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The positive effect of nano-magnesium oxide (MgO) on Expansion the cement paste in concrete

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Abstract

Based on the application of MgO in clinker and light burnt MgO to the thermal and autogenously shrinkage compensation of dam concrete, the variation of expansion properties of cement paste with nano-MgO was studied. Results indicated that the maximum content of nano-MgO added in ordinary Portland cement reached up to 8% for soundness. The hydration rate of nano-MgO cured in water at 20 C was low, and a little of nano-MgO existed till the age of 365 days. The paste expansions increased gradually with the increase of the nano-MgO content cured at 20 C in water within 365 days and through autoclaving after the ages of 365 days. The results suggest that added with nano-MgO and mixed with light burnt MgO, the shrinkages of dam concrete may be completely compensated in safety.

Keywords: Cement paste, Dam concrete, Expansion.

Introduction

The free MgO in clinker at the clinkering temperature of 1400– 1500 C is in a dead-burnt state in the form of periclase crystals. In normal conditions of exposure to ambient conditions of humidity and temperature it may take several years for the periclase to hydrate (White, 1928). As the conversion of MgO to Mg(OH)2 involves a molar volume expansion of 117% (Ramachandran, Feldman, & Beaudoin, 1981) , the presence of excessive amounts of MgO in hardened cement-based materials may lead to expansion and crack formation. However, the expansive forces can be used to advantage in the chemical prestressing of concrete.

Although free MgO in the form of periclase in cements causes expansion on hydration, the expansion does not be proportional to the amount of periclase present. Coarse periclase particles cause more expansion than fine ones. For a particular percentage of MgO, the expansion is related particle size, cement containing particles of <5 lm showing the least expansion (Ramachandran, Feldman, & Beaudoin, 1981) . Because of the possible deleterious effects of MgO, most specifications have placed a limit on the amount of MgO that can be present in cement, and the MgO content does not exceed 6%. The expansion caused by the hydration of MgO, if it is controlled, could be used to compensate the shrinkage of cement-based materials, such as dam concrete. In the 1970s, the Baishan dam was constructed by using cement with high MgO (4.5% by mass of cement) in China, and no temperature-controlling measures were taken during the constructing process (Cao & Xu, 2003) , and several years later, no penetrating cracks were found in general. Several studies indicated that the thermal shrinkage of dam concrete generated during the cooling stage has been effectively compensated by the delayed expansion attributed to the slow hydration of MgO in cement (Cao & Xu, 2003; Zonghan et al, 1998; Qing et al, 2004). And in the 1990s, the Three Gorges Dam was constructed also by using cement with high MgO in clinker (Zonghan et al, 1998; Qing et al, 2004) . To avoid dead burnt MgO in cement and for good control of the properties of MgO, some Mg-bearing minerals such as magnesit were calcined separately under much lower temperatures ranging from 900 to 1200 C to produce light (caustic) burnt MgO.

Some researches (Cao & Xu, 2003; Wang, 2002; Xu & Deng, 2005) indicated that the expansion properties of the 190Q. Ye et al. /Construction and Building Materials 78 (2015) 189–193

light burnt MgO depended on the calcining temperature and residence time. For example, the light burnt MgO produced under higher calcining temperature, resulted in slower and smaller expansion at early age but larger expansion at later age (Wang, 2002). Mehta (Mehta & Pirtz, 1980) also reported that the carefully calcined (under the temperatures of 900–950 C) and sized (300–1180 lm) MgO powders had the potential of being used as expansive agents for compensating thermal shrinkage and thus preventing cracks in mass concrete due to thermal stresses. In the 1980–1990s, about twenty dams were constructed by using cement added with light burnt MgO in China (Cao & Xu, 2002).

In this new century, the technology of nano-structured material is developing at an astonishing speed and will be applied extensively with many materials. Although cement is a common building material, its main hydrate C–S–H gel is a natural nanostructured material. Ye (Qing et al, 2007; Qing et al, 2006) reported that added with a small amount of nano SiO2, the CH crystals at the interface between hcp and aggregate at early ages were effectively absorbed in high performance concrete. And, Moradpour (Moradpour et al, 2013) reported that the effects of nanoscale expansive agents on the mechanical properties of non-shrink cement-based composites were studied and the autoclave expansions of Portland cement paste containing 3% and 5% nano-MgO were 0.10% and 0.12%, respectively.

