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INVESTIGATIONS INTO ALKALI-SILICA REACTION IN CALCIUM SULFO-ALUMINATE CEMENT MORTARS AND ITS BLENDS WITH POZZOLANS

Venkatanarayanan K Harish, Prasada Rao Rangaraju*

Clemson University, Clemson, SC, USA

Abstract

Calcium sulfo-aluminate cements (CSA) are a special type of cement used for rapid setting applications. In this study, CSA cement and its blends with pozzolans were used as a binder for mitigating alkali silica reaction (ASR). Standard ASTM C1260/C1567 test procedures were used to assess the performance of CSA cement and their blends to mitigate ASR. Fourteen mortar mixtures were cast using 3 aggregates of different reactivity. In these mixtures, fly ash, meta-kaolin and slag were used at different replacement levels. The results obtained were then compared with Ordinary Portland Cement (OPC) mixtures and their blends with pozzolans at same replacement levels. Results from these investigations indicate that the mortar bar expansion due to ASR in CSA mixtures was either similar or lower compared to OPC mixtures, depending on specific aggregates. However, in the presence of pozzolans, the CSA mixtures were more effective compared to OPC mixtures in mitigating ASR.

KEYWORDS: calcium sulfo-aluminate, pozzolan, alkali-silica reaction, rapid setting, binary blend

1.0 INTRODUCTION

Calcium sulfo-aluminate cements (CSA cements), are a special type of hydraulic cements that are manufactured at a lower temperature (~ 1250^0 C) as compared to that of ordinary portland cement (1500^0 C). Since less heat is involved during their production, these cements are softer and consume less energy during grinding process. Consequently these cements are 2 to 6 times greener than OPC when they are used as binders in concrete [1]. The CSA cements are usually used for special applications such as in self-stressing concrete pipes, self-leveling screeds, repair material, etc., most of which requires high shrinkage-resistance, rapid hardening and high early-age strengths. These special properties are derived from the hydration reactions of calcium sulfo-aluminates, which are different from that of calcium aluminate cements and OPC [2, 3]. The principle hydration in CSA cement involves reaction between the calcium sulfo-aluminates and gypsum to form ettringite. The chemical reaction associated with CSA hydration is shown below [4]:

$$C_4A_3\check{S} + \underset{\text{(gypsum)}}{2C\check{S}H_2} + 36H \rightarrow \underset{\text{(ettringite)}}{C_6A\check{S}_3H_{32}} + 2AH_3 \text{ (In absence of calcium hydroxide)} \quad \text{--- (1)}$$

$$C_4A_3\check{S} + \underset{\text{(gypsum)}}{8C\check{S}H_2} + 6CH + 74H \rightarrow \underset{\text{(ettringite)}}{3C_6A\check{S}_3H_{32}} \text{ (In presence of calcium hydroxide)} \quad \text{--- (2)}$$

CSA cements also contain dicalcium silicate (C_2S) to a lesser extent and consequently are capable of generating C-S-H gel and calcium hydroxide as hydration reaction products. In addition, the pH of the pore solution in CSA cement is between 10.5 and 11, which is several times less alkaline than that of the OPC [1]. Previous micro-structural studies conducted on ettringite formation in OPC pastes suggested that only colloidal ettringite formed in the presence of lime during hydration process is expansive in nature [5] while that which forms in the absence of lime is non-expansive [6]. This expansive property of ettringite in the former can be utilized for shrinkage-resistant and self-stressing purposes [7] while that in the latter can be

* Correspondence to: prangar@clemson.edu

utilized for high-early strength of the cementitious systems [6]. It is believed that the ettringite behavior in CSA cement hydration is similar to that observed with OPC.

In addition to the above applications, CSA cements can also be used for applications in high performance concretes in which protection against corrosion (carbonation and chloride resistance) to embedded steel and sulfate exposures in marine environments are required. The resistances of CSA cements to carbonation, chlorides and sulfates may be due to its chemical stability, its ability to self-desiccate faster, its high sulfate content and its very low porosity [8, 9]. Blends of CSA with OPC and slag cements have also been employed to improve the strength and durability of concrete [10, 11], understanding how these cements perform in mixtures containing reactive aggregate is important.

