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Effect of MgO and gypsum content on long-term expansion of low heat Portland slag cement with slight expansion

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Abstract

The expansion of low heat Portland slag cement with slight expansion (LSE cement) was studied by XRD, SEM and test methods for strength and expansion. Results indicated that under the condition of 4.5–5.0% MgO in clinker and 2.8–3.4% SO_3 in cement, ettringite expansion and brucite expansion produced by periclase hydration in the paste had continuity, entirety and stability. Periclase hydration in the paste started at about 60 days and was completed up to 2000 days and ettringite was stable from 3 to 2000 days. At the ages of 28, 90, 365, 730 and 2000 days the expansion of the paste reached 0.08–0.13%, 0.09–0.14%, 0.12–0.17%, 0.13–0.18% and 0.15–0.21%, respectively. At the ages of 2, 28 and 180 days the autogenous volume deformation of mass concrete made out of LSE cement was positive and was 0.0042%, 0.0050% and 0.0066%, respectively and the prestress of the concrete with 2.0% steel bar content was 0.069, 0.060 and 0.082 MPa, respectively. The results suggest that using this cement in mass concrete may compensate for a part of its thermal shrinkage and autogenous shrinkage.

Keywords: Brucite; Ettringite; Expansion; Long-term performance; Low heat Portland slag cement

1. Introduction

Low heat Portland slag cement has been used worldwide in dam construction for 60 years. Concrete for huge projects, such as the Three Gorges Dam in China must be made mainly from this type of cement. It has high durability, but the cement has no expansive property in itself. Much research work has been done over the years, aimed at achieving shrinkage-compensating concrete with magnesia (MgO) and sulphate (SO_3).

Mehta [1] tried to use the expansive property of light-burnt MgO in order to solve the problem of thermal shrinkage in mass concrete for dams in general. White [2] investigated the expansion of cement made from high MgO clinker (4.45–7.21% MgO, clinker formation at about 1500 °C) and showed that the expansion produced by periclase hydration reached stability at 4–6 years and the expansive increment during the period from 1 to 5 years was 0.15–0.20%. In the 1980s Lou et al. [3] studied Portland slag cement with high MgO clinker, which was used in the Baishan dam, and with the concrete made from this cement having slightly long-term expansion there is no crack in the dam in general. A majority of practical expansive cements have depended on the modification of a Portland cement in such a way as to increase the formation of ettringite. Type S cements are Portland cements high in C_3A and with suitable contents of calcium sulphate. In the 1970s Lou et al. [4] investigated low heat slag cement with ettringite expansion, which was used in the weir (81 m in length) of the Jinshuitan dam, and using slip-form construction no crack exists in the weir without construction joint. Odler et al. [5] studied the property of cements with high C_4AF content and low C_3A content, the expansion of these cements remained insignificant even after additions of up to 4.5–6% SO_3, and expansive hydrate ettringite remained stable at long-term ages. Cohen [6] reviewed theories of the expansion mechanism and a majority of

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workers [7,8] have attributed expansion to forces exerted by the growth of the ettringite crystals.

In order to compensate for the thermal shrinkage and autogenous shrinkage of the mass concrete for this dam which is the subject of this paper, a low heat Portland slag cement with slight expansion (LSE cement) has been investigated. The expansive properties have been achieved not only by increasing the gypsum addition to produce suitable expansive source ettringite, but also by using high MgO clinker in order to produce expansive source brucite. Owing to the use of both gypsum and periclase, the expansive property of this LSE cement must be monitored over a long period.

2. Preparation of sample and test methods

2.1. Test materials

The chemical composition of the clinker that comes from the plant in trial production and those of the gypsum and slag are shown in Table 1.

2.2. Preparation of LSE cement sample

All of the LSE cement samples with variable SO_3 content were made out of the above clinker, slag and gypsum, and the ratio of clinker to slag was kept at 1:1. Their codes are L*i* and the SO_3 content is *i*%. All of the samples were ground to a specific surface area of 300–350 m^2/kg (Blaine).

