

Novel alkali silica reaction inhibitors for concrete

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Abstract

Current strategies used for the mitigation of alkali-silica reaction (ASR) includes the use of non-reactive aggregates, reducing concrete alkali loading, lithium-based admixtures, and supplementary cementitious materials. While these strategies have been useful, there are a variety of challenges with their future use including cost, availability, variability in performance, and logistical problems. Development of an economical new generation chemical admixture that is produced with consistent quality and wide availability will ensure that the concrete industry has a reliable solution to address the ASR problem. Our research has shown that certain soluble salts which meet the above requirements have the capacity to mitigate ASR by reducing the pore solution pH of concrete. This paper summarizes the protocol developed for the identification of such salts and evaluates the impact of the promising salts on workability, setting time, and strength development of mortar mixtures. Data from concrete prism tests are used for demonstrating the validity of this strategy. Drying shrinkage of mortar containing two of the promising salts are also presented. The salts identified here will be explored further in future studies to understand their effects on the microstructure, performance, and durability of concrete.

Keywords: alkali-silica reaction; chemical admixtures; mitigation

1. INTRODUCTION

Concrete industry has been searching for a cheaper, more available, and more effective alternative to lithium admixtures for mitigation of alkali-silica reaction (ASR). While other strategies for ASR mitigation exists, such as use of non-reactive aggregates, reducing alkali loading of concrete (e.g., by using cements with low alkali content), and using supplementary cementitious materials (SCMs) [1, 2], each of these solutions suffer from challenges that place their long-term sustainability in question. Non-reactive aggregates are not available in many locations. Reducing the alkali loading of concrete is not always sufficient for mitigating ASR while lithium admixtures may not be economically feasible [1, 3–5]. The consistency and availability of SCMs such as fly ash and slag have become a source of great concern recently. Fly ash supply has declined steadily over the last decade due to aging and retirement of coal-fueled power plants across the world in addition to more stringent air quality regulations which have impacted fly ash composition and performance in concrete. While the use of landfilled, ponded, or other off-spec fly ashes could partially compensate for this deficit, the use of these materials is in its infancy and their uniformity and performance in concrete are not fully understood [6, 7]. The world supply of slag cement is only 5% of Portland cement clinker and therefore slag is not available in sufficient quantities to meet the demand for ASR mitigation of concrete globally [8]. Overall, the introduction of new generation of ASR inhibitors which are cheap, reliable, and widely available will be highly beneficial for the concrete industry.

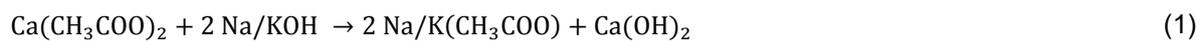
As is known from literature, ASR initiates when the reactive silica in aggregates are attacked by the hydroxyl (OH⁻) ions in concrete's pore solution. As such, the concentration of OH⁻ ions, alternatively presented as the pH of the pore solution, plays a crucial role in triggering ASR. Cements with lower alkali content and SCMs both mitigate ASR primarily by reducing the pH of concrete [3, 9]. For example in a typical concrete mixture with w/c=0.45, 350 kg cement per m³ of concrete, and at 70% degree of hydration, a portland cement with alkali content Na₂O_{eq}=0.90% produces a pH=13.82, while a cement with alkali content Na₂O_{eq}=0.60% (historically designated as "low-alkali" cement) leads to a pH=13.64 [10]. Concrete alkali loading of 1.8 kg/m³ achieved with low-alkali cement as the lone mitigation strategy is sufficient for managing ASR in moderately reactive aggregates as per ASTM C1778 [1]. The pore solution pH corresponding to this alkali loading and the above-mentioned conditions is 13.57 [10]. For aggregates with higher reactivity, reduction in concrete alkali loading needs to be combined with use of

SCMs for mitigation. It is also known from literature that ASR cannot be sustained below a hydroxyl ion concentration of 0.2 to 0.25 M [9, 11]. This corresponds to a pore solution pH of 13.30 to 13.40. While such low pH values will be conservative, it is often practically not necessary.

