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Communication

Interaction of anhydrite and melamine–formaldehyde polycondensates in aqueous suspensions

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Abstract

The interactions of molecules of melamine–formaldehyde (MF) polycondensates in aqueous suspensions with synthetic anhydrite were studied. The sorption is selective. The medium molar fractions of additives are preferably sorbed on the surface of anhydrite and its product of hydration after 10 and 30 min of interaction. After 180 min, all high molar fractions are sorbed out. The results indicate that molecules of polycondensate tested interact with calcium ions in suspension and have a tendency to transform from R-SO_3Na to R-$(SO_3)_2Ca$ form. Any other changes in the structure of molecules after interaction in aqueous suspension of anhydrite were not proved by the tests carried out.

Keywords: Admixture; Adsorption; Anhydrite; Hydration

1. Introduction

Synthetic anhydrite has been widely used in building industry for a long time. Its application in aqueous suspensions for floor constructions is one of the most effective methods. Those suspensions have very low viscosity even at low water content and possess a so-called self-leveling effect. This effect can be achieved only when about 2% of K_2SO_4 and 0.5% to 1% of melamine–formaldehyde (MF) polycondensate (by mass of binder) are present in suspension. Rheological properties mentioned cannot be achieved by other types of additive. A number of publications deal with the influence of additives on the properties of samples with cement binders, for instance Refs. [1–15]. The plastifying effect of organic additives is usually explained by two main principles. Molecules of additives are sorbed on the surface of solid particles in suspension and their ξ potential increases. The repulsive forces between particles increase and, as a result of ξ potential growth, the friction forces in suspension decrease. This conception does not presuppose chemical interaction of sorbed molecules with compounds of solid particles. Other authors presuppose chemical interactions, for instance, Ref. [5]. Organic complexes are formed on the surface of cement particles after interaction with molecules of MF polycondensate according to the author's hypothesis. The plastifying effect of additives mentioned is attributed to the complexes mentioned. However, experimental proof of those complexes has not been published. Only very limited publications deal with the influence of additives on the properties of samples with gypsum binder. The studies usually contain results of the tests with additives having retarding action, for instance, Ref. [16]. Quite rare are publications describing the interaction of laboratory-made MF polycondensates in suspensions with synthetic anhydrite. One of the aims of this publication is to broaden the knowledge in this field.

2. Materials and method

2.1. Binder

The synthetic anhydrite used was a product of Spolchemia, Ústí nad Labem. The result of chemical analysis is in Table 1. X-ray diffraction analysis (apparatus: Philips APD 15) showed that the sample analyzed is a pure soluble anhydrite modification III with very low content of other compounds, mainly $Ca(OH)_2$ and CaF_2. The specific surface area of anhydrite was 378 m^2/kg. The particle size distribu-

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Table 1
Chemical composition of anhydrite

Ignition loss (%)		Component (%)								
230°C	600°C	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
0.8	1.13	2.36	0.31	0.17	0.32	40.08	0.06	0.05	0.10	54.54

tion of sample was: >90 μm = 0.5%, 63–90 μm = 0.5%, <63 μm = 99%.

2.2. Catalyst

K_2SO_4 p.a. was used. Its optimal dose was found to be 2% by weight of anhydrite binder.

2.3. Additives

Different samples of polycondensates of MF were prepared (see Fig. 1) with significant difference in the conditions of synthesis. The total chromatograph characteristics (for illustration) of one chosen sample are shown in Fig. 2. The distribution functions of M_w of the chosen samples before and after sorption are shown in Fig. 3. Similar dependencies were obtained for other polycondensates tested. The basic parameters of additives are in Table 2.

2.4. GPC analysis

Liquid chromatographs model 8000 (Spectra Physics Association, USA) and model 8500 (Varian, USA) were used. Further refractometer model R 401 (Waters Association, USA), plotter model 9179 (Varian) and stan-

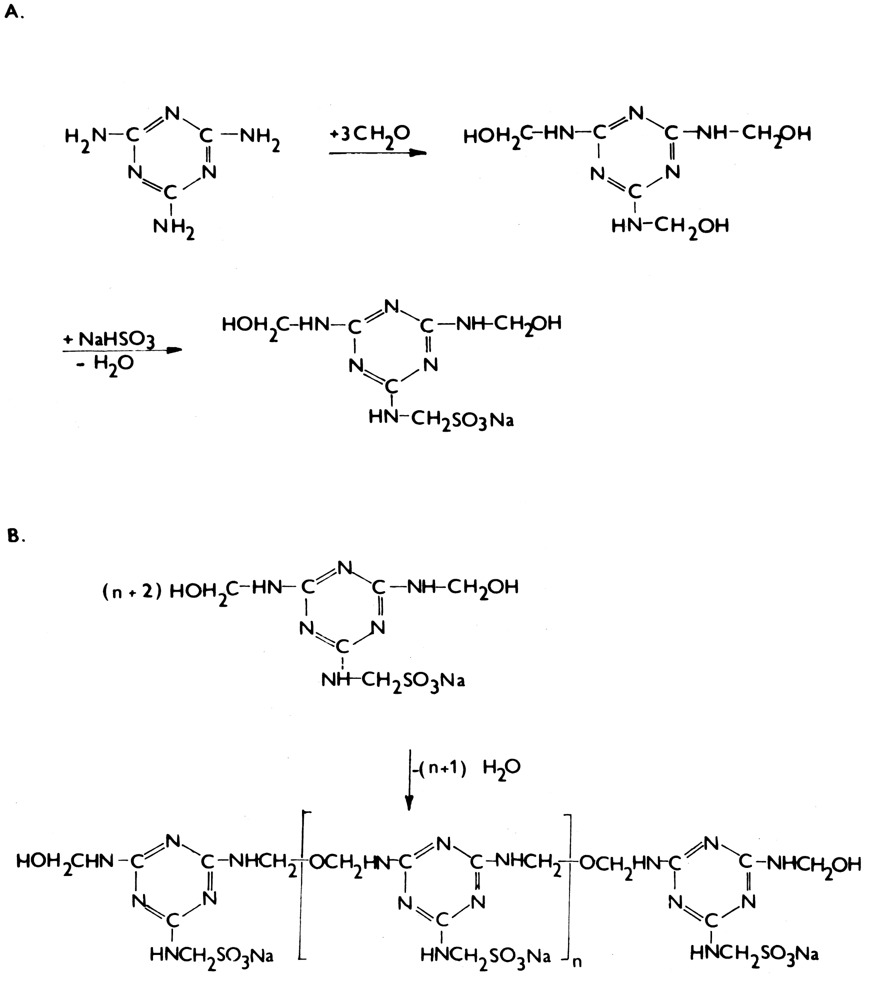

Fig. 1. Scheme of polycondensates preparation.

