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Communication

Gypsum-free cements as binders of suspensions for injections

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Abstract

The affinity of chosen organic pollutants present in polluted natural gravels and soils to gypsum-free cement and its hydrates was tested. The organic hydrophobic pollutants are emulsified and bound to the rapidly created solid structure of the binder because of the favourable action of the combined additive. It seems that the suspensions based on gypsum-free cements with suitable additives, because of their very good fluidity and affinity to pollutants tested, can be used for elimination of pollutants migration in strata of permeable gravels.

Keywords: Waste management; Admixture; Rheology; Workability; Curing

The prevention of pollutant penetration from polluted soils into the surrounding environs is one of the main problems that must be often urgently solved in environmental engineering. The urgency is greater when the polluted locality of rocks or soil is created by a permeable layer of gravel saturated permanently or temporarily with water. The reduction or elimination of permeability can be reached, for example, by injection of the permeable layer mentioned. The water:binder ratio of suspensions based on an industrial cement binder must be about 0.5 to have satisfactory fluidity. The tendency of suspension to segregation (bleeding) is in direct proportion to the third of free-water content and in reverse proportion to the quadrate of specific surface area of solid compounds [1], as is evident from Eq. (1):

$$Q = K \cdot \frac{1}{\eta} \cdot \sigma \cdot \frac{V^3}{S^2} \quad (1)$$

Q = flow rate of water to the surface ($m^3 \cdot s^{-1}$)
η = dynamic viscosity of liquid phase of suspension valid for chosen temperature ($Pa \cdot s$)
σ = power causing the sedimentation proportional to the mass of solid compounds in m^3 of volume (N)
V = volume of free (not bound) water (m^3) in m^3 of suspension
S = specific surface area of solid phase (m^2) in m^3 of suspension
K = constant

The so-called filtration effect may occur due to the tendency of the suspension to segregation. It means that a vacant area of a certain volume of gravel in some distance from the drill-hole orifice aperture is filled with a penetrating suspension having a higher concentration of the solid phase. The rate of filling has a tendency to decrease with an increase in distance. The phenomenon mentioned may cause the impermeability of the gravel layer after treatment to be less than perfect.

It seems that for ecological use as well as for the building industry there are much more suitable injection suspensions based on gypsum-free ground clinker. These type of binders have very good fluidity (low viscosity) even if the water:binder ratio is about 0.22–0.25 [2–4]. That is why the tendency to segregation of the suspensions is markedly lower as is evident from Eq. (1). A very serious barrier for the application of the binders mentioned for the purpose described is their $\geqslant$1% sodium carbonate content. Furthermore, 0.5–1% of organic additives are mainly those based on ligninsulphonates and sulphonated polyphenolates [5–11]. The acceptable amount of anionactive tensides in leachate prepared by the leaching of 100 g of solid materials in l L of distilled water during 24 hours in accordance with prescription [12] is about 0.1 mg/L. The phenol index of leachate prepared from a sample containing sulphonated polyphenolates under the same conditions must be below 0.005 mg/L. Those limits are higher in the case of suspensions with the binders mentioned. That is why they cannot come into contact with water from natural resources. The favourable properties of suspensions for injections based on gypsum-free cements can only be taken full advantage of

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Table 1
The content of the pollutants in analysed samples

	Content of pollutants in the water extract (μg/L)			
Substance	Polluted gravel	Solidification of gravel	Polluted soil	Binder + water + soil
Trichloroethylene	5.58	0.98	2.25	1.4
Tetrachloroethylene	44.38	0	18.71	3.22
Cis1,2 dichloroethylene	0	0	0	0
N1	—	0	—	0
N2	393	0.39	223.16	0.84
N3	—	0	—	0

N1, N2, N3 = not identified substance: Rt = 39.3 minutes, Rt = 44.1 minutes (probable 1,3-dichlorobenzene), Rt = 48.7 minutes.

when the organic additive used is not classified as a pollutant from the point of view of ecological requirements. That is why the research was carried out using a new polyfunctional organic additive having equivalent efficiency on the fluidity and hardening of samples with gypsum-free cements as well as satisfactory ecological properties.

