Suppressing alkali-silica reaction through incorporation of calcined kaolinite–montmorillonite clay blends

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ABSTRACT

Cement substitution with calcined kaolinite–montmorillonite clay blends as an effective way to suppress alkali-silica reaction in cement composites containing reactive aggregates is investigated. Expansion, cracking behavior, mechanical properties and microstructure of the cement composites were investigated. Hydration of the ternary cement blends was also characterized. The results indicate that cement modification with a combination of calcined kaolinite–montmorillonite clays can effectively mitigate alkali-silica reaction-induced deteriorations. By incorporating 30% clays, the volume expansion of the cement composites was decreased from deleterious to innocuous level. Amount of cracks was decreased with increasing clay incorporations. In the presence of combined calcined clays, the strength gain of the cement composites is more significant the strength loss caused by alkali-silica reaction indicating the effective mitigation of this virulent reaction in concrete.

1. INTRODUCTIONS

Alkali-silica reaction (ASR) is one of the major degradation mechanisms causing volume expansion, cracking and even substantial damages of concrete. Due to the internal attribute, pessimum, and irreversibility of the induced degradation, ASR is commonly referred to as “concrete cancer”(Subasi, et al. 2010). Prerequisites of ASR include reactive aggregates (metastable silica) (Bérubé, et al. 2002, Maraghechi 2014), alkaline concrete pore solution (Mukhopadhyay 2013), and sufficient moisture (Chatterji, et al. 1989). Therefore, theoretically effective approaches to avoid or mitigate ASR are the use of inert aggregates, reduce the ambient relative humidity and modification of the cement matrix to decrease alkalinity. However, the selection of service environment and use of non-reactive aggregates and are not practical, especially in some regions where reactive aggregates dominate the rock resource (Rajabipour, et al. 2015).

In addition to reactive silica, alkali is the most important reactant of ASR reactions. For concrete with moderate or higher ASR risk, low-alkali cement should be used. However, for concrete structures with high ASR risk, limiting cement’s alkali content, even controlling alkali content in supplementary cementitious materials (SCMs) and aggregates, cannot be the sole strategy (Rajabipour, et al. 2015). The most common approaches to suppress ASR is the use of lithium admixture and SCMs. Lithium can reduce silica dissolution rate and impede formation and swelling of ASR gel by forming protective layers (Feng, et al. 2010, Kawamura & Fuwa 2003). It is worth to note that limited availability of lithium, which accounts for <0.002% earth’s crust, is the main change of their pervasive applications in concrete. More practically, the use of SCMs can not only improve concrete properties but also reduce the alkalinity of the pore solution. Various SCMs, such as fly ashes (Shafaatian, et al. 2013), slag (Wang 1995), silica fume (Shehata & Thomas 2002), ground clay brick (Afshinnia & Poursaee 2015), rice husk ash (Munir, et al. 2016) and metakaolin (MK) (Trümer & Ludwig 2015) have been investigated. Although good results have been obtained in suppressing ASR, high volume SCMs can significantly impact concrete’s setting and strength development. Moreover, the local availability of high-quality SCMs (i.e. low alkali, low-calcium, and narrowly variable chemistry) is uncertain.

Clays, due to their abundance, low-cost, carbon efficiency and high pozzolanic activity, are promising mineral admixtures for high-performance concrete with a great potential to replace the conventional SCMs. Metakaolin (MK) is a calcined kaolinitic clay, one of the richest natural clay minerals. Due to the penta-coordinated aluminum ions, disordered and strained nature of the alumina layers formed during the calcination process (>600 °C), MK has high pozzolanic activity comparable to or exceeding the activity of silica fume (Antoni, et al. 2012, Fernandez, et al. 2011). Aquino et al. (2001) reported that MK performed similarly with SF in controlling ASR expansion of mortars. Depending on the aggregate, the amount of MK between 10% and 15% that is required to control ASR expansion to <0.04% at 2 years was reported by Ramlochan et al. (2000). In the work reported by Chappex and Scrivener (2013), reduced ASR expansion and increased the concentration of aluminum in pore solution was observed by incorporating MK. Montmorillonite (MT) is an aluminum phyllosilicate clay and, according to the amount of exchangeable ion, it can be classified as sodium-MT, potassium-MT or calcium-MT (King 2017). Because of its high swelling behavior, absorption capacity and cation exchange ability, MT has been extensively used as heavy metal cations adsorbent (Brtáňová, et al. 2012), radionuclide barrier (Galamboš, et al. 2012, Galamboš, et al. 2013) and healing agent for self-healing concrete (Qureshi, et al. 2016). However, the role of this clayey mineral in mitigating ASR has not been fully understood.