Based on the successful application of periclase in clinker and light burnt MgO to the thermal and autogenous shrinkage compensation of dam concrete, and based on the use of nano materials in the material fields, the present work aims to find out the variation of expansion properties of cement based materials with nano-MgO.

Experimental procedure

Raw materials

Commercial ordinary Portland cement (42.5 grade, Blaine specific surface area310 m2/kg) complying with Chinese standard (GB 175–2007) was used. Its ingredients (wt%) were 80% clinker, 5% gypsum, 5% coal shale and 10% fly ash, respectively, and its compressive and flexural strengths at the age of 28 days were 47.9 and 7.6 MPa respectively. Its chemical composition is reported in Table 1 and its mineral composition is presented in Fig. 1.

Nano-MgO used was marketed by Hangzhou Wanjing new-material CO., Ltd. in China, with specific surface area 30–50 m2/g and average diameter 50 nm. Its chemical composition is reported in Table 1 and its mineral composition is presented in Fig. 2.

Table 1. Chemical compositions (% by weight) of ordinary Portland cement and nano-MgO.

	CaO	SiO2	Al2O3	Fe2O3	MgO	SO3	K2O	Na2O
Ordinary Portland cement	59.53	21.63	5.85	4.90	2.02	2.80	0.65	0.23
Nano-MgO					99.90			

Preparation of cement paste and expansion test

Linear expansion of cement pastes was tested in accordance with the linear expansion test for cement paste (JC313, Chinese Standard). Cement with nanoMgO was fully mixed under dry conditions beforehand. The cement paste was prepared using a planetary mixer (ISO 9597). For the pastes, a cement (containing nano-MgO) to water ratio of 0.28 was used. The mixing consists of a sequence of mixings involving 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 prismatic moulds 25 mm 25 mm 280 mm. The paste samples which were cured at 20 ± 2 C and above 90% RH moisture were demoulded at 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 prisms were tested for each sample at the ages of 2, 3, 7, 14, 28, 120, 180 and 365 days, and after autoclave curing at 365 days.

Soundness test for cement containing nano-MgO

The soundness of cement containing nano-MgO was tested in accordance with the method of the autoclave expansion test for soundness of common Portland cement (Chinese Standard GB/T 750). Cement with nano-MgO was fully mixed under dry conditions beforehand. The preparation of cement paste and squarebar sample for expansion test was the same the above section.

The paste samples which were cured at 20 ± 2 C and above 90% RH moisture were demoulded at 24 h when the initial length was measured by screw micrometer (precision 0.01 mm). Then the samples which were stored in water were boiled for 3 h, after cooling in water till 20 ± 2 C when the length was measured. And then the samples which were stored in the saturated steam were autoclaved at 216 C and 2.0 MPa for 3.0 h, after cooling in water till 20 ± 2 C when the final length was measured. Small autoclave utilized as steaming equipment is a vertical autoclave, cylin-drical in shape, 160 mm in inside diameter and 0.0085 m3 in volume. It is a product (type YZF-2A) of Cangzhou Luyi Test Instrument Co., Ltd, PRC and has a maximum pressure of 2.5 MPa.

Preparation of mortar and strength test

Cement strength was determined in accordance with the plastic mortar strength test (Chinese Standard GB17671, or ISO 679). At first, cement with nanoMgO was fully mixed under dry condition. For the mortars, a cement (containing nano-MgO): sand: water ratio of 1:3.00:0.50 was used and the sand with the size range of 0.08–2.0 mm is ISO Standard sand. The mortars were prepared according to ISO 679. The fresh mortar was cast into prismatic moulds 40 mm 40 mm 160 mm on a jolting table. The mortar samples which were cured at 20 ± 2 C and above 90% RH moisture were demoulded at 24 h and then stored in water at 20 ± 1 C till test. Three prisms were tested for each sample at each age. The span for flexural strength and the area for compressive strength is 100 mm and 40 40 mm2, respectively.