1. Materials

1.1. Clinker

The content of the main minerals of clinker used determined by an optical method was as follows: C_3S = 71%, C_2S = 8.2%, C_3A = 7.9%, C_4AF = 12.6%, and free CaO = 0.3%. The clinker was ground in a laboratory ball mill. The specific surface area was 422.8 m^2/kg (binder).

1.2. Polluted samples

Two mixtures of natural sand, gravel, and soil (gravel) was taken from a chemical enterprise where decontamination of the locality was made. The content of pollutants in the samples is shown in Tables 1 and 2.

1.3. Additives

The dose of sodium carbonate was 1% by weight (b.w.) of gypsum-free binder. The organic polyfunctional additive with preliminary signature Inject was obtained from Rokospol (Uhersky Brod, Czech Republic). The dose was 0.7% b.w. Inject is based on derivatives of saccharides according to the data of the producers of additive and has emulsifying properties.

2. Methodology

2.1. Rheology

A rotary viscometer Rheotest (Mechanik Prüfgeräte, Medingen, Germany) was used. Sedimentation of the suspension was observed when the system of cylinder-cylinder was used. Hence the rotating cylinder was replaced with the treated cylinder, which secured the homogenization of suspension during testing. The rheological characteristic is expressed as a moment of torsion (mN · m) at maximal velocity of rotation 12a II. The binder was mixed with ground gypsum on the portion 95:5 b.w. Suspensions were prepared from that cement with different water:cement ratio. Further binder without gypsum was mixed with different amounts of water containing the dissolved previously mentioned additives. The rheological characteristics of all samples was determined. The results of the tests are in Fig. 1.

2.2. Strength

Samples 4 × 4 × 16 cm were prepared from suspension containing binder:polluted gravel:water with additives = 1:3:0.32 b.w. The additives were dissolved in the mixing water. The suspension had a flowing consistency and filled the moulds without intensive compaction. The moulds with samples were stored in different thermal conditions in the range of 5–30 °C. The temperature and time of storing influence the compressive strength with a portion of 93% as it was derived from the coefficient of multiple determination obtained by regression analysis using the computer program Statgraphics 2. The results are in Fig. 2. The samples in the shape of a cylinder were prepared from the same suspension for leaching tests.

Table 2
The remaining parameters of leachate

	Water extract	
Determined quantity	Contamined gravel	Solidificate
Conductivity (mS/m)	5	147
pH (−)	5	12.34
PAH—12 pollutants (ng/L)	398.6	60
No extractable substances (mg/L)	2.7	1.3

PAH, polyaromatic hydrocarbons.

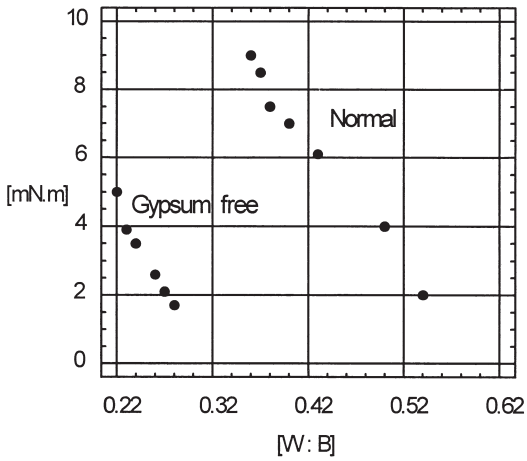

Fig. 1. Rheological characteristic vs. water:binder ratio.

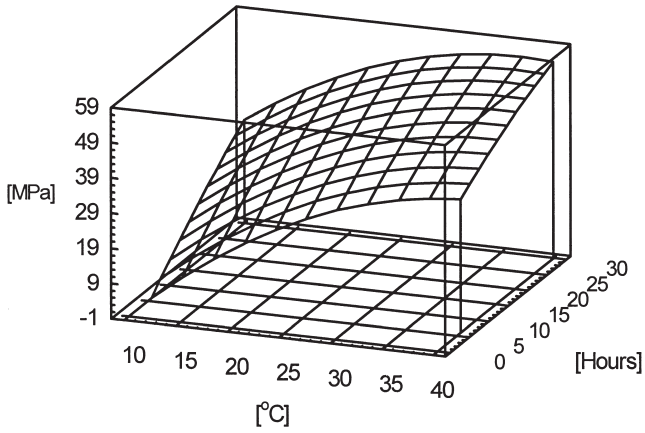

Fig. 2. Compressive strength vs. time and temperature of hardening.

