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ASR SUPPRESSION BY LITHIUM COMPOUNDS

J.S. Lumley
Blue Circle Industries PLC
Technical Centre, 305 London Road
Greenhithe, Kent, DA9 9JQ, UK

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ABSTRACT

Concrete prism tests have been carried out to test the effectiveness of lithium compounds in reducing the expansion of concrete due to alkali silica reaction. Calcined flint cristobalite was used as the reactive aggregate in concrete mixes with material proportions close to those of field concretes.

With respect to the quantity of lithium required to alleviate asr in a given mix the results are broadly in agreement with those published by other laboratories using other reactive aggregates. The work also showed that adding only half the necessary quantity of lithium to a concrete mix does little or nothing to reduce asr expansion, so that full measures of lithium compounds need always to be used wherever the addition of lithium for this purpose is considered desirable. The supply and cost of lithium compounds are also briefly discussed in this report. © *1997 Elsevier Science Ltd*

Introduction

In 1950 McCoy and Caldwell (1) investigated the ability of various substances to reduce or even suppress the expansion of concrete caused by asr. Some copper and ammonium salts were found to be effective, but lithium compounds were the best. Other workers (2-6) have since found similar results. The possible commercial use of lithium for asr suppression was initiated in the 1980's when the Portland Cement Association started a fresh programme of experimental work on the topic and Stark (5) reported the interim findings in 1992. In many of the following papers much of the work was carried out on mortar prisms stored at elevated temperatures.

McCoy and Caldwell (1) using Pyrex glass in the ASTM C 227 test found asr expansion involving cements of eq Na_2O 0.57% and 1.15% to be almost completely suppressed by lithium carbonate at $Li_2O : Na_2O$ of 0.40 : 1 by mass. A ratio of 0.20 caused partial reduction of expansion. A mixture of lithium carbonate and fluoride at a combined ratio of 0.31 reduced expansion by three quarters.

Lawrence and Vivian's report (2) did not provide data to calculate ratios, but where they achieved complete inhibition of expansion by means of lithium hydroxide, asr gel spots were still seen on the mortar prisms stored at 43°C.

The paper by Sakaguchi et al. (3) quoted Li : Na ratios which were not clear, but working from their additions of lithium hydroxide given on a mass per 100g cement basis, the results of their work are similar to those found by other workers.

Ohama et al. (4) autoclaved at 128°C mortar prisms containing an opaline amorphous silica. Expansion was reduced by only one half by lithium fluoride and hydroxide at Li_2O : Na_2O ratios 0.50 and 0.41 respectively; though how relevant this result is to concrete at ordinary temperatures is open to speculation.

Stark's (5) C 227 tests with a natural reactive aggregate and a cement of 0.92% eq Na_2O produced complete expansion suppression with lithium carbonate at Li_2O : Na_2O of 0.44 and with the fluoride at 0.34. Half these dosage rates of the compounds had no noticeable effect on inhibiting expansion.

A reactive andesite aggregate was used by Bian et al. (6) in mortar prisms cured at 20°C for 4 months and then stored at 40°C. At high alkali contents of 11 and 19 kg/m^3 eq Na_2O, an Li_2O : Na_2O ratio of 0.8 reduced expansion substantially. At low eq Na_2O contents of the mortars lithium addition slightly increased the small expansion caused by the cement's alkali.

After the 8th ICAAR Conference at Kyoto in 1989, Blue Circle Technical Centre decided to carry out similar work using calcined flint cristobalite as the reactive aggregate in expansion tests on concrete prisms cured and stored at 20°C.

The Occurrence and Uses of Lithium

Lithium is widely distributed through the Earth's crust being a very minor component of many rocks. It is also present in vegetable and animal species.

Only a few sources contain sufficient concentrations of lithium to permit extraction on a commercial scale. The two types of source are brine lakes in North and South America, and pegmatite rocks which are very coarse grained granites consisting of quartz, alkali feldspar, and possibly mica. The principal lithium bearing minerals are spodumene, petalite, amblygonite, lepidolite, and eucryptite.

