

STUDY OF THE EFFECT OF CHEMOGYPSUM AS SETTING
RETARDER ON THE PROPERTIES OF CEMENT PASTES

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Waste gypsum from chemical works contains various proportions of impurities according to the character of the respective production technology. If the chemogypsum is used as a setting retarder in portland cement, the hexafluoro-silicates present exhibit considerable additional retarding effects with respect to early strength, whereas the fluorides, such as CaF_2 , do not influence the hydration processes to any substantial degree. The early strengths of cement are mostly affected by Na_2SiF_6 .

INTRODUCTION

Utilization of secondary raw materials, which is a necessary precondition for introduction of waste-free technologies, is of primary importance in all industrial developed countries. Some of them, including Czechoslovakia, have also limited resources of natural gypsum of adequate purity. For these reasons it is desirable to make use of gypsum produced as waste in some fields of industry.

The manufacture of superphosphate and titanium dioxide yields considerable amounts of gypsum with a high content of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; however, when used as a setting retarder in Portland cement, it is responsible for excessive retardation of early strength. Even with the smaller proportions of fluorides and silicofluorides involved, it was considered necessary to study their effect on the properties of cement. No comprehensive survey of the effects of these substances on the development of early strength of Portland cement has so far been available.

Schwiete et al. [1] as well as Ludwig with Schwiete and Seiler [2] showed that MgSiF_6 is mainly responsible for prolonging the setting time above all of mixed cements. Recent studies [3—5] were concerned with the influence of some silicofluorides on the retardation of early strength and on delaying the initial setting of cement pastes.

EXPERIMENTS

The initial substances employed

The study made use of 3 samples of chemogypsum (Chemopetrol, C.C., Přerov Chemical Works, Přerov) of different purity, as well as natural gypsum from the Koberžice locality (class II). The results of chemical analyses are given in Table I. Natural gypsum of comparatively high purity was employed as standard. The largest amounts of impurities are contained in industrial gypsum types CH (I) and CH (II), whereas sample CH (III) exhibits the highest content of SO_3 .

The content of total fluorine was as follows:

CH (I): 0.58%; CH (II): 0.28%; CH (III): 0.14%.

Table I
Chemical composition of the gypsum types employed

Characteristic component (wt. %)	Natural gypsum KO	Chemo- gypsum CH(I)	Chemo- gypsum CH(II)	Chemo- gypsum CH(III)
Ignition loss (230 °C)	20.16	17.36	17.36	18.74
Ignition loss (900 °C)	1.01	1.38	1.55	1.63
SiO ₂ + insoluble residue	0.90	7.67	6.63	3.68
Al ₂ O ₃	0.04	1.03	2.49	2.42
Fe ₂ O ₃	0.04	10.21	8.18	7.99
TiO ₂	0.02	1.44	2.00	2.26
CaO	32.16	25.14	26.75	25.85
MgO	0.02	1.04	0.94	0.75
K ₂ O	0.02	0.06	0.05	0.05
Na ₂ O	0.04	0.17	0.16	0.13
SO ₃	45.53	34.67	34.24	36.25
Total	99.94	100.17	100.35	99.75
CaSO ₄ . 2 H ₂ O*	97.91	74.56	73.63	77.96

* The proportion of CaSO₄ . 2 H₂O was calculated from SO₃, as the gel of Fe(OH)₃ contained in the chemogypsum is already decomposed in the course of thermal treatment.

Table II
Chemical and phase composition of the Portland cement clinkers

Characteristic (component) (wt. %)	Hranice clinker (HR)	Prachovice clinker (PR)	Quantitative microscopical analysis		
Ignition loss	0.72	0.27	Component (wt. %)	HR	PR
SiO ₂ + insoluble residue	21.46	21.34	3 CaO . SiO ₂	76.9	58.8
Al ₂ O ₃	6.42	5.79	2 CaO . SiO ₂	10.0	24.3
Fe ₂ O ₃	3.16	2.97	3 CaO . Al ₂ O ₃	6.1	9.5
TiO ₂	0.27	0.30	4 CaO . Al ₂ O ₃ Fe ₂ O ₃	6.4	7.2
CaO	64.53	62.43	CaO	0.6	0.2
MgO	1.06	3.77	total	100.0	100.0
K ₂ O	1.13	1.32	pores	11.1	18.3
Na ₂ O	0.16	0.30			
SO ₃	0.76	1.22			
MnO	0.07	0.06			
Total	99.74	99.77			

X-ray diffraction analysis showed that all of the samples contained high proportions of CaSO₄ . 2 H₂O (gypsum). The diffraction at 2.73 Å with the industrial samples indicates a lower content of ilmenite (FeO . TiO₂). Iron was contained in the form of X-ray amorphous Fe(OH)₃, as no other diffractions appeared in the respective X-ray diffraction patterns.