2.3. Preparation of cement paste and expansion test specimens

Linear expansion of cement was tested in accordance with the linear expansion test for cement paste (JC313, Chinese Standard). The cement paste was prepared at standard consistency using a planetary mixer (ISO). For the pastes, a cement: water ratio of 1:0.25–0.27 was used. The mixing consists of a sequence of mixings that involve a total of 2.0 min at a paddle speed of both 62 rpm (revolution) and 140 rpm (rotation), a 15 s stop and a total of 2.0 min at a speed of both 125 rpm (revolution) and 285 rpm (rotation). The fresh paste was cast into square-bar molds 25 mm × 25 mm × 280 mm. The paste samples which were cured at (20 ± 2) °C and above 90% R.H. moisture were demolded after 24 h when the initial length was measured by screw micrometer (precision 0.01 mm), and then stored in water at (20 ± 2) °C till next test. Three square-bars were tested for each sample at 2, 3, 7, 14, 28, 60, 90, 180, ..., 1600 and 2000 days.

2.4. Preparation of mortar and strength test specimens

Cement strength was determined in accordance with the plastic mortar strength test (GB177, Chinese Standard). For the mortars, a cement:sand:water ratio of 1:2.5:0.44 was used and the sand with the size range of 0.25–0.65 mm is silica sand. The mixing involves a total of 3.0 min both at a paddle speed of 137 rpm and at a pot reverse speed of 65 rpm. The fresh mortar was cast into square-bar molds 40 mm × 40 mm × 160 mm on a vibrating table. The mortar samples which were cured at (20 ± 2) °C and above 90% R.H. moisture were demolded after 24 h and then stored in water at (20 ± 2) °C till test. Three specimens were tested for each sample at each age. The span for flexural strength and the area for compressive strength are 100 mm and 62.5 mm × 40 mm, respectively.

2.5. Preparation of concrete and tests of autogenous volume deformation and prestress

Autogenous volume deformation (namely autogenous expansion or shrinkage) of concrete was tested according to SD105 (Chinese Standard), and the sample was ∅200 mm × 500 mm cylinder and was cured at (20 ± 1) °C or (38 ± 1) °C under the sealed environment (no exchange of water or moisture between sample and environment) (Fig. 1). Method for prestress of concrete was acted also in accordance with SD105 and the sample was ∅150 mm × 450 mm cylinder with 2.0% or 2.6% bar content and was cured at (20 ± 1) °C under the sealed environment (Fig. 1). For the above concrete, a cement:water:sand:coarse aggregate (5–80 mm crushed granite stone) ratio of 1:0.55:3.66:8.46 was used. The coarse aggregate consists of 50% the large crushed stone 40–80 mm, 20% the middle 20–40 mm and 30% the small 5–20 mm. A forced concrete mixer was used for concrete mixing. The fresh concrete, from which 40–80 mm coarse aggregate was sifted out, was cast into above cylinder molds. Three cylinders were tested for each sample at

Table 1
Chemical composition of test materials wt%

Specimen	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Periclase	f-CaO	SO_3	C_3S	C_2S	C_3A	C_4AF
Clinker	20.33	5.39	5.86	61.40	4.84	2.8–3.1	0.30	0.95	49.7	20.8	4.3	17.8
Gypsum	11.95	2.97	1.26	25.10	2.05	/	/	30.31	/	/	/	/
Slag	34.51	14.62	1.07	36.10	8.81	/	/	/	/	/	/	/

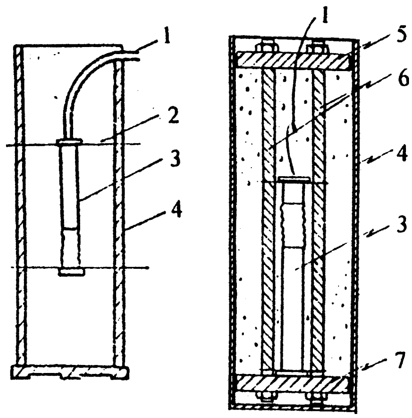

Fig. 1. Test installations of autogenous volume deformation (left) and prestress (right) for concrete. 1: Conducting wire; 2: iron wire; 3: strain gage; 4: water or moisture insulation layer made from steel plate with tin soldering; 5: upper steel plate; 6: steel bar; 7: lower steel plate.

some ages. The apparatus for both autogenous volume deformation and prestress was a strain gage (DI-25 type, made in China). The basic value for deformation and prestress was determined at the age of 1 day.