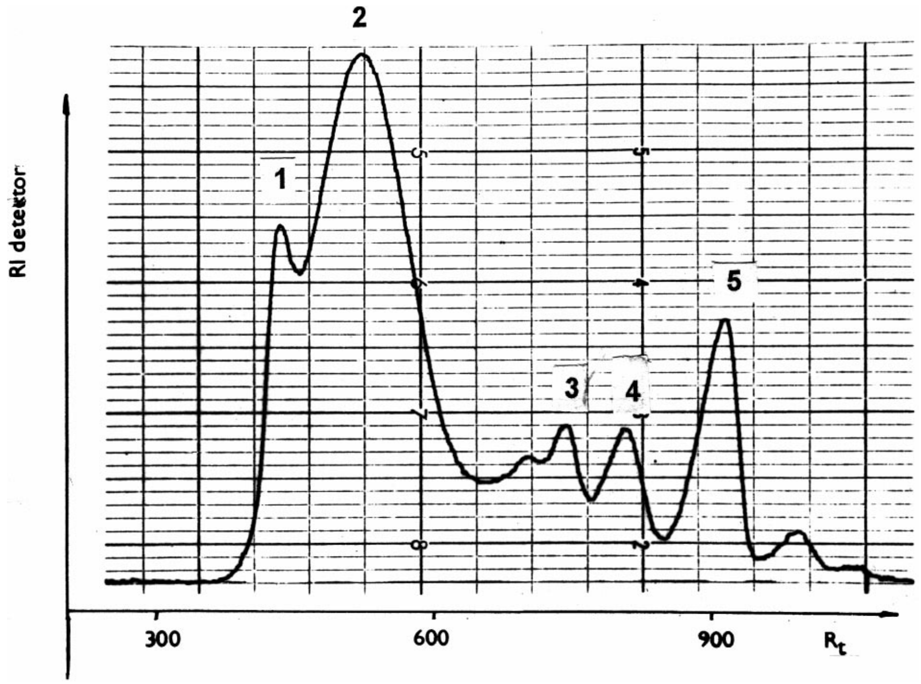

Fig. 2. Characteristic total chromatograph of polycondensate. Rt = retention time (second). (1) High molar, (2) medium molar, and (3, 4 and 5) low molar fractions.

dards of fermentation gums (Fine Chemicals, Uppsala) for calibration were used. The tests were carried out according to the program for "method 7" prescribed in Ref. [13]. Determined molar parameters are valid only

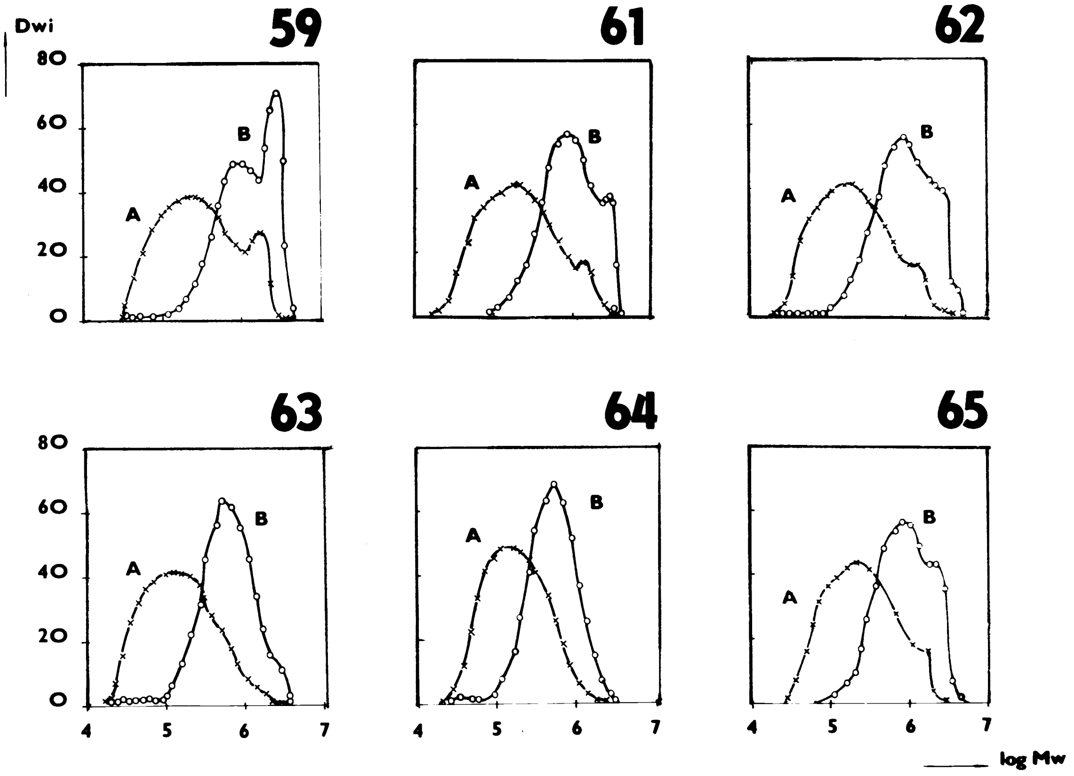

Fig. 3. Distribution functions of molar weight of chosen polycondensates before (A) and after sorption (B) in term 20 min. Calculated from medium and high molar part of chromatographs.