Two types of Portland cement clinker were chosen: one from "wet technology" (Hranice) and one from "dry one" (Prachovice). Their chemical and phase compositions are listed in Table II. The clinkers were ground separately in order to get very similar specific surface areas (HR): $267.1 \text{ m}^2 \text{ kg}^{-1}$; (PR): $265.9 \text{ m}^2 \text{ kg}^{-1}$, and only then thoroughly homogenized with the powdered gypsum at a weight ratio of 93 parts clinker to 7 parts gypsum.

RESULTS AND THEIR DISCUSSION

Determination of thermal differences in the course of hydration

Each sample was first mixed with tempered distilled H_2O ($w = 0.30$; $t = 20^\circ\text{C}$) and then placed in a calorimeter. Water was used as standard medium, by recording continuously the temperature difference between the cement paste and water for 24 hours.

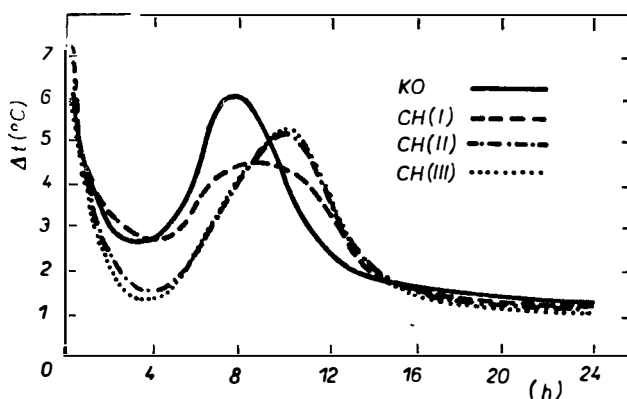


Fig. 1. Calorimetric curves of cement HR.

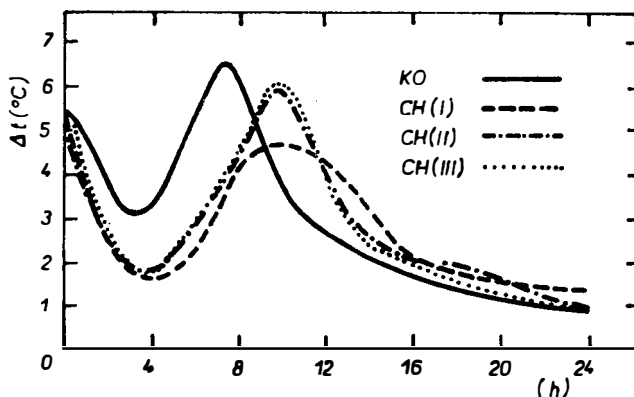


Fig. 2. Calorimetric curves of cement PR.

The calorimetric curves of cement HR indicate that a temperature difference arises after mixing with water, the temperature of the sample increasing after 4 hours, attaining maximum after about 8 hours of hydration in the case of the specimen with the natural gypsum (KO), only then decreasing, at first at a comparatively high rate and then slowly.

The course of hydration curves of cement with chemogypsum show quite distinct differences. At the beginning of hydration, the lowest difference with all of three samples is obtained after about 4 hours, followed by a rapid increase, which in the case of pastes with gypsum CH (III) and CH (II) is most pronounced and almost identical.

In comparison with sample (KO), the maximum was shifted by almost 2 hours towards the longer time of hydration.

The cement with gypsum CH (I) exhibits a quite different course of hydration, as its maximum of temperature difference shows a gradual character and is generally much lower (Fig. 1). In the case of cement prepared from clinker PR, the character of the temperature difference curves (Fig. 2) does not show any substantial differences compared with the series mentioned above.

Specification of the effect of fluorides and silicofluorides on the degree of cement hydration

The types of chemogypsum investigated contain smaller amounts of fluorides and silicofluorides.

For this reason it was considered desirable to investigate their effect on the hydration of cement. The following fluorine compounds were used in the experiments: CaF_2 , NaF , CaSiF_6 , Na_2SiF_6 and K_2SiF_6 . The basic mix again contained 93 parts of Portland cement clinker and 7 parts of natural gypsum (KO). Stepped up amounts of the compounds mentioned were added to this basic mix in amounts from 0 to 5 wt. %, calculated per 7% of the gypsum being present. PR clinker was used in this instance. The pastes were cured in a medium saturated with water vapour for a period of 24 hours (20 °C, 100% r.h.). The hydration was interrupted following removal of the specimens and their grinding by repeated washing with absolute ethanol and finally with acetone.