2.6. Preparation of hydrated sample of LSE cement and test

Using the above cement pastes cured in water at (20 ± 2) °C at some ages, hydrated samples were observed by SEM. And the samples which were ground to a specific surface area of 300–350 m^2/kg (Blain) were analysed immediately by XRD in order to indicate the variation of expansive hydrates with time.

2.7. Preparation of hydrated sample of clinker and test

The above clinker added with 3.0% gypsum was ground to a specific surface area of 300–350 m^2/kg (Blain). The preparation of the clinker paste sample was the same as that of the above cement paste. The samples were cured first at (20 ± 2) °C and above 90% R.H. moisture at 24 h and then in water at (20 ± 2) °C, (50 ± 3) °C, (70 ± 3) °C and (90 ± 3) °C, respectively. The hydrated samples in water at different temperatures at some ages, which were ground to a specific surface area of 300–350 m^2/kg, were analysed by XRD in order to know when the periclase started to hydrate into brucite and when periclase hydration was almost completed.

2.8. Equipment and test conditions

X-ray diffraction analyser: D/Max-α A type, Cu Kα radiation, tube electric current 50 mA and tube voltage 40 kV. Scanning electron microscope: ASM-SX type, its energy spectrum is EDAX-9100.

3. Results and discussion

3.1. Variation of hydration of periclase in clinker with curing temperature

Fig. 2 shows the variation of hydration of periclase in clinker with curing temperature according to the characteristic peak of periclase at 42.8°(2θ) and the characteristic peak of brucite at 37.9°(2θ) in XRD powder pattern. When the hydrated samples of clinker with 3.0% gypsum were cured in water at 90 °C, the characteristic peak of periclase declined gradually during the period from 7 to 120 days and almost disappeared till 120 days, and coincidentally the peak of brucite increased gradually during the same time. When cured in water at 50 °C, the peak of periclase almost disappeared till 300 days and the peak of brucite appeared for the first time at 28 days. And when cured in water at 20 °C, the peak of brucite appeared for the first time at 60 days, and the peak of periclase declined slowly during the period from 60 to 300 days. These results appear that the rate of periclase hydration increased sharply with the curing temperature increasing, and cured in water at 20 °C the periclase hydration was slow and the periclase started to hydrate into brucite at about 60 days.

3.2. Variation of ettringite and periclase with time in hardened LSE cement paste

Fig. 3 shows the variation of ettringite with time in paste determined by XRD powder pattern. From 3 to 28 days the characteristic peak of ettringite at 9.1°(2θ) increased with time. From 28 to 2000 days the peak was stable and did not decrease. And from images (Fig. 4) of hydrates of hardened LSE cement paste by SEM, the morphology of ettringite is known. There were many fibrous crystals of ettringite in the pore of paste, 7.5–15 μm in length, 0.3 μm in diameter, and aspect ratio

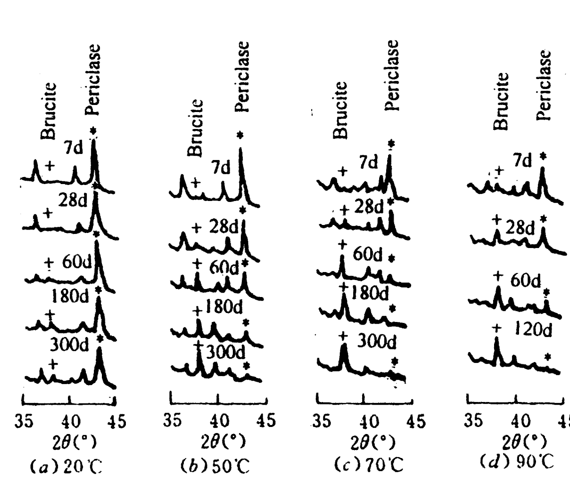

Fig. 2. XRD patterns of paste sample of clinker added with 3.0% gypsum hydrated at different temperatures.