For a practical estimate of the upper limit of pore solution pH for ASR mitigation, the data provided by Thomas [9] can be used. This study provides the SCM dosage level required for mitigation of ASR in the case of a very highly reactive (R3 [1]) aggregate as estimated by the concrete prism test [12]. It also provides data on the pore solution pH achieved for various dosages of the SCMs. Based on relating the ASR mitigation dosage of an SCM with the corresponding pore solution pH; 13.50 can be set as a practical upper limit for mitigation of ASR in most cases. Thus, admixtures developed in this study capable of maintaining the pH below 13.50 are classified as “highly effective” formulations. Additionally, pore solution pH of 13.50 to 13.64 will be more effective than low alkali cements in mitigating ASR but may not be sufficient in all cases. Admixtures capable of maintaining the pH within this range are classified as “moderately effective” formulations. The capacity of the formulations to reduce the pore solution pH was experimentally measured as described in the subsequent sections.

2. NEW CHEMICAL ADMIXTURES FOR MITIGATING ASR

Certain soluble salts are capable of forming low solubility complexes with hydroxyl ions, and as such remove them from the pore solution of concrete. For example, calcium acetate can react with the sodium and potassium hydroxide in the pore solution and decrease the pH by precipitating calcium hydroxide as per the following reaction.



In addition to the precipitation of the cation hydroxide, the pore solution of concrete is modified such that a portion of the alkali ions are charge balanced by the anion from the salt rather than the hydroxyl ion. It is crucial that these anions stay in the pore solution to balance the alkali ions and not get captured by hydration products in order to maintain the reduced pH. For example, nitrates, nitrites, sulfates, and chlorides are known to form AFm phases and as such salts containing these anions would be less effective at maintaining the reduced pH [13]. The list of anions which are capable of producing the necessary effect needs to be experimentally determined.

There are over 700 salts that can be considered for this purpose. However, only a very small subset will meet various considerations based on performance, safety, economy, and consistency. Out of all the cations that could be used, it is best to limit it to calcium, magnesium, aluminum, and iron for two reasons. First, these are the most abundant metals in the earth's crust other than sodium and potassium which cannot be used due to the high solubility of their hydroxides [14]. Secondly, other cations would be foreign to the chemistry of cement and could potentially have negative side effects in addition to some of them being heavy metals which raises concerns regarding environmental toxicity. In addition to the cation criterion, the salt added needs to be more soluble than the cation hydroxide complex at the prevailing pH in order to encourage the capture of hydroxyl ions. As an example, if calcium acetate is used, then it should have a higher solubility than calcium hydroxide at pH = 13 (which is typical for fresh concrete) in order to effectively precipitate the hydroxide ions. In addition, the salts also need to meet certain other requirements such as being easily available, stable, inexpensive, non-hazardous, and not harmful to concrete. For the cost criteria, only salts that are cheaper than lithium nitrate, the current ASR mitigating admixture, were chosen. The availability and hazard level were determined using the information in chemical vendor websites. With respect to harmful effects on concrete, primarily chloride salts were eliminated. Following these theoretical considerations, the salts were also tested for certain practical requirements which are discussed in subsequent sections.

The final list of ASR-mitigating salts may be introduced into concrete in several ways:

- 1) In powder form, inter-ground with Portland cement clinker;
- 2) In powder form, pre-blended with Portland cement;
- 3) In powder form, pre-blended or inter-ground with SCMs like fly ash;
- 4) In powder form added to fresh concrete during mixing;

- 5) In pre-dissolved aqueous form (i.e., as a liquid chemical admixture) added to fresh concrete during mixing; and
- 6) In pre-dissolved aqueous form sprayed onto SCMs.