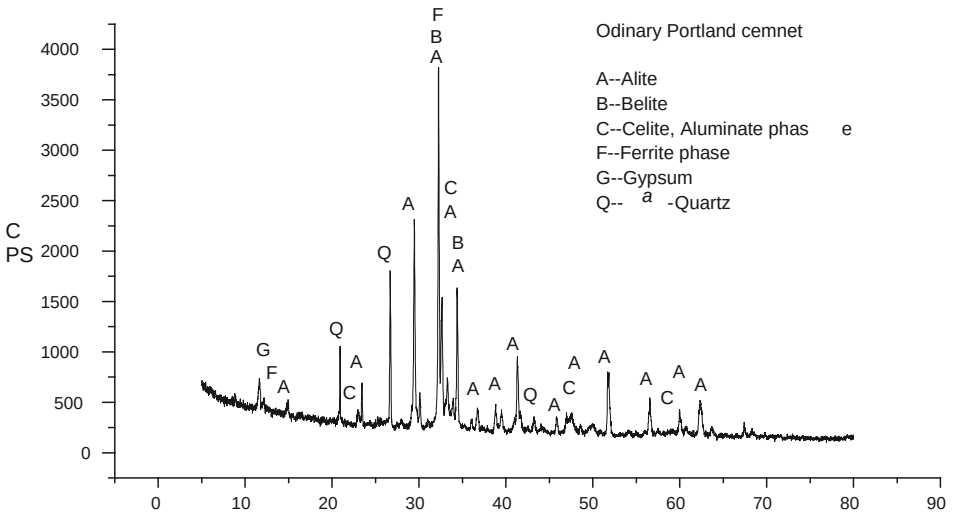

Figure 1. XRD patterns of ordinary Portland cement.

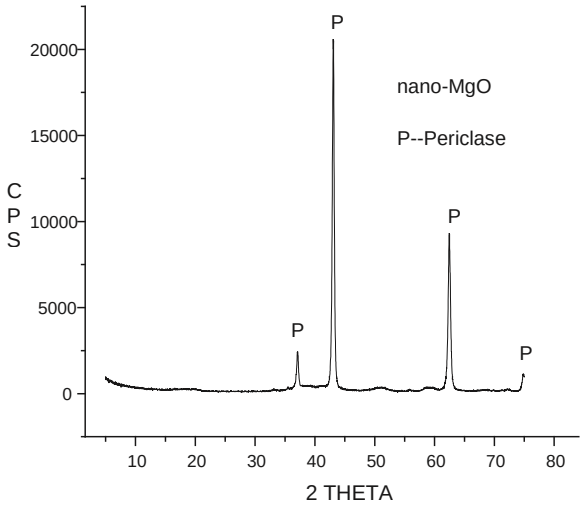

Figure 2 XRD patterns of nano-MgO.

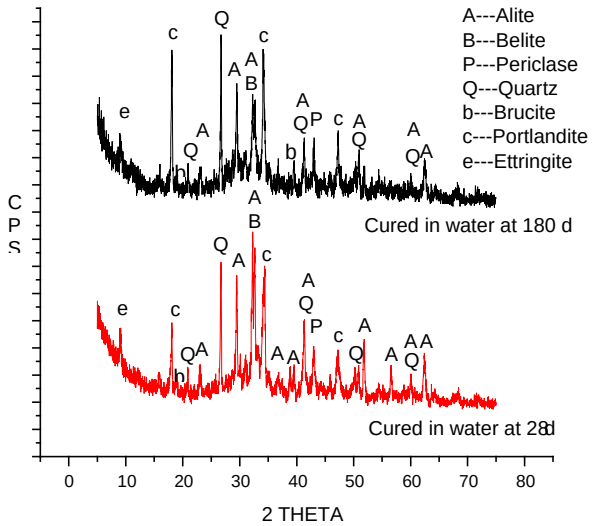

Figure 3 XRD patterns of cement pastes containing 6% nano-MgO cured at 20°C in water at the ages of 28 d and 180 d.

Autoclave curing after 365 days

For the above paste and mortar samples of cement containing nano-MgO, the autoclave curing (autoclaving after 365 d in this study) refers to ‘‘curing in water at 20 ± 2 C for 365 days, and then curing autoclaved in the saturated steam at 216 C and 2.0 MPa for 6.0 h’’.

Preparation of hydrated sample for XRD test

Using the above cement pastes cured in water at 20 ± 2 C at some ages or through autoclaving after 365 d, the hydrated samples which were ground to a specific surface area of 350–400 mm2/kg (Blaine) were analyzed immediately by XRD in order to indicate the variation of periclase (MgO) or hydrates with time.

X-ray diffraction analyzer used is Thermo ARL SCINTAGX’ TRA type with the following conditions: Cu Ka radiation, tube electric current 40 mA and tube voltage 40 kV, and scanning speed 4/min.