Table 2
Basic parameters of polycondensates before and after sorption

	Concentrate					Filtrate		
Sample	M_wE − 4 (g/mol)	SO_3Na (%)	CH_2O (%)	Ac805 (−)	Ac1035 (−)	Af805 (−)	Af1035 (−)	Af675 (−)
MF 59	50.80	12.50	0.72	0.289	0.277	0.165	0.227	0.101
MF 61	37.41	12.71	0.44	0.308	0.678	0.218	0.311	0.124
MF 62	38.34	10.63	0.45	0.229	0.495	0.159	0.289	0.202
MF 63	25.90	10.25	0.46	0.241	0.492	0.183	0.321	0.182
MF 64	25.60	12.95	0.51	0.261	0.503	0.176	0.282	0.133
MF 65	43.37	16.67	0.79	0.273	0.546	0.113	0.178	0.116
MF 66	35.60	10.90	0.50	0.261	0.395	0.185	0.295	0.149
MF 67	43.60	15.90	0.82	0.325	0.422	0.190	0.212	0.036

for the calibration, method and the ion power of the eluent used.

2.5. Preparation of filtrates

Anhydrite (20 g) + water (20 g), containing additive, were homogenized. Doses of additives were 2% K_2SO_4 and 1% of dry content of polycondensates from mass of anhydrite. Filtrates were separated and analyzed in term 20 min. The relationship between M_{ws} and M_w (molar weight of filtrate after sorption and that of concentrate before sorption) of polycondensates tested is in Fig. 4. The chosen additive MF 65 was used for the determination of time dependencies in distribution functions of polycondensates. The distribution functions of filtrates (except that in term 5 min) are in Fig. 5. The same chromatographs were used for the calculation of dependencies in Figs. 6 and 7. Relative sorption, S_r (%), of MF molecules on the surface of solid particles was calculated using following formula:

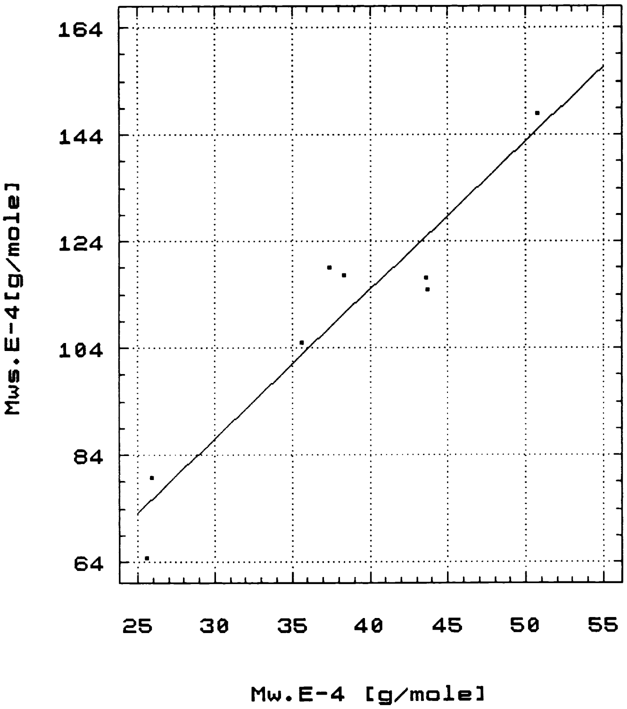

Fig. 4. Relationship between the molar weight of additives before (M_w) and after sorption (M_{ws}) in term 20 min. Calculated from medium and high molar part of chromatographs.

$$S_r = \frac{F_c - F_f}{F_c} 100 \qquad (1)$$

where F_c and F_f are the areas under the chromatographic waves of sorption-active high and medium molar fractions of concentrate (M_w over 10^4 g/mol) before and the same of filtrate after sorption (cm^2). Further analysis of filtrates containing anhydrite, anhydrite + 2% K_2SO_4, anhydrite + 2% K_2SO_4 + polycondensate MF 66, and K_2SO_4 only were made. Results are given in Fig. 8.

One disadvantage of this method of sorption determination is that the low molar fractions of organic and inorganic compounds (up to about 10^4 g/mol) coincide, as is certain from Figs. 5 and 8. Therefore, this low molar part of the area under the chromatographic waves was not taken into account in our calculations. It means that relative sorption calculated using Eq. (1) is valid only for sorption-active medium and high molar fractions creating decisive part of additives dry content.

Determined molar weight of polycondensates are given in Table 2.

2.6. IR spectroscopy

Apparatus model 283 Perkin-Elmer was used. Aqueous solutions of polycondensates tested with concentration of 1% (concentrates) were prepared. Volume aliquot of 0.3-ml size was immediately dehydrated (liquid nitrogen + vacuum). The dry content was homogenized with 1 g of KBr in vibrator mill for 20 min. Tablets were prepared and analyzed after 24 h of storing in vacuum over P_2O_5. The total spectra of analyzed polycondensates are in Fig. 9.

The filtrates were prepared by the same method as for GPC analysis. The 0.3-ml portions were used for the preparation of samples and were analyzed by the same method as in the case of concentrates. It appeared that the

