

PREPARATION AND PROPERTIES OF LOW HYDRATION HEAT PORTLAND CEMENT

HAMDY EL-DIDAMONY, AHMED AMER, SOLIMAN EL-HEMALY*, SAYED EL-ALFI*

Faculty of Science,
Zagazig University,
Zagazig, Egypt

*National Research Centre,
Dokki, Cairo, Egypt

Received August 14, 1997.

Several types of Portland cement having different characteristics are distinguished. The most important variables are the rate of hardening, the rate and total extent of heat evolution during hydration, and the resistance of hardened cement to chemical attack by sulphate and chloride solutions. The aim of the present work was to prepare three types of Portland cement, namely types I, II and IV, in the laboratory from locally available raw materials, and to study their hydration kinetics, development of compressive strength as well as the aggressive attack of 4 wt.% MgCl₂ solution on hardened pastes of the three Portland cements and of sulphate resisting cement pastes. The results show that the kinetics of hydration and the susceptibility to corrosion by chlorides increase with increasing LSF of the cement.

INTRODUCTION

Portland cement is a heterogeneous material comprising mainly alite (C₃S), belite (β-C₂S), tricalcium aluminate (C₃A) and ferrite solid solution (C₄AF), which make up about 90 % of the whole. It is to be therefore expected that the properties of the cement will be determined by the properties of the individual constituents and their relative contents in the cement as well as by the relative characteristics of the four major phases of Portland cement; namely, the rate of hardening, cementing quality, extent of heat of hydration and resistance to corrosion by sulphates [1].

Preparation and hydration of belite-rich cements was studied [2]. Three laboratory clinkers with different C₂S contents (28 - 57 wt.%) were prepared from available local raw materials. The clinkers were air-cooled and examined by X-ray diffraction. By fast cooling, the active crystal forms of α- and α'-C₂S were stabilized in the belite-rich clinker. The hydration phenomena were also studied on the cements prepared from the clinkers by DTA, TG and XRD at 3, 7, 28 and 90 days. The combined water and the liberated Ca(OH)₂ were quantitatively determined by TG and the hydration rate was studied. The hydration rate differs in the early stages, but progresses at the same rate after 28 days. No significant differences in the hydration products formed in the three cements were observed by XRD.

The properties of concrete made from low-heat cement containing a large amount of belite were studied [3]. The fundamental properties of concrete using 3 kinds of belite cements of which the belite content was

25 - 53 wt.% higher than that in moderate-heat Portland cement were investigated. The ultimate adiabatic temperature rise of concrete from the belite cements was between that of moderate-heat Portland cement and blended moderate-heat Portland cement containing blast-furnace slag and fly ash.

Hydraulic cement with a low heat of hydration was investigated [4]. Cement consisting of 60 - 95 wt.% C₂S and crystalline or glassy interstitial material comprising C₂AS, 3CaO.2SiO₂ (C₃S₂) and/or CaO.SiO₂ (CS) was mixed with 0.5 - 5.0 wt.% gypsum to give the product. Alternatively, 40 and more parts of mixtures consisting of 30 - 95 wt.% C₂S and crystal or glassy interstitial material comprising C₂AS, C₃S₂ and/or CS and moderate heat Portland cement, ordinary Portland cement and/or high-early strength Portland cement, were combined with 0.5 - 5.0 parts gypsum to give the product.

The hydration of the low-heat cement and its resistance to sea water and acid soils were studied [5]. It consisted of a 1:1 mixture of Portland cement and a cement containing predominantly 2CaO.SiO₂ and a glassy phase consisting of alkalis, CaO, Al₂O₃ and iron oxide. This latter cement was made from lime-deficient marl by firing and rapid cooling. The sulphate resistance of this cement results from its low C₃A content (< 5 wt.%) as compared to at least 10 wt.% in normal Portland cement.

The aim of the present work is to prepare three types of Portland cement, type I, II and IV cements, in laboratory from local commercial raw materials which are currently used for the production of Portland cement, and to study the course of hydration kinetics, development of compressive strength as well as the

aggressive attack of 4 wt.% $MgCl_2$ solution on the three Portland cements in comparison with pastes of sulphate resisting cement (SRC).

EXPERIMENTAL PART

The materials used in this study, namely limestone, clay and pyrite ash, were provided by Torah Portland Cement Company, Egypt. Table 1 shows the chemical analyses of these materials. The materials were ground in laboratory steel ball mill of 50-litre capacity to pass through a 200-mesh sieve. On the other hand, the prepared clinkers were ground using a porcelain mortar.