In this study, an attempt has been made to understand how alkali-silica reactive prone aggregates perform in CSA concretes, both in the presence and the absence of supplementary cementing materials (SCMs). In this study, CSA blends containing fly ash, meta-kaolin and slag were investigated to determine their effectiveness to mitigate ASR.

2.0 OBJECTIVES

The principle objectives of this study are:

1) To compare the expansions of mortar bars containing reactive aggregate with virgin CSA and OPC cements in the accelerated mortar bar tests.
2) To determine the efficacy of CSA blends containing fly ash, meta-kaolin and slag on their ability to mitigate ASR.
3) To compare the ASR mitigation performance of mortars containing blends of CSA and OPC cements

3.0 MATERIALS, MIXTURE PROPORTIONS AND METHODS

3.1 Materials and their properties

Cement

Two types of cements were used in this study, namely, CSA and OPC. The chemical compositions of these cements are shown in Table 1.

Pozzolans

The pozzolans that are used along with these cements to form binary blends include low-lime fly ash (Class F fly ash), meta-kaolin and slag. The replacement levels of low-lime fly ash and meta-kaolin used in these blends were 0%, 10% and 20% while that of slag was 0%, 30% and 40%. The chemical compositions of the various pozzolans used are shown in Table 1.

Fine Aggregates

Three types of aggregates were used, namely, a non-reactive siliceous sand from North Augusta, South Carolina, a moderately reactive siliceous limestone (Spratt Aggregate) and a highly-reactive New Mexico Aggregate (highly reactive aggregate) designated as Aggregate No. 1, No. 2 and No. 3, respectively. The aggregate gradation used for preparing the blended mixtures were as per the ASTM C 1260/C 1567 test procedure. The basic properties of the aggregates are shown in Table 2. Of the three aggregates, Aggregate No. 1 was natural river sand and Aggregate No. 2 and No. 3 were crushed stone. Aggregate No. 1 was sieved to obtain different size fractions that were recombined in required proportions per ASTM C 1260 to meet the gradation specifications. The Aggregate No. 2 and 3 were crushed and sieved to obtain smaller size fractions that were recombined to meet the gradation specifications.

3.2 Mixture proportions and methods

The mixture proportions of the mortars used in various tests in this study are shown in **Table 3**. All the mixtures are cast at a constant w/cm ratio of 0.47 and tested after a defined curing period. The various properties investigated include setting time, strength activity index and mortar-bar expansions due to alkali silica reaction.

The setting time test was conducted on cementitious paste containing the CSA and the OPC cements using the Vicat's apparatus as per the standard ASTM C 191 test procedure. The strength activity index (SAI) test was conducted on 50 mm x 50 mm x 50 mm mortar cubes containing these cements based on the ASTM C 311 test procedure. In this test, only non-reactive aggregates were used to determine the SAI after 3, 7 and 28 days curing period.

The effectiveness of the blends containing various pozzolans on their ability to mitigate ASR was determined by the ASTM C 1567 test procedure. In this test, mortar bars of size 25 mm x 25 mm x 285 mm, containing the CSA and OPC blends were cast using the mixture proportion, the aggregate gradation and the condition of exposure as per this method. The cast mortar bars were demolded after 24 hours, kept in hot-water bath maintained at 80^0 C for 24 hours and reference readings were taken with a comparator before immersing the bars in IN NaOH solution. The expansion of these mortar bars were recorded after specified immersion period till 28 days. The effectiveness of the blends to mitigate ASR was then evaluated based on the 0.10% limited expansion at 14 days as set by the ASTM C 33 specification. Both non-reactive (No. 1) and reactive aggregates (No. 2 and 3) were used to determine the ASR expansions of the blended mixtures. Comparative studies were conducted using these cements with no pozzolans using the ASTM C 1260 test method. The mixture IDs and the experimental program for this study are shown in **Table 4**.

4.0 RESULTS AND DISCUSSIONS

4.1 Setting time

The initial and final setting time of the OPC cement pastes were found to be 228 and 350 minutes, respectively, while that of the CSA cement pastes were found to be < 12 and < 45 minutes, respectively. Thus, the setting time of CSA cements were extremely faster compared to that of OPC cements, indicating rapid setting mechanism of CSA cements.