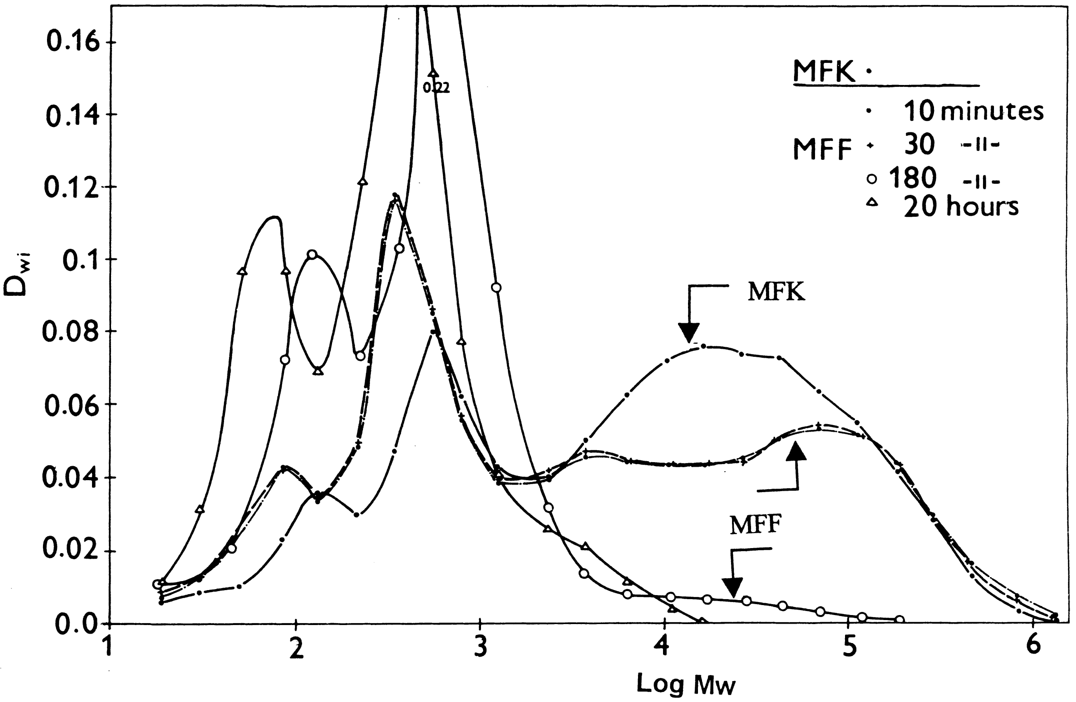

Fig. 5. Distribution functions of polycondensate MF 65 fractions before sorption (MFK) and after 10, + 30, ○ 180 min and △ 20 h of sorption (filtrates MFF). Calculated from total chromatographs.

sample of filtrate containing 2% K_2SO_4 was not transparent for IR radiation. Therefore, that salt was not used for preparation of suspensions and filtrates. Total spectra of filtrates are given in Fig. 10. IR spectra of samples in Fig. 11

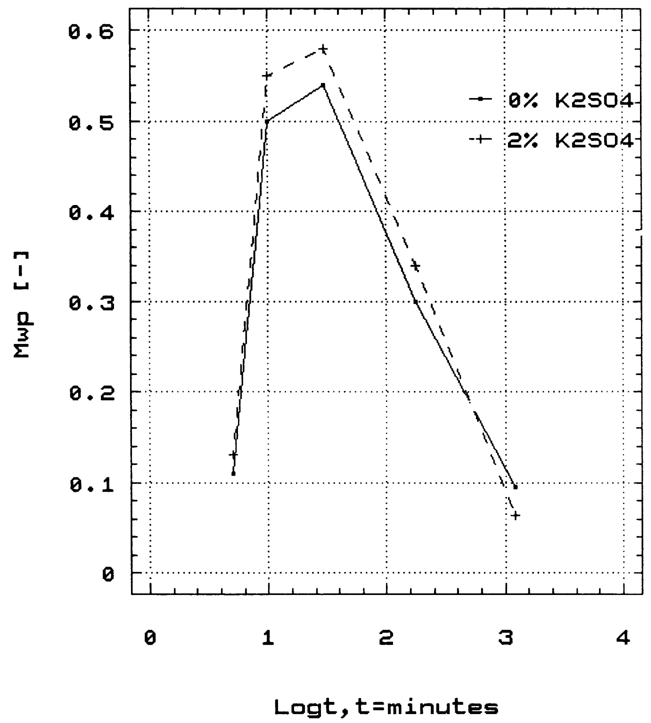

Fig. 6. Changes of M_{wp} (ratio of molar weight after:molar weight before sorption—M_{ws}:M_w) of filtrates after various time of interaction. Calculated from total chromatographs.

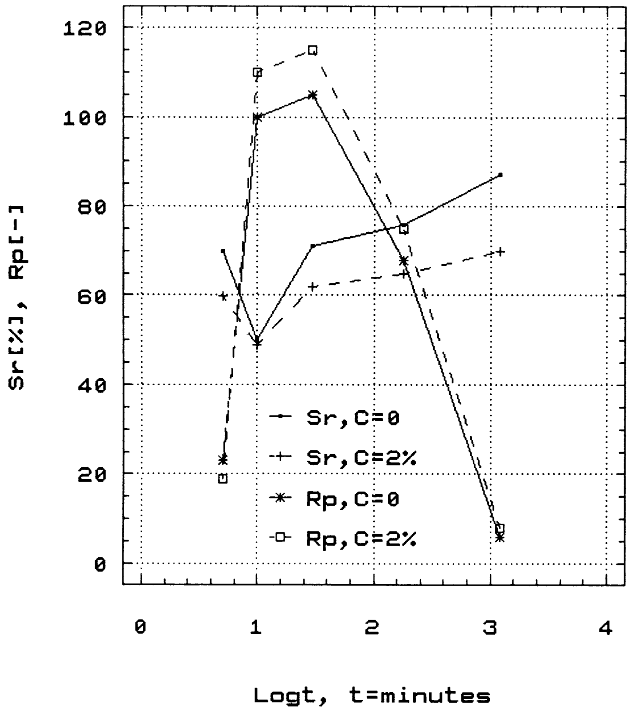

Fig. 7. Sorption S_r and polydispersivity R_p of filtrates versus time of interaction. C—dose of catalyst.

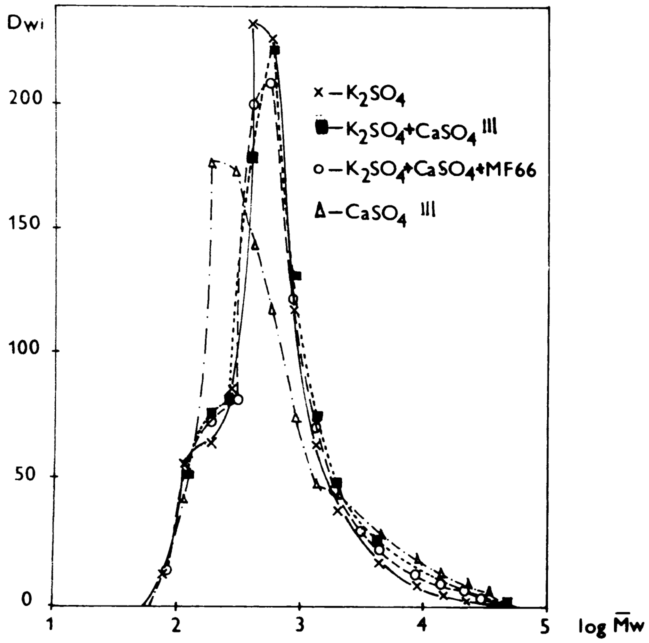

Fig. 8. Distribution functions of organic and inorganic low-molar components of suspensions (filtrates) after 20 min of interaction.

were prepared for better interpretation of spectra in Figs. 9 and 10. The sample MF 65 was treated by HCl and also by $BaCl_2$. Coagulates of MF-SO_3H and MF-$(SO_3)_2Ba$ were filtered out, treated for analysis and analyzed using the above described method. Determined absorbencies are given in Table 2.