Calcium and aluminum play critical roles in the occurrence and development of ASR. The alkalinity of concrete’s pore solution can be maintained or even increased in the presence of calcium through “alkali recycling” (Hanson, Thomas 2001), which thereby keeps facilitating the occurrence of ASR over years. Although some studies show that the diffusion of silica from the reactive aggregates can be prevented in the presence of calcium (in the form of portlandite) (Chatterji 1979), the incorporation of calcium is critical for the formation of gels with increased viscosity, stiffness and yield strength of ASR gel and hence results in more destructive internal pressure (Gholizadeh Vayghan, et al. 2016). On the contrary, aluminium, which is known interact with calcium-silicate hydrates (C–S–H) to form the aluminum-modified calcium silicate hydrates (C–A–S–H), can mitigate ASR’s occurrence and development by reducing alkalinity of pore solution, repelling dissolution of silica in alkaline environments, and densifying microstructure of the cement paste (Chappex & Scrivener 2013). To address the challenges of conventional SCMs and utilize the merits of aluminum, this study investigates the coupled cement substation of MK and sodium-MT and its role in ASR suppression. Development of ASR expansion,

cracking and mechanical properties of cement composites containing reactive fine aggregates are monitored. Correlations between hydration and ASR mitigation are discussed.

2. MATERIALS AND METHODS

2.1 Materials

Low alkali Type II/V Portland cement with a Na_2O equivalent of 0.58 and a mean particle size of 12.9 μm produced by CalPortland was used in this study. The MK with a specific density of 2.6 g/cm^3, containing 52 wt.% SiO_2 and 42 wt.% Al_2O_3 is produced from Aiken, South Carolina (USA), with a thermal treatment temperature near the upper end of the normally adopted temperature range (600°C to 800°C). The sodium MT used in this study has a relative density of 2.4 g/cm^3, a molecular weight of 180.1 g/mol, SiO_2 content of 62 wt.% and Al_2O_3 content of 17%. It can be noted that the content of silicate and aluminate phases (SiO_2+Al_2O_3) of MK and MT are higher than 94wt.% and 79wt.%, respectively. Particle size distributions of MK and MT was measured by laser diffraction and it was observed that MK has a specific surface area of 2.9 m^2/g and a median particle size of 3.8 μm which is finer than MT, the specific surface area of which is 0.87 m^2/g. In addition to composition and particle size, it is also worth to note that the molecular structure of clays (e.g. MK has a metastable atomic structure of 1:1 layering of Si and Al (Claire, et al. 2011, White, et al. 2010), while MT has a 2:1 three-layer structure consisting of two silica tetrahedral layers sandwiching a central alumina octahedral layer (Murray 2006)) can also impact their performance in concrete. The reactive sand was obtained from El Paso, TX (USA). Sodium hydroxide pellets (certified ACS) with a purity of ⩾97% and high-performance water-reducing admixture (Sikament 686) were also used.

2.2 Mixture proportion and specimen preparation

According to ASTM C1260 (2014), a water/cement (w/c) ratio of 0.47 and a binder-to-sand ratio of 1:2.25 were used for all mortar mixtures. Three cement binders with plain cement (PC), 10% (B10) and 30% (B30) cement substitutions were adopted. With increasing cement replacement, the substitution of MK by MT was increased from 0% to 3% (B10-0, B30-1, and B30-3). The mixture proportions with different MK to MT ratios are summarized in Table 1. After mixing, the mortar was cast in 25 mm × 25 mm × 285 mm stainless steel molds with pre-embedded studs. After 1 day, the specimens were removed from the molds and immersed in tap water at 23.0 ± 2 °C and were place in an oven with a temperature of 80.0 ± 2 °C for 24h. Then the specimens were immersed in 1N NaOH at 80.0 ± 2 °C to accelerate ASR. ASTM C109 (2016) was followed for strength measurement. 25.4 mm × 25.4 mm × 25.4 mm cubic specimens were cast. After de-molding at 1 day, the cubes were conditioned in two environments: one group (G1) was immersed in saturated lime water at 23.0 ± 2°C and the other group (G2) was immersed in 1N NaOH solution at 80.0 ± 2°C. Cement pastes for TGA analysis were cast in sealed bottles until testing.