4.2 Strength activity index

The strength activity index (SAI) of mortars containing CSA cement at any given age was calculated by considering the strength of the OPC mortar at that specific age as 100%. The SAI values of mortar cubes containing the CSA cements after 3, 7 and 28 days curing period were found to be 142%, 131% and 105%, respectively. As observed, these SAI values decreases with increase in the curing period. At 3 and 7 days curing period, the SAI values were very high indicating the rapid hardening behavior of CSA cements. Sherman et al. 1995 had also obtained very high early-age strengths for both dry- and wet-cured specimens containing calcium sulfo-aluminates and other pozzolans. The reasons for such higher early-age strengths of CSA cement compared to OPC may be due to the formation of non-expansive ettringite at early ages [7]. However, at 28 days curing period, the SAI values of CSA cements were only slightly higher than OPC cements.

4.3 Alkali silica reaction

The 14-day and the 28-day expansions of mortar bars containing non-reactive and reactive aggregates with the two different cements are shown in Table 5.

Comparison of expansions of mortars containing virgin CSA and OPC cements in the ASTM C 1260/1567 Tests

The expansions of mortars containing CSA and OPC cements are shown in Figure 1 (a) and (b), respectively. As expected, with increase in the reactivity of the aggregate, the mortar bar expansions also increased for mortars containing both CSA and OPC cements. Among the three aggregates used, the

Aggregate No. 3 showed the highest expansions while the Aggregate No. 1 showed the least expansion, as expected.

In order to understand the comparative performance of CSA and OPC cements, a plot of the 14-day expansion of mortars containing these cements is shown in Figure 1 (c). For mortars prepared with non-reactive Aggregate No. 1 and with moderately reactive Aggregate No. 2, the 14-day ASR expansions of specimens containing CSA cements were similar or only slightly higher than that containing OPC cements. However, for mortars prepared from highly-reactive Aggregate No. 3, the 14-day ASR expansions of specimens containing CSA cements were significantly lower than that containing OPC cements. Such lower expansions may be due to the rapid setting and hardening of CSA pastes as indicated in the setting time and strength activity index tests. This setting and hardening of CSA cement may result in the formation of impermeable cementitious matrix that delays the attack of aggregates by the external alkalis present in the 1N NaOH soak solution. Further, the availability of lime in the hydrated matrix of CSA cement is significantly lower than that is available in the OPC cement paste [1]. It is well known that the expansive nature of ASR gel is promoted with the free availability of lime in the system.

Efficacy of blends of CSA with Pozzolans on ASR mitigation

Figure 2 (a) through (f) shows the expansions of mortars containing CSA cement with different pozzolans and different aggregates. As seen from all these figures, the ASR expansions decreases with increase in the replacement level of the pozzolans, namely, fly ash, meta-kaolin and slag, evaluated in this study.

In order to ascertain the replacement level of pozzolans at which effective ASR mitigation is achieved, the reduction in the 14-day expansions of all the mortar bars are plotted against the replacement level of pozzolans used as shown in Figure 3 (a) and (b). The dashed line in the plots indicates the minimum percent reduction in expansion required below which one can expect complete ASR mitigation (i.e. expansion less than 0.10% at 14 days) in the ASTM C 1567 test procedure. The minimum percent reduction in expansion was found to be 77.5% and 83% for Aggregate No. 2 and Aggregate No. 3, respectively. From Figure 3 (a), effective ASR mitigation was achieved with Aggregate No. 2 using a minimum replacement level of 7%, 6% or 26% of fly ash, meta-kaolin and slag, respectively. At higher replacement levels of these pozzolans, the mortar bar expansions were found to be well below the limit line. These values of replacement levels indicate that fly ash and meta-kaolin appear to perform similarly despite their different varying chemical compositions. However, significantly higher replacements levels of slag are needed to achieve a comparable level as obtained with fly ash and meta-kaolin. From Figure 3 (b) it can observed that effective ASR mitigation for Aggregate No. 3 was achievable only when fly ash and meta-kaolin were used at a minimum replacement level of 17.5% and 11%, respectively. These values are higher compared to those replacement levels obtained for Aggregate 2, which indicates that the replacement level of pozzolans for complete ASR mitigation is dependent on the individual degree of reactivity of the aggregates. However, the use of slag at a replacement level up to 40% was not enough to completely mitigate ASR in mortars containing Aggregate No. 3.