3. MATERIALS AND METHODS

3.1 Materials

The properties of the ASTM C150/C150M [15] compliant Type I portland cement (OPC) used in this study are shown in Table 3.1.

Table 3.1: Properties of OPC used in the study

Oxide Composition (%)							Limestone %	Blaine Fineness (m ² /kg)
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O _{eq}		
61.71	19.61	3.86	4.24	2.79	3.18	0.79	4.1	400

For the mortar tests such as flow, setting time, and compressive strength of cubes, concrete sand ("Northumberland") was used instead of standard sand. The Northumberland concrete sand sourced from Pennsylvania had an oven-dry specific gravity of 2.62 and absorption of 1.66%. The aggregates used for ASTM C1293 [12] were a highly ASR reactive Spratt coarse aggregate from Ontario, Canada and a non-reactive Oley fine aggregate from Pennsylvania. Spratt aggregate had an oven dry specific gravity of 2.64, absorption value of 0.74%, and the Oley fine aggregate had an oven dry specific gravity of 2.70 and absorption of 0.46%. Various manufacturers supplied the salts used in this study including Alfa Aesar, Spectrum, ACROS organics, etc. and all salts had a minimum purity of 95%.

3.2 Methods

3.2.1 Pore fluid analysis

To test the effectiveness of the salts, they were used to prepare paste mixtures and tested for pore fluid pH at fresh state, 7, and 28 days. The paste mixtures consisted of OPC, salt, and water at a w/cm (here 'cm' includes the salt and cement) of 0.45. The salts were incorporated on an OPC replacement basis – for example, a dry mixture with 2% calcium acetate contained 98% OPC and 2% calcium acetate by weight. Compressed air was used to extract the pore fluid from fresh paste while a high-pressure die was used for extracting pore fluid at 7 and 28 days from the hardened cement paste. The high-pressure die was operated at a loading rate of 90 to 180 kN/min (age-dependent) and a maximum pressure of 215 MPa. The pore fluid was filtered through a 0.45 μm filter and titrated with hydrochloric acid and phenolphthalein indicator for pH determination. For all of these tests, the salt was dry blended with the cement before mixing. The salts were also tested pre-dissolved in the mix water (suspended in the mix water in the case of salts with lower solubility) to check for any difference in pH reduction.

3.2.2 Mortar tests

Mortars mixtures were prepared by incorporating any given salt along with cement, water, and concrete sand. The proportions for flow and strength tests were fixed based on ASTM C109/C109M [16]. The testing protocol was based on the standards for the various tests – flow test based on ASTM C1437 [17], compressive strength of mortar cubes based on ASTM C109/C109M [16]. Setting time tests were done on prepared mortar mixtures with composition similar to that of the compressive strength cubes, except the w/cm ratio, which was lowered to 0.45. The procedure for setting time by penetration resistance was based on ASTM C403 [18]. Drying shrinkage of two salts (calcium formate and calcium bromide) and pure OPC mortar mixtures was also tested according to ASTM C157/C157M [19]. The mortar mixture proportions were based on ASTM C109/C109M [16] but the w/cm was adjusted to achieve a flow of 110 ± 5% as recommended in ASTM C157/C157M [19]. The final w/cm ratio was 0.464 for OPC and calcium bromide mixtures while it was 0.454 for calcium formate mixture. After casting, the mortar bars were stored in a moist room and were demolded at 24 hours for taking the initial length reading. Following this, the bars were stored in lime saturated water at 23 °C until 28 days of age. After the curing period, the bars were stored at 23 °C and 50% RH to observe the shrinkage behavior.

3.2.3 ASR testing – concrete prism test

Concrete prism tests were performed according to the requirements of ASTM C1293 [12]. We tested the effect of 10% aluminum nitrate and 10% iron (III) nitrate on a highly reactive Spratt coarse aggregate and a non-reactive Oley fine aggregate, the properties of which were described earlier. The two salts which were used for the ASTM C1293 test did not make it into the final list of promising salts (reasons discussed in the next section) but nevertheless demonstrate the effectiveness of reducing pore solution pH using soluble salts as an ASR mitigation strategy.

