Periclase, and the autoclave who cried "Wolf!" — determining the influence of ASTM C151 cement autoclave expansion on the volume stability of concrete

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INTRODUCTION

From the early use of Portland cement, there was a concern with preventing the use of "unsound cement" in concrete. Initially, a pat test was chosen in 1904 as an accelerated method to detect unsound cement and was used until 1940 when this technique was replaced with the ASTM C151 autoclave expansion test (AET) [1]. In addition to detecting expansion from excessive amounts of free lime (CaO), the AET can also accelerate the crystalline MgO (periclase) to brucite ($Mg(OH)_2$) transformation. Expansion limits are set at 0.8% in ASTM C150 and 1.0% in CSA A3001. Additionally, the MgO content of cement is restricted in different standards internationally: 6% in ASTM C150 and 5% in CSA A3001. Recently, some cements from one source failed the AET but were well below the MgO limit. In contrast, some cements with similar MgO contents passed the autoclave expansion limit. The primary objective of the current project is to determine if the ASTM C151 AET is serving any purpose in protecting the consumer beyond that provided by the chemical limit on MgO content.

Adoption of the autoclave test was controversial from the very beginning, and many were unsure whether or not this test was representative of the long-term expansion of a moist cured specimen. For example, creep of the hardened paste in normal curing condition compensates for the MgO expansion and, unlike the AET, can provide stress relief which would not cause any durability issue in long-term moist curing condition [2]. It was mentioned that the AET destroys the cohesive forces of a one-day cured specimen and hence this accelerated test method exaggerates the expansion. This suggests that if the duration of curing before the AET is increased, the matrix strength would be increased and consequently, there would be more chance for the paste matrix to endure the disruptive forces during the autoclave test [3]. Also, the potential expansion of concrete is the main concern, not the cement paste specimen. Literature reviews and test reports have found a general lack of correlation between the cement autoclave expansion and the concrete expansion except for cements with 15% or more of crystalline MgO [4]. Since the AET method has always been controversial, this test was not adopted outside of North America, and sometimes, the limit on the MgO content coupled together with the Le-Chatelier soundness test are the only constraints applied on cement. It is worth noting that there is no direct correlation between the crystalline MgO content of the cement and the AET results [5]. As well, autoclave expansion could be influenced by other things including the MgO crystal size, and impurities found inside the periclase crystals [6].

The technology being used for cement production has changed considerably during the last century, including the better homogenization of raw mix, and rapid cooling of clinker which reduces the crystalline MgO content of cement. Also, the cement particles produced these days are much finer than previously, which enhances the strength development of paste specimen that constraints the paste bar expansion [7]. Besides, the AET has safety hazards, and in some locations this equipment is no longer available, especially in smaller labs [8]. In the current study, two types of cement from a single source and with almost the same MgO content were selected. One of these cements passed the AET (subsequently referred to as AP), and the other one failed the test, (subsequently referred to as AF). The purpose of this research is to determine the factors affecting the reactivity of periclase in each cement, including: the MgO crystal size, shape, and impurities. Furthermore, the effect of the duration of the moist curing period before being subjected to the AET was also examined.

MATERIALS AND METHODS

The chemical analysis for each of the two ASTM Type I cements is provided in Table1. To determine if there were any differences between the periclase crystals in each cement, the anhydrous AP and AF cement powders were impregnated with fluorescent epoxy, and a thin section was made from each cement type for scanning electron microscopy (SEM) analysis. During the SEM study, X-ray Energy Dispersive Spectroscopy (EDS) spot analysis was used as a tool for identification and quantification of different phases in the cement, and especially inside the crystalline magnesia particles, as based on mineral standards and the OXFORD INCA software. The ability to detect low concentration impurities inside the MgO crystals can be problematic with EDS, therefore, a wavelength dispersive detection system (WDS) was also used. As well, third-point loading tests were performed on paste bars after different periods of moist curing.

Table 1: Cement Chemical Analyses

Cement	Oxide wt. %								Auto-clave expan-sion%
	SiO_2	MgO	CaO	Fe_2O_3	SO_3	Na_2O	K_2O	Al_2O_3	
AP	20.27	4.02	60.85	3.19	4.34	0.09	1.11	4.91	0.55
AF	20.32	4.63	60.5	3.67	4.17	0.1	1.31	4.07	6.6

RESULTS AND DISCUSSION

SEM analysis of unreacted cement powder

Figure1 compares backscattered electron images of AF and AP cement particles. The rate of clinker cooling has a significant impact on the autoclave expansion of cement. Slowly-cooled clinker provides larger periclase crystals leading to excessive autoclave expansion [9]. Therefore, that might be the reason why the AF cement has a relatively larger magnesia grain size than that found in the AP sample.