Comparative performance of CSA and OPC blends on ASR mitigation

Figure 4 shows the comparison of 14-day ASR expansions of mortars containing blends of pozzolans with CSA and OPC cements using Aggregate No. 2. This figure shows that for the control mixtures (i.e. with no pozzolans), the expansion values of mortars containing CSA cements were slightly higher than that of OPC cements, as also indicated in Figure 1 (c). However, the blends of CSA cement with pozzolans yielded significantly lower expansions compared to corresponding blends of OPC cement with pozzolans, with exception of SP-MK-20% mixture. This synergistic behavior of CSA cement with pozzolans in mitigating ASR is very advantageous from a practical standpoint, in that ASR prone aggregates can be effectively used with CSA cements using minimal amount of pozzolans. In SP-MK-20% mixtures, though the expansion of mortars with CSA cement and meta-kaolin was only slightly higher than the corresponding blend with OPC cement, both of their expansion values were well below 0.10% expansion limit.

5.0 CONCLUSIONS

From the investigations conducted to understand the performance of CSA cements and its blends with pozzolans in the presence of alkali-silica reactive aggregates, the following conclusions can be drawn:

(1) The SAI test results indicate that the strength gains are faster and higher in CSA cements than OPC cements. However, there is only a slight increase in the 28 days SAI index above control (100%).

(2) The use of virgin CSA cement in mortars instead of OPC was not effective in reducing the ASR expansion in mortars containing reactive aggregates below 0.10% at 14 days. Since, this study was helpful only in understanding the fundamental performance of CSA cements, detailed study is required to assess their accurate behavior.

(3) The blends of CSA cement with pozzolans were more effective than corresponding blends of OPC cement with pozzolans in mitigating ASR.

(4) For effective ASR mitigation with a moderately reactive aggregate (i.e. exp. less than 0.10% at 14 days in ASTM C 1567 test), the minimum replacement levels of Class F fly ash, meta-kaolin and slag in the CSA cement blends were found to be 6%, 5% and 26%, respectively, which are significantly lower compared to what is needed with OPC to achieve similar level of ASR mitigation.

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Table 1 – Major oxides present in the various cements and pozzolans used in this study

Sl. No.	Materials	Oxide contents by mass (%)							
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O_{equi}
1	CSA cement	15.40	13.78	2.38	50.87	1.26	12.52	-	-
2	OPC cement	19.78	4.98	3.13	61.84	2.54	4.15	-	0.82
3	Dolet Hill	58.67	20.86	11.57	3.35	1.15	0.40	1.12	1.20
4	Meta-kaolin	50.38	42.57	0.45	0.022	0.16	-	0.13	0.22
5	Slag	38.20	7.31	0.78	39.10	12.50	2.56	0.34	-

Table 2 – Properties of aggregates used in the study

Aggregate Property	Aggregate Type		
	No. 1	No. 2	No. 3
Water absorption (%)	0.2	0.456	0.344
Bulk specific gravity	2.65	2.69	2.75
Bulk specific gravity (SSD)	2.66	2.706	2.76

Table 3 – Mixture proportions of the cementitious mixtures

Cementitious mixtures	Blended Mixture	Quantity of materials (g)					w/cm
		Cement	Pozzolan	Fine Agg.	Water	SP	
Pastes	Control	440	0	0	206.7	RQ	0.47
	Blend	440 (1-x*/100)	440 (x*/100)	0	206.7	RQ	0.47
Mortars	Control	440	0	990	206.7	RQ	0.47
	Blend	440 (1-x*/100)	440 (x*/100)	990	206.7	RQ	0.47

Note: SP – Superplasticizer; RQ – Required quantity; x – RHA Replacement levels for cement in %