Compositions are given in Table 1. Lithium compounds are extracted from ores occurring in the North and South Americas, parts of Africa, Western Australia, China and Russia, not far from the Mongolian border (7). In the extraction process the ore is roasted; the temperature and time being critical. After removal of the lithium the residue is principally aluminium silicate (except from amblygonite).

The principal uses of lithium are in the manufacture of glasses, ceramics, lubricating greases, and pharmaceuticals. It has several other smaller applications and worldwide consumption is of the order of 30,000 tonnes of lithium compounds, as carbonate equivalent per year. Spodumene costs about $300 per tonne. The pure mineral contains 8.03% lithium as Li_2O; the commercial products having from 3% to over 7%. Bagged and drummed lithium carbonate is currently available in the USA at $4 per kilogram.

Lithium compounds are not particularly hazardous to handle, though contact with the eyes and skin is to be avoided. The industry carefully monitors the health of its employees, and sickness caused by contact with lithium seems to be very rare.

TABLE 1

The Principal Lithium Minerals and their Sources

Mineral	**Formula**	**Locations of deposits**
Spodumene	$Li_2O.Al_2O_3.4SiO_2$	USA, Australia, China, Russia, Brazil, Canada
Petalite	$Li_2O.Al_2O_3.8SiO_2$	Zimbabwe, Namibia, Australia, Brazil, Sweden, Russia
Amblygonite	$LiAl(PO_4)$ (F,OH)	Canada, Brazil, Zimbabwe, Namibia, Mozambique, South Africa, Rwanda, Surinam
Lepidolite	$K_2(Li,AL)_{5-6}\{Si_{6-7}Al_{2-1})_{20}\}$ (OH,F)$_4$	Zimbabwe, Namibia, Canada, Brazil
Eucryptite	$Li_2O.Al_2O_3.2SiO_2$	Zimbabwe
Brines		Nevada, Chile, Argentina and Bolivia

Several other significant deposits around the world have been identified.

Experimental

The experimental work consisted of long term expansion tests on seven sets of concrete prisms having stainless steel measuring studs cast into their end faces. Five sets each included control prisms devoid of lithium. The compounds tested were the carbonate, hydroxide, and fluoride of lithium. The solubilities, along with other salts are given in Table 2.

Approximate solubilities are expressed as grams of each compound soluble in 100 ml of water at 20°C (8). Stark et al. (9) reported that it is difficult to produce solutions of the above concentrations in deionized water. However, the solubilities of lithium carbonate and lithium fluoride are greater in the high pH pore solution of cement paste than they are in pure water.

The essential factor tested in six of the prism series was the effect of varying the lithium dosage in the mix. The aim was to cover a range of lithium additions from largely ineffective to complete asr suppression, in order to determine the most economic dosage in the given mix. The seventh series consisted of four prisms to test the effect of varying the calcined flint cristobalite content.

TABLE 2

Solubilities of Lithium Compounds

Lithium Hydroxide	LiOH	12.8
Lithium Hydroxide monohydrate	$LiOH.H_2O$	22.5
Lithium Carbonate	Li_2CO_3	1.33
Lithium Fluoride	LiF	0.27
Lithium Chloride	LiCl	70
Lithium Nitrate	$LiNO_3$	85
Lithium Sulfate	Li_2SO_4	25

TABLE 3

Cement Analyses

	Cement S	**Cement T**
SiO_2	20.6	20.7
IR	0.13	0.4
Al_2O_3	5.0	4.9
Fe_2O_3	2.1	3.3
Mn_2O_3	0.05	0.06
P_2O_5	0.04	0.06
TiO_2	0.22	0.27
CaO	65.4	63.0
MgO	1.8	2.7
SO_3	2.4	3.15
LOI	1.0	0.8
K_2O	1.13	1.05
Na_2O	0.12	0.44
eq Na_2O	0.86	1.13
Free Lime	1.4	-
SSA m^2/kg	362	360

All specimens were 75 × 75 × 270 mm prisms cast in two layers by hand tamping. The concrete for each prism was mixed on the bench with trowels, the lithium salt being dissolved or dispersed in the mixing water. The undissolved part formed a fine suspension in the mixing water in each case.

