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THE INFLUENCE OF ORGANIC ADDITIVES ON SOLIDIFIED FBC-P PARAMETERS

The influence of organic plasticizers based on Mg^{2+} lignin-sulphonates (LS), naphthalene derivatives (NF) and melamine-formaldehyde polycondensates (PC) on the parameters of solidified FBC-P (fluidised bed combustion product) was tested. Water-reducing effectiveness of the additives tested increases in the following order: NF, PC, LS. All additives cause a marked increase in compressive strength of solidified specimens prepared from suspension of constant workability and reduced amount of mixing water. The compressive strength increases predominantly with the volume weight of specimens and the time of hardening. The conductivity of leachate of modified specimens has tendency to decrease with the dose of additives and to increase with the time of leaching up to about 100 days of leaching and afterwards it decreases. UV spectral analysis showed that the content of LS and PC molecules in the leachate after 24 hours of leaching is very low, near to the detection limits of the method used.

1. INTRODUCTION

Organic additives are widely used for modification of mortars and concrete with cement binder. The results show that they markedly influence a number of their parameters. FBC-P has very good cementitious properties. Their practical use in building industry is limited mainly owing to the high content of sulphates and CaO. A great amount of FBC-P is therefore stored in waste dumps. Durability of solid structure and leaching of pollutants are very important parameters of solidified ash. It was found [1] that the integrity of samples from FBS-P tested immersed in the water is limited and the structure is relatively soon destroyed. The resistance of specimens against the action of water can be reached by over 3% addition of cement.

Parameters and leaching of pollutants from solidified specimen of FBC- P without any organic additive were studied by a number of authors as, for instance, [1]–[10].

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They depend on a number of variables. The porosity of specimen seems to be one of the most important parameters influencing the compressive strength and the movement of water in the structure of a solid body. The total volume of capillary pores and their parameters depend mainly on the amount of mixing water used when structural pores are removed by compaction.

Conductivity changes of leachate depend on the kinetics of ions' diffusion from the solid sample into the surrounding water as is well known. It depends on the rate of moistening of surface of capillaries and pores of a solid body. The content of mixing water in mortars can be reduced, and the volume weight can be increased by the use of plasticizers. Organic plasticizers belong to the group of polyelectrolytes and are regarded as pollutants over certain limits in the leachate. Therefore experiments were also carried out to determine the leaching of PC and LS additives (as representatives) from solidified FBC-P. The results of leaching tests showed that the content of heavy metals in the leachate is very small and within the limits fixed for drinking water. Therefore, NaCl was used as a representative of a very good soluble pollutant. The second reason for its use were the results [1] showing that NaCl causes a marked increase of compressive strength. It was found out that it influences favourably the formation of ettringite and its morphology [2]. Therefore all those observations were respected in the conception of our tests.

2. EXPERIMENTAL PART

2.1. CEMENT

Clinker was ground in laboratory ball mill without gypsum because superfluous amount of calcium sulphate is present in the ash. Mineralogical composition was determined according to [11]. The content of main minerals (%) is: C_3S = 64.4%, C_2S = 12.9%, C_3A = 8.9%, C_4AF = 13.2%, CaO = 0.29%. Specific surface area of cement was 385 m^2/kg.

2.2. ADDITIVES

Three different organic plasticizers were used. Basic parameters of the specimens tested are in table 1.

2 g of NaCl p.a. was used in all suspensions as a representative of readily soluble pollutants. Additives were dissolved in the mixing water.

Table 1

Basic parameters of fluid additives used

Additive	Parameter	Unit	Value
	Molar weight	g/mole	8 125
LS	Concentration	%	35
Waste sulfite liquor	Saccharides	%	8
	Lignin-sulphonates and minor compounds	%	27
PC	Molar weight	g/mole	48 150
Melamine-formaldehyde polycondensate	Concentration	%	20
	Sulpho group content	%	12.8
NF	Molar weight	g/mole	601
Naphthalene derivative	Concentration	%	35

2.3. FLY ASH

Flying product caught by the fabric filters from a central heating plant was used for the tests. Results of X-ray analysis are presented in table 2. The content of main compounds was estimated (weight %) as follows: quartzite = 4%, $CaSO_4$ = 22%, hematite = 3.1%, CaO = 8.6%. The content of periclas, calcite, feldspar and portlandite was estimated up to 5%.