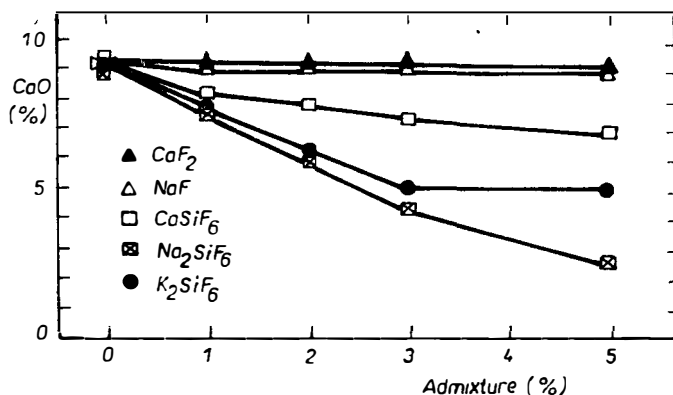


Fig. 3. The influence of fluorides and hexafluorosilicates on the degree of hydration of cement (24 hours).

The degree of hydration of the cement studied was determined on the basis of liberated portlandite [$\text{Ca}(\text{OH})_2$] and CaCO_3 ; the contents of the two components were determined thermogravimetrically and expressed as CaO . The graphic plot (Fig. 3) indicates that the hydration is neither positively nor negatively affected by the addition of CaF_2 . As regards NaF , the addition of the compound somewhat decrease the degree of hydration of the cement. Substantial suppression of hydration after 24 hours of curing is induced by hexafluorosilicates, among which Na_2SiF_6 exhibits the highest influence over the concentration range employed.

In another series of experiments, use was made of the same clinker (PR), to which 7% of natural gypsum were added either without additions or containing the same amounts of CaF_2 or Na_2SiF_6 , corresponding to 5 wt. %. Following thorough homogenizing, the mixtures were placed in a medium saturated with water vapour (20 °C; 100% r.h.) for 3 days; at certain time intervals (1, 8, 24 and 72 hours) the hydration was chemically interrupted, similarly to the series described above. Portlandite and secondary CaCO_3 were again determined by the thermogravimetric method. The results plotted in Fig. 4 show that the addition of fluorite (CaF_2) has virtually no effect on the hydration process.

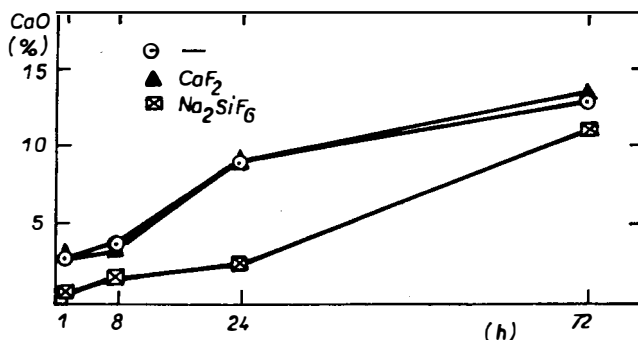


Fig. 4. The influence of CaF_2 and Na_2SiF_6 on the degree of cement hydration.

Quite different is the case of the cement containing Na_2SiF_6 . The hydration process is significantly retarded, above all during the first 24 hours of curing the cement paste. Only after this period the main clinker mineral alite begins to be hydrated at a higher rate and the degree of hydration approaches that of cement paste without addition, or with CaF_2 only, after 72 hours. This corresponds to the development of strength, as after 7 days of curing the strengths are almost identical, and after 28 days of curing the paste with Na_2SiF_6 often shows a higher strength than the cement containing natural gypsum only.

Determining the effect of gypsum types on the strength of cement pastes

The powdered clinkers were mixed with the individual types of gypsum (93 parts clinker: 7 parts gypsum), and thoroughly homogenized; the pastes prepared ($w = 0.32$) were cured for 12 and 24 hours (20 °C, 100% r.h.). The compressive strengths were determined immediately afterwards are listed in Table III.