Table 1. Chemical composition of the starting materials (wt.%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
limestone	1.73	0.98	0.45	53.14	0.95	0.34
clay	71.71	8.76	4.35	3.88	1.19	0.53
pyrite ash	8.20	10.44	65.20	4.00	2.90	0.79
SRC	20.01	4.01	4.98	63.77	2.29	2.08

SRC: Sulphate resisting cement

Three laboratory clinkers of various compositions were prepared directly from the raw materials. The ingredients of each mix were thoroughly homogenized, mixed with water, moulded into a compact mass and heated at 1200 °C for two hours, then ground, remoulded with CCl_4 and fired at 1450 °C for two hours. The completeness of the solid-state reactions was checked by determining free lime and insoluble residue. The resulting clinkers designated OPC, MHPC and LHPC (Ordinary Portland cement, Moderate heat Portland cement and Low heat Portland cement respectively) were separately mixed with gypsum (2.5 wt.% SO_3) and ground to pass completely through a 200-mesh sieve. The chemical and phase compositions of the cements are given in tables 2 and 3.

Table 2. Chemical composition and properties of the prepared cements (wt.%).

	surface area (cm ² g ⁻¹)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LSF
OPC	2976	21.64	5.03	3.40	65.12	3.57	2.68	92.00
MHPC	3056	22.81	4.53	4.64	63.44	3.35	2.51	85.29
LHPC	3134	22.71	4.62	5.43	62.45	3.36	2.54	83.50

LSH: Lime saturation factor

OPC: Ordinary Portland cement.

MHPC: Moderate heat Portland cement.

LHPC: Low heat Portland cement.

Table 3. Phase composition of the prepared cements (wt. %).

	alite	belite	aluminate	ferrite
OPC	53.56	16.86	7.58	10.34
MHPC	39.41	35.75	4.16	14.11
LHPC	34.44	39.53	3.06	16.50

OPC: Ordinary Portland cement.

MHPC: Moderate heat Portland cement.

LHPC: Low heat Portland cement.

The X-ray diffraction patterns of the cements prepared are shown in figure 1 and show single peaks at 29.4, 32.3 and 34.4° (2θ), indicating the presence of the alite phase in the three cement compositions in the decreasing order: OPC, MHPC and LHPC. Also, the presence of a single peak at 33.3° (2θ) indicates the presence of C_3A , in smaller amounts in MHPC and LHPC in comparison with OPC. The results of chemical and mineralogical analyses show that the prepared cements are similar to Portland cement types I, II and IV, respectively, according to ASTM specification (C150-68) for OPC (type I), modified (type II) and low-heat (type IV).

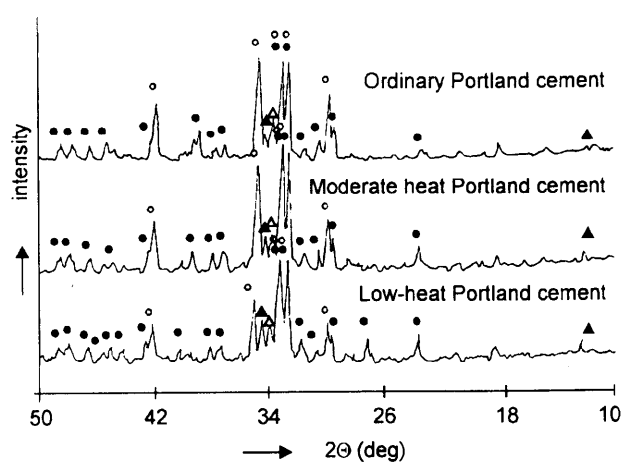


Figure 1. XRD patterns of prepared cements.

○ - C_3S , ● - $\beta-C_2S$, Δ - C_3A , ▲ - C_4AF

The mixing of the pastes was done as described in a previous work [6]. The pastes were moulded in 0.5 inch cubic moulds, cured in humidity chamber at 23 ± 1 °C for 24 hours, then demoulded and immersed in water till the time of testing. The kinetics of hydration was followed by determining the heat of hydration, and free lime and combined water contents after 3, 7, 28 and 90 days. Compressive strength was also measured at these intervals. Following the compressive strength test

the hydration was stopped [6]. The heat of hydration of cement was determined as described in BS 1370: 1991. The free lime content was determined as described elsewhere [7]. The combined water content was estimated on the basis of ignition loss of dried sample heated at 1000 °C for 30 minutes minus the weight of water in Ca(OH)₂.

Some selected hardened samples cured for 28 days (zero time) in tap water were separated and tested for their resistance to 4 wt.% magnesium chloride solution as aggressive solution. The samples were immersed in the solution for additional 1, 3, 6 and 9 months. At the end of each period, 3 cubes representing each mix were tested for their physico-mechanical properties as well as their kinetics of hydration. To compare the degree of chemical durability of all prepared cements, a commercially-produced sulphate resisting cement was also tested.