Table 2

Results of XRD analysis of dry FBC-P. Di = diffraction intensity of certain compounds expressed as a height of the peaks in number of division parts of recording paper used. Meaning of symbols: Q = quartzite, H = hematite, A = anhydrite II, C = calcite, An = anortite, P = portlandite

Q 4.25 Å	H 2.51 Å	A 3.48 Å	C 3.03 Å	An 3.18 Å	P 2.63 Å	Clay 4.45 Å	Periclas 2.1 Å	CaO 2.4 Å
17.5	17.5	77.6	16.7	14	9.2	10.0	17.8	69.2

2.4. PREPARATION OF SAMPLES

Mixtures were prepared from fly ash, binder and water using a laboratory mixer. The composition of specimens is given in table 3. The dose of water was reduced to reach constant consistency of all suspensions (limiting shear stress of 150 ± 5 mN/cm^2) determined by cone method published in [13]. Cubes with 25 mm edges were prepared from the suspensions having plastic consistency. The suspensions in the moulds were compacted by a laboratory vibrator. Optimal time of vibration (10 seconds) was determined experimentally. This time was sufficient for removal of structural and air pores without separation of mixing water. The

cubes for determination of compressive strength were stored at humidity of about 90% and a temperature of 21–23 °C (wet conditions) up to 28 days and afterwards in water up to 4 years of testing. The parameters of specimens are gathered in table 3.

Table 3

Basic parameters of specimen tested

No.	Water	Additive (%)		NaCl	Ash	Cement	28 days		1 year	4 years	
	(g)	Liquid	Dry	(g)	(g)	(g)	g/cm^3	MPa	MPa	g/cm^3	MPa
1	130	0.1LS	0.035	2	225	25	1.50	27.6	38.0	1.51	43.0
2	126	0.3LS	0.105	2	225	25	1.50	26.0	35.0	1.53	41.3
3	122	0.5LS	0.165	2	225	25	1.51	25.7	33.8	1.51	42.9
4	134	0.1PC	0.020	2	225	25	1.48	26.6	32.8	1.48	37.8
5	132	0.3PC	0.060	2	225	25	1.48	26.5	30.1	1.52	41.3
6	130	0.5PC	0.100	2	225	25	1.41	24.0	29.0	1.53	42.0
7	134	0.1NF	0.035	2	225	25	1.48	24.6	30.9	1.51	42.3
8	132	0.3NF	0.105	2	225	25	1.50	25.5	31.4	1.48	33.4
9	130	0.5NF	0.165	2	225	25	1.44	21.9	28.1	1.46	37.2
Control	135	0.0	0.00	2	225	25	1.31	13.3	25.9	1.34	30.1

2.5. LEACHING TESTS

The cubes, after 26 days of storing in wet conditions, were stored for 48 hours in laboratory conditions. They were not dehydrated at a high temperature to avoid the thermal activation of reactions and due to the parameters of specimens (leaching of compounds). Each cube was immersed separately in re-distilled water. Solid to liquid ratio was 1:10. After 24 hours of shaking (reciprocating shaker) pH value, conductivity and the content of additives were determined in the leachate of cubes. The basic parameters of leachate after different time of leaching are given in table 4.

Table 4

Basic parameters of leachate tested

No.	(mS/m), hours			After 24 hours		(mS/m), days		After 4 years	
	2 h	4 h	6 h	pH	(mS/m)	28 d	180 d	pH	(mS/m)
1	49.4	70.7	96.0	12.12	165	402	400	11.67	366
2	44.4	63.2	78.0	12.11	141	337	330	11.57	294
3	40.8	60.8	75.5	12.10	151	334	335	11.45	283
4	46.0	86.3	106.8	12.17	191	389	410	11.67	353
5	42.8	64.8	92.5	12.12	161	340	352	11.59	312
6	42.4	64.4	91.1	12.05	157	345	348	11.51	294
7	55.5	77.7	97.2	12.02	175	372	386	11.64	352
8	50.5	76.7	91.2	12.04	168	350	374	11.50	303
9	47.7	72.6	88.3	11.94	165	349	344	11.38	294
Control	59.8	82.8	131.0	12.21	287	563	472	11.8	415

2.6. ULTRAVIOLET SPECTRAL ANALYSIS (UV)

Apparatus Specord M 42, Carl Zeiss Jena, was used for analyses. Solutions of waste liquor of different concentrations were analysed in the first step. Total spectra of additive LS in figure 1 show one distinctive (λ = 203 nm) and two less distinctive (λ = 231 nm, λ = 283 nm) peaks. The peak λ = 203 nm coincides with the peaks of other compounds dissolved in the leachate. Further analyses showed that the peak λ = 283 nm is the most suitable for determination of concentration changes of lignin-sulfonate in the leachate. The total UV spectra of PC additive show that only one distinctive peak is present (λ = 221 nm). Calibration dependences showed that the relationship between the concentration of solution and the absorbance A is linear in the range from 0 to 2000 mg/dm^3. It was found out that the content of both additives in the leachate after 24 hours of leaching is very low and varies within the limits of detection sensitivity of the method used.