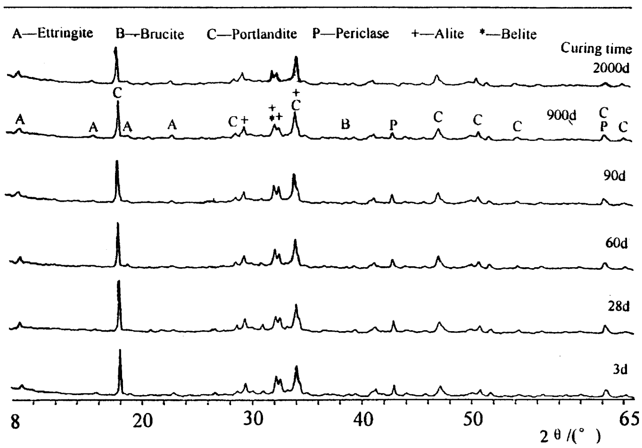

Fig. 3. Variation of expansive hydrates in hardened LSE cement paste with time (XRD, sample L3.1).

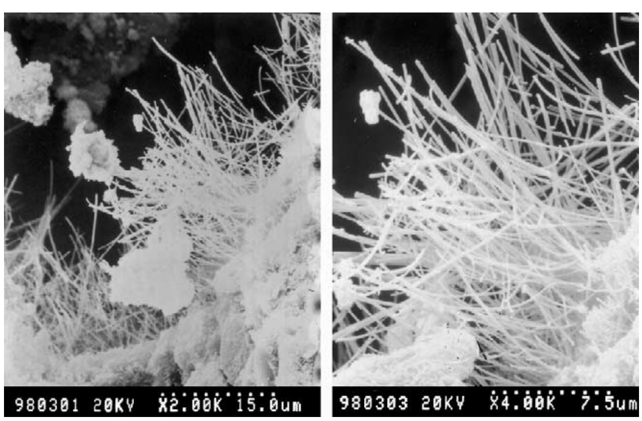

Fig. 4. SEM images of ettringite in hardened LSE cement paste (sample L3.1, at the age of 28 days).

25–50. It is clear that ettringite is stable during the period from 3 to 2000 days.

Fig. 3 also shows the periclase hydration in the long term. From 3 to 28 days these characteristic peaks ($2\theta = 42.8°, 62.2°$) of periclase did not decrease. During the period from 28 days to 900 days these peaks declined gradually, and disappeared till 2000 days. These results appear that the periclase starts to hydrate into brucite at about 60 days and periclase hydration has almost been completed till 2000 days.

3.3. Long-term strength development of LSE cement

Table 2 shows the strength development of LSE cement up to 2000 days. Flexural strengths decreased obviously at early age, but increased slightly at 365, 900 and 2000 days with SO_3 content increasing. Compressive strengths also decreased obviously at 3 day, and increased later. In summary both flexural and compressive strengths from 3 to 2000 days increased gradually in spite of variable SO_3 content. The results seem to indicate that the hydration of periclase does not harm strengths and the strengths develop regularly. According to the variation of compressive strengths with variable SO_3 contents, those of sample L2.8, L3.1 and L3.4 were well both at the early age and in the long term.

3.4. Variation of expansion of hardened LSE cement paste with variable SO_3 content

Fig. 5 shows variation of expansion of hardened LSE cement paste with variable SO_3 content. At the age of 28 days, the expansion increased mainly with SO_3 content increasing. For example, the expansion of samples L2.0, L2.8, L3.1, L3.4, L3.7 and L4.0 was 0.056%, 0.079%, 0.116%, 0.132%, 0.189% and 0.279%, respectively. Among them, the expansion of L3.1 and L4.0 was 107% and 398%, respectively, more than that of L2.0. The results seem to indicate that with SO_3 content increasing the necessary ettringite expansion is obtained, which makes the hardened cement paste more compacted and produces internal prestress and external volume expansion. The suitable ettringite expansion can help the following expansive energy produced by periclase hydration to be transformed greatly into external volume expansive work.