RESULTS AND DISCUSSION

The water of consistency as well as the time of initial and final set of cement pastes are listed in table 4. The results show that the water of consistency tends to increase with the increase in lime saturation factor (LSF). Higher LSF values indicate that the cement contains higher amounts of alite which needs more water to form paste of normal consistency. The results indicate that LHPC has a lower water consistency value than OPC and MHPC. As the belite content increases, the water of consistency diminishes due to the lower hydraulicity of the belite phase in early stages of hydration. The results also indicate that the LHPC followed by MHPC pastes have longer setting times than OPC pastes. This delay of setting is due to the increase in belite content and the decrease of water of standard consistency.

Table 4. Water of consistency and setting time of the prepared cement.

	cement type		
	I	II	III
water of consistency (wt.%)	27.5	26.0	24.5
initial setting time (min)	165	240	310
final setting time (min)	215	290	350

The values of heat of hydration for the cement pastes cured for 3, 7, 28 and 90 days are plotted in figure 2. It can be observed that the values of heat of hydration increase with curing time for all cement pastes. This is due to the continuous hydration of the clinker phases liberating heat during the hydration process. Also, as the alite and aluminate contents increase, the amount

of heat liberated in early stages rises. On the other hand, as the belite content increases, the heat of hydration is diminished. This is due to the higher hydraulicity of calcium aluminate and alite in early stages. Alite is considered to be thermodynamically unstable in comparison to belite [8]. Type I Portland cement pastes have higher values of heat of hydration than those of the low-heat as well as medium-heat Portland cement pastes. The latter have relatively higher contents of belite than the former. Since belite is characterized by lower hydraulicity towards water at early ages, the liberated amounts of heat are accordingly diminished and hence the total heat of hydration becomes lower.

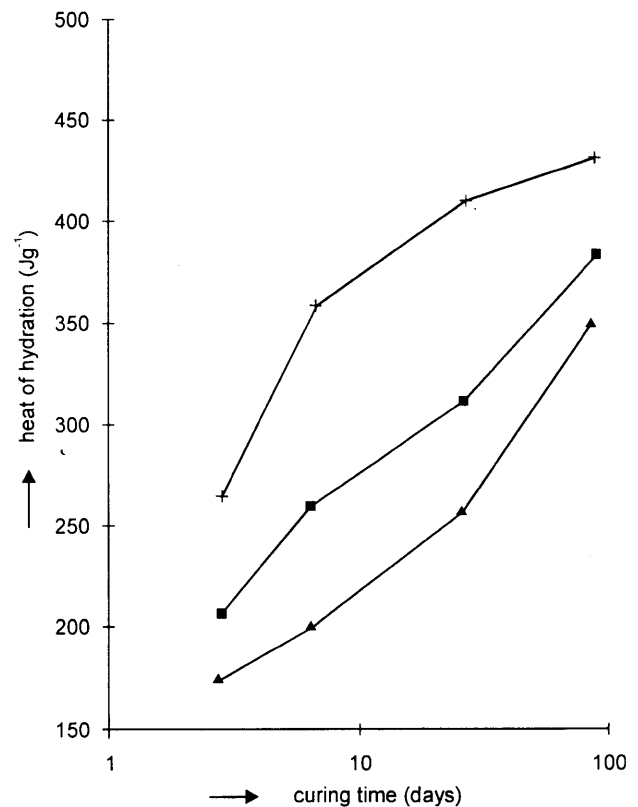


Figure 2. Heat of hydration of hardened Portland cement pastes. + – OPC, ■ – MHPC, ▲ – LHPC

The values of chemically combined water content for the different cement pastes cured for 3, 7, 28 and 90 days are plotted in figure 3. It can be seen that the combined water contents increase gradually with curing time for all hardened cement pastes, due to the progress of hydration and to the increasing amounts of hydration products formed. The value of LSF (lime saturation factor) is directly associated with the content of chemically combined water. This is mainly attributed to the fact that a cement of higher LSF usually contains a higher amount of alite. The results of OPC pastes exhibit

higher rates of hydration than those of the MHPC and LHPC pastes up to 28 days. Moreover, the MHPC and LHPC pastes possess higher rates of hydration at later ages (90 days). This is due to the relative contents of alite, aluminate and belite in the particular cement and to the high rate of hydration of belite at later ages.