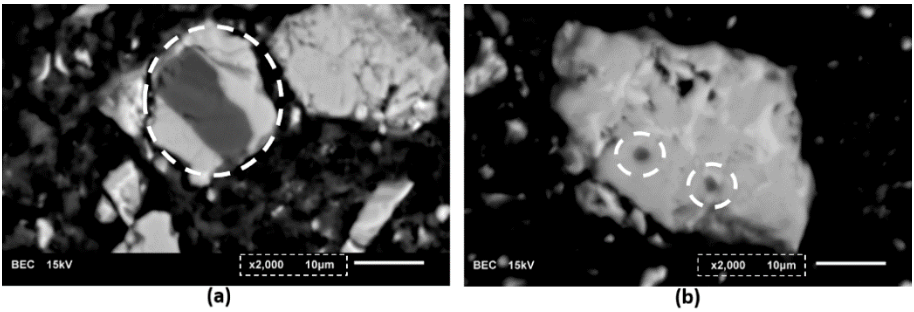

Figure1: SEM analysis of unreacted cement powders (a) AF cement, and (b) AP cement

Apart from the clinker cooling rate, the impurities inside the periclase crystals can have an impact on the size of crystalline MgO and the cement autoclave expansion as well. Interestingly, tetragonal zirconia contributes to increasing the periclase crystal size [10], and the shape of the periclase particles would be changed from rounded to angular as the zirconia impurity increases [11]. Additionally, iron oxide and chromic oxide affect the periclase-periclase bond and result in the increment and decrement of magnesia crystal size respectively. Furthermore, increasing the iron-oxide impurity in periclase crystals results in effective sintering and enhances the periclase bond leading to pronounced crystal growth. [12]. EDS and WDS spot analyses were performed on both cements, and the average weight percentage for each element is reported in Figure 2. The iron content of MgO crystals found in the AF cement is higher than that of the AP cement, and this could enhance the reactivity and size of periclase of the AF cement relative to the AP sample. There is no significant difference in zirconia and chromium contents between the two samples, and both elements were below the minimum detection limit. The calcium content of the AP cement is higher, but this may be an artifact of the excitation volume of the beam current (around one cubic micrometer); approximately the same volume as these smaller periclase crystals. Hence due to the small crystal size of magnesia in AP cement, exciting the periclase phase would also excite the surrounding calcium compounds.

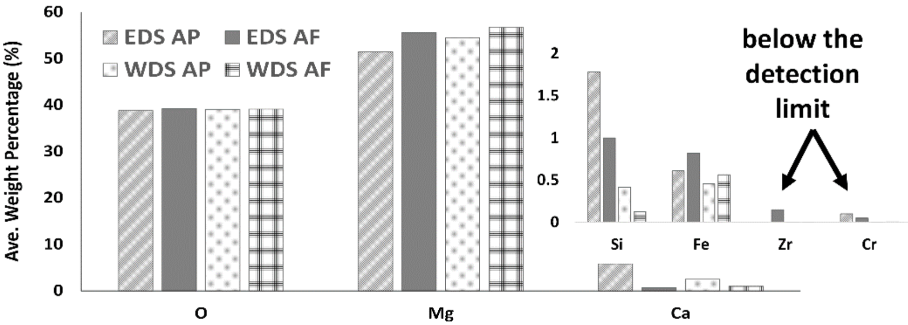

Figure 2: EDS and WDS analyses on unreacted cement powders

Analysis of autoclaved paste bars

The effect of the moist curing period, before the AET, on the autoclave expansion of paste bars made with AF and AP cement is investigated. As shown in Figure 3, the paste bars made with AF cement and cured for only one day (AF-1) as specified in ASTM C151, had almost 6.6% autoclave expansion and failed the test. The elemental mapping provided in Figure3 suggests that about 25% of the paste matrix was densely cracked and hence the porosity is high. Surprisingly, samples cast from the same mix but moist cured for 7 or 28 days before the AET had autoclave expansions of only 0.55% and 0.21% respectively and passed the expansion limit. This might be attributed to the increased tensile strength of paste bars with an increased moist curing period. In addition, as illustrated in Figure3, the cracks pass through the magnesium particles, i.e. the red particles shown in the elemental mapping, which accelerates the periclase to brucite transformation by providing more water access to hydrate the magnesia.

In Figure 4, the flexural strength of paste bars made with AP and AF cements were measured before the other bars were subjected to AET. The procedure used to measure the paste modulus of rupture (MOR) is the similar to that described in ASTM C78-18, see Figure 4 (a). As shown in Figure 4 (b), the curing period before the AET has a significant impact on the paste tensile strength development especially during the first week. It is reported that higher paste tensile strength would constrain the excessive autoclave expansion (Gonnerman et al. 1953), and that might be one of the reasons why the autoclave expansion decreases significantly after a single week of moist curing.