Results and discussion

Soundness of cement containing nano-MgO

The influence of the nano-MgO content on the expansion of hardened cement pastes after boiling and after autoclaving is presented in Table 2. When the contents of nano-MgO were 0, 4%, 8% and 10%, the expansions after boiling (or during boiling) reached 130, 470, 770 and 890 lm/m, respectively; and the expansions after autoclaving (or during boiling and autoclaving) reached 260, 1600, 3990 and 5670 lm/m, respectively.

Table 2. Mix proportions and expansion results of hardened cement pastes containing nano-MgO after boiling and autoclaving

	OP cement	Nano-MgO	Water	During boiling	During boiling and autoclaving
PM0	100	0	28	130	260
PM4	96	4	28	470	1600
PM8	92	8	28	770	3990
PM10	90	10	28	890	5670

A part of nanoMgO in cement paste boiled for 3 h after the age of 24 h was hydrated and it causes some expansions increased with the content of nano-MgO increasing. Also, a large number of nano-MgO in cement paste autoclaved for 3 h after boiling have been hydrated and it causes large expansions increased with the content of nano-MgO increasing.

According to the current Chinese standard (GB/T 750), when the autoclave expansion of hardened ordinary Portland cement

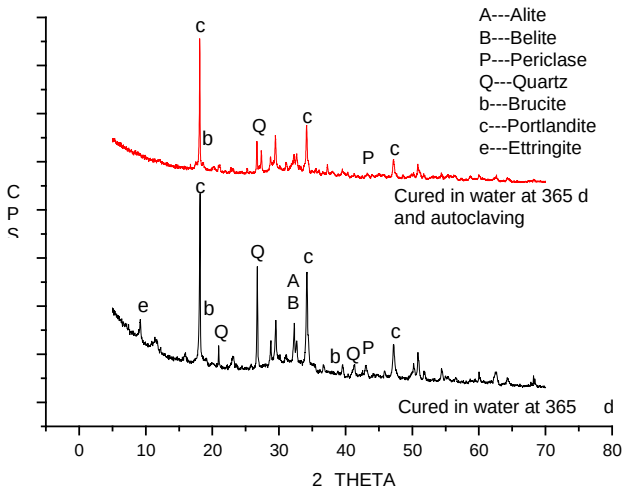

Figure 4. XRD patterns of cement pastes containing 6% nano-MgO cured at 20 C in water at the ages of 365 d and autoclaving after 365 days.

Hydrates and periclase (nano-MgO) varied with time

Fig. 1 shows XRD patterns of ordinary Portland cement. It was a type of normal cement, and a few of a-quartz, originated from mineral addition (coal shale and fly-ash), existed in the cement.

Fig. 3 shows XRD patterns of cement pastes containing 6% nanoMgO cured in water at 20 C at the ages of 28 days and 180 days.

Note: The autoclaving after 365 d refers to curing in water at 20 C for 365 days, and then autoclaving in the saturated steam at 216 C for 6.0 h.The cement hydration was normal. Crystal hydrates such as portlandite, ettringite and brucite existed, and a-quartz and periclase (nano-MgO) also existed.

Fig. 4 shows XRD patterns of cement pastes containing 6% nanoMgO cured in water at 20 C at the age of 365 days and through autoclaving after 365 days. When cured in water at 20 C at the age of 365 days, the cement hydration was normal, crystal hydrates such as portlandite, ettringite and (a little) brucite existed, and a-quartz and periclase also existed. Through autoclaving after the age of 365 days, the cement hydration was almost completed, and both periclase and its hydrate brucite barely existed. Most of the a-quartz had reacted with portlandite, and a little also existed.

The result shows that the hydration rate of nano-MgO cured in water at 20 C is low, and a little of nano-MgO exists till the age of 365 days. Through autoclaving after the age of 365 days the hydration of nano-MgO is completed.

Strengths of cement mortars containing nano-MgO

Table 3 shows the strengths of cement mortars containing nano-MgO cured at 20 C in water and through autoclaving after 365 days. At the age of 28 days the flexural and compressive strengths increased with the content of nano-MgO increasing. At the age of 365 days flexural and compressive strengths increased slightly when the nano-MgO content increased.