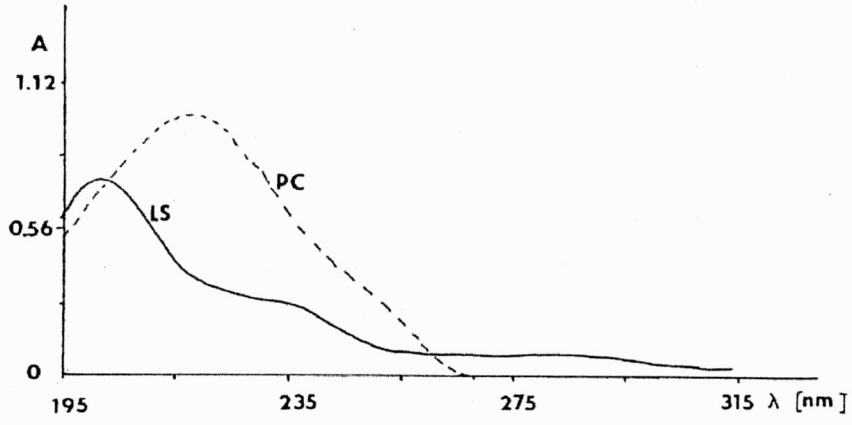

Fig. 1. Total UV spectra of LS and PC additives.
Concentration, 100 mg/dm^3

2.7. REGRESSION ANALYSIS

Computer program Statgraphics 2 (product of Statistical Graphic Corporation, U.S.A.) was used for determination of functional relations between the dependent and independent variables tested. In order to judge every correlation significance, the limits of coefficient of multiple determination R^2 were used [12]. $R^2 < 30\%$ – low or any correlation, R^2 from 30% to 60% – quite good correlation and $R^2 > 60\%$ – high correlation between the variables exists.

3. RESULTS AND DISCUSSION

The results in figure 2 show that the water reducing effectiveness of additives increases in the following order: NF, PC, LS. The volume weight of all modified specimens is markedly higher than that of control as is evident from table 3. Regression analyses involving the compressive strength, dose of additive, water content and the volume weight of specimens were carried out. High single correlation between the compressive strength and the volume weight of specimens after 28 and 360 days was found. Further analyses showed that the increase in a dose of additives proportionally

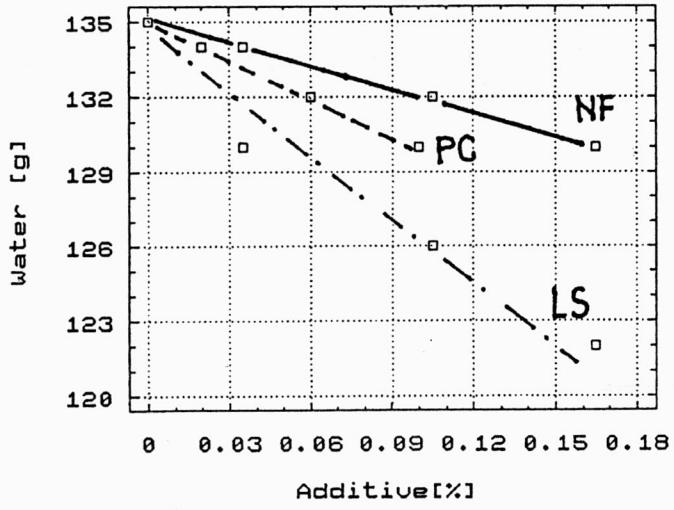

Fig. 2. Water content in suspension at constant plasticity versus dose of additives (% of dry content of solid compounds)

reduced the compressive strength of specimens after 28 days and also after 4 years of hardening. Volume weight of specimens has predominant influence on the compressive strength as is shown in figures 3 and 4. The molecules of the organic additives tested have good affinity with the solid phase of modified suspensions of ash. The analyses of UV spectra showed that 34–50% of them are sorbed out after 20 minutes of interaction and their content in the leachate after 24 hours is near to detectability. They may react with calcium ions and transform from sodium to calcium form as can be derived from [14]. They may be preferably bond in active centres on the surface of cement or ash particles and prevent their interaction with molecules of water. On the other hand, they contribute to the increase of repulsive forces between the particles and to the decrease of friction forces in the suspension even if the content of mixing water is reduced.