3.5. Variation of long-term expansion of hardened LSE cement paste with periclase hydration

Fig. 6 shows variation of long-term expansion of hardened LSE cement paste with periclase hydration. The periclase hydration (brucite expansion) started at about 60 days and the expansive increment produced by periclase hydration was considerable during the period from 60 to 730 days, which amounted to 50–60% of the total increment. Then the expansive increment increased slightly and then the expansion tended to be stable during the period from 1600 to 2000 days, when periclase hydrated almost completely. Taking sample L3.1 as an example, its expansion was 0.116%, 0.119%, 0.155%, 0.156%, 0.178%, 0.182% and 0.188%, respectively, at the ages of 28, 60, 365, 730, 1200, 1600 and 2000 days.

Despite of each sample's MgO content being nearly equal, the same expansive energy produced by periclase hydration did not do the same external volume expansive work, which increased with SO_3 or ettringite content increasing at early age. For example of sample L2.0, L3.1 and L4.0 (containing the same MgO content in clinker, and containing 2.0%, 3.1% and 4.0% SO_3 content in cement, respectively), their expansive increments were 0.068%, 0.069% and 0.103%, respectively, during the period from 60 to 2000 days.

In summary, the expansion and strength of sample L3.1 at some ages was better than other samples, so it was taken as the control sample in this paper and in industrial production.

Table 2
Variation of mortar strengths of LSE cement with variable SO_3 content

Sample	SO_3 content (%)	Flexural strength (MPa) (days)						Compressive strength (MPa) (days)					
		3	28	90	365	900	2000	3	28	90	365	900	2000
L2.0	2.0	3.4	7.4	9.6	9.3	9.3	9.6	13.0	42.4	67.7	74.5	76.4	81.6
L2.5	2.5	3.2	7.5	9.8	9.7	10.6	10.2	13.0	43.1	64.7	73.8	73.3	78.2
L2.8	2.8	3.1	7.6	10.2	9.7	9.3	10.0	12.6	42.8	63.9	71.3	72.9	79.6
L3.1	3.1	2.8	7.7	9.7	9.9	9.6	10.4	11.4	39.2	59.4	69.4	70.1	77.0
L3.4	3.4	2.3	7.4	9.9	9.4	10.5	10.2	9.5	40.3	59.6	67.0	71.3	76.0
L3.7	3.7	2.2	7.6	9.8	9.8	10.1	10.6	8.3	38.2	56.9	65.1	66.9	77.7
L4.0	4.0	2.1	7.6	10.0	9.6	9.8	10.4	8.1	39.3	56.6	62.8	67.3	77.9

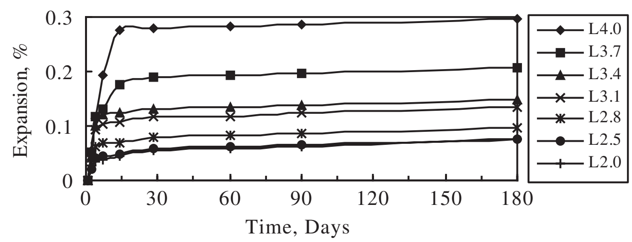

Fig. 5. Variation of expansion of hardened LSE cement paste with variable SO_3 content.

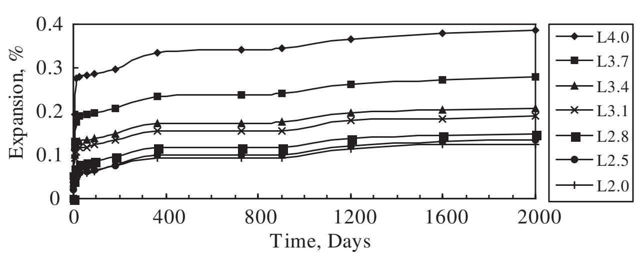

Fig. 6. Variation of expansion of hardened LSE cement paste with periclase hydration and variable SO_3 content.