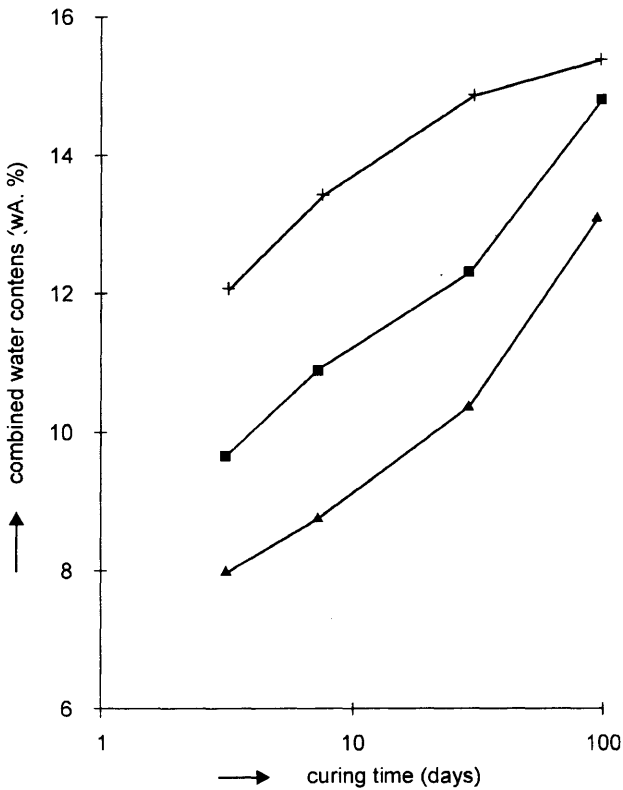


Figure 3. Combined water content in hardened Portland cement pastes.

+ - OPC, ■ - MHPC, ▲ - LHPC

The free lime contents in the hardened cement pastes are plotted as a function of curing time in figure 4. The free lime content increases with curing time for all cement pastes due to the continuous hydration of the silicate phases which liberates free $\text{Ca}(\text{OH})_2$. Also, the free lime content increases as the LSF as well as the alite content increase. It is also obvious that LHPC followed by MHPC pastes shows lower values of free lime content in comparison with OPC pastes at all ages due to the higher contents of belite in LHPC and MHPC. Belite liberates less $\text{Ca}(\text{OH})_2$ than alite in addition to its lower rate of hydration during the early stages of curing.

The compressive strength values of the hardened cement pastes cured for 3, 7, 28 and 90 days are plotted in figure 5. The compressive strength increases with curing time for all cement pastes. This is attributed to the increase of the amounts of hydrated products, in particular phases of tobermorite type. The calcium silicate hydrate (tobermorite-like gel) is the main source of com-

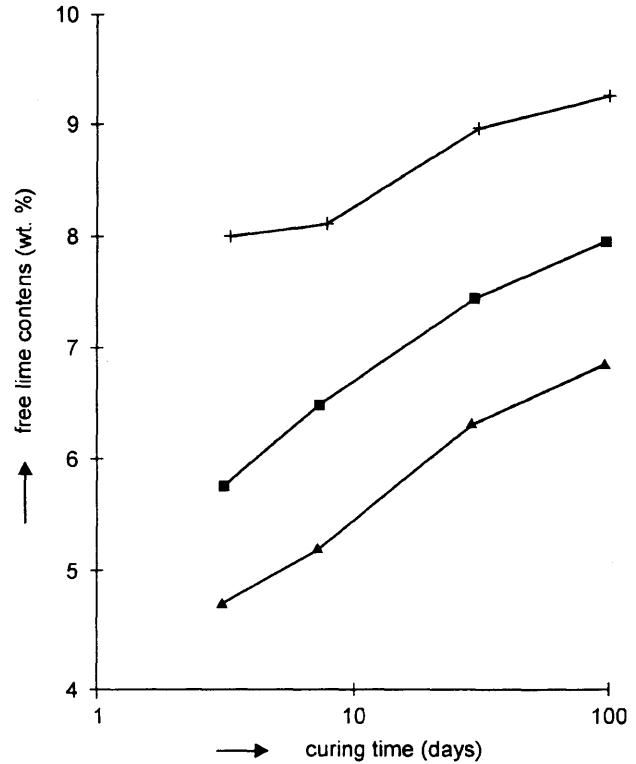


Figure 4. Free lime content in hardened Portland cement pastes.