Most mixes were formulated to have a cement content of 400 kg/m^3 with Cement S, a British high alkali cement. This gave an equivalent soda content of the concretes of 3.44 kg/m^3. Cement T was produced from a high alkali clinker from Scandinavia ground in the UK. This was used in Series 164 at 304 kg/m^3 in order to achieve the same alkali content. Cement analyses are shown in Table 3.

The aggregates consisted of quartz sand for the fine, and 5-10 mm Mountsorrel granodiorite for the coarse. Essential details of all prisms are given in Table 4 which also shows how much of each lithium compound would have dissolved in the mixing water if saturation had been achieved. The mix proportions were 1 : 1.80 : 2.675 : 0.50 for the cement S mixes and the assumed pessimum value of the calcined flint cristobalite was 12% of the total aggregate volume except for Series 164. Freshly cast prisms were cured in their moulds in fog at 20°C for 24 hours and then demoulded, marked for identification, weighed, and initial comparator readings taken. They were then wrapped around their four long faces with polythene sheeting, which overlapped each bare end of the prisms by 5 cms, and placed horizontally on the shelves of the high humidity room for permanent storage in fog at 20 ±1°C. This mode of storage ensured that the prisms could imbibe water from the fog through their open ends, while minimising leaching by the covering of the large rectangular faces. The prisms have since been re-weighed and measured in the comparator at intervals to follow the expansions.

TABLE 4

Details of Test Prisms' Compositions

Series Number and Prism Identity	Cement	$\frac{W}{C}$	Calcined Flint Cristob. Content %	Lithium Compound	Compound Mass (kg) Per Cubic Metre of Concrete	Theoretical % of LiR Dissolved in Mixing Water	eq Li_2O kg/m^3	$\frac{\text{eq } Li_2O}{\text{eq } Na_2O}$
118 A	S	0.50	12		Nil		0	0
B		0.50	12	Lithium	4.95	53.8	2.00	0.58
C		0.50	12	Carbonate	9.89	26.9	4.00	1.16
D		0.50	12		14.84	17.9	6.00	1.74
119 A	S	0.525	0		Nil	-	0	0
B		0.525	12	Lithium	Nil	-	0	0
C		0.525	12	Carbonate	3.30	84.8	1.33	0.39
D		0.525	12		6.60	42.4	2.67	0.77
E		0.525	12		9.89	28.3	4.00	1.16
120 A	S	0.525	12	Lithium	1.87	100	0.67	0.19
B		0.525	12	Hydroxide	3.75	100	1.33	0.39
C		0.525	12	Monohydrate	5.62	100	2.00	0.58
121 A	S	0.525	0		Nil	-	0	0
B		0.525	12		Nil	-	0	0
C		0.525	12	Lithium	1.16	49.1	0.67	0.19
D		0.525	12	Fluoride	2.32	24.5	1.33	0.39
E		0.525	12		3.47	16.4	2.00	0.58
163 A	S	0.525	0		Nil	-	0	0
B		0.525	12		1.20	100	0.48	0.14
C		0.525	12	Lithium	2.00	100	0.81	0.23
D		0.525	12	Carbonate	2.80	99.9	1.13	0.33
E		0.525	12		3.60	77.7	1.46	0.42
164 A	T	0.64	0		Nil	-	0	0
B		0.64	11.2		1.20	100	0.48	0.14
C		0.64	11.2	Lithium	2.00	100	0.81	0.23
D		0.64	11.2	Carbonate	2.80	92.5	1.13	0.33
E		0.64	11.2		3.59	72.0	1.45	0.42
165 A	S	0.525	7.5		1.20	100	0.48	0.14
B		0.525	7.5	Lithium	2.00	100	0.81	0.23
C		0.525	10	Carbonate	1.20	100	0.48	0.14
D		0.525	10		2.00	100	0.81	0.23

Notes:
1. Equivalent soda content of all prisms 3.44 kg/m^3
2. Calc. flint cristob. content is percentage of total aggregate on a volume basis.

Results

Expansion curves are shown in Figure 1. From these, the failure of any prism to expand significantly between 2½ years age and the present ages of 5 and 6 years suggests that the lithium has a long term effect on inhibiting asr.