The accelerated mortar bar test (ASTM C1567 [20]) was not used to evaluate the effectiveness of the salts for two reasons. First, storage of mortar bar in water followed by a 1N sodium hydroxide solution leads to significant leaching of the anions of the salt from the pore solution. The leached anions are replaced with hydroxide ions from the alkali bath thus negating the pH reduction effect. Secondly, the salt dosage has to be carefully selected for the appropriate pH reduction. The large quantities of 1N sodium hydroxide solution used for storing the mortar bars would significantly increase the amount of admixture necessary for neutralizing the pore fluid.

4. RESULTS AND DISCUSSION

4.1 Pore solution pH

In addition to the criteria mentioned above, one of the first experimental criterion determined was a lower limit for pH. It is shown in literature that aluminum ions can bind to C_3S when the pH of the pore solution is below 12. pH of 12 to 12.5 is a grey area for this effect, therefore further testing is required [21]. In practice, this effect leads to significant strength loss at early ages. This can be seen in Figure 4.1 wherein the compressive strength at 1-day of the mixtures with the admixture dropped by roughly 70%. The fresh pore solution pH corresponding to mixtures containing 10% aluminum nitrate (AN) and 10% iron (III) nitrate (FN) are shown in the legend. Therefore, the next criterion is that the pore solution pH should be greater than 12 at all ages. This also led to the elimination of 10%AN and 10%FN from the final list of promising salts.

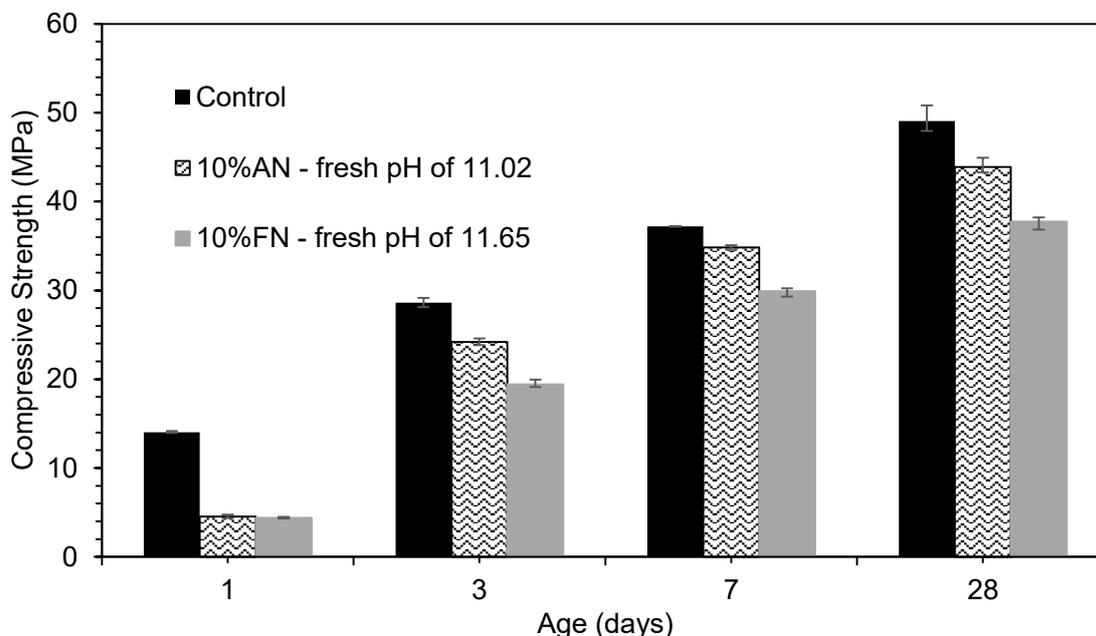


Figure 4.1: Compressive strength of 10%AN and 10%FN compared to OPC

Ten salts that were successful in maintaining the pH within the necessary range when used at a dosage rate of less than or equal to 5% cement replacement are shown in Table 4.1. Further, the “highly effective” salts that maintained the pH below 13.50 at all ages are in bold whereas the salts which had 28-day pH between 13.50 and 13.64 (“moderately effective” salts) are in plain text. It can also be seen

from the table that the performance of the admixture is independent of the mode of introduction (dry blended with cement vs dissolved/suspended in mix water).

Table 4.1: Pore fluid pH at 0, 7, and 28 days of the most promising salts used at dosage rate of less than or equal to 5% cement replacement

Mixture	Binder age (days)		
	0	7	28
OPC	13.00	13.75	13.77
Aluminum Nitrate	12.32	13.54	13.55
Ferrous Fumarate	12.80	13.30	13.40
Ferrous Fumarate – pre-suspended	12.87	13.32	N/A
Magnesium Acetate	12.50	13.38	13.41
Magnesium Acetate – pre-dissolved	12.62	13.36	N/A
Magnesium Bromide	12.62	13.44	13.53
Magnesium Bromide – pre-dissolved	12.50	13.45	N/A
Magnesium Nitrate	12.32	13.53	13.57
Magnesium Nitrate – pre-dissolved	12.50	13.55	N/A
Calcium Acetate	12.50	13.32	13.33
Calcium Acetate – pre-dissolved	12.62	13.30	N/A
Calcium Benzoate	12.72	13.44	13.47
Calcium Bromide	12.50	13.30	13.42
Calcium Bromide – pre-dissolved	12.62	13.30	N/A
Calcium Formate	12.62	13.32	13.34
Calcium Formate – pre-dissolved	12.62	13.30	N/A
Calcium Nitrate	12.62	13.50	13.55
Calcium Nitrate – pre-dissolved	12.62	13.51	N/A

4.2 Mortar tests

Mortar mixture tests were performed on the 10 salts shortlisted at dosage rates found to be suitable using the pore fluid pH test. The salts that did not provide satisfactory performance were eliminated from the final list of promising salts. Thus, mortar performance is the last selection criterion in the preliminary study. In the future, additional criteria such as performance in concrete prism test, effect on concrete durability, and so on will be tested. The difference in the flow of the mortar mixtures incorporating the salt when compared to the control pure OPC mixture is reported in **Erro! Autorreferência de marcador inválida.** Most of the salts improved the flow of the mortar. When there was a drop in flow, it is typically less than 10%, except for aluminum nitrate which showed a significant drop.

The compressive strength of the mortar cubes incorporating various salts were tested at 1, 7, and 28 days. The results of the strength test are shown as a percentage of the OPC mortar cube strength at the same age in Table 4.3. It can be seen that calcium benzoate has poor strength at all ages and thus can be eliminated. Additionally, aluminum nitrate has poor 1-day strength similar to the 10% dosage level. The fresh pH of 5%AN was 12.32, and as mentioned before, pH between 12 and 12.5 can sometimes be bad for C₃S hydration which seems to be the case here. Therefore, aluminum nitrate can also be eliminated.

Table 4.2: Difference in flow of mortar incorporating various salts when compared to OPC mortar

Mixture	Flow difference
AN (aluminum nitrate)	-19%
F2Fu (iron-II fumarate)	+10%
MAc (magnesium acetate)	+3%
MB (magnesium bromide)	+6%
MN (magnesium nitrate)	-6%
CAC (calcium acetate)	+3%
CBz (calcium benzoate)	+10%
CB (calcium bromide)	-2%
CN (calcium nitrate)	+17%
CF (calcium formate)	+4%

Table 4.3: Compressive strength of mortar cubes incorporating the salt as a percentage of control OPC cube strength

Mixture	Percentage of control OPC strength		
	1	7	28
CF	80%	96%	105%
CB	107%	109%	105%
MB	113%	96%	99%
CN	78%	89%	98%
MN	62%	84%	86%
F2Fu	72%	82%	83%
CBz	54%	70%	75%
MAc	71%	87%	92%
CAC	73%	93%	99%
AN	34%	85%	82%

Table 4.4 shows the initial and final setting time of all the mixtures containing the salts and OPC. Once again it can be seen that AN has very poor performance probably due to the C_3S hydration issue. While many of the salts are behaving as set accelerators, calcium benzoate (which was already eliminated due to poor strength) behaved as a set retarder. At the optimum dosage level, calcium acetate and magnesium acetate produced setting performance that is comparable to OPC.

Finally, the effect of calcium formate and calcium bromide on the drying shrinkage of mortar is shown in Figure 4.3. It can be seen that the mixtures incorporating the salts show a slightly higher drying shrinkage than OPC, but it is not a cause of concern. The other salts will be tested subsequently, and the results will be published in the future.

Table 4.4: Initial and final setting time of each mixture tested compared to OPC

Mixture	Setting time (hh:mm)	
	Initial set	Final set
OPC	05:18	07:10
CB	02:18	03:21
CF	03:16	04:57
MB	02:42	03:55
CN	02:59	05:04
MN	02:51	04:24
F2Fu	02:31	06:20
AN	>10:00	>10:00
CAC	05:25	07:50
MAC	05:57	08:18
CBz	06:19	09:21

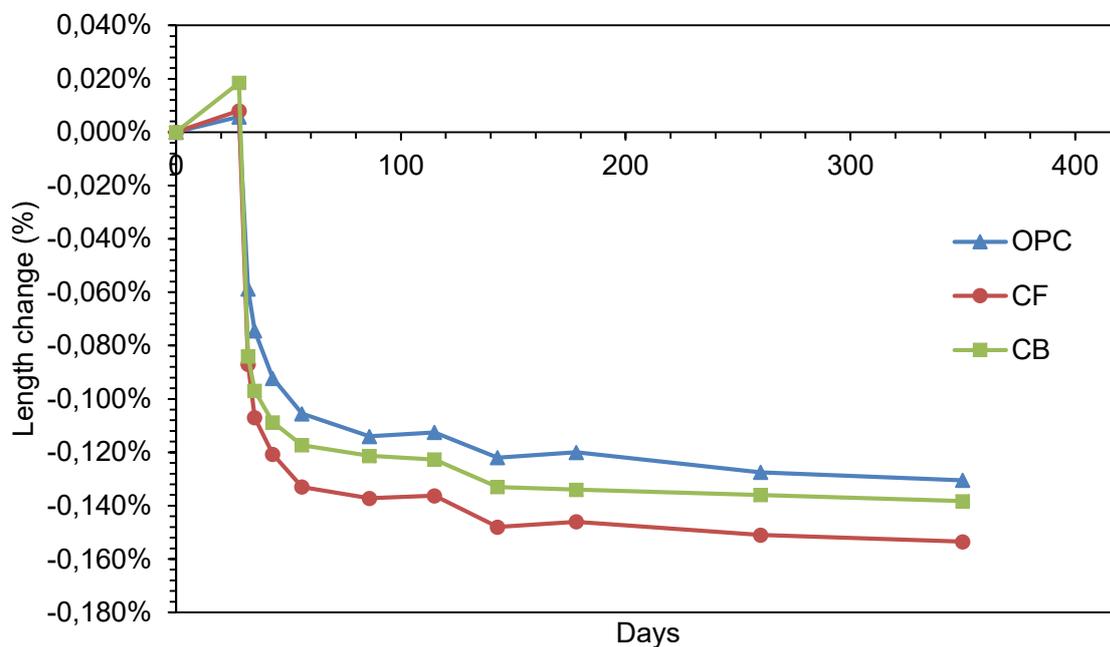


Figure 4.2: Drying shrinkage performance of CF and CB when compared to OPC

4.3 Concrete prism test results

The ASTM C1293 concrete prism test result is shown in Figure 4.3. 10%AN had a pore fluid pH of 13.53 at 180 days and 10%FN had a pore fluid pH of 13.56 at 90 days. Both salts are within the 0.04% expansion threshold at the end of 2 years as required in ASTM C1293 for successful mitigation. This

clearly demonstrates that pore fluid pH reduction using soluble salts is a valid strategy for ASR mitigation.

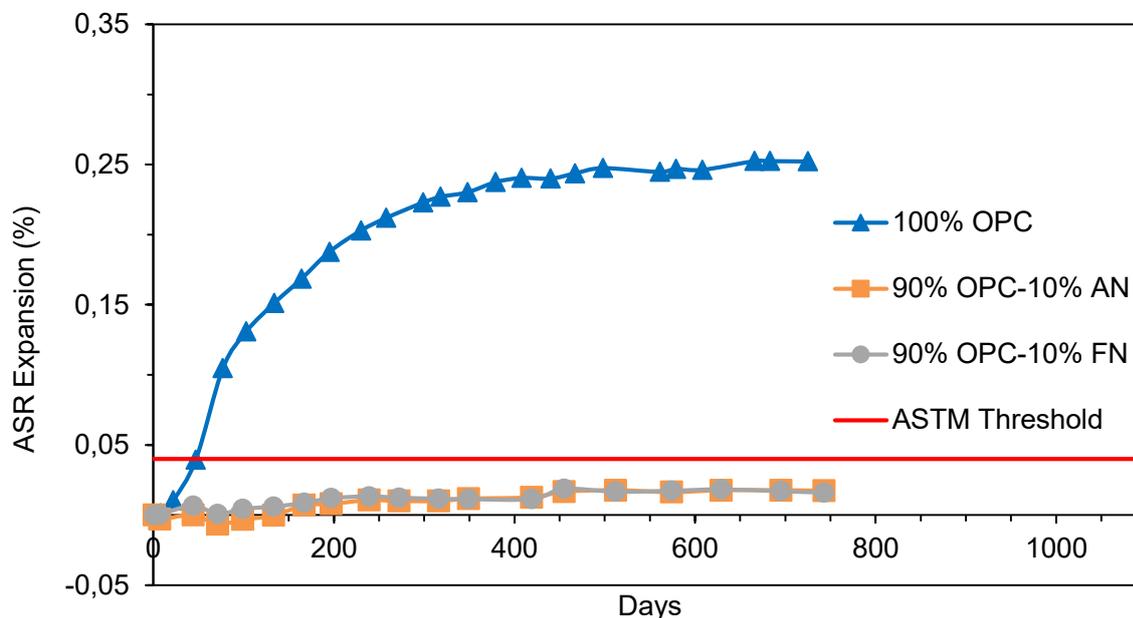


Figure 4.3: ASTM C1293 results for 10%AN and 10%FN with highly reactive aggregate

5. CONCLUSIONS

A new class of ASR inhibitors for concrete was explored in this study. These admixtures mitigate ASR by reducing the pore solution pH of concrete below that which can be achieved with low alkali cement. A number of criteria (based on theory and experimental data) was developed for the identification of suitable salts. Currently, the most promising 8 salts for this application are calcium acetate, magnesium acetate, calcium formate, ferrous fumarate, calcium bromide, magnesium bromide, calcium nitrate, and magnesium nitrate. The effectiveness of this strategy in mitigating ASR was demonstrated using ASTM C1293 concrete prism test. Future work will involve proving the capability of all the salts using the concrete prism test and assessing the microstructure and performance of concrete mixtures incorporating these salts.

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