Table III
Compressive strength of cement pastes

Cement (HR)			Cement (PR)		
Gypsum type employed	Compressive strength (MPa)		Gypsum type employed	Compressive strength (MPa)	
	12 h	24 h		12 h	24 h
Natural gypsum (KO)	21.55	40.08	Natural gypsum (KO)	10.45	34.45
Chemogypsum CH(I)	13.42	34.90	Chemogypsum CH(I)	8.79	35.68
Chemogypsum CH(II)	19.38	34.83	Chemogypsum CH(II)	10.28	37.68
Chemogypsum CH(III)	21.13	36.32	Chemogypsum CH(III)	10.91	38.48

After 12 hours of curing, the largest difference in compressive strength values was exhibited by cement with chemogypsum CH(I) showing the highest fluorine content, followed by the cement with chemogypsum CH (II); the last specimens, containing the relatively purest chemogypsum CH (III) with the lowest fluorine contents, exhibited almost identical strengths as compared to the cement containing the natural Koberice gypsum. After 24 hours of curing, the difference in the compressive strengths attained decreased with chemogypsum CH (I).

In the case of cement PR with natural gypsum after 12 hours of curing, the compressive strength value was distinctly lower than in that of cement HR. This fact is associated with a distinctly higher proportion of alite in clinker HR. A considerable difference in compressive strength was found only with the cement containing chemogypsum of the lowest purity (CH(I)) whereas the cement with the next gypsum attains almost identical values compared with the standard; in the case of chemogypsum of the relatively highest purity (CH(III)), the strength is even somewhat higher. After 24 hours of curing, the cement paste exhibited a somewhat anomalous behaviour in the sense that the standard samples of paste with the natural gypsum exhibited the lowest value of compressive strength. With decreasing content of fluorine in the chemogypsum added to clinker, the cements showed increasing strength, both after 12 and 24 hours of curing.

Determining the effect of Na_2SiF_6 on the setting and strength of cement paste

On the basis of the results obtained it was deemed desirable to determine the effect of stepped up amounts of sodium hexafluorosilicate on the time of initial and final set, as well as on the value of compressive strength. For this purpose, mixtures of powdered clinkers HR or PR with 7 wt. % of natural gypsum (KO) and with the identical dihydrate, containing stepped-up amounts of Na_2SiF_6 (0, 1, 3 and 5 wt. %) were prepared.

The mixtures were homogenized and prepared to make pastes ($w = 0.32$) which were again cured for 24 hours (20 °C, 100% r.h.).

The results obtained with clinker HR are given in Table IV.

Table IV
Cement pastes (HR)

Content of Na_2SiF_6 (wt. %) in natural gypsum (KO)	Compressive strength (24 h/22 °C)		Initial setting (h)	Final setting (h)
	MPa	%		
0	39.00	100.00	2.10	3.00
1	22.80	58.46	4.30	7.10
3	17.08	43.79	5.15	8.15
5	13.43	34.43	6.00	8.55

As indicated by the results obtained, if the gypsum added as setting retarder to Portland cement clinker (HR) contains only 1% Na_2SiF_6 , the strength of paste after 24 hours of curing will fall almost to the half and at a content of 5% of Na_2SiF_6 , to almost one third of that of the standard mix (cement) free of silico-fluoride.

At the maximum content of Na_2SiF_6 (5%) in gypsum, the time of initial setting increased by a factor of almost three. The time of final setting was also substantially increased from 3 to 8.55 hours.

The results indicate that an increase in the content of Na_2SiF_6 in the gypsum employed tends to impair significantly the strength of the paste, while simultaneously increasing the time of both initial and final setting.

Identical experiments were carried out with clinker PR and the results are summarized in Table V.

Table V
Cement pastes (PR)

Content of Na_2SiF_6 (wt. %) in natural gypsum (KO)	Compressive strength (24 h/22 °C)		Initial setting (h)	Final setting (h)
	MPa	%		
0	34.40	100.00	1.40	3.20
1	27.02	78.55	2.50	4.45
3	16.70	48.54	2.55	5.20
5	12.07	35.10	3.45	5.40

With clinker PR and particularly at the lower contents of Na_2SiF_6 (1%) in gypsum, the strength did not decrease as considerably as in the previous series. The time of both initial and final setting did likewise not increase as markedly as with cement HR. This phenomenon is due to the great difference in the mineralogi-

cal composition of the two clinkers and is associated above all with alite content. It can be assumed that at higher contents of alite, the silicofluoride will exert a more intensive retarding effect on early strength and the time of setting.

CONCLUSION

The study was concerned with the possibility of using chemogypsum, a secondary raw material from superphosphate and titanium dioxide production, as a setting retarder for Portland cements.