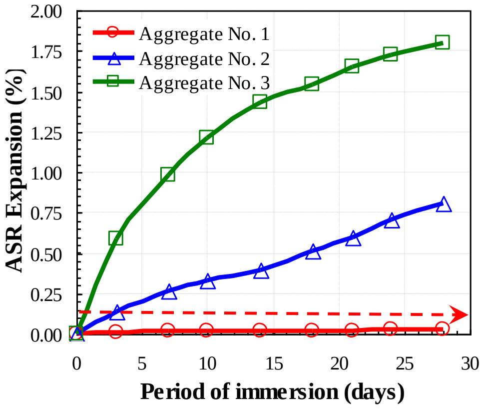
Table 4 – Mixture IDs and experimental program for this study

Aggregate Type	Mixture IDs	Replacement level of pozzolans (%)	Type of cement	
			CSA	OPC
No. 1 (Non-Reactive)	NR-Control	0	X	X
No. 2 (Spratt Reactive)	SP-Control	0	X	X
	SP-FA-10%	10	X	X
	SP-FA-20%	20	X	X
	SP-MK-10%	10	X	X
	SP-MK-20%	20	X	X
	SP-SL-30%	30	X	*
	SP-SL-40%	40	X	X
No. 3 (New Mexico Reactive)	NM-Control	0	X	-
	NM-FA-10%	10	X	-
	NM-FA-20%	20	X	-
	NM-MK-10%	10	X	-
	NM-MK-20%	20	X	-
	NM-SL-30%	30	X	-
	NM-SL-40%	40	X	-

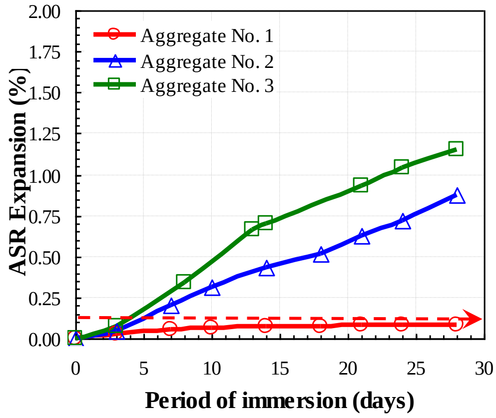
Note: *CSA-Calcium Sulfo-Aluminate cement; OPC-Ordinary Portland Cement; NR-Non-Reactive aggregate (No. 1); SP-Spratt Reactive aggregate (No. 2); NM-New Mexico Reactive aggregate (No. 3); FA-Fly ash; MK-Meta-kaolin; SL-Slag*

Table 5 – 14-day and 28-day ASR expansion of mortar bars containing different cements (SP – Agg. No. 1; NM – Agg. No. 2)

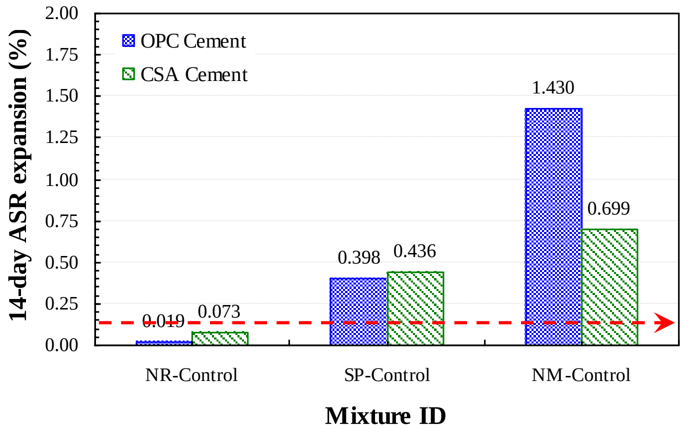
Mixture IDs	Expansion of mortar bars containing different cements after specified immersion period (%)			
	CSA Cement		OPC Cement	
	14-day	28-day	14-day	28-day
NR-Control	0.07	0.08	0.02	0.02
SP-Control	0.44	0.63	0.40	0.60
SP-FA-10%	0.06	0.09	0.29	0.32
SP-FA-20%	0.02	0.02	0.08	0.14
SP-MK-10%	0.04	0.04	0.10	0.19
SP-MK-20%	0.04	0.03	0.01	0.02
SP-SL-30%	0.05	0.13	-	-
SP-SL-40%	0.03	0.07	0.13	0.20
NM-Control	0.70	0.93	-	-
NM-FA-10%	0.07	0.10	-	-
NM-FA-20%	0.020	0.02	-	-
NM-MK-10%	0.14	0.14	-	-
NM-MK-20%	0.15	0.15	-	-
NM-SL-30%	0.14	0.25	-	-
NM-SL-40%	0.07	0.17	-	-