2.7. Atomic absorption spectroscopy (AAS)

The apparatus spectrometer GBC 933 AA (GBC Scientific Equipment, Australia) was used. A solution of one chosen polycondensate having 10% concentration was prepared. The contents of the Ca^{++} and Na^{+} ions were determined in it. Then, 30 ml of the above mentioned solution was mixed for 20 min with 20 g of anhydrite and filtered. Also, a filtrate of anhydrite (20 g) and distilled water (20 g) was prepared. The contents of Ca^{++} and Na^{+} ions were determined in all filtrates. Results are shown in Table 3.

2.8. Content of sulphogroups in polycondensates

The sulphogroup content was determined in all additives in Table 2 using an ion exchanger. The sulphogroup contents were calculated from the determined amount of NaOH made by titration. For the determination of sulphogroup content in samples used for AAS analysis, a method based on conductometric titration was applied [15]. The determined content of sulphogroups in polycondensate tested was 13.32% of dry content. The theoretical content of sodium ions in all sulphogroups of sample tested was calculated to be 2.97%.

2.9. Regression analysis

The approximation of functional dependencies between tested dependent and independent variables was determined by a computer using program Statgraphics 2. The following limits were used for determination of each R_d coefficient's significance (coefficient of multiple determination): $R_d < 30$: low or any correlation, R_d = 30–60%: medium to good correlation, $R_d \geq 60$: very good correlation between analyzed variables exists [17].

3. Evaluation of results

The scheme in Fig. 1 shows that the preparation of samples consists of two steps. Step A: preparation of sodium salt of trimethylol–melamine and step B: polycondensation. The characteristic total chromatograph in Fig. 2 shows that tested sample contains various fractions of final product. High and medium molar sorption-active fractions are represented by peaks 1 and 2. Peaks 3, 4 and 5 represent low molar fractions containing various intermediate products of reactions further products of neutralization of acid by NaOH, and also free formaldehyde. The aim of industrial practice is to achieve maximal content of sorption-active medium and high molar fractions. The results in Table 2 show that various conditions of synthesis have influence on the determined parameters of polycondensates prepared.

The relationships in Fig. 3 prove that sorption of MF molecules in term 20 min is selective. Medium molar fractions are preferably sorbed out from all tested additives. These results are proved by relationship in Fig. 4 either. It shows that molar weight of filtrates (M_{ws}) is markedly higher than that of concentrates (M_w) before sorption. Selective sorption is evident also from courses of distribution functions in Fig. 5. Medium molar fractions of additive MF 65 are sorbed out after 10 and 30 min of interaction in the range of about log M_w = 3.6–5.2. All the high and a substantial part of medium molar fractions, in the range of about log M_w = 5.2–6.1, are sorbed out in the period 180 min. Only the low molar fractions, first of all inorganic components (log M_w < 4.2), remain in the filtrate after 20 h of interaction. More illustrative and complementary information can be obtained by comparison of dependencies in Figs. 5–7 because all of them were calculated from the same chromatographs. After 5 min of interaction, about 60% to 70% of MF 65 molecules are sorbed out. M_{wp} (M_{ws}:M_w) value decreases from 1 (concentrate) to about 0.1 (filtrate) and is low. The determined value of polydispersivity of concentrate was R_p = 66. This value decreases after interaction to about 20 (filtrate). R_p value decreases on the one hand due to the sorption of organic medium molar fractions and on the other hand because inorganic compounds in intergrain solution are present

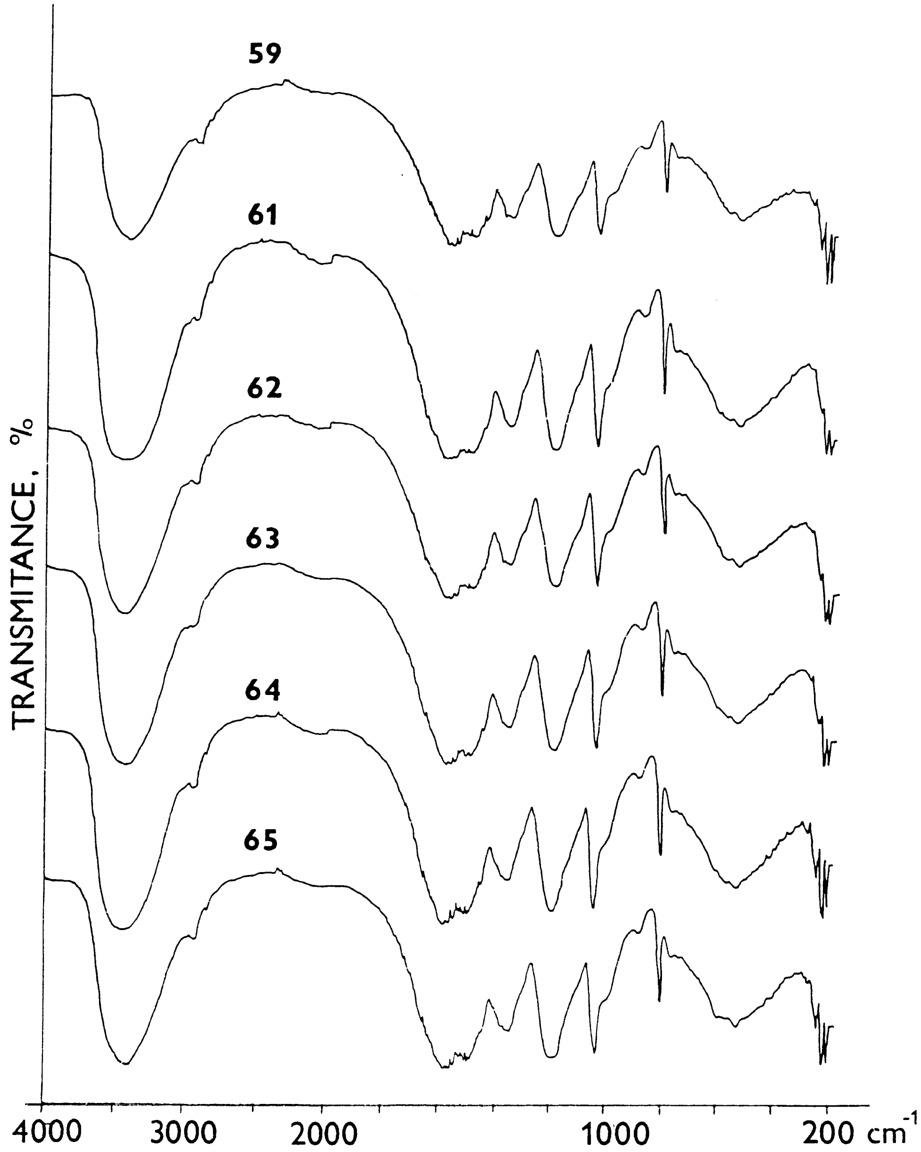

Fig. 9. Total IR spectra of additives before sorption (concentrates).