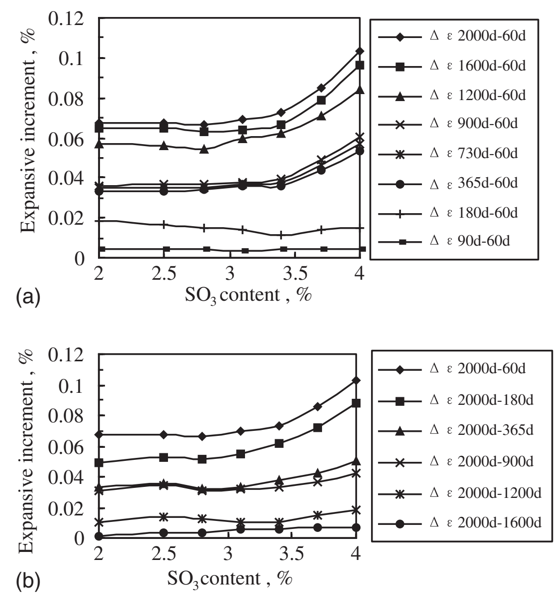

Fig. 7. Variation of expansive increments of hardened LSE cement paste with variable SO_3 content and time.

3.6. Variation of expansive increment of hardened LSE cement paste with variable SO_3 content

Fig. 7a shows variation of expansive increment of hardened LSE cement paste with variable SO_3 content and time. Expansive increments of samples L2.0, L2.5, L2.8, L3.1 and L3.4, during the period from 60 to 365 days, to 730 days, to 1200 days and to 2000 days, were almost equal, and were 0.036%, 0.037%, 0.057–0.063% and 0.068–0.073%, respectively. These increments had almost nothing to do with SO_3 content, but mainly with periclase hydration (brucite expansion). However expansive increments of both L3.7 and L4.0 during the same periods as above were higher than those of the above samples, moreover these increased with SO_3 content increasing. Especially for sample L4.0, its increments reached 0.053%, 0.057%, 0.084% and 0.103% during the same periods. Furthermore, during the period from 60 to 2000 days the increment of L4.0 was 1.53 times over that of L2.0.

According to Fig. 7b expansive increments of L2.0, L2.5, L2.8, L3.1, L3.4 decreased gradually during the periods from 60, 180, 365, 730, 900, 1200, 1600 days to 2000 days. And among them the expansive increment of the above samples was only 0.001–0.006% during the period from 1600 to 2000 days. The results indicate that during the period from 1600 to 2000 days the expansion of the above samples tends to stability and periclase hydrates almost completely.

3.7. Autogenous volume deformation of concrete made out of LSE cement

Fig. 8 shows the variation of autogenous volume deformation of C20 mass concrete sample made out of LSE cement (sample L3.1) with temperature and time. Within 2 days the autogenous volume deformation of the sample cured at 20 °C increased quickly and reached 0.0042%, and then the deformation increased very slowly. At 28, 40, 90 and 180 days the deformation was 0.0050%, 0.0053%, 0.0059% and 0.0066%, respectively.

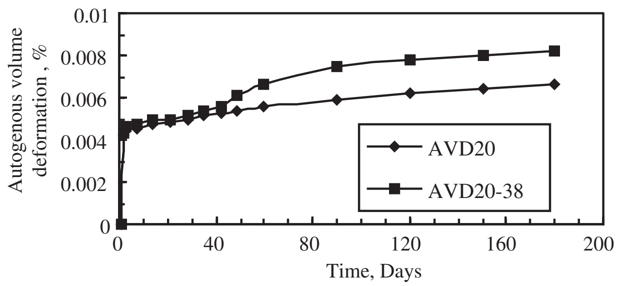

Fig. 8. Variation of autogenous volume deformation of C20 mass concrete made out of LSE cement with temperature and time.

Among them the deformation increment during the period from 40 to 180 days only produced 0.0013%. For the sample cured at 20 °C till 40 days at first and then cured at 38 °C, the deformation increment during the period from 40 to 180 days reached 0.0026%, which was 2.0 times over that of the sample cured at 20 °C all the time. These results can be explained by noting that periclase hydration is sensitive to temperature, namely with temperature increasing the hydration increases. The results seem to indicate that the concrete made from LSE cement may compensate for a part of its temperature shrinkage and autogenous shrinkage.