(a) ASR Expansion behavior of mortar bar containing OPC cement



(b) ASR Expansion behavior of mortar bar containing CSA cement



(c) Comparison of 14-day ASR expansions of mortar bars containing OPC and CSA cement

Figure 1 – Influence of aggregate reactivity on mortar-bar expansions containing CSA cement (SP – Agg. No. 1; NM – Agg. No. 2)

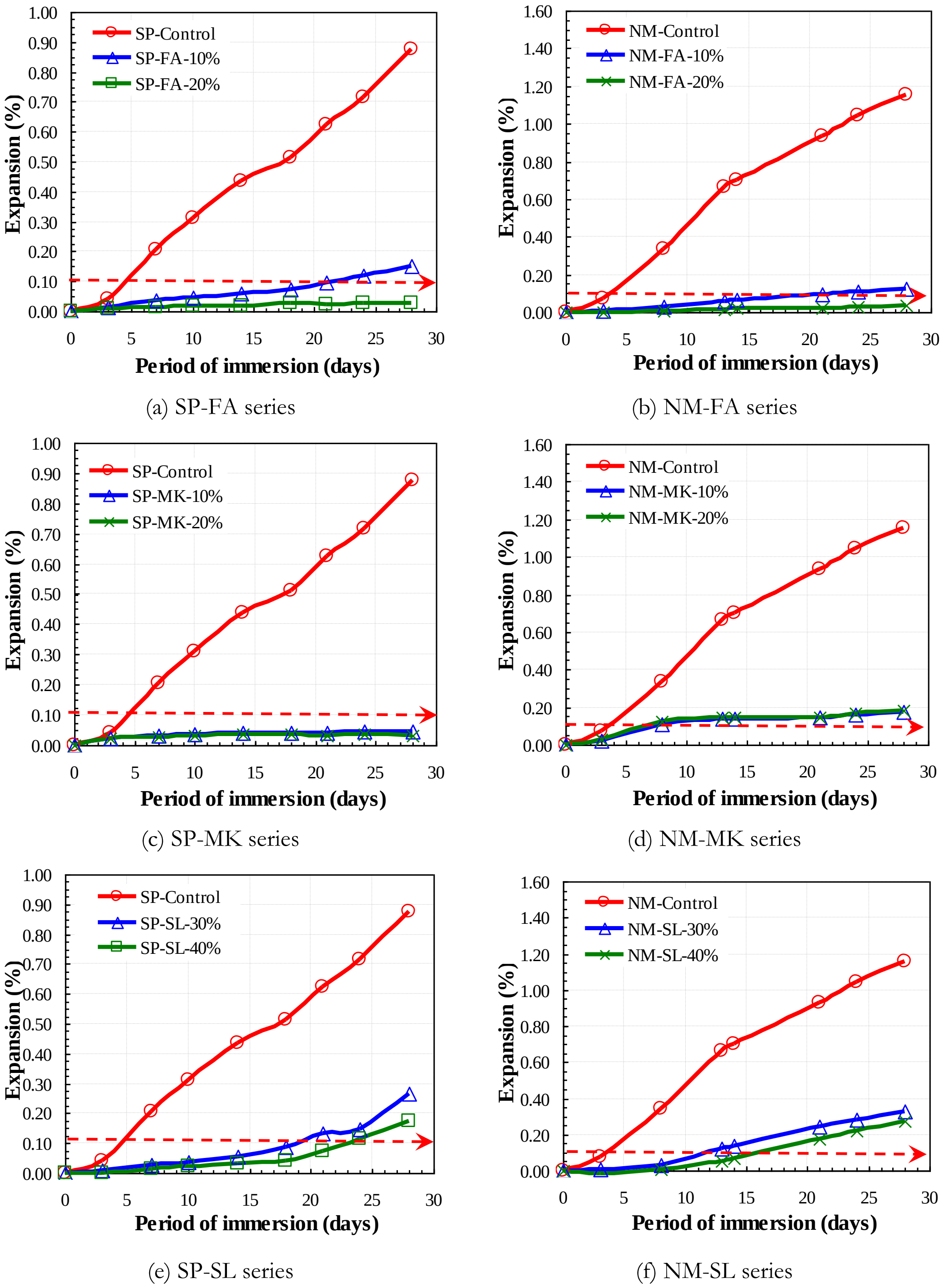
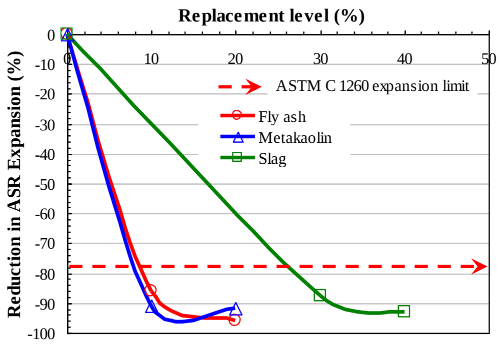
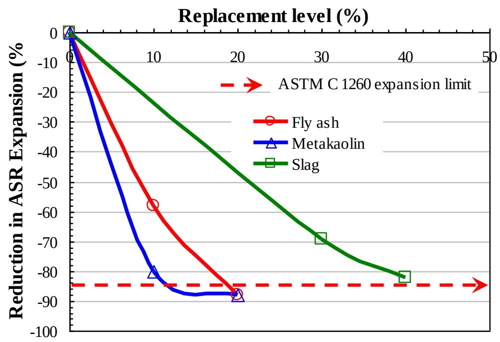