2.3. Leaching tests

The samples after 14 days of hardening at 20°C were immersed into distilled water (100 g of solid:1000 g of water) and agitated for 6 hours. After 18 hours of subsequent storing the leachate was filtered and analysed. The leachate for volatile pollutants determination was prepared in thoroughly closed vessels. The volume of air over the liquid level in the vessel was only 50 cm^3. The content of the vessel was remixed for 1 minute by hand in intervals of 20 minutes over 8 hours. After 18 hours of storing without any treatment the leachate was analysed using GC-FID (gas chromatography–flame ionization detector, Series II, Hewlett Packard) method. The results are shown in Tables 1 and 2.

The affinity of organic pollutants to bind with additives in water suspension was tested also. The composition of suspension was as follows: polluted gravel:gypsum-free binder:water with additives = 0.70:0.3:0.26 b.w. Furthermore, 8.74 parts of the distilled water were added to the suspension after 5 minutes of mixing by hand. After 24 hours (8 hours agitated by hand, 16 hours stored) the sample was filtered and analyzed. The results are given in Table 1.

3. Conclusions

1. The rheological characteristic of suspension containing additives and binders is the same at water:binder ratio = 0.26 as that of cement with gypsum at about water:binder ratio = 0.52.
2. The content of pollutants analyzed in the leachate of solidified samples is markedly smaller than in the polluted gravel (see Table 1). The combined action of binder and additives probably increases the affinity of organic pollutants to binder and its hydrates.
3. The affinity mentioned above is without a doubt confirmed by the results in Table 1. The results are not influenced by the prevention effectiveness of the solid structure of the sample against the migration of organic pollutants tested in the liquid phase. This is due to fact that the suspension was dispersed in the water throughout the duration of the experiment without creating dense solid structure as in the case of the solid samples. The results indicate that the suspension injected into the structure of polluted gravel is able to bind the pollutants from the intergrain solution or from the surface of gravel particles. The solid structure subsequently created only increases the decontamination ability of the binder. The organic additive has polyfunctional action: It contributes to good fluidity of suspension, emulsifying of organic pollutants, and their transfer from the surface of the grains of gravel to the liquid phase. They can in such a way come into the contact with particles of binder and its hydrates and interact with them.
4. The remaining parameters of leachate are shown in the Table 2. They are very favourable and considerably under the limits of prescriptions.

The gypsum-free binder is suitable for preparation of suspensions used for injections of undergrounds (or permeable layers) in environmental and civil engineering because all organic compounds are free of ecologically unsuitable components and they are biologically degradable. The other advantage is the very good fluidity at low water content and rapid rise of strength even at low temperature.

Acknowledgments

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References

[1] J. Stork, Technology of Concrete Part I, Slovak Academy of Sciences, Bratislava, 1954, pp. 254–255.
[2] O.I. Lukyanova, E.E. Segalova, P.A. Rebinder, Koll Journal 19 (1957) 82.

[3] O.I. Lukyanova, E.E. Segalova, P.A. Rebinder, Dokl Akad Nauk SSSR 117 (1957) 1034.
[4] S. Brunauer, M. Yudenfreund, J. Skalny, J. Odler, Cem and Concr Res 3 (1973) 129.
[5] F. Škavára, K. Kolář, Z. Zadák, Z. Bažantová, Stavivo (Czechoslovakia) 57 (1979) 44 (1979).
[6] F. Škavára, K. Kolář, J. Novotný, Z. Zadák, Cem and Concr Res 10 (1980) 253.
[7] F. Škavára, K. Kolář, J. Novotný, Z. Zadák, Cem and Concr Res 11 (1981) 247.
[8] M. Collepardi, S. Monosi, G. Moriconi, Cem and Concr Res 10 (1980) 455.
[9] M. Pauri, G. Ferrari, M. Collepardi, Cem and Concr Res 13 (1983) 61.
[10] F. Škvára, Stavivo (Czechoslovakia) 62 (1984) 298.
[11] F. Škvára, T. Všetečka, Stavivo 67 (1989) 262.
[12] Czech Government Issue 513/92Sb.