Table 1. Mixture proportion of mortars

Index	Content (g)					
	Cement	Sand	Water	MK	MT	Superplasticizer
PC	990	440	465.3	0	0	0
B10-0	891	440	465.3	99	0	3
B30-1	693	440	465.3	287.1	9.9	6
B30-3	693	440	465.3	267.3	29.7	7

2.3 Expansion test

ASTM C1260 (2014) was followed to determine the ASR expansion of the cement blends. The initial length of the mortar bar was measured as zero points. Then the mortar bar samples were immersed in a NaOH 1 M solution at 80°C. Length change of the mortar bars was measured every 2 days for the first 12 days and then four additional measurements were carried out from 16 days to 40 days.

2.4 Microstructure analysis

The microstructure of the mortars from G1 after 28 days and G2 after 9 months was investigated on a polished surface using a Hitachi 4700 SEM under an accelerating voltage ranging from 10 kV to 20 kV and a JSM-7001F-LV Field Emission Scanning Electron Microscope (SEM) under an accelerating voltage of 3.0 kV, respectively.

2.5 Compressive strength

Effects of cement substitutions and ASR on strength of the cement composites were evaluated according to ASTM C109. The mortar cubes, with 3 repetitions, were tested by using a static servo-hydraulic universal testing machine (SATEC 135HVL UTM).

2.6 Thermogravimetric analysis

TGA test was carried out on ground powders of the pastes for pure cement and cement-MK-MT blends of G1 to understand the influence of clays on cement hydration products, which is strongly related to the occurrence and development of ASR. Q50 thermogravimetric analyzer (TA Instruments) was used in this study. A heating rate of 10ºC/min from room temperature to 150ºC followed by 15ºC/min up to 800ºC in N2-atmosphere was adopted. Contents of calcium hydroxide (*CH*) and non-evaporable water in the pastes, expressed as a percentage of the dry sample weight at 550°C, were determined by using the following equations.

$$CH = [(W_{440} - W_{550}) / W_{550}] \times M_{Ca(OH)2} / M_{H2O} \quad (1)$$

where *CH* is calcium hydroxide content, W_n is the mass at temperature n°C, and M is the molar mass.

$$W_{ne} = (W_{105} - W_{550}) / W_{550} \quad (2)$$

where W_{ne} is non-evaporable water content, W_n and *M* are same as in Eq. (1).

According to W_{ne}, degree of cement hydration (*DOH*) was calculated as follows

$$DOH = 100\% \times W_{ne}(t) / (W_{ne}(\infty) \times F_c) \quad (3)$$

where $W_{ne}(t)$ is the content of non-evaporable water in cement at time *t*, $W_{ne}(\infty)$ is the non-evaporable water content of 1 g fully hydrated cement (0.24 g (de Larrard 1999, Fagerlund 2009, Feng, et al. 2004)), and F_c is the fraction (mass ratio) of cement in the cement blends;