Figure 2 – Expansions of CSA blended mortar bars containing different aggregate (SP – Agg. No. 1; NM – Agg. No. 2)



(a) Spratt aggregate (Aggregate No. 2)



(b) New Mexico (Aggregate No. 3)

Figure 3 – Effect of replacement level on 14-day expansions of mortar bars containing CSA blends

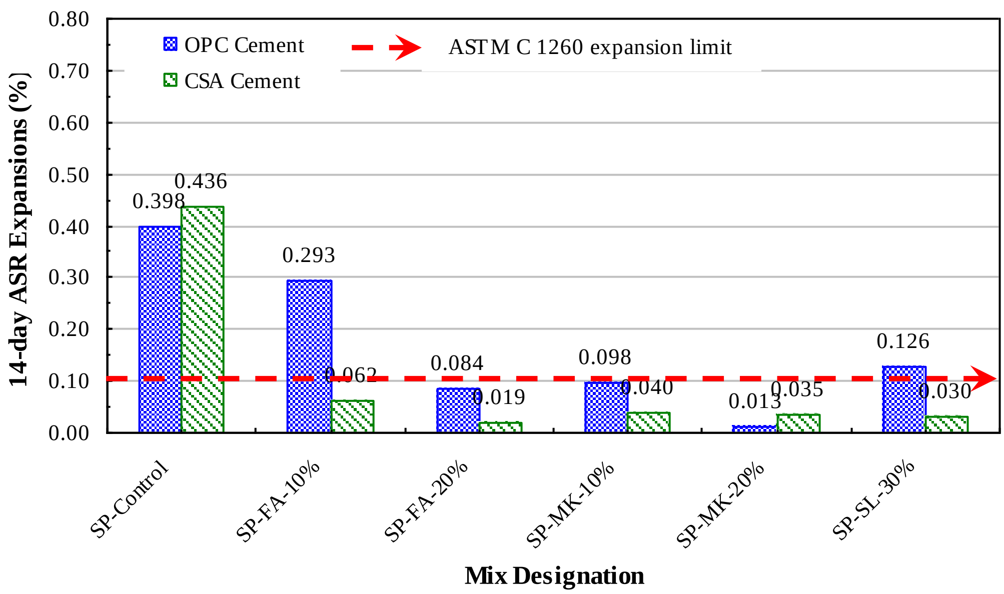


Figure 4 – Comparison of 14-day ASR expansions of mortar bars containing OPC and CSA cements and their blends