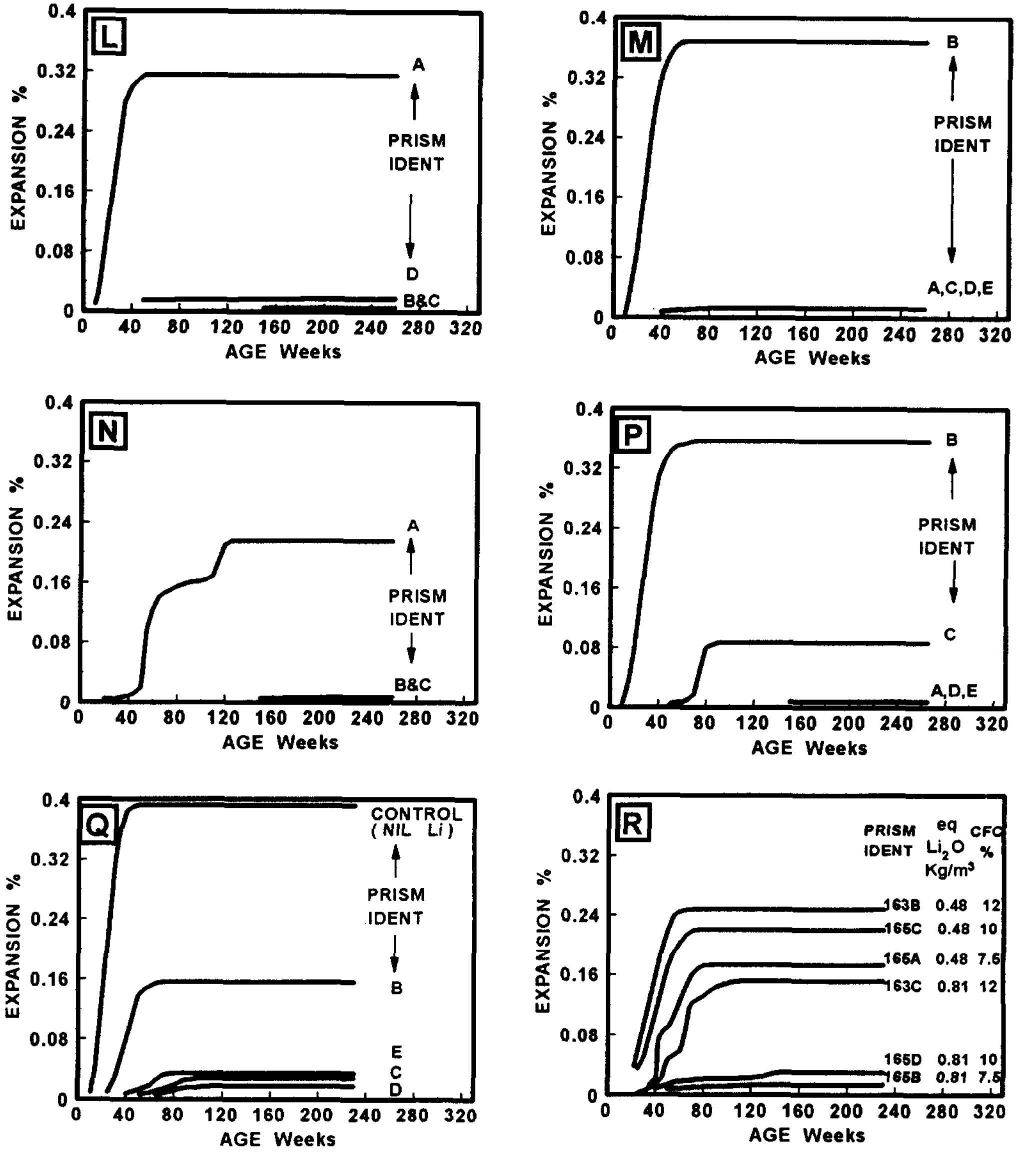

FIG. 1.

Expansion curves of the test prisms. L. Series 118 containing lithium carbonate. M. Series 119 containing lithium carbonate. N. Series 120 containing lithium hydroxide. P. Series 121 containing lithium flouride. Q. Series 164 containing lithium carbonate. R. Series 163 and 165 containing lithium carbonate.