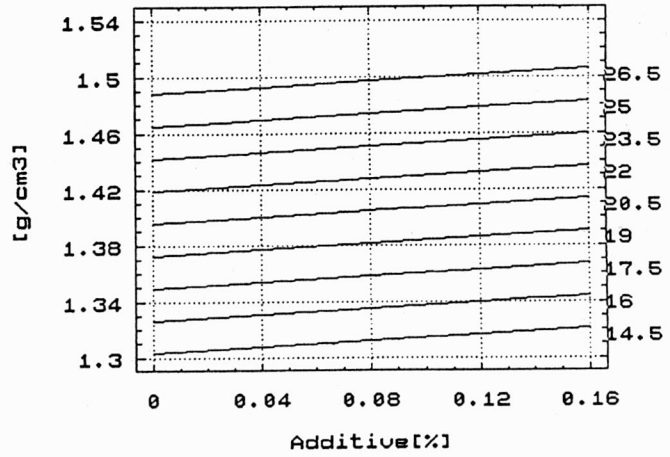

Fig. 3. Relationship between the compressive strength after 28 days (MPa-numbers at lines) versus volume weight of samples and dose of additives (% of dry content of cement)

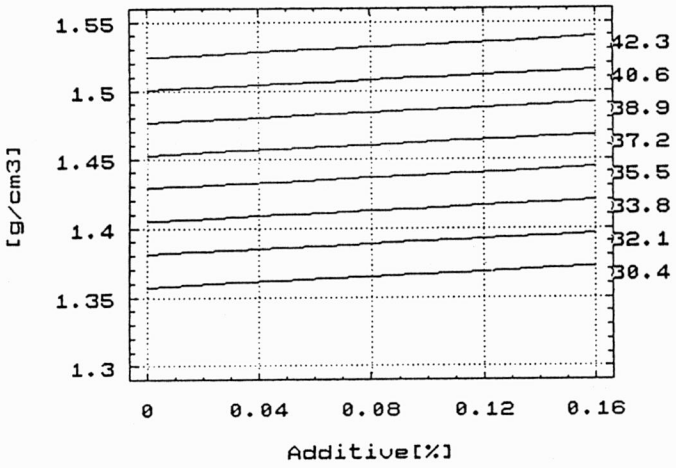

Fig. 4. Compressive strength of samples after 4 years (MPa-numbers at lines) versus their volume weight and dose of additives (% of dry content of cement)

The results in table 4 show that the diffusion of ions from the solid specimen to the liquid phase is relatively intensive in the first hours of leaching. The relationships between the dose of additives and the conductivity of leachate were found. Chosen representatives of those relationships are shown in figure 5. The parameters of leachate after 24 hours of standard leaching are regarded as having a decisive influence on the classification of the waste product tested in accordance with standard specifications. Therefore a number of regression analyses were carried out. The correlation between the conductivity of leachate after 24 hours was higher when the volume weight of solid specimens and the dose of

additives were chosen as independent variables. The representative of results of multiple regression analyses in figure 6 (R^2 = 81.57%) shows that the increase of both independent variables results in the decrease of conductivity. Both independent variables influence the conductivity changes by about 82%. Results in figure 7 (R^2 = 74.7%) and in table 4 show that the time of leaching has a decisive influence on the conductivity of leachate. The conductivity increases up to about 100 days of leaching and then it has a tendency to decrease. This tendency was observed also during our earlier experiments. The explanation of phenomena observed will be carried out in a separate publication.

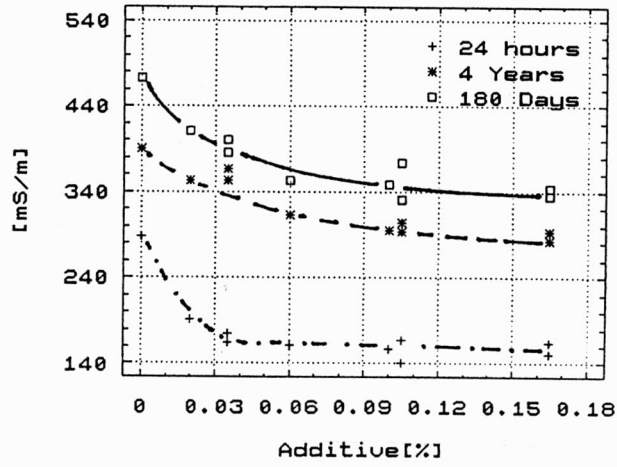

Fig. 5. Conductivity of leachate after different time of leaching versus dose of additives (% of dry content of cement)