3. RESULTS AND DISCUSSION

3.1 ASR Expansion

Figure 1 shows the ASR expansion behavior of the blended cement mortars with a period of up to 40 days. It can be seen that PC experienced a significant increase at an early age and shows the highest expansion (0.60% at 16 days) among the specimens suggesting the high reactivity of the fine aggregates. According to ASTM C1260 (ASTM 2014), the mortar bar length changes of less than 0.10% and more than 0.20% after 16 days are indicatives of innocuous and potentially deleterious expansions, respectively. The expansion rate of PC decreases over time and the final expansion of 0.8% was obtained after 40 days. By incorporating 10% MK, the expansion, especially at an early age, was decreased. No significant expansion was observed during the first 8 days. At 16 days, B10-0 showed an expansion of 0.16%, which is in the range of indecisive expansion according to ASTM C1260 (ASTM 2014). Compared with PC, the expansion of B10-0 was reduced by 52% at 40 days and did not exceed the threshold of deleterious expansion. This indicates that, with a low-volume MK, development of ASR at an early age can be effectively suppressed, but the slow reaction due to leached metastable silica cannot be mitigated. Increased clay incorporation resulted in a considerable reduction of ASR expansion. After 16 days, B30-1 and B30-3 showed an expansion of 0.07% and 0.04%, respectively, both of which are lower than 1.0% suggesting that the expansion of mortars was suppressed to an innocuous level. Compared with PC, the 40-day expansions of B30-1 and B30-3 were decreased by 79% and 87%, respectively. From the figure, it is worth to note that the increased incorporation of MT can help to further mitigate the ASR expansion. This indicates that synergistic effects between these

two clays might be generated in concrete. The author's previous work showed that MK and MT can work synergistically to enhance cement hydration in terms of CH consumption, the formation of additional C-S-H, incorporation of aluminum in C-S-H, growth of silicate chains length and increased dissolution of MK in cement system. There are evidences that the reduced calcium in pore solution (Hanson 1944, Thomas 2001), incorporation of soluble aluminium (Aquino, et al. 2001), consumption of CH (Bleszynski and Thomas 1998) and formation of C–A–S–H (Hong and Glasser 2002) due to pozzolanic reactions can effectively against ASR.

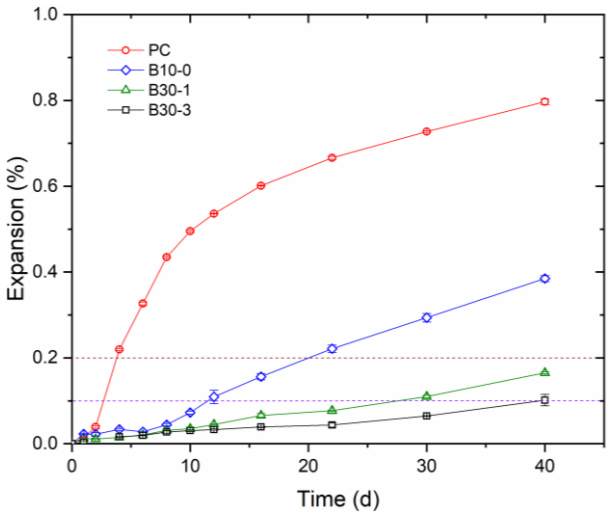

Figure 1. ASR expansion of mortar bar specimens and thresholds suggested by ASTM C1260.

3.2 Cracking behavior

Cracking on the surface of mortar bars conditioned in accelerated aging condition (1 N NaOH solution at 10ºC) induced by ASR was observed. As shown in Figure 2, the PC shows the severest cracking in terms of crack width, length, and density. Agreeing well with the expansion results, by mixing 10% MK, less cracks with reduced crack width were observed (Figure 2c). When 30% cement was replaced, cracking resistant of mortar was effectively improved (Figures 2d and 2e), this might be attributed to (i) pozzolanic reactions that can help to improve mechanical properties of the cement matrix, (ii) increased tolerance to volume change and (iii) suppressed ASR expansion as discussed above. The partial replacement of MK with MT shows benefit again to mitigate ASR induced cracking. After 9 months, no cracks can be visually observed on the surface of B30-3 (Figs 2a and 2e).