+ - OPC, ■ - MHPC, ▲ - LHPC

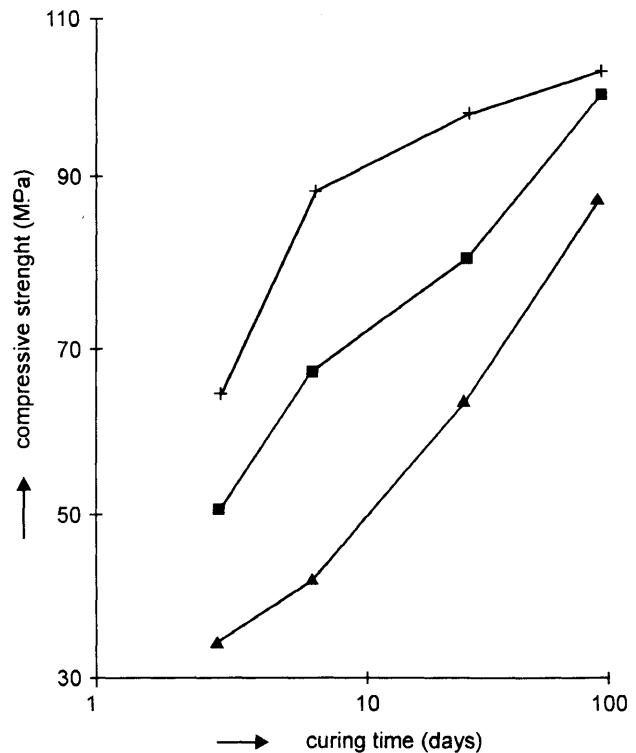


Figure 5. Compressive strength of hardened Portland cement pastes. + - OPC, ■ - MHPC, ▲ - LHPC

pressive strength. As the hydration proceeds, more hydration products and more cementing materials are formed. This leads to a corresponding increase in the compressive strength of hardened cement pastes. It is also seen that as the value of lime saturation factor (LSF) decreases, the amount of calcium silicate hydrate becomes less in early stages, but the rate of hydration increases linearly at later ages. The data also indicate that the rate of hardening of OPC pastes increases in early stages. On the other hand, LHPC and MHPC pastes give lower values of compressive strength in early stages up to 28 days and then increase (90 days). This is due to the fact that alite is responsible for most of early strength of cement pastes. With the decrease of LSF, the early strength development is lower whereas the rate of strength increase becomes more pronounced at later ages.

The compressive strength of cement pastes cured up to 9 months in 4 wt.% $MgCl_2$ solution is plotted as a function of time in figure 6. The compressive strength increases up to one month and then decreases gradually up to 9 months for OPC whereas the strength of sulphate-resisting cement goes on rising up to 3 months, then decreasing gradually up to 9 months. Sulphate resisting cement has a minimum content of C_3A . The loss in compressive strength of hardened cement pastes immer-

sed in $MgCl_2$ solution is attributed to the formation of calcium chloroaluminate hydrate $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 12H_2O$ which makes softening of the pastes and thus impairs the structure [9]. On the other hand, it can be observed that the compressive strength increases with curing time up to 9 months in the case of MHPC and LHPC pastes. This is attributed to the fact that these cements have lower amounts of alite which liberates $Ca(OH)_2$ than the commercial sulphate-resisting cement. The attack of $MgCl_2$ on cement paste is due to the reaction between $MgCl_2$ and the liberated $Ca(OH)_2$. The MHPC and LHPC have a high content of $\beta-C_2S$, a low one of C_3S and a small percentage of C_3A . Therefore, they show more resistance to chloride ions than commercially produced sulphate resisting cements.

The content of free lime in hardened cement pastes immersed in 4 wt.% $MgCl_2$ solution for up to 9 months is shown in figure 7. It is clear that with all of the Portland cement types involved the free lime content gradually decreased with exposure time. As the hydration proceeds, magnesium chloride reacts with liberated $Ca(OH)_2$ to produce $Mg(OH)_2$ and $CaCl_2$. The results show that LHPC and MHPC yield less free $Ca(OH)_2$ than OPC and sulphate resisting cements at all ages. This is due to the lower contents of alite in the former cements