Table 3.Mix proportions and strengths of mortars containing nano-MgO

	Cement	Nano-MgO	Water	Sand	28 d	365 d	Autoclaving after 365 d	28 d	365 d	Autoclaving after 365 d
PM0	450	0	225	1350	7.6	11.5	7.2	47.9	68.1	62.1
PM2	441	9	225	1350	8.0	11.7	7.0	49.8	70.6	61.9
PM4	432	18	225	1350	8.5	11.8	6.7	50.7	69.8	58.8
PM6	423	27	225	1350	9.1	11.9	5.8	50.9	69.9	52.2
PM8	414	36	225	1350	9.0	11.8	4.9	50.7	69.7	44.6
PM10	405	45	225	1350	9.3	11.7	3.2	50.6	69.4	39.0

However through autoclaving after the age of 365 days the flexural and compressive strengths decreased obviously with the nano-MgO content increasing. For example, when the contents of nano-MgO were 0%, 2%, 4%, 6%, 8% and 10%, the compressive strengths were 62.1, 61.9, 58.8, 52.2, 44.6 and 39.0 MPa, respectively, and the ratios of the above strengths to that of the control sample PM0 were 1.00, 1.00, 0.95, 0.84, 0.72 and 0.63 in proper order.

The results seem to indicate that the hydration of nano-MgO does not harm strengths and the strengths develop regularly within 365 days cured at 20 C in water, but it harms the strengths obviously through autoclaving after the age of 365 days especially when the nano-MgO contents are 8% and 10%.

Expansion of cement pastes containing nano-MgO

Table 4 shows the relationships between the development of paste expansion at some ages or through autoclaving after 365 days and the content of nano-MgO. The expansion increased gradually with the increase of the content of nano-MgO and the time cured at 20 C in water. For example, at the ages of 28, 120, 180 and 365 days, the expansions of the control sample PM0 paste reached 500, 680, 740 and 880 lm/m, respectively; when the content of nano-MgO was 6%, the expansions of sample PM6 paste reached 710, 1120, 1340 and 2300 lm/m, respectively; when the content of nano-MgO was 8%, the expansions reached 810, 1340, 1640 and 3070 lm/m, respectively; and when the content of nano-MgO was 10%, the expansions reached 930, 1590, 1990 and 3940 lm/m, respectively.

Table 4. Expansion of cement pastes containing nano-MgO

				1 d	2 d	3 d	7 d	14 d	28 d	120 d	180 d	365 d	
PM0	100	0	28	0	90	170	250	400	500	680	740	880	1010
PM2	98	2	28	0	110	190	270	430	550	780	880	1210	1630
PM4	96	4	28	0	140	220	310	460	630	930	1100	1710	2340
PM6	94	6	28	0	160	260	360	520	710	1120	1340	2300	3430
PM8	92	8	28	0	180	300	400	590	810	1340	1640	3070	4740
PM10	90	10	28	0	210	350	470	690	930	1590	1990	3940	6750

Furthermore, through autoclaving after the age of 365 days the expansion and its increment increased obviously with the nano MgO content increasing. For instance, with the contents of nanoMgO being 0%, 2%, 4%, 6%, 8% and 10%, the expansions through autoclaving were 1010, 1630, 2340, 3430, 4740 and 6750 lm/m, respectively, and the ratios of the above expansions to that of the control sample PM0 were 1.00, 1.61, 2.32, 3.40, 4.69 and 6.68 in proper order. And the expansion increments between after and before autoclaving were 130, 420, 630, 1130, 1670 and 2810 lm/ m, respectively, and the ratios of the above expansion increments to that of the control sample PM0 were 1.00, 3.23, 4.85, 8.69, 12.85 and 21.62 in proper order. Only when the nano-MgO

content was 10%, its expansion was more than 5000 lm/m, and the soundness of the sample PM10 was unqualified.

The results seem to indicate that the expansions cured at 20 C in water within 365 days increase gradually and the expansion increments through autoclaving after the age of 365 days increase obviously with the increase of the nano-MgO content. Only when the nano-MgO content is 10%, its cement paste soundness is unqualified.

Conclusion

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

Nano-MgO was able to be used as the expansive agent for cement and concrete.The maximum content of nano-MgO added in ordinary Portland cement reached up to 8% for soundness.

The hydration rate of nano-MgO cured in water at 20 ± 2 C was low, and a little of nano-MgO existed till the age of 365 days.

The paste expansions increased gradually with the increase of the content of nano-MgO cured at 20 C in water within 365 days and through autoclaving after the ages of 365 days.

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