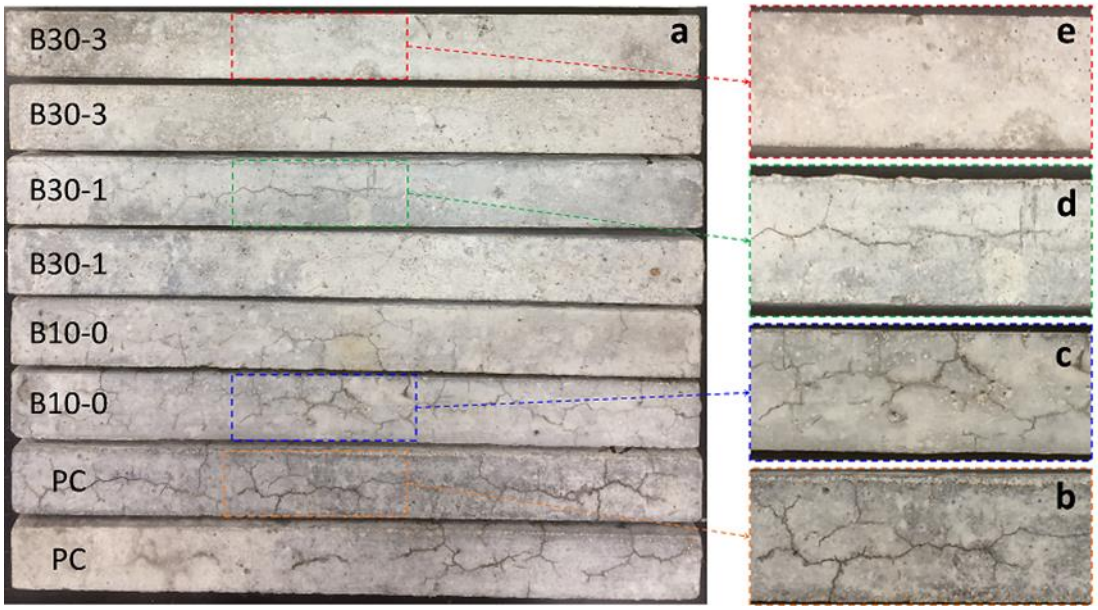

Figure 2. Images from mortar bars after immersion in 1 N NaOH for 9 months: (a) comparison between groups, cracks on the surface of (b) PC, (c) B10-0, (d) B30-1 and (e) B30-3.

3.3 Development of strength

The 7-day and 28-day compressive strength of the mortars conditioned in the two environments are illustrated in Figures 3a and 3b, respectively. As shown in Figure 3a, after 7 days, PC and B10-0 cured in lime water exhibit higher strength than that immersed in thermal 1N NaOH solution, while B10-0 shows a smaller difference. This is in agreement with the observations of Smaoui et al. (Smaoui, et al. 2005) and Garci et al. (Maria & Hamlin 2001). It was found that the NaOH solution can increase the rate of cement reaction prior to 1 day, hydration is retarded at later ages and alkalis has a significant influence on the percolation of the porosity in cement hydrating systems (Bentz 2006, Maria & Hamlin 2001). B30s yield higher 7-day strength in the alkali solution than those cured in water. This might be attributed to the alkaline activation of MK in the cement systems (Granizo, et al. 2002). It was observed that B30-1 cured in 1N NaOH solution has the highest 7-day compressive strength and the strength decrease with MT incorporation in both water and alkali solution immersions. This trend was modified for 28-day strength. From 7 days to 28 days, the strength of PC immersed in lime water increased by 19%, while the one cured in the alkali solution yielded an increase of 13% with a higher variation. This might be caused by the enhanced ASR deterioration in the alkali-thermal condition, which can in a certain extent counteract the strength gain. It should be noted that B30-3 yield higher strength than B30-1 and the strength of both B30s samples in the condition of NaOH solution are higher than that obtained from lime water curing. This is a result of two things: (1) MK's dissolution and reactivity in the cement systems was improved in the presence of alkali and MT, and (2) ASR was suppressed effectively in the presence of incorporated clay minerals.