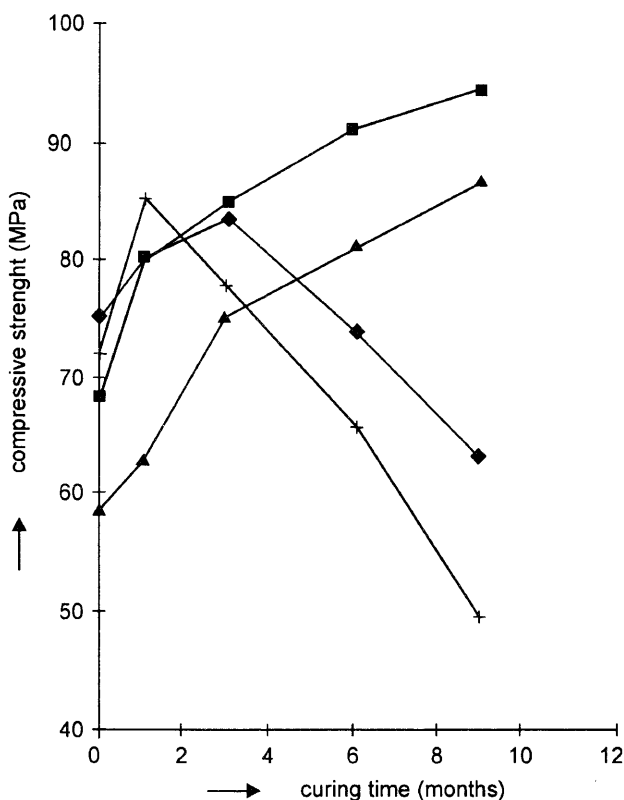


Figure 6. Compressive strength of hardened Portland cement pastes immersed in 4 wt.% $MgCl_2$ solution.
 + - OPC, ■ - MHPC, ▲ - LHPC, ◆ - SRC

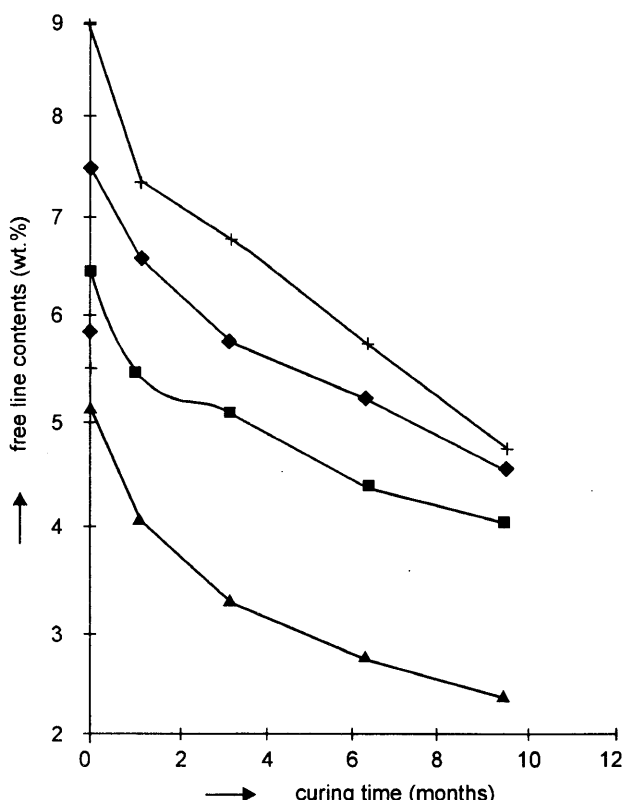


Figure 7. Free lime content in hardened Portland cement pastes immersed in 4 wt.% $MgCl_2$ solution.
 + - OPC, ■ - MHPC, ▲ - LHPC, ◆ - SRC

and higher contents of β - C_2S as well as lower C_3S and C_3A contents in the latter. The respective compositions seem to be more suitable with respect to chemical durability for the effects of chloride ions. These results are in a good agreement with the results of compressive strength determinations.

The contents of chloride ions in cement pastes immersed in 4 wt.% $MgCl_2$ solution up to 9 months are plotted in figure 8. The total chloride content increases gradually with time for all cement pastes due to the continuous diffusion of chloride ions into the cement paste. The LHPC and MHPC pastes show much lower contents of chloride ions than OPC and SRC at all ages. This is explained by the fact that these two types of Portland cement have the lowest content of free $Ca(OH)_2$ as a result of the higher amounts of alite which produces a large quantity of $Ca(OH)_2$ during hydration. Figure 9 shows the XRD patterns of hardened MHPC and LHPC pastes immersed in 4 wt.% $MgCl_2$ solution for 0, 3 and 9 months. Samples hydrated for 28 days (zero time) in fresh water show broad peaks of calcium sulphoaluminate hydrates, either ettringite or monosulphate, as well as of calcium aluminate hydrate. After a three-month immersion in 4 wt.% $MgCl_2$, the peak of calcium-chloro-