For the purposes of assessing the effectiveness of lithium compounds, and quantifying their effect in suppressing asr, ratios of equivalent Li_2O to equivalent Na_2O will be considered. Here, the calculation of eq Li_2O involves theoretically splitting a compound LiR into Li and R, and then converting the Li to Li_2O; all carried out on a mass basis. Thus eq Li_2O is not analogous to eq Na_2O which latter means Na_2O plus an equivalent amount of another species, namely K_2O. Examination of Figure 1 with Table 5 shows that in these tests, where the eq Li_2O : eq Na_2O ratio was 0.33 : 1 by mass, or above, asr expansion was virtually totally eliminated. At a ratio of 0.14, expansion was only partially reduced. Ratios of 0.23 and 0.19 gave partial reduction in two cases - prisms 120 A and 163 C - considerable reduction in prism 121 C, and complete suppression in the three prisms 164 C, 165 B and 165 D.

In Figure 1 R the expansion curves of those prisms containing 0.81 kg/m^3 of Li_2O suggest that asr performance is somewhat sharply influenced by the proportion of calcined flint cristobalite in the aggregate. This is in contrast to most of the other asr work carried out with the cristobalite where the pessimum value, although requiring to be targeted fairly closely, is not particularly critical. However, too much significance should not be placed on one set of results. Further work would be necessary to establish the true acuity of the pessimum. For clarity Fig. 1R does not show prisms 163 A, D, or E because their expansions were recorded as nil or 0.01%.

The lithium carbonate caused noticeable stiffening of the concrete during the early part of the three minute mixing period. The effect was massive in the case of prism 118 D, thus the water : cement ratio was increased for subsequent mixes to improve prism compaction. It was then found that the lithium carbonate content of prism 163 D at only one-fifth that of 118 D caused total suppression of expansion. Thus, the higher water content was probably unnecessary for carbonate additions sufficient to prevent any expansion where much of the early stiffening would have been worked out. In this connection Gajda (10) found Li_2CO_3 addition to increase setting times by a factor of 2 or 3.

The lithium hydroxide produced much stiffening of prism 120 C, shortly before mixing was complete at 3 minutes. If the stiffening process had continued for a few more minutes, compaction of the prism would have been impaired. It is also possible that compaction of 120 B was affected. Lithium fluoride caused only minor stiffening of the mixes.

Prisms imbibed between 30g and 50g each from the fog over the first four years of their lives. Prisms which expanded more than 0.15% took up between 3g and 17g more water than sister prisms in the same series, which did not expand. Prisms 118 D and 120 C both imbibed some 10g more than sister prisms, doubtless because impaired compaction had left them porous as had been indicated by their lower demoulding weights. Series 163 showed somewhat anomalous behaviour in that 163 B, which expanded the most, gained one gram of water less than 163 D which showed only moisture movement.

Discussion

In these tests, conducted with concretes stored at 20°C and containing calcined flint cristobalite as the reactive aggregate, an eq Li_2O : eq Na_2O ratio of 0.33 to 1 by mass was found to be effective in almost completely inhibiting asr expansion. This result agrees reasonably well with those in the published papers referred to in the introduction.

Ultimate expansions in the current work are plotted against Li_2O : Na_2O ratios in Figure 2. A smooth curve could be drawn on the chart about which the points would be only slightly scattered. This suggests that none of the three anions involved had a significant effect on asr suppression. As CO_3^{2-}, OH^-, and F^- would not necessarily have the same effect as one another