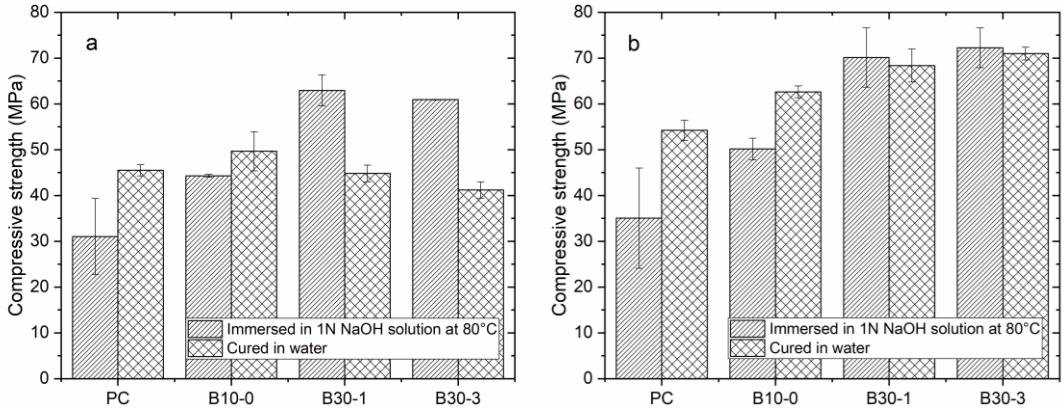

Figure 3. Compressive strength development of mortar cubes for the two groups: (a) 7-day strength and (b) 28-day strength.

3.4 Microstructural analysis

The microstructure of the mortars was investigated on polished sections after 9 months immersion in 1N NaOH at 80°C. As shown in SEM images of PC (Figure 4a), cracks in both cement paste and aggregates can be observed indicating the severe ASR gel's swelling and destructive impact on concrete. This is in agreement with the observations of expansion and cracking above. From Figure 4b it can be seen that, with 10% MK incorporation, cracks can still occur displaying a rim with ASR gels. Moreover, gel-filled micro-cracks extended from inner aggregate to the paste can also be observed. As the cement replacement increased to 30%, see Figure 4c, cracking in aggregate was significantly suppressed, while the surrounding cement paste still experienced cracking. This again indicates that cement substitution with the combination of MK and MT is an effective way to suppress ASR induced deterioration of concrete containing active aggregates, while this also indicates that future works for high-volume clays substitution for robust ASR suppression are needed.

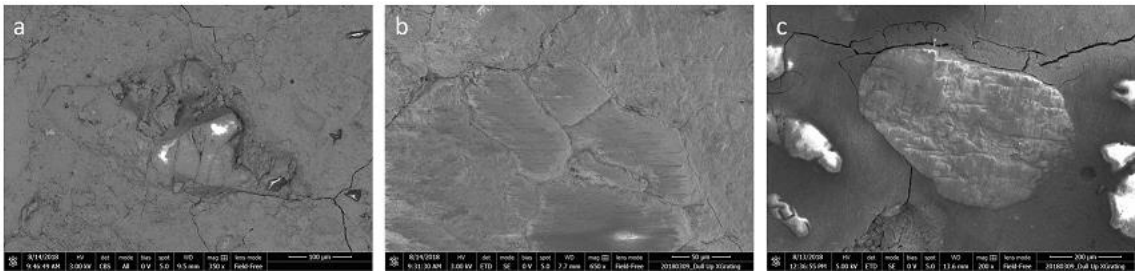

Figure 4. Microstructure selected mortars cured in 1N NaOH solution at 80°C after 9 months: (a) PC, (b) B10-0 and (c) B30-1.

3.5 Thermogravimetric analysis

Figures 5a and 5b show the development of a degree of hydration for cement and content of calcium hydroxide, respectively, calculated from the TGA results. It is seen that with more MK incorporation, a higher DOH of cement was obtained suggesting that this clay mineral is an effective cement hydration accelerator. This is a result of several mechanisms related to physical and chemical modification of cement pastes including (i) improved homogeneity, reduced coagulation and increased dispersion of clinker particles and hydrates; (ii). increased particle packing due to extra physical nucleation sites (Kadri, et al. 2011, Wu & Young); (iii) additional reactive aluminate and siliceous surfaces (Madani, et al. 2012); (iv) increased shearing between particles (Berodier & Scrivener 2014). With a similar particle size as PC and higher amorphous silica content than MK, the incorporation of MT results in a further improvement in DOH of cement. Figure 5b shows that the coupled substitution of MK and MT results in a decrease of CH content. The amorphous phases, i.e., silicate and aluminate, of MT and MK react with CH in the presence of water producing cementing compounds like C–S–H (C-A-S-H) (Hakamy, et al. 2015). The further decrease of calcium hydroxide content caused incorporation of MT was observed again after 28 days.