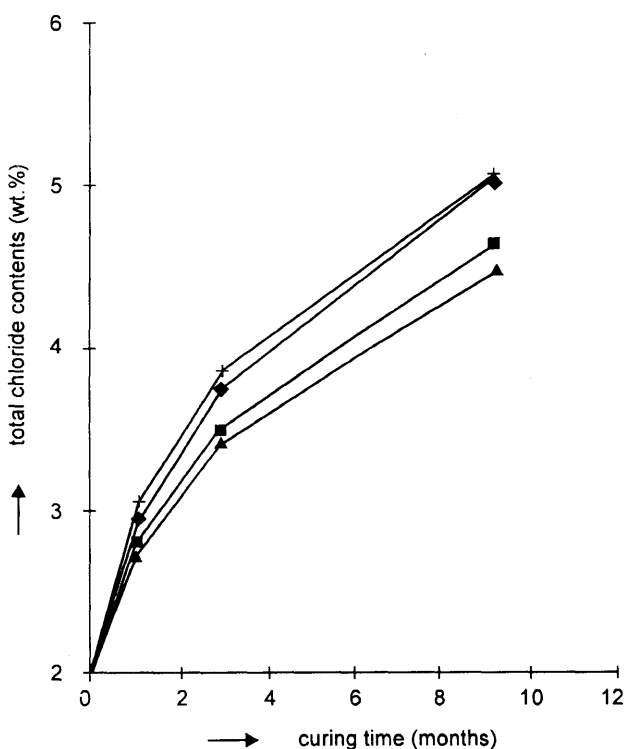
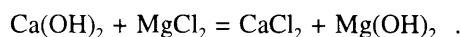


Figure 8. Total chloride content in hardened Portland cement pastes immersed in 4 wt.% $MgCl_2$ solution.

+ - OPC, ■ - MHPC, ▲ - LHPC, ◆ - SRC

aluminate hydrate has grown and there is some little growth of sulphoaluminate hydrate peaks. On prolonged

hydration, the intensity of chloroaluminate peaks is enhanced and the peaks of $Ca(OH)_2$ diminish. The increase in chloroaluminate content is due to the continuous interaction of calcium aluminate with the chloride ions from the surrounding medium. Magnesium chloride reacts with liberated $Ca(OH)_2$ and produces $Mg(OH)_2$. The low solubility of $Mg(OH)_2$ shifts the equilibrium to the right:



Therefore, the content of $Ca(OH)_2$ in the samples immersed in $MgCl_2$ solution for 9 months is lower than in samples immersed in tap-water. LHPC obviously liberates smaller amounts of $Ca(OH)_2$ than MHPC, so that the former has a higher resistance to the chloride solution.

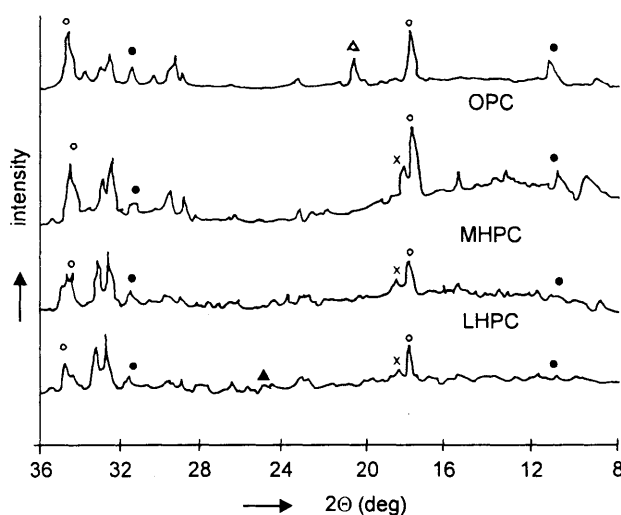


Figure 9. XRD patterns of hardened Portland cement pastes immersed in 4 wt.% $MgCl_2$ solution. O - $Ca(OH)_2$, ● - $3CaO \cdot Al_2O_3 \cdot CaCl_2$, × - $Mg(OH)_2$, Δ - $3CaO \cdot Al_2O_3 \cdot 3Ca(SO_4) \cdot 0.31H_2O$

CONCLUSION

The following conclusions may be reached on the basis of the above findings:

1. The water of consistency increases with increasing LSF; LHPC has the lowest standard water to cement ratio values in comparison with MHPC and OPC pastes. On the other hand, the times of initial and final set of LHPC are longer than those of MHPC and OPC. Ordinary Portland cement pastes need more water of consistency and shorter setting times than MHPC and LHPC pastes.
2. The free lime content and combined water content in the cement pastes increase with the increase of LSF or decrease in the order OPC, MLPC and LHPC.
3. LHPC shows a lower rate of hardening in early stages but a higher one at later ages.

4. LHPC shows a good resistance to $MgCl_2$ solution, followed by MHPC and OPC. The compressive strength of LHPC and MHPC increases on exposure to chloride solution up to 9 months. On the other hand, the compressive strength of SRC (sulphate resisting cement) paste increases up to 3 months and then decreases, while the paste of OPC gains strength for one month and then starts to lose it. It can be concluded that the chemical durability of Portland cement increases with decreasing LSF (lime saturation factor).