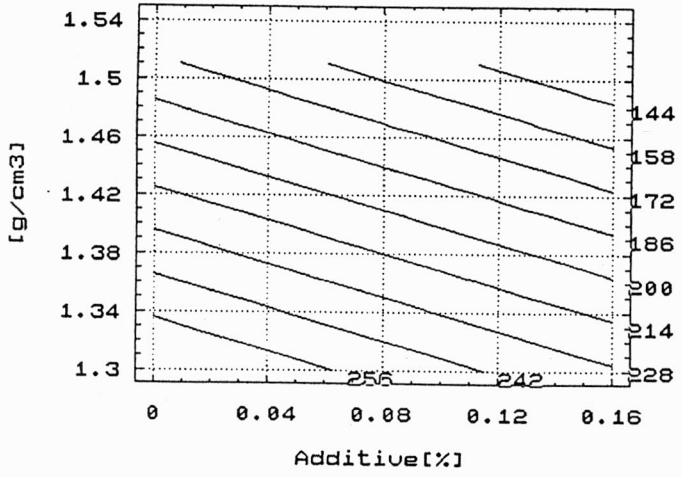

Fig. 6. Conductivity (mS/m) of leachate after 24 hours of leaching versus volume weight of specimens and dose of additives (% of dry content of solid compounds)

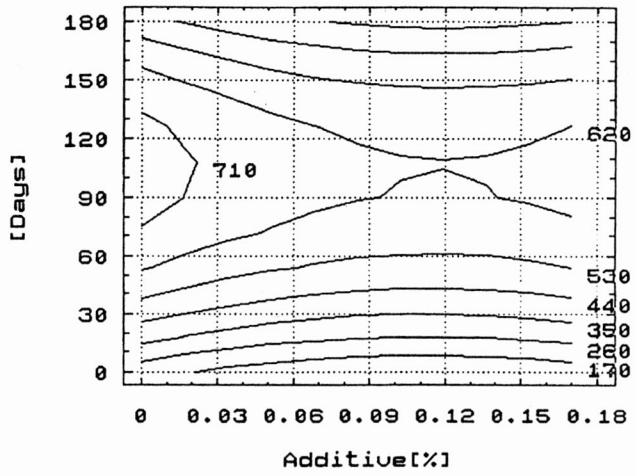

Fig. 7. Conductivity (mS/m) of leachate
versus time of leaching and dose of additives (% of dry content of cement)

The content of additives tested in the leachate after 24 hours of leaching was extremely low, i.e. <2 mg/dm^3. Those results confirm that the organic molecules are bond in the structure of solid phase.

4. CONCLUSIONS

1. Water-reducing effect of the additives tested increases in the following order: NF, PC, LS.

2. The compressive strength of specimen increases in all terms of testing. Increasing the dose of additives we slightly retard their effect on the compressive strength development. The intensity of the retarding action after 28 days and also after 4 years of hardening is similar. The results of regression analyses show that the volume weight of specimens has a decisive influence on the growth of compressive strength. The solid specimens do not lose their integrity even after 4 years of hardening in water in spite of very high content of anhydrite II and CaO favourable for creation and action of destructive ettringite.

3. The conductivity of leachate after 24 hours decreases with an increase of volume weight of specimens and dose of additives.

4. The time of leaching has a decisive influence on the long-term conductivity of leachate. It lenghtens up to about 110 days and then has a tendency to decrease.

5. The differences in the effect of separate additives on the parameters tested are not significant (except water-reducing effect) as can be derived from correlation coefficients of the relationships obtained.

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WPŁYW DODATKÓW ORGANICZNYCH NA PARAMETRY ZESTALONEGO PRODUKTU SPALANIA ZŁOŻA FLUIDALNEGO

Badano wpływ organicznych plastyfikatorów opartych na sulfonianach ligninowych (SL), pochodnych naftalenu (PN) i polikondensatach melaminowo-formaldehydowych (PMF) na parametry zestalonego produktu spalania złoża fluidalnego. Skuteczność w ograniczaniu niszczącego wpływu wody w badanych dodatkach zwiększała się w następującym porządku: PN, PMF, SL. Wszystkie dodatki znacznie zwiększały wytrzymałość na ściskanie zestalonych próbek otrzymanych z zawiesiny

o stałej podatności na obróbkę i obniżonej zawartości dodanej wody. Wytrzymałość na ściskanie zwiększa się najczęściej z ciężarem objętościowym próbek i czasem twardnienia. Przewodność właściwa odcieku po ługowaniu zmodyfikowanych próbek zmniejsza się z dawką dodatków, a zwiększa się z czasem ługowania przez około 100 dni, po czym spada. Analiza w zakresie UV wykazała, że zawartość cząsteczek SL i PMF w odcieku po 24 godzinach ługowania jest bardzo mała, bliska granicy wykrywania stosowanej metody.