As discussed above, the most important factor from cement contributing to ASR is the pH value. From the view of thermodynamics, the network dissolution of silica is caused by OH^- ion attack of the ≡Si-O- bonds. Then, in the presence of high pH, the ionization of the non-ionic $Si(OH)_4$ can result in further dissolution. If free calcium (in the form of portlandite) is available, this two-step dissolution process can be enhanced through the aforementioned alkali recycling. Another negative contribution of calcium is to link silica ions to form poly-metalsilicates(Iler 1979). These negative impacts of calcium can be suppressed by decreasing the content of calcium hydroxide.

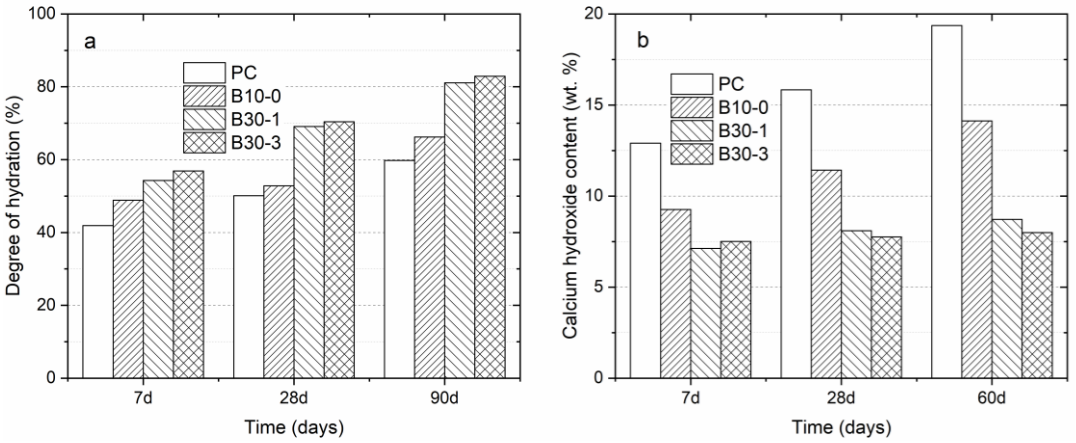

Figure 5. Degree of hydration of cement (a) and content of calcium hydroxide (b).

4. CONCLUSIONS

This study presents experimental investigations documenting the role of combined incorporation of MK and MT in mitigating expansion, cracking and strength loss of Portland cement mortars induced by ASR. To explain the mitigating mechanisms, hydration of the cement in the presence of MK and MT were studied. The results obtained in the study allow the following conclusions:

The incorporation of MK and MT in cement can effectively suppress ASR expansion. With 10% cement substitution, the expansion of mortar at an early age (first 10 days) can be effectively suppressed, but the slow reaction and expansion due to leached metastable silica cannot be arrested. With increasing incorporation of MK and MT, expansion of mortars was decreased to an innocuous level. It was found that with the replacement of MK by MT, the expansion of mortar was further decreased.

Agreeing well with the expansion behavior, a significant amount of cracks can be observed on the surface of the PC. Amount of cracks was decreased with increasing clay incorporation and no crack can be visibly detected from the surface of B30-3 specimens.

At an early age (7 days), due to the retarded hydration and the modified percolation of the porosity in cement, PC and the cement blends with a low substitution (B10-0) cured in lime water exhibit higher strength than that immersed in 1 N NaOH solutions at 80°C. While attributed to the alkaline activation of clay minerals, B30-1 and B30-3 yield higher 7-day strength in the alkali solution than those cured in lime water. With increasing MK and MT incorporation, strength gain of the cement blends is more significant in the alkali environment as a result of enhanced MK dissolution and reactivity in the presence of alkali and MT and the suppressed ASR deterioration.

The microstructure of the samples influenced by ASR indicates that expansion of mortar was induced by the swelling and destructing nature of ASR gels formed on the surface and inside the aggregates. In the presence of MK and MT, less crack with decreased crack width can be observed. This again reveals the effective roles of MK and MT in suppressing ASR induced deterioration. Synergistic effects between MK and MT in enhancing cement hydration and consuming calcium hydroxide were observed, and this provides benefits in suppressing ASR by mitigating the “virulent” influence of calcium.

5. ACKNOWLEDGMENTS

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