References

1. Lee F.A.: *The Chemistry of Cement and Concrete*, 3rd Ed., Edward Arnold Ltd., London 1979.
2. Ftikas C., Philippou T.: *Cem.Concr.Res.* 20, 934 (1990).
3. Sone T., Fujiama O., Tanimura M.: *Semento Konkurito Ronbunshu* 46, 392 (1992).
4. Hobara T., Sawaki D., Nomura K., Nunma T.: *Jpn. Kokai Tokyo Koho JP 0560*, 192 [93 570 192] (1991).
5. Hessling H.W.: *Ger.Offen.* 2,322, 889 (Cl CO 4b), 6 (1973).
6. El-Didamony H., Haggag M.Y., Abou-El-Enein S.A.: *Cem.Concr.Res.* 8, 351 (1978).
7. Kondo R., Abou-El-Enein S.A., Diamon M.: *Bull.Chem.Soc.Japan* 48, 222 (1975).
8. Brunauer S., Greenberg S.A.: *Proc. 4th Int. Symp. Chem. Cem.*, Vol. 43 VI, p.153, Washington 1960.
9. Biczok I.: *Concrete Corrosion and Concrete Protection*, Akadimial Kiado, Budapest 1972.

Submitted in English by the authors.

PŘÍPRAVA A VLASTNOSTI PORTLANDSKÉHO CEMENTU SE SNÍŽENÝM HYDRATAČNÍM TEPEM

HAMDY EL-DIDAMONY, AHMED AMER,
SOLIMAN EL-HEMALY*, SAYED EL-ALFI*

*Faculty of Science,
Zagazig University,
Zagazig, Egypt*

**National Research Centre,
Dokki, Kairo, Egypt*

Vlastnosti cementu jsou určovány vlastnostmi jeho složek a jejich relativními obsahy v cementu, a dále čtyřmi relativními charakteristikami portlandského cementu, jmenovitě rychlostí tvrdnutí, hydratačním teplem, a odolností proti síranům a chloridům. Celkové hydratační teplo betonu z belitického cementu leželo mezi hydratačním teplem betonu s cementem se středním hydratačním teplem, a hydratačním teplem betonu se smíšeným cementem se středním hydratačním teplem, obsahujícím struskový granulát a popílek. Cílem této práce bylo laboratorně připravit tři typy portlandského cementu, jmenovitě I, II a IV, a to z místních dostupných surovin, a zjišťovat jejich kinetiku hydratace, pevnosti v tlaku a odolnost proti síranové a chloridové korozi ve srovnání se síranuvzdorným cementem.

Příslušné tři slínky byly připraveny vypálením surovin při teplotě 1450 °C, pomletím a opětovným výpalem při teplotě 1450 °C po dobu dvou hodin. Úplnost výpalu byla zjišťována stanovením volného vápna a nerozpustného zbytku. Kinetika hydratace byla sledována stanovením hydratačního tepla, obsahu volného vápna, obsahu vázané vody a zjišťováním pevnosti v tlaku zatvrdlých kaší až do stáří 90 dnů.

Výsledky ukazují, že množství záměsové vody pro získání normální konsistence stoupá s obsahem alitu a klesá s obsahem belitu. Doba tuhnutí se prodlužuje a hydratační teplo se snižuje s obsahem belitu. Množství vázané vody a také obsah volného vápna se snižují s obsahem belitu, a nejnižší hodnoty těchto charakteristik poskytuje portlandský cement s nízkým hydratačním teplem. Kaše z běžného portlandského cementu vykazují vyšší krátkodobé pevnosti. Cementy s nízkým a středním hydratačním teplem mají naopak nižší 28-denní a vyšší 90-denní pevnosti. Pevnost v tlaku tělísek z běžného portlandského cementu ponořená ve 4% roztoku $MgCl_2$ se zvyšuje do stáří jednoho měsíce, pak se postupně snižuje až do stáří 9 měsíců, zatímco pevnost síranuvzdorného cementu vzrůstá do 3 měsíců a pak klesá do 9 měsíců. Pevnost v tlaku zatvrdlých kaší z cementu s nízkým a středním hydratačním teplem se zvyšuje až do stáří 9 měsíců. Obsah volného vápna a chloridů v tělískách ponořených v roztoku chloridu během doby klesá, a je rovněž nižší v cementech s vyšším obsahem belitu. Ukázalo se, že vůči roztoku $MgCl_2$ vykázal nejvyšší odolnost cement s nízkým hydratačním teplem, a po něm následoval cement se středním hydratačním teplem a posléze běžný portlandský cement.