mainly in a dissociated form. In term 10-min sorption, S_r slightly decreases and other parameters increase. Probable interactions up to term 10 min can be described as follows. Immediately after mixing of compounds, interaction of water catalyst and MF molecules with surface of solid particles starts. The surface of solid particles (base for sorbed MF molecules) rapidly changes its parameters. Part of it is simultaneously dissolved and also hydrated. The concentration of organic molecules in intergrain solution decreases due to sorption, and on the contrary, the concentration of dissociated inorganic ions increases in it. The electrokinetic properties of anhydrite particles and the affinity of MF molecules to their gradually hydrated and dissolved surface may change and may cause the slight desorption of certain fractions or molecules having lower affinity to hydrated surface in term 10 min. Dissociated inorganic ions react and create the particles of new formation in solution having a greater diameter than the dissociated ions. The outline characteristic of particles changes due to the growth of their diameter and that supports the M_{wp} increase. In period 10 to 30 min, S_r reaches similar value as in term 5 min and slight growth of M_{wp} and R_p of filtrates can be observed. The R_p parameter reaches the maximal value because the filtrate contains, in 30 min, dissociated ions of catalyst and anhydrite compounds, low molar fractions of additive, solid particles of new formations and unsorbed portion of medium and mainly high molar fractions. In term 180 min, M_{wp} and R_p values decrease and S_r value slightly grows. The filtrate contain high content

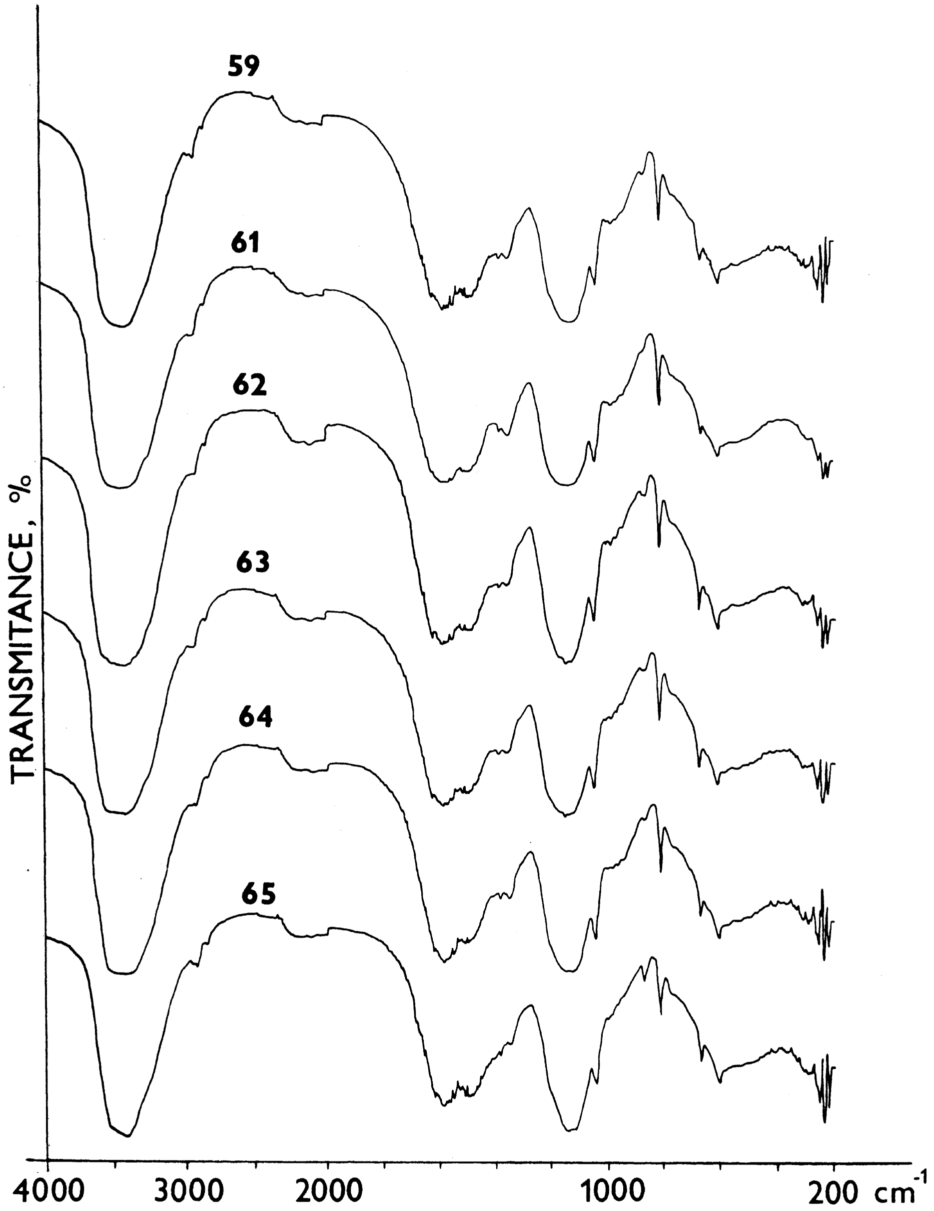

Fig. 10. Total IR spectra of additives after sorption (filtrates) in term 20 min of interaction.

of low molar fractions represented by log $M_{\mathrm{peak}} = 2.7$ (molar weight belonging to maximal value of peak). The prevailing parts of filtrate after 20 h are low molar compounds because the medium and high molar fractions of additive are quite sorbed out as is evident from Fig. 5. Also, the particles of new formations, having greater diameter than pores of filter used (about 500 nm) are filtered out. M_{wp} and R_{p} values rapidly decrease. S_{r} increases and reaches its maximum value. The influence of catalyst used on determined parameters of filtrates can be derived from Figs. 6 and 7. It seems that catalyst retards the sorption of organic molecules and therefore causes increase of M_{wp} in all range of log t. The catalyst causes also increase of R_{p} owing to its very good solubility. Changes in chemical structure of polycondensates as a result of interactions in suspension cannot be proven by the above given results. This problem was studied using infrared and AAS analysis. The total infrared spectra of tested polycondensates in Fig. 9 can be interpreted as follows.