In addition to natural gypsum, experiments were carried out with three types of industrial dihydrate with various contents of total fluorine, namely 0.58, 0.28 and 0.14 wt. %. The results have borne out the assumption that the compounds of fluorine being present promote retardation of the actual hydration, also affecting the initial strength of the cement paste. This was also demonstrated by stepped up additions of selected fluorides and hexafluorisilicates to natural gypsum used as setting retarder. The admixture of CaF_2 has almost no effect on the degree of cement hydration, which is most strongly retarded by Na_2SiF_6 . Apart from reducing strength, the compound increases the time of both initial and final setting of the cement.

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STUDIUM Vlivu CHEMOSÁDROVCE JAKO REGULÁTORU TUHNUTÍ NA VLASTNOSTI CEMENTOVÝCH PAST

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Byla zjišťována možnost použití odpadního sádrovce z výroby superfosfátu a titanové běloby jako regulátoru tuhnutí cementu.

Ke studiu bylo užito vedle přirozeného dihydrátu 3 vzorků chemosádrovce, které se vyznačovaly rozdílným obsahem nečistot a dvou průmyslových slinok portlandského cementu z „mokrého“ a „suchého“ technologického procesu.

Prokázalo se, že cementy obsahující chemosádrovec se vyznačují retardací nárůstu pevnosti v počátečním časovém období za současného prodloužení počátku i doby tuhnutí.

Dále byl studován vliv odstupňovaného přídatku fluoridů a silikofluoridů (CaF_2 , NaF , CaSiF_6 , Na_2SiF_6 a K_2SiF_6), které mohou být v chemosádrovci v menším množství obsaženy, na stupeň hydratace cementu. Výrazným retardačním účinkem se vyznačují hexafluorosilikáty, z nich nejvyšším přísada Na_2SiF_6 , zatím co CaF_2 téměř neovlivňuje vlastní hydratační proces.

Již velmi nízký obsah Na_2SiF_6 v sádrovci (1%) značně snižuje pevnosti cem. pasty po 24 h ošetření. Po delší době (7—28 dnů) pevnosti, jak bylo zjištěno pokusy — které nejsou v textu zahrnuty — dosáhnou úrovně cementu s přirozeným sádrovcem.

Obr. 1. Kalorimetrické křivky cementu (HR).

Obr. 2. Kalorimetrické křivky cementu (PR).

Obr. 3. Vliv fluoridů a hexafluorosilikátů na stupeň hydratace cementu (24 h).

Obr. 4. Vliv CaF_2 a Na_2SiF_6 na stupeň hydratace cementu.

ИССЛЕДОВАНИЕ ВЛИЯНИЯ ХЕМИГИПСА В КАЧЕСТВЕ РЕГУЛЯТОРА СХВАТЫВАНИЯ НА СВОЙСТВА ЦЕМЕНТНЫХ ПАСТ

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Автором исследовалась возможность использования отходного гипса из производства суперфосфата и титановых белий в качестве регулятора схватывания цемента.

Для исследования кроме обыкновенного дигидрата использовали три образца хемигипса, отличающиеся различным содержанием загрязнений, и два промышленных клинкера портландского цемента, полученных мокрым и сухим путем технологического процесса.

Было доказано, что цементы, содержащие хемигипс, выделяются ретардацией роста прочности в начальном временном этапе при одновременном продолжении начала и времени схватывания.

Исследовали влияние фторосиликатов добавки фторидов и схватывания (CaF_2 , NaF , CaSiF_6 , Na_2SiF_6 и K_2SiF_6), которые могут входить в состав хемигипса в меньшем количестве, на степень гидратации цемента. Резким ретардационным действием отличаются гексафторосиликаты. Наибольшим ретардационным действием обладает Na_2SiF_6 , в то время как CaF_2 почти не оказывает влияния на собственный процесс гидратации.

Даже весьма низкое количество Na_2SiF_6 , содержащееся в гипсе (1 %), значительно понижает прочности цементной пасты после суток обработки. После более длительного времени (7—28 суток) прочности (данные, полученные экспериментальным путем в нашей статье не приводятся), достигли уровня цемента с природным гипсом.

Рис. 1. Калориметрические кривые цемента (HR).

Рис. 2. Калориметрические кривые цемента (PR).

Рис. 3. Влияние фторидов и гексафторосиликатов на степень гидратации цемента (сутки).

Рис. 4. Влияние CaF_2 и Na_2SiF_6 на степень гидратации цемента.