3.8. Prestress of concrete made out of LSE cement

Fig. 9 shows the variation of prestress of C20 mass concrete sample made out of LSE cement (sample L3.1) with steel bar content and time. Within 2 days prestresses of the concrete with 2.0% and 2.6% steel bar content increased quickly and reached to 0.069 and 0.092 MPa, respectively, and then prestresses increased very slowly. Owing to relaxation of stress the prestress went to a valley during 14–28 days. After 28 days the expansion produced from ettringite and periclase hydration compensated for the relaxation of stress. At 28, 40, 90 and 180 days the prestress was 0.060, 0.066, 0.078 and 0.082 MPa (2.0% steel bar content), and 0.070, 0.082, 0.092 and 0.096 MPa (2.6% steel bar content), respectively. Among them the prestress increment during the period from 28 to 180 days was 0.022 MPa (2.0% bar content) and 0.026 MPa (2.6% bar content), respectively. The results seem to indicate that the concrete made out of LSE cement may make itself more compacted and may compensate for a part of its thermal shrinkage and autogenous shrinkage.

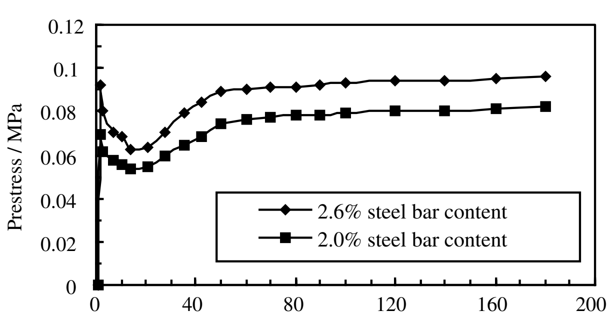

Fig. 9. Variation of prestress of C20 mass concrete made out of LSE cement with steel bar content and time.

3.9. Continuity, entirety and stability of ettringite and brucite expansion in hardened LSE cement paste

We choose the high MgO clinker, slag and gypsum to produce the LSE cement. We make full use of not only the ettringite expansion at early and medium ages, but also the brucite expansion (periclase hydration) at medium and later ages. Only when SO_3 content reached 2.8–3.4%, the hardened cement paste could produce necessary ettringite expansion before the age of 28–60 days to fill up capillary, to compact the paste and to produce some prestress and external volume expansion. Only on the above basis, brucite expansive energy after the age of 60 days could be fully used as external volume work to compensate for the autogenous and thermal shrinkage effectively. So it is concluded that ettringite and brucite expansion in hardened LSE cement paste has continuity, entirety and stability.

4. Conclusion

The following conclusions may be drawn from the obtained experimental data:

(1) Periclase hydration in hardened LSE cement paste started at about 60 days and was completed up to 2000 days. The expansive increment produced by periclase hydration during the period from 60 to 730 days was 50–60% of the total increment and then the increment increased slowly, and the expansion produced by periclase hydration tended to stability during the period from 1600 to 2000 days.
(2) In LSE cement containing 2.8–3.4% SO_3, ettringite in hardened LSE cement paste was stable from 3 to 2000 days. At the age of 28 days, the expansion of hardened LSE cement paste reached 0.08–0.13%.
(3) The flexural and compressive strengths of LSE cement mortar from 3 to 2000 days age increased gradually and the strength development was normal.
(4) At the ages of 90, 365, 730 and 2000 days, the expansion of the LSE cement with 4.5–5.0% MgO in clinker and 2.8–3.4% SO_3 in cement was 0.09–0.14%, 0.12–0.17%, 0.13–0.18% and 0.15–0.21%, respectively. The autogenous volume deformation of C20 mass concrete made out of LSE cement was positive and was 0.0042%, 0.0050%, 0.0066% and the prestress of the concrete with 2.0% steel bar content

was 0.069, 0.060, 0.082 MPa at the ages of 2, 28, 180 days, respectively.

(5) Not only ettringite expansion but also brucite expansion was utilized in LSE cement. It was concluded that ettringite and brucite expansion in hardened LSE cement paste had continuity, entirety and stability.

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