Wave number about 3400 cm $^{-1}$: The characteristic vibrations N–H and O–H bonds of amines and alcohols can be observed in this part. Wave numbers 2940 and 2850 cm $^{-1}$ of low intensity belongs to the antisymmetric and symmetric valency vibrations of the methylene group. The same group shows itself by scissoring deformative vibrations at 1490 cm $^{-1}$ and rocking vibrations at 730–780 cm $^{-1}$. Alcoholic group shows itself, except

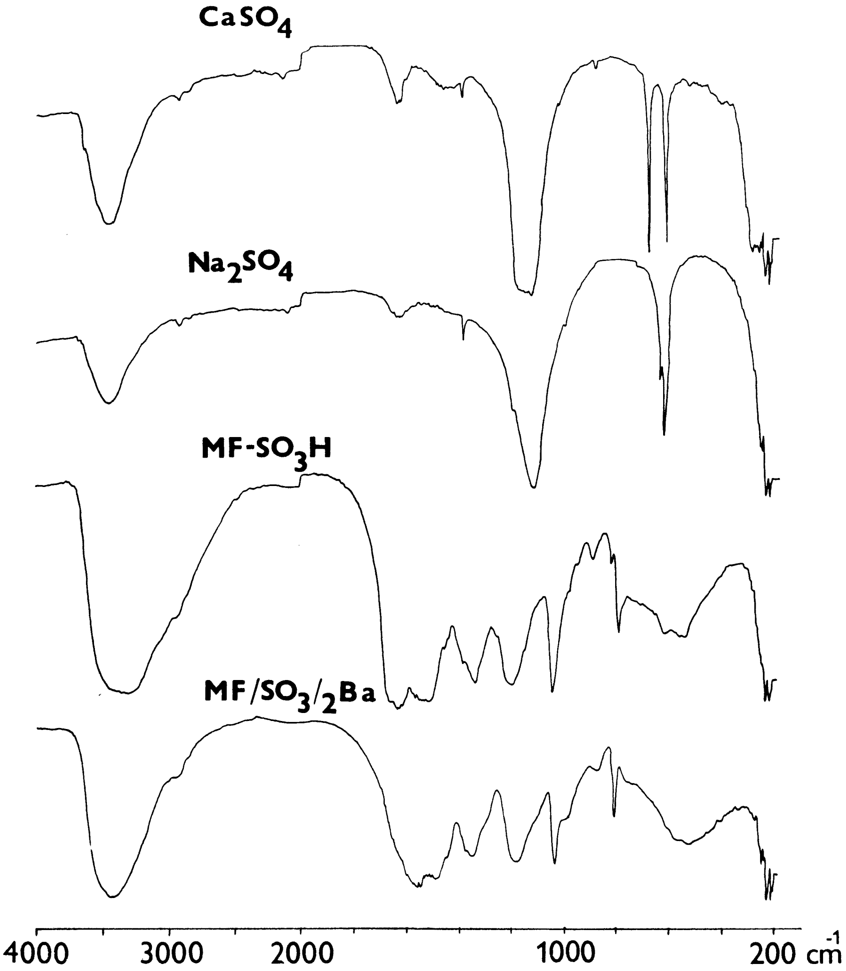

Fig. 11. Total IR spectra of treated MF additive and complementary compounds.

in the mentioned wave number 3400 cm $^{-1}$, in the form of plain deformation vibration C–O–H, and in addition, at 1350 cm $^{-1}$ and extending to 1140–1030 cm $^{-1}$. Present secondary amine groups show themselves by skeleton C–N–C vibrations at 1190–1130 cm $^{-1}$. The group $-SO_3Na$ manifests itself by valence vibration v-SO_2 at 1220–1190 cm $^{-1}$ (antisymmetric) and 1030–1040 cm $^{-1}$ (symmetric) vibrations. A certain number of deformation vibrations of that group can be found between 500 and 600 cm $^{-1}$. The intensive wave of extraplain deformative vibration at 820 to 805 cm $^{-1}$ may be assigned to the 1,3,5-triazine ring. It is evident from the total spectra in Fig. 9 that the wave number of triazine ring can be used, with great advantage, for the judgement of degree of sulphonation. In comparison with it, the changes in intensities of symmetric and antisymmetric valence vibration of R-SO_3Na (respectively, R-SO_3H) group can be identified. It can be declared, after the comparison of spectra in Fig. 9, that additives tested do not differ from each other from standpoint of infrared spectra characteristics. The spectra of tested filtrates with the same additives are in Fig. 10. It can be concluded, by comparison of spectra in Figs. 9 and 10, that after interaction of compounds in modified suspension, the characteristic absorptive wave (band) did not disappear from basic spectra. It can be observed on the contrary that the filtrates tested are reached by a new component as can be dedicated from the absorption at 3650, 605 and 672 cm $^{-1}$. This indicates the presence of calcium sulphate. Bright diffusion band can be observed extending to wave numbers 1100–1200 cm $^{-1}$. It is caused by presence of $-SO_4^{2-}$ group.

Table 3
Content of ions in analyzed samples

Sample	Na^+ (mg/30 ml)	Ca^{++} (mg/30 ml)
Additive 10% solution	378.72	1.18
Additive + anhydrite (filtrate)	358.56	80.10
Anhydrite (filtrate)	0.97	29.90

No direct proof of the answer to the question whether ions Na^+ in sulphogroups are not replaced by Ca^{++} ions is

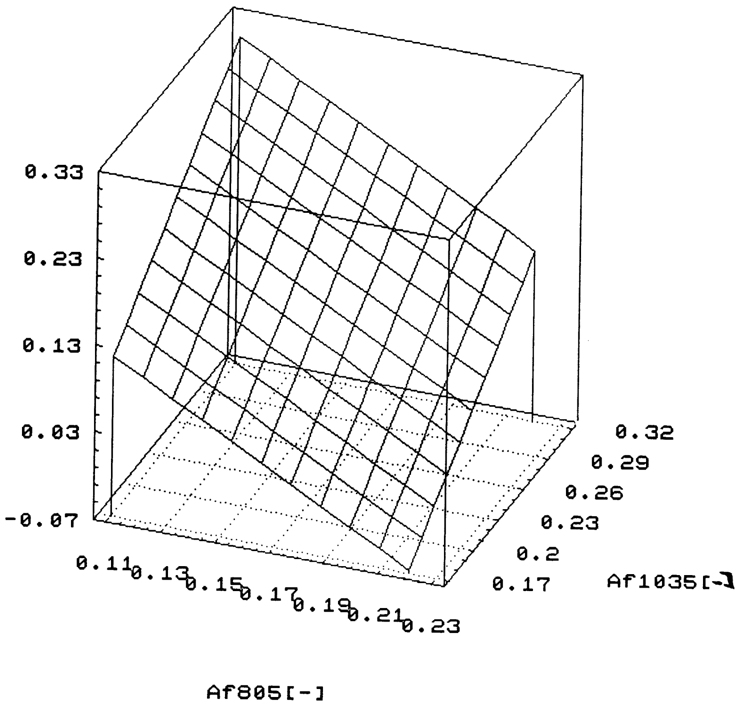

Fig. 12. Absorbance Af 675 (calcium sulphate) versus absorbances Af 805 (triazine cycles) and Af 1035 (sulphogroups). All absorbances of filtrates are valid for term 20 min of interaction.

obtained from the IR spectra presented. The absorption band belonging to the calcium sulphate (wave number 605 cm $^{-1}$) coincides with that of Na_2SO_4 (wave number 610 cm $^{-1}$), as is evident from Figs. 10 and 11. Therefore, we try to gain indirect proof of this reaction. It is valid, in general, that equilibrium concentration of inorganic components in an intergrain solution is influenced by concentration and properties of additive present (unsorbed part) when other conditions are constant. Equilibrium concentration of components in filtrates in term 20 min of interaction can be derived from absorbencies in Table 2. Regression analysis of variables from Table 2 showed that very good correlation exists among A675 (calcium sulphate in dry of filtrate) and absorbances of filtrate Af805 and Af1035 (R_d = 96.55%). The results in Fig. 12 show that hydrophobic part of unsorbed portion of MF molecules (triazine cycles) causes decrease and hydrophilic part ($-SO_3Na$) contributes to the increase of main calcium-based compound in filtrate. These results are in accordance with theory of reaction kinetics and thermodynamic laws. Free energy of MF salts decreases and their thermodynamic stability grows in this order: MF-SO_3Na, MF-$(SO_3)_2Ca$, MF-$(SO_3)_2Ba$. Therefore, sodium salt, in solutions saturated by calcium ions, has a tendency to transform to more stable form from the standpoint of thermodynamic laws. The relationship in Fig. 12 shows that there exists a linear relationship between the content of calcium ions in filtrate (or main calcium compound in dry filtrate) and content of sulphogroups.

A direct proof of ion exchange by AAS method is based on the presupposition that all or a decisive part of Na^+ ions, bound in sulphogroups or present in the form of dissolved sodium compounds in concentrate, passes to intergrain solution after interaction of MF molecules with anhydrite. Theoretical (anticipated) concentration of Na^+ ions in filtrate can be calculated from data in Table 3 as a sum of Na^+ in concentrate and in filtrate of only anhydrite as follows: $378.72 + 0.97 = 379.69$ mg/30 ml. The determined content of Na^+ in filtrate (polycondensate + anhydrite + water) is 358.56 mg/30 ml. The difference between calculated and determined content of sodium ions is $378.72 - 358.56 = 20.16$ mg. This difference may represent all imperfections in the preparation of samples and reproducibility of the method used. It may also represent the part of Na^+ ions that bond in surface or structure of hydrates or hydrated surface of anhydrite particles. The theoretical content of Na^+ only in sulphogroups of concentrate (30 ml of 10% solution) is 89.22 mg. The remaining amount $378.72 - 89.22 = 289.5$ mg/30 ml is present in concentrate due to neutralization of additive tested with NaOH in the final process of laboratory preparation. The following inequality can be written using the above given results: $20.16 < 89.22$. These results indicate that the decisive portion of Na^+ ions present in the sulphogroups of sorbed and unsorbed molecules is present in the filtrate after interaction of additive with compounds of anhydrite. The results obtained indicate that the anhydrite suspension can be regarded as an ion exchanger.

The results in Table 3 show that the content of calcium ions in the filtrate with MF additive is higher than in the filtrate without additive. This result is proven by the relationship in Fig. 12. Ideal proof of such ion exchange would exist if the stoichiometric ratio between exchanged sodium and calcium ions in solution could be proven. This is not possible because the calcium content in the filtrate represents not only dissociated ions but also the calcium in created particles of new formation having lower diameter than the pores of the filter used (about 500 nm). All the calcium ions are detected by AAS method used. Sodium ions, on the contrary, are present in solution in a dissociated form. One of the possible reactions, which may be in progress in the intergranular solution of modified suspension, can be written as follows.

$$\mathrm{MF} - (\mathrm{SO_3Na})_2 + \mathrm{CaSO_4} \rightarrow \mathrm{MF} - (\mathrm{SO_3})_2\mathrm{Ca} + \mathrm{Na_2SO_4}$$

4. Conclusions

1. The sorption of organic molecules on the surface of solid particles is selective. Medium molar fractions are preferably sorbed out in terms 10 to 30 min. In term 180 min, the total amount of high molar fractions is sorbed out.
2. The results obtained indicate that ions $\mathrm{Na^+}$ in sulphogroups of polycondensate are replaced by $\mathrm{Ca^{++}}$ ions. The suspension of anhydrite can be considered as an ion exchanger.
3. The proportion of sorbed low, medium and high molar fractions of polycondensate tested changes in dependence on the time of interaction.
4. The results presented are valid only for the materials and methods used.

Acknowledgments

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