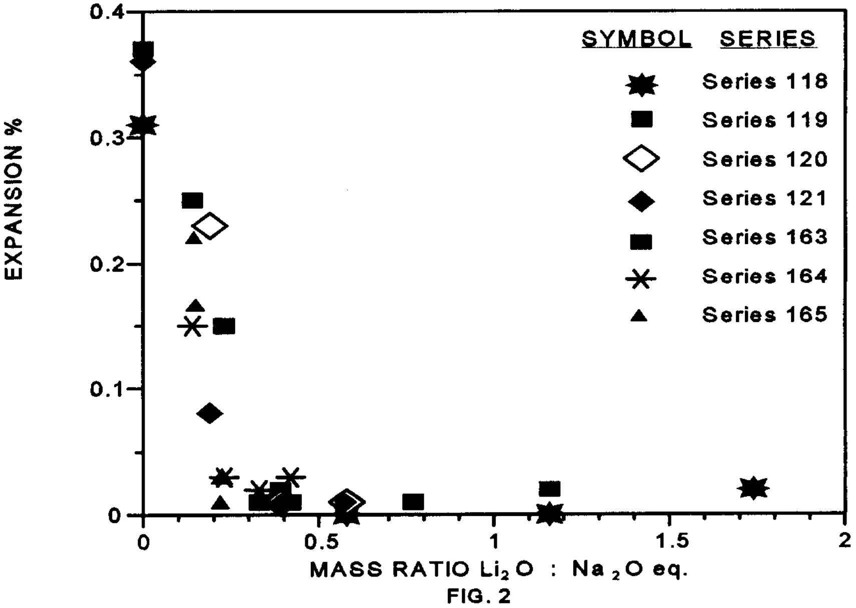

FIG. 2.

on OH^- concentration it is conceivable that the Li : Na : K ratios are the dominant factor with respect to asr and that any minor pH change is relatively unimportant.

If a provisional ratio of 0.35 : 1 is taken as that required to greatly reduce the chance of any concrete cracking through the action of asr, then a mix of 450 kg/m^3 of OPC of 1.0% eq Na_2O would require 3.885 kg of lithium carbonate/m^3, raising the material cost of the concrete by $15 per cubic metre.

Diamond and Ong (11) investigated the chemistry of lithium with respect to its effect on asr using a white Portland cement having the low equivalent soda content of 0.08%. Mortars prepared from this cement and a non-reactive aggregate were dosed with lithium hydroxide and cured at 38°C. Pore solution studies showed that much lithium became absorbed by the cement hydrates. Similar tests with the lithium replaced by NaOH and KOH indicated that sodium and potassium were also taken up by the hydrates, but to a rather less extent.

Further pore solution work with mortars containing reactive aggregates suggested that lithium forms an asr product, but in smaller quantities than sodium and potassium. Length change measurements on mortar bars confirmed that this lithium gel - in the near absence of Na and K - does not induce expansion. It was also found that when a reactive mortar contained lithium plus Na or K, each at say 0.25% of the mass of the cement, the asr gel contained both lithium and the other alkali ion and was less expansive than the pure Na or K gel.

The authors therefore concluded that when a sufficiently high dosage of lithium is added to a reactive mortar of typical eq Na_2O content, some lithium will enter the C-S-H, but sufficient will enter the asr gel at a later stage and render it non-expansive.

They also found that intermediate dosages of lithium increased expansion above the extent reached when no lithium was added. A speculative explanation of this phenomenon is that with their particular cement the lithium is taken up more quickly by the hydrates than the Na and K so that when the hydrates become saturated with alkali ions, more Na^+ and K^- ions remain in solution, balancing more OH^- ions. Thus the higher alkalinity of the pore solution, than would be the case in the absence of lithium, produces more gel and expansion; this notwithstanding the presence of a small but significant concentration of sulfate found in the pore solutions at ages up to several months.

The greater affinity of C-S-H for lithium over other alkali metals had been similarly demonstrated by Bhatty and Greening (12) who also found that the lower the Ca/Si ratio of the C-S-H, the greater the retention of alkali. Their work suggested that the lower Ca/Si ratio hydrates retained alkali metal ions by an additive process while a hydrate of 1.32 Ca/Si ratio could also exchange calcium ions for alkali.

Stade (13) found no particular trend of alkali retention with Ca/Si ratio with pastes prepared at 22°C by precipitation from sodium silicate solution and then immersed in molar alkali hydroxide solution. The tests confirmed that more lithium enters C-S-H than Na or K, and that much less of the larger molecule tetramethylammonium hydroxide is taken up by C-S-H. Stade further detected that pastes containing aluminium would incorporate less alkali metal than Al-free C-S-H.

That the combining power of C-S-H for Li is greater than that for Na and K is therefore well established. Also, this combined lithium is not available for suppressing asr. Thus the importance of not underestimating the dosage of lithium salt required to avoid asr problems is clear. However, since concretes containing reactive aggregate have a threshold alkali content below which expansion would be absