EFFICACY OF ALKALI-SILICA REACTIVITY MITIGATION MEASURES AND THEIR EFFECTS ON THE ENGINEERINGPROPERTIES OF CONCRETE

Tom Pyle, John Gage, Vijay Jain, Benjamin Lenz*, and Doran Glauz

California Department of Transportation,
5900 Folsom Boulevard, SACRAMENTO, California 95819

Abstract

The incorporation of supplementary cementitious materials in concrete enhances concrete durability by reducing permeability and increasing resistance to alkali-silica reaction, sulfate attack, and corrosion. The results of test methods ASTM C1260, ASTM C1567, and ASTM C1293, performed on two highly reactive California aggregates with various mitigation measures using supplementary cementitious materials and lithium nitrate are presented. Some ternary blends are also examined. In addition, the results of compressive strength, flexural strength, modulus of elasticity, permeability, and drying shrinkage testing of concrete made with these additives are presented.

KEYWORDS: AAR prevention and remediation, admixtures, durability, lithium

1 INTRODUCTION AND SCOPE OF WORK

Alkali-Silica Reactivity (ASR) is defined as the reaction between reactive components of aggregate (reactive silica) and alkalis in the pore solution of concrete. Alkali-Silica reactivity may cause expansion resulting in deterioration of concrete.

Much progress has been made over the years to prevent ASR induced damage in new concrete construction. New and improved test methods and specifications have provided the necessary tools to mitigate ASR in concrete. The use of low alkali cements, supplementary cementitious materials like fly ash, ground granulated blast furnace slag, silica fume, Metakaolin, natural pozzolanic materials and chemical admixtures such as lithium compounds (primarily lithium nitrate) have helped in mitigating ASR in concrete.

Test method ASTM C 1293 is currently considered the most reliable for evaluating the potential alkali-silica reactivity of aggregates. However, the one-year testing period is often unacceptable for projects that require a rapid turn-around of results. A number of studies have been carried out to develop new test methods and also to accelerate ASTM C 1293 by increasing the temperature from 38°C to 60°C so that potential reactivity of aggregates can be evaluated in a shorter time.

This research paper is aimed to investigate the effect of mitigation measures on ASR in concrete. This study also includes the effects of supplementary cementitious materials and lithium nitrate on the various engineering properties of hardened concrete.

2 MATERIALS AND TEST PROCEDURES

2.1 ASTM C 1260/ASTM C 1567 testing

Two highly reactive aggregates, namely Saticoy aggregate and Desert aggregate available in California were selected for use in this study. The reactive elements of these siliceous aggregates consist mainly of rhyolite, chert, and volcanic glass. The cement used was California Portland Cement Type I/II. The chemical analysis of the cement is reported in Table 1. Class F fly ash, metakaolin, silica fume, Micron^3 (ultra fine fly ash), and the natural pozzolans Lassenite and Pozzolite were used as supplementary cementitious materials by mass replacement of Portland cement. The chemical analysis of these materials is given in Table 1. The samples were stored in containers containing 1N NaOH at 80±2 °C and readings were taken at intervals as described in ASTM C 1260. The test results are plotted in Figures 1 and 2.

---

* Correspondence to: ben_lenz@dot.ca.gov

2.2 ASTM C 1293 TESTING

Lehigh Portland Cement, Type 1, with an alkali content of 0.89% (Na_2O equivalent) was used to make the concrete prisms. In accordance with ASTM C 1293, reagent grade sodium hydroxide (NaOH) was added to the mixing water to increase the total alkali level to 1.25% (Na_2O equivalent). Triangle Soledad aggregate was used as an innocuous coarse aggregate, and met the grading requirements shown in Table 1 of ASTM C 1293. The highly reactive Desert aggregate was used as the fine aggregate in all concrete mixes for ASTM C 1293 testing. Cement content and water/cement ratios for all mixes conformed to ASTM C 1293. Class F fly ash, metakaolin, silica fume, Micron^3 (ultra fine fly ash), and ground granulated blast furnace slag were used as supplementary cementitious materials by mass replacement of Portland cement. Lithium nitrate was also used, both alone and with fly ash. The amount of lithium nitrate used was based on the alkali content and quantity of the cement used in the mix. Based on the manufacturer's recommendation, 4.56 liters of lithium nitrate solution was used per kilogram of alkalis in the concrete. A reduced amount was used in the mix in which it was combined with fly ash.

The concrete samples were stored in screw-top 19 liter plastic buckets, supported over water on plastic grids, and maintained in a chamber at 38°C, as per ASTM C 1293. Measurements were taken at intervals for one year. The test results are presented in Table 3 and plotted in Figure 3.

2.3 ENGINEERING PROPERTIES OF HARDENED CONCRETE

Eight concrete mixes of 0.113 cubic meters were made using Teichert coarse and fine aggregates and a Type I/II portland cement with 0.60% (Na_2O equivalent) alkalis. The cementitious material in each mix was 390 kg/m^3 and the water cement ratio was held constant at 0.41. Rheobuild 1000 (from BASF Inc.) was used as a high range water reducer. Class F fly ash, metakaolin, silica fume, Micron^3 (ultra fine fly ash), and the natural pozzolan Pozzolite were used as supplementary cementitious materials by mass replacement of Portland cement. One mix was made with a ternary combination of 15% fly ash and 5% metakaolin. Lithium nitrate addition, where used, was based on the alkali content and quantity of the cement used in the mix.

The objective of this part of the study was to investigate the effect of various additives on the engineering properties of hardened concrete, such as compressive strength, flexural strength, modulus of elasticity, drying shrinkage and permeability.

Cylinders of Ø102×203 mm were fabricated from the concrete for testing compressive strength. The samples were cured in a fog room up to 90 days and tested for compressive strength at various ages according to ASTM C39. The modulus of elasticity testing was performed on identical cylinders in accordance with ASTM C469.

Flexural strength and shrinkage tests were performed on 76×76×286 mm concrete prisms according to ASTM C78 and ASTM C 157 respectively. Samples for rapid chloride ion penetration testing were 51 mm thick slices of the Ø102×203 mm cylinders, as described in ASTM C1202.

The results of the above tests are presented in Table 2, and in Figure 4.

3 RESULTS AND DISCUSSION

3.1 ASTM C 1260/ASTM C 1567 Testing

The results reported in Figures 1 through 2 are percentage expansion versus number of days in 1N NaOH solution. For interpretation of results, expansion at 14 days immersion in 1N NaOH solution (16 days after casting samples) was considered the value for comparison.

The California Department of Transportation considers aggregates that show less than 0.15% ℓ/ℓ expansion at 14 days when tested by ASTM C 1260 to be innocuous. The same 0.15% ℓ/ℓ value is also used as a criterion for determining adequate mitigation when testing by ASTM C 1567.

Saticoy aggregate

The results of tests using metakaolin showed that a minimum of 10wt% metakaolin is required to mitigate ASR. Results when using Class F fly ash substitution showed that a minimum of 25wt% fly ash is required to reduce the 14-day expansion to less than 0.15% ℓ/ℓ. A 10% substitution of Micron^3 was effective in lowering the expansion from 0.70% ℓ/ℓ to 0.14% ℓ/ℓ. A silica fume substitution of 12wt% was required to mitigate ASR. A substitution with 15wt% of the natural pozzolan Lassenite was insufficient for complete mitigation, lowering expansion only to 0.34% ℓ/ℓ at 14 days. A ternary blend of 15wt% fly ash and 5wt% metakaolin was very effective, lowering the expansion to 0.05% ℓ/ℓ.

Desert Aggregate

Desert aggregate, when tested without mitigation, showed a 14-day expansion of 0.64% ℓ/ℓ. A substitution of 10wt% metakaolin was effective in lowering the expansion to 0.12% ℓ/ℓ. Class F fly ash substitution at various rates showed that approximately 25wt% fly ash is required to reduce expansion to below 0.15% ℓ/ℓ. A Micron^3 substitution of 12wt% reduced the expansion to 0.13% ℓ/ℓ. Substitution of 10wt% silica fume did not adequately mitigate expansion, reducing it only to 0.44% ℓ/ℓ at 14 days. Pozzolite natural pozzolan at 20wt% substitution reduced the expansion to 0.13% ℓ/ℓ. Three ternary blend substitutions were tested, 15wt% fly ash plus 5wt% Metakaolin, 15wt% Pozzolite plus 5wt% metakaolin, and 15wt% fly ash plus 5wt% Micron^3. All were very effective in reducing expansion to below 0.15% ℓ/ℓ.

In summarizing the results of the ASTM C1260 / ASTM C1567 testing, it can be concluded that a minimum of 25wt% Class F fly ash, or 10wt% metakaolin or Micron^3, or a ternary blend of 15wt% Class F fly ash plus 5wt% of either metakaolin or Micron^3 is required to mitigate alkali-silica reactivity in concrete with highly reactive aggregates.

3.2 ASTM C 1293 RESULTS

In this study, for the purpose of interpretation of the results, an expansion value of 0.04% ℓ/ℓ is considered the maximum allowable for an aggregate to be considered innocuous or for a mitigation attempt to be considered successful. The results plotted in Figure 3 show that Desert fine aggregate produced a one-year expansion of 0.218% ℓ/ℓ, which is much higher than the maximum allowed 0.04% ℓ/ℓ. Therefore this aggregate can be classified as highly reactive.

Eight separate mitigation measures were tested in this study. Four were straight mass substitutions of Portland cement, namely 25wt% Class F fly ash, 10wt% metakaolin, 10wt% Micron^3, and 50wt% ground granulated blast furnace slag. Additionally, two dual-pozzolan ternary mixes were tested. These used 15wt% fly ash plus 5wt% metakaolin and 15wt% fly ash plus 5wt% Micron^3, respectively. Finally, two mixes were made with lithium nitrate, one with lithium nitrate alone, and the other including a 15wt% substitution of fly ash.

In summary, each of the mitigation measures was very successful, reducing expansion to less than 0.03% ℓ/ℓ.

4 ENGINEERING PROPERTIES OF CONCRETE

The results of testing for compressive strength, flexural strength, modulus of elasticity, drying shrinkage, and rapid ion chloride permeability are presented in Table 2 and compressive strength is plotted in Figure 4.

Steam curing concrete samples at 100°C significantly improved compressive strength at 24 hours age. Two mixes, one with lithium nitrate alone and the other the ternary mix with 15wt% fly ash plus 5% metakaolin, showed the greatest increases in 24-hour compressive strength over the control. These mixes may be good choices for the manufacture of precast elements.

In general, addition of supplementary cementitious materials did not provide any appreciable improvement in flexural strength, modulus of elasticity or drying shrinkage over the control samples.

The ternary mix using 15wt% fly ash plus 5wt% metakaolin showed the most improvement in engineering properties of all the mixes tested, especially in the chloride permeability test. Another positive aspect of this ternary mix is that the metakaolin improved the early strength gain over the mix which used fly ash alone.

The concrete mixes using 10wt% metakaolin and 10wt% silica fume replacements show overall improvement in compressive strength and permeability.

Lithium nitrate acts as a set accelerator, assisting early strength gains. However, its addition did not reduce permeability.

The 25wt% fly ash substitution clearly delayed the early strength gain of the concrete as compared to the control, and reduced permeability, though not as well as silica fume, metakaolin or the ternary mix.

The use of Micron^3 improved compressive strengths, but had no effect on permeability.

Pozzolite used at a 15wt% substitution rate delayed early strength gains to an even greater extent than 25wt% substitution with fly ash.

In summary, it can be concluded that the best overall engineering properties were achieved by the ternary mix using 15wt% fly ash and 5wt% metakaolin. The mixes with 10wt% substitutions of metakaolin and silica fume each showed good performance.

5 CONCLUSIONS

1. A minimum 25wt% (mass substitution of Portland cement) Class F fly ash is required to mitigate alkali-silica reactivity in concrete with highly reactive California aggregates.
2. Metakaolin and Micron^3 each require a minimum of 10wt% (mass substitution of portland cement) for effective control of alkali-silica reactivity
3. A ternary blend of 15wt% (mass substitution of Portland cement) Class F fly ash plus 5wt% (mass substitution of Portland cement) metakaolin provided effective protection against alkali-silica reactivity and also showed the most overall improvement in engineering properties.
4. Lithium nitrate addition to the concrete provided adequate protection against alkali-silica reactivity. It also acts as an accelerator, assisting in early strength gain. However, its use does not improve the permeability of concrete compared to the use of supplementary cementitious materials.
5. This study supports ASTM C1293 as a good test method for evaluating the use of supplementary cementitious materials in concrete to control alkali-silica reactivity.
6. ASTM C 1567 is a fast, effective method for evaluating the use of supplementary cementitious materials in concrete for control of alkali-silica reactivity.
7. Within this study, ASTM C1260 / ASTM C1567 test results correlated well with test results using ASTM C1293.

6 ACKNOWLEDGEMENTS

The authors would like to thank Larry McCrum and his staff for the help they provided in the fabrication and testing of samples for this study.

7 REFERENCES

---

[1] ASTM C 1260 (2006): Potential alkali reactivity of aggregates (mortar-bar method). Annual Book of ASTM Standards (04.02), Concrete and Aggregates. American Society for Testing and Materials, West Conshoshocken, PA.

[2] ASTM C 1293 (2006): Determination of length change of concrete due to alkali-silica reaction. Annual Book of ASTM Standards (04.02), Concrete and Aggregates. American Society for Testing and Materials, West Conshoshocken, PA.

[3] ASTM C 1567 (2006): Determining the potential alkali-silica reactivity of combinations of cementitious materials and aggregate (accelerated mortar-bar method). Annual Book of ASTM Standards (04.02), Concrete and Aggregates. American Society for Testing and Materials, West Conshoshocken, PA.

[4] Fournier, B, Nkinamubanzi, P, and Chevrier, R (2004): Comparative Field and Laboratory Investigations on the Use of Supplementary Cementing Materials to Control Alkali-Silica Reaction in Concrete. In: Tang, M, and Deng, M (editors): Proceedings of the 12th International Conference on Alkali-Aggregate Reaction in Concrete, Beijing, China: 528-537.

[5] Hooper, R, Nixon, PJ, and Thomas, MDA (2004): Considerations when specifying lithium admixtures to mitigate the risk of ASR. In: Tang, M, and Deng, M (editors): Proceedings of the 12th International Conference on Alkali-Aggregate Reaction in Concrete, Beijing, China: 554-563.

TABLE 1: Chemical composition of materials

	Portland Cement Type II	Class F Fly Ash	Ground Granulated Blast Furnace Slag	Metakaolin	Silica Fume	Micron3
SiO_2, %	21.32	59.30	33.00	97.10 (sum of Si, Al, Fe)	94.30 (sum of Si, Al, Fe)	48.32
Al_2O_3, %	3.04	16.50	11.80			26.23
Fe_2O_3, %	3.75	4.95	1.60			3.74
CaO, %	64.68	10.00	41.30	--	0.50	14.08
MgO, %	2.23	--	9.00	--	0.66	2.50
SO_3, %	2.91	0.96	0.13	--	0.31	0.90
Loss on Ignition, %	1.94	2.61	0.80	--	2.26	0.13
Alkalis (as Na_2O equivalent), %	0.59	0.83	0.66	--	0.72	0.10
Fineness (Blaine), m^2/kg	377	--	295	--	--	--
Specific Gravity	3.15	2.40	2.80	2.50	2.20	2.57
Percent Retained on No. 325 (45um) sieve	--	24.81	--	--	--	2.20
Strength Activity Index @ 28 days, % of control	--	87.00	100.00	--	--	116.20

TABLE 2: Engineering properties of concrete.

Mix No.	mix design	compressive strength (MPa)					
		fog cure	steam cure	DAYS			
		1		7	28	56	90
1	Control	11.50	22.53	30.99	43.80	50.52	54.25
2	10wt% silica fume	10.80	26.19	31.63	48.43	52.28	51.30
3	10wt% metakaolin	12.84	28.68	33.30	47.39	49.43	50.48
4	25wt% fly ash	6.63	19.48	21.46	36.48	44.17	47.10
5	15wt% Pozzolite	6.67	16.95	21.55	37.82	43.28	44.63
6	lithium nitrate	16.04	34.03	40.89	46.40	54.06	53.30
7	15wt% fly ash + 5wt% metakaolin	15.75	34.76	37.72	51.87	54.53	55.14
8	10wt% Micron^3	12.62	29.94	36.49	48.72	51.99	55.21

TABLE 2 (cont'd): Engineering properties of concrete.

Mix No.	mix design	flexural strength (MPa)			modulus of elasticity (MPa ×1 000)			drying shrink.*	chloride perme.‡
		DAYS			DAYS				
		7	28	90	7	28	90		
1	Control	5.08	6.81	6.79	39.6	37.6	46.1	0.0547	3080
2	10wt% silica fume	5.04	6.40	7.40	33.1	34.8	48.3	0.0497	980
3	10wt% metakaolin	4.23	5.78	6.15	31.8	41.4	40.7	0.0467	1073
4	25wt% fly ash	4.50	5.45	6.74	30.7	38.2	37.3	0.0500	2143
5	15wt% Pozzolite	3.72	5.07	5.86	34.8	38.4		0.0720	1497
6	lithium nitrate	5.50	5.88	6.55	37.1	44.1	48.5	0.0557	3248
7	15wt% fly ash + 5wt% metakaolin	5.21	5.72	6.39	32.2	35.0	46.3	0.0530	1386
8	10wt% Micron^3	5.56	5.85	6.79	31.3	44.6	44.2	0.0550	3092

TABLE 3: Expansion results of ASTM C 1293 testing

mix	percent expansion ℓ/ℓ after exposure in days							
	0	**7**	**28**	**56**	**91**	**182**	**273**	**364**
control	0.000	-0.099	0.008	0.014	0.025	0.043	0.118	*0.218*
25wt% fly ash	0.000	-0.002	0.002	0.005	0.010	0.014	0.015	*0.019*
15wt% fly ash + 5wt% metakaolin	0.000	-0.005	0.000	0.005	0.010	0.014	0.017	*0.019*
10wt% metakaolin	0.000	-0.018	-0.015	-0.010	0.000	-0.002	0.000	*0.007*
10wt% micron^3	0.000	0.007	0.010	0.012	0.020	0.020	0.021	*0.026*
15wt% flyash + 5wt% micron^3	0.000	-0.006	0.000	0.006	0.007	0.009	0.012	*0.017*
lithium nitrate	0.000	0.002	0.011	0.020	0.022	0.023	0.025	*0.003*
lithium nitrate + 15wt% flyash	0.000	0.000	0.008	0.016	0.016	0.021	0.022	*0.029*
50wt% slag	0.000	-0.001	0.004	0.006	0.010	0.014	0.015	*0.020*

Figure 1: ASTM C 1260/ASTM C 1567 testing on Saticoy aggregate

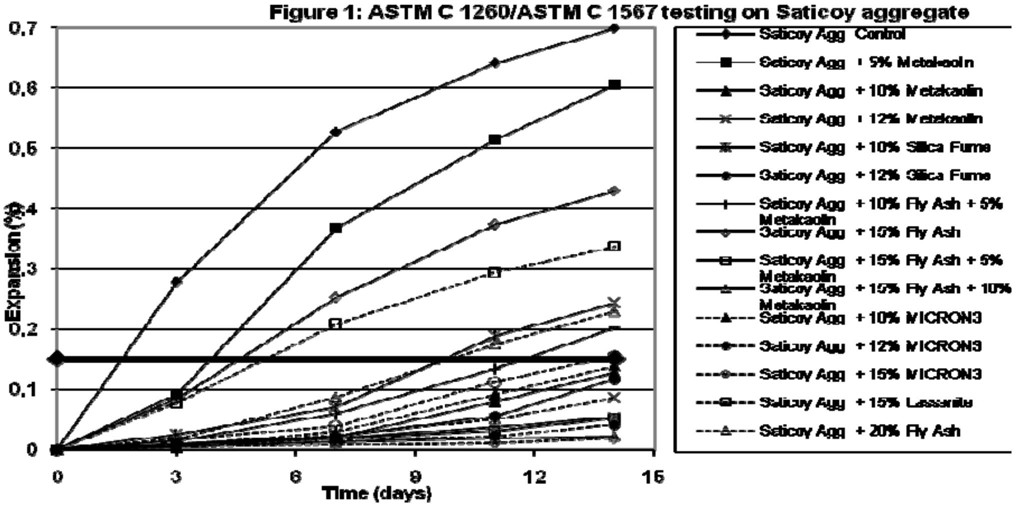
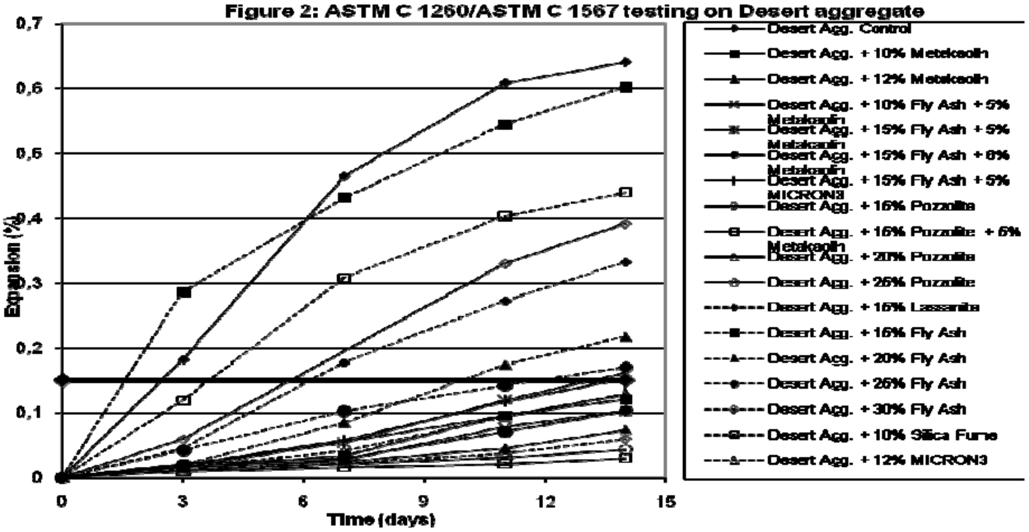


Figure 2: ASTM C 1260/ASTM C 1567 testing on Desert aggregate



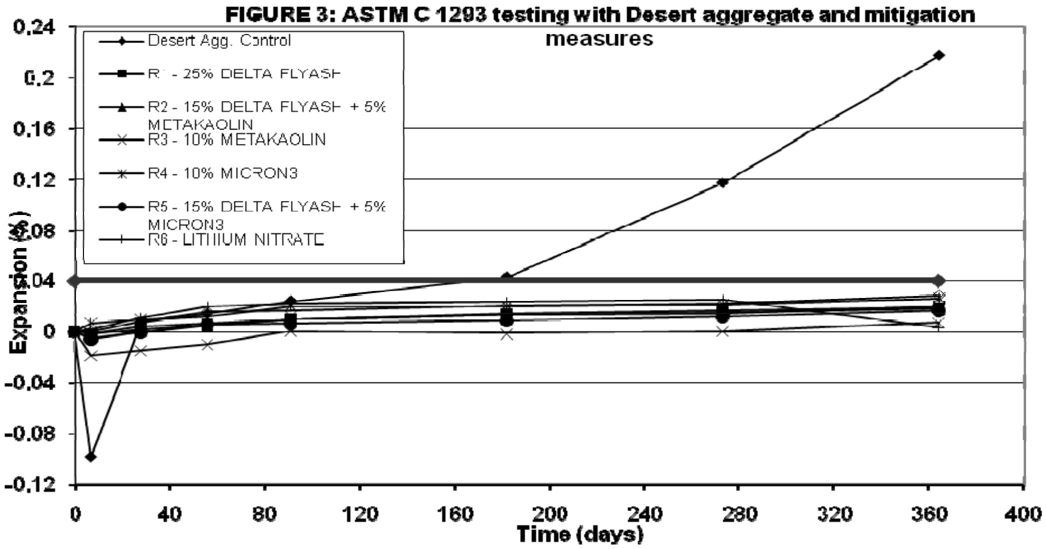


FIGURE 3: ASTM C 1293 testing with Desert aggregate and mitigation measures

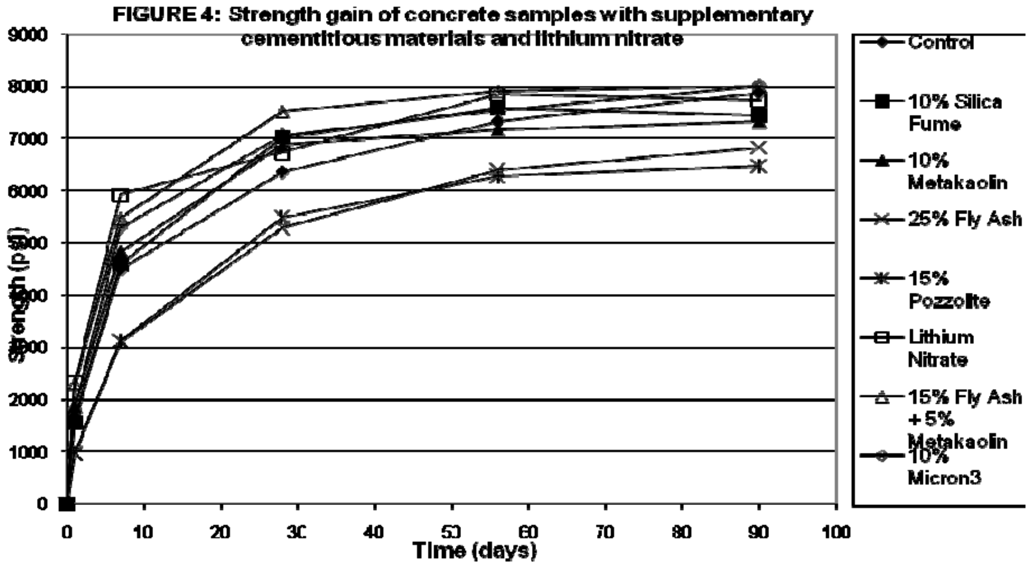


FIGURE 4: Strength gain of concrete samples with supplementary cementitious materials and lithium nitrate