As discussed earlier, for the AF paste bar moist cured for 28 days (AF-28) the autoclave expansion is negligible. Apart from the increased tensile strength development theory for mitigating the paste bar expansion, some periclase crystals were left unreacted inside the unreacted cement particles in the AF-28 sample, as shown in Figure 5 (a). In Figure 5, “P” refers to the periclase crystals, and “B” refers to brucite crystals. The crystalline magnesia particles at these protected locations are less likely to react with water since the water cannot easily reach them. Additionally, for the AF-28 sample, periclase hydration could have ceased after becoming partially encapsulated with brucite, as appears to be the case in Figure 5(c) [2]. Another possible explanation for the low autoclave expansion of the AF-28 samples would be the formation of monoaluminate phases (AFm) around the periclase compounds that isolate them from hydration, a feature also observed in Figure 5(c) [13].

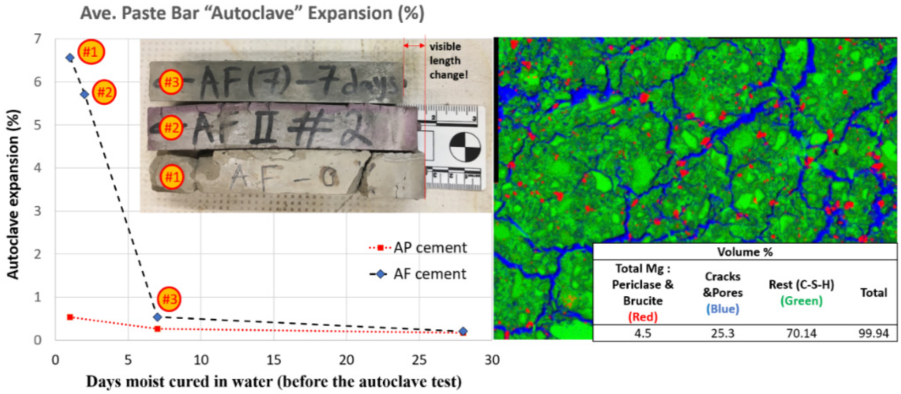

Figure 3: Autoclave expansion of paste bars with different moist curing period before subjected to AET.

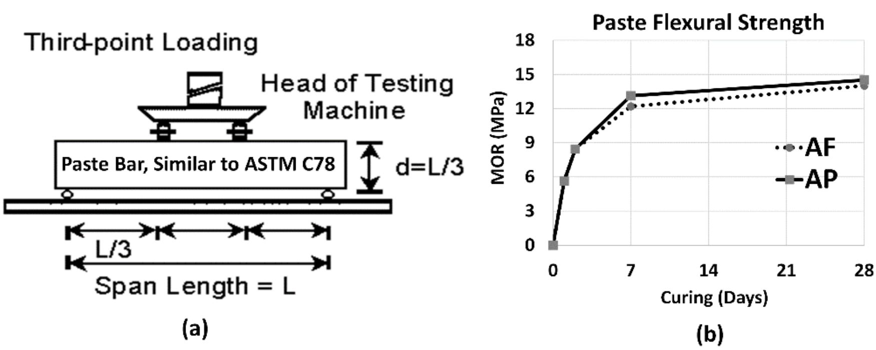

Figure 4: Measuring paste bar flexural strengths vs. the curing period.

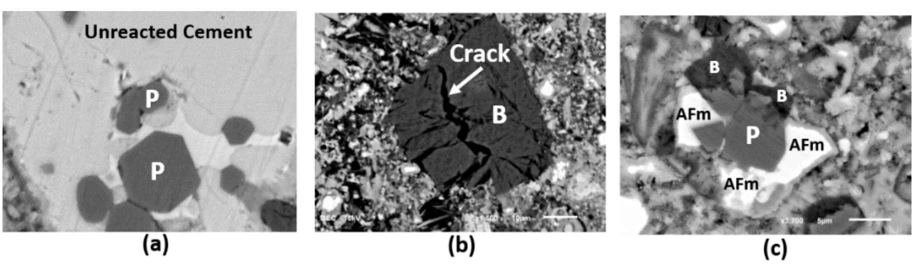

Figure 5: SEM of autoclaved paste bars made with AF cement and moist cured at different periods before the AET

CONCLUSIONS

It is of interest to determine whether or not the autoclave expansion test is a true representative of the long-term expansion of moist cured samples. The effect of the duration of the moist curing period in reducing the autoclave expansion is remarkable and likely due to the tensile strength development of paste matrix. Furthermore, the longer the samples are moist cured prior to autoclaving, the formation of monoaluminate phases around the unreacted periclase particles together with their encapsulation with an impermeable brucite layer would contribute to the reduction in paste bar expansion. Another interesting point is that impurities might affect the size and shape of MgO crystals, but this needs further investigation. This would affect the reactivity and vulnerability of periclase crystals at the 215°C autoclave temperature while not having much effect on expansion at ambient temperature.

ACKNOWLEDGMENTS

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