occurs or it is very subtle and so constitution of expansive pressures is limited. It univocally follows that there is a possibility to improve concrete resistance to sulphates, when choosing a suitable type of active hydraulic admixture diminishing the quantity of $Ca(OH)_2$.

Another aspect, very important in the viewpoint of cement matrix stability in sulphate medium, is chemical and mineralogical composition of cement. Higher content of C_2S in cement decreases concentration of forming $Ca(OH)_2$ and so the resistance to sulphates increases; and vice versa, higher content of C_3S initiates higher content of arising $Ca(OH)_2$, whereas concrete resistance using such cement decreases.

Resistance of cement matrix to sulphates can be also substantially influenced by presence of tricalciumaluminate C_3A in cement. According to Solacolm´s research, cement resistance to impact by sulphate dilutions can be derived from calculation of its aluminate modulus M_{hl}. The aluminate modulus of cement is given by relation (3):

ISSN 1582-3024

$$M_{hl} = \frac{Al_2O_3}{Fe_2O_3} \quad (3)$$

On the basis of aluminate modulus values, cements are ranked into five classes, whereas very resistant cements with M_{hl} = 0.0 – 0.7 belong to the first class and cements no resistant to sulphates, where M_{hl} = 2.4, fall into the utmost class five. It univocally follows that, should pozzuolana admixture be able to eliminate degradation of concrete resp. mortar exposed to sulphates impact, the content of active Al_2O_3 may not be too high.

2.2. Degradation of Cement Composite by Acids

Concrete based on Portland cement is a strong basic substance. When exposed to impact of acids (eventually to certain salt solutions thereof), the material reactions are principally neutralizing. A consequence of such reactions is degradation of cement matrix, attended by descent of concrete strength characteristic. The effect of single acid types is determined not only by acid strength (resp. its dissociative constant), but also by the present cation type etc. Principally, the impact of single acid types may be described as follows:

Acids causing decomposition of cement matrix are those, destructing the cement matrix step by step (so called concrete „acid extraction“). To exemplify, we can mention the affect of mild carbonic acid, de facto present in „famished“ waters. Initially, such waters quickly leach $Ca(OH)_2$ present in concrete, later it comes to slower decomposition of hydrated silicates and aluminates. This fact leads to decreasing of pH value, reflecting in negative impact on corrosion of reinforcement as well as on stability of some hydrated clinker minerals.

Acids causing cement matrix destruction – this group particularly encompasses acids, creating voluminous crystalline new formations in concrete microstructure, when reacting with cement mastic. Initially, the impact of such acids may reflect in soft decrease of compactness and impermeability or, even in strength increasing. Continued swelling of crystalline new formations creating in cavities and pores, however, leads to crakes and, in extreme cases, to total destruction of concrete.

3. WORK METHODOLOGY

To investigate concrete resistance to corrosion, there were prepared test specimens (blocks 40 × 40 × 160 mm each) conformable to the ČSN 73 1340.

After manufacturing, the test specimens were placed into moist environment for 24 hours, followed – after form removal and before exposure to corrosive medium –

by placing into water bath at 19 to 21°C. After 28 hours of hardening, the specimens were exposed to corrosive medium action. Selection of parameters under evaluation is based on the ČSN 73 1340.

Tested specimens were monitored in the light of parameters as follows:

- appearance (visually)
- density ***D*** (EN 12390-7)
- ultrasonic pulses velocity ***V*** (EN 12504-4)
- dynamic modulus of elasticity E_{bu} (ČSN 731371)
- compression strength f_{cc} (EN 1015–11)
- tensile strength under flexure f_{cf} (EN 1015–11)

Specimen strength was destructively tested before exposure to corrosive medium and after 2, 4, 6, 9 and 12 months of exposure.

- Corrosive environment effect during other time periods was evaluated, based on both, ultrasonic pulse speed variation and dynamic modules of elasticity.

Corrosive media:

- sulphates - sodium sulphate solution (10,000 mg of SO_4^{2-} in 1 litre)
- acidic environment – solution with pH 3±0.2 value.

4. CONCRETE COMPONENTS AND COMPOSITION

- Binder: Portland cement CEM I 42.5R
- Aggregates: fraction 0/4 mm hoisted from Bratčice locality, crashed; fraction 4/8 mm from Olbramovice locality (granodiorit) – basic parameters, see Table 1.
- Admixtures: fine-ground blast-furnace slag granules (Nová Huť, Ostrava) – parameters, see Table 2; chemical composition, see Table 3; result of X-Ray analyse, see Figure 1. Slag contains a low portion of crystalline phases)
- Plasticizer: Stachement 2000
- Mixing water: fulfils demands of EN 1008
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Table 1. Basic Parameters of Aggregates

Parameter	Unit	Bratčice 0/4 mm	Olbramovice 4/8 mm
Volume weight	[kg/m^3]	2530	2610
Bulk weight, jolted	[kg/m^3]	1650	1625
Porosity	[%]	34.8	37.7

Table 2. Basic Parameters of Blast-Furnace Slag

Parameter	Unit	Slag
Specific surface *S*	[m^2/kg]	380
Specific weight ρ	[kg/m^3]	2830
Basicity modulus M_z	[-]	1.07

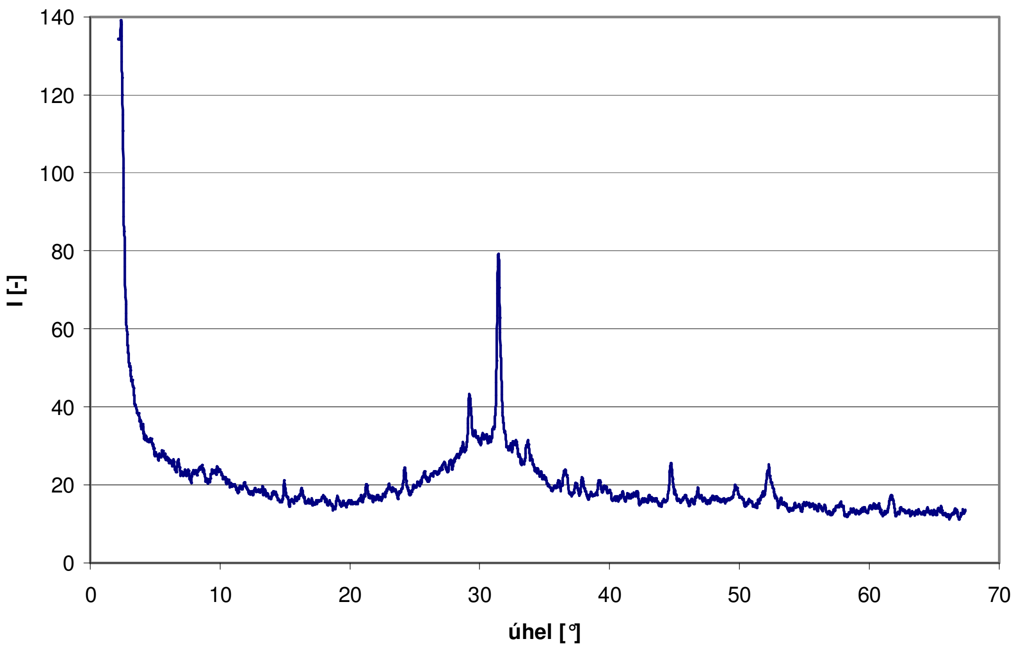

Figure 1. Result of X-Ray analyse blast-furnace slag

Table 3. Chemical Composition of Slag

Component	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO
Content [%]	32.7	6.59	0.19	0.5	41.4
Component	MgO	S^{2-}	Annealing Loss	Non-Decomposable Portion	
Content [%]	12.2	0.55	1.08	6.99	

– Concrete composition and basic physical and mechanical characteristics are shown in Tables 4 and 5 below.

Table 4. Composition of 1 m^3 Concrete

Component	Quantity (BS0-BS50 concrete)
CEM I 42.5 R Hranice Cement	416 kg
Fine-Ground Slag	0-50% of cement weight
Sand 0 to 4 mm from the Bratčice Gravel Pit	725 kg
Aggregates 4 to 8 mm from the Olbramovice Gravel Pit	1087 kg
Plasticizer Stachement 2000	4.16 kg
Mixing Water	159 kg
Cement/Water Ratio	0.382

Table 5. Basic Parameters of Concretes

Parameter		Unit	BS0	BS10	BS20	BS30	BS40	BS50
f_{cc}	7 days	[MPa]	55.8	53.3	49.7	46.4	43.2	41.1
f_{cf}	7 days	[MPa]	7.7	8.5	8.3	8.9	7.4	8.2
D	7 days	[kg/m^3]	2364	2325	2335	2346	2305	2315
f_{cc}	28 days	[MPa]	63.1	66.8	62.5	65.9	55.3	59.4
f_{cf}	28 days	[MPa]	8.9	8.7	9.0	9.5	9.6	9.4
D	28 days	[kg/m^3]	2366	2309	2303	2313	2303	2323

5. FINDINGS OF CONCRETE RESISTANCE MONITORING

Concretes have been exposed to aggressive environment impact for 12 months. Variation results of parameters monitored in the course of time are graphically demonstrated in:

– Figure 2: progress of tensile strength under flexure during the exposure period – concretes stored in aggressive acid environs
– Figure 3: progress of compression strength during the exposure period – concretes stored in aggressive acid environs
– Figure 4: modulus of elasticity progress during the exposure period – concretes stored in aggressive acid environs
– Figure 5: progress of tensile strength under flexure during the exposure period – concretes stored in sulphates
– Figure 6: progress of compression strength during the exposure period – concretes stored in sulphates
– Figure 7: modulus of elasticity progress during the exposure period – concretes stored in sulphates.

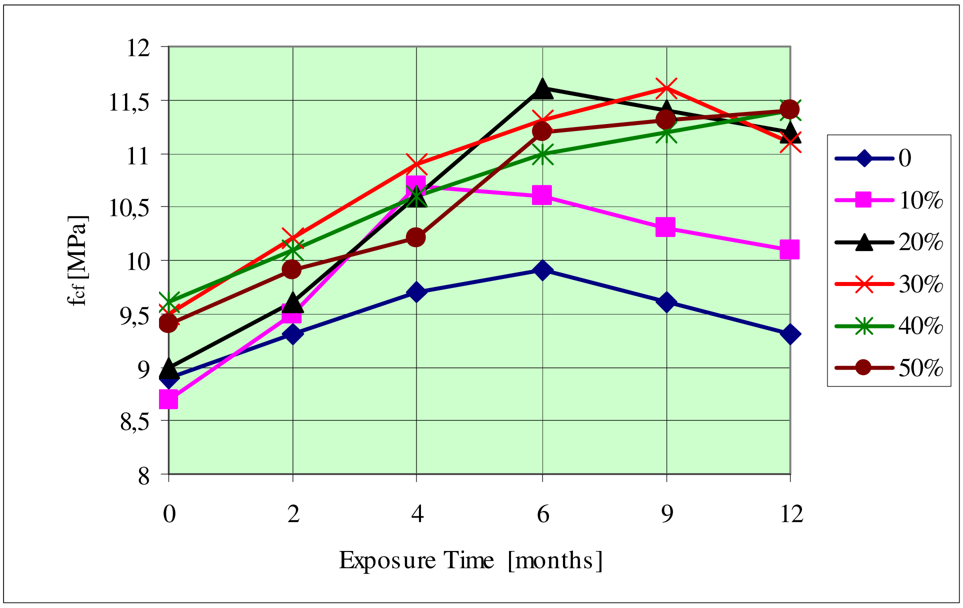

Figure 2. Tensile Strength under Flexure of Concretes Stored in Aggressive Acid Environs

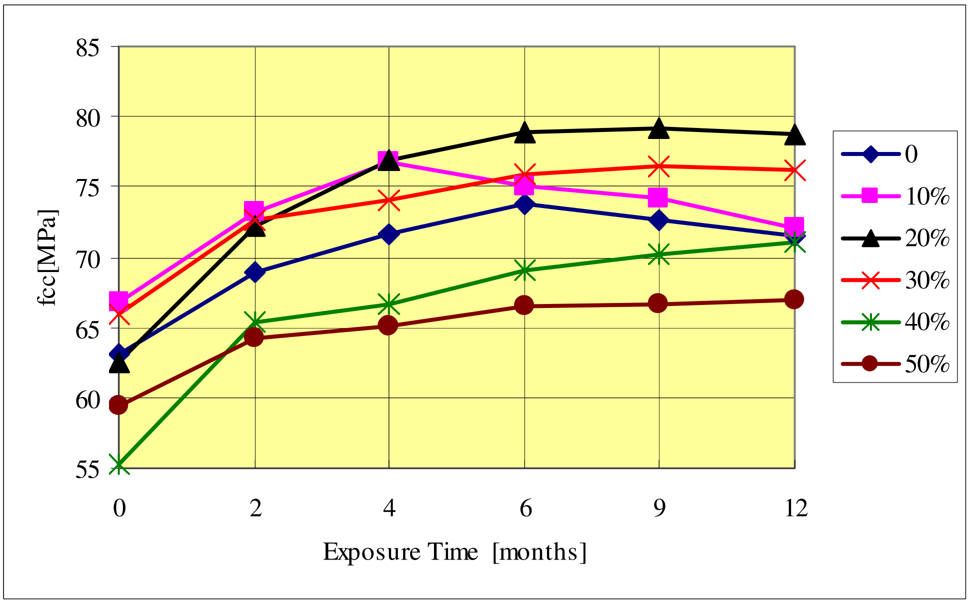

Figure 3. Compression Strength of Concretes Stored in Aggressive Acid Environs

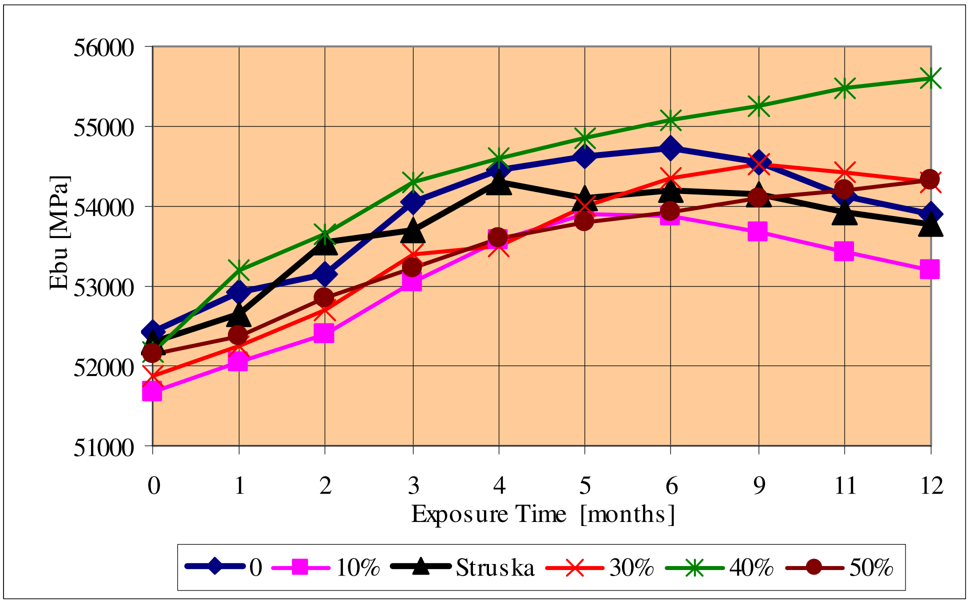

Figure 4. Dynamic Modulus of Elasticity Related to Concretes Stored in Aggressive Acid Environs

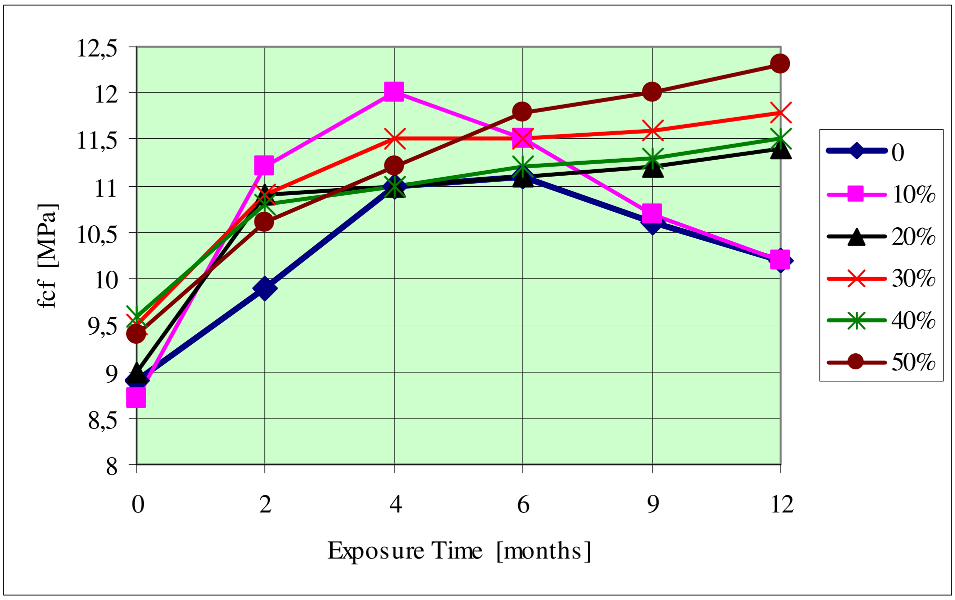

Figure 5. Tensile Strength under Flexure of Concretes Stored in Sulphates

ISSN 1582-3024

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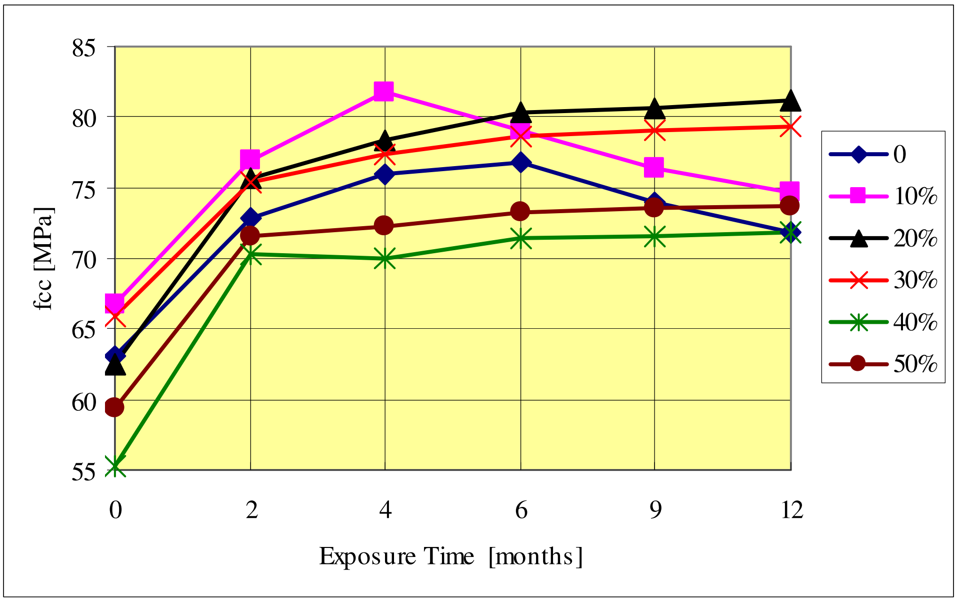

Figure 6. Compression Strength of Concretes Stored in Sulphates

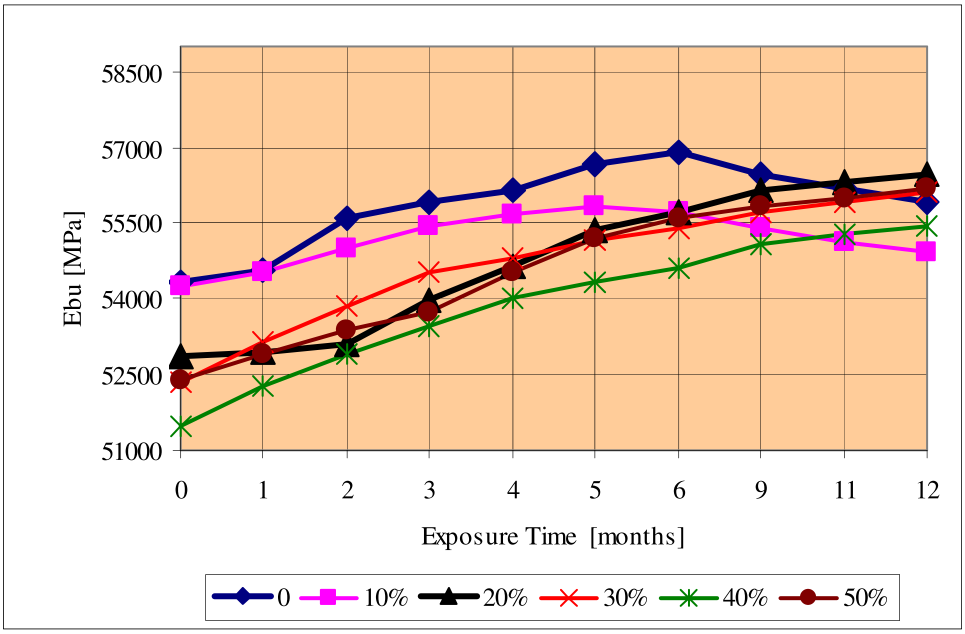

Figure 7. Dynamic Modulus of Elasticity Related to Concretes Stored in Sulphates

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6. CONCLUSION

Partial substitution of Portland cement by blast-furnace slag granules had a positive influence on resistance of concretes exposed to aggressive acid and sulphate environment for the period of 12 months.

Specifically, concretes using slag amounting to 40 or 50% of cement weight show increased resistance to aggressive acid and sulphate environment, whereas slag content amounting to 20 – 50% of cement weight increases concrete resistance to sulphates.

Contributions occurs in the environmental viewpoint (liquidation of wastes, diminished power consumption for manufacturing of cement, heavy on energy) as well as in relation to economy (lower consumption of expensive cement).

Acknowledgements

The work was supported by the MSM 0021630511 Plan: Progressive Building Materials with Utilization of Secondary Raw Materials and Impact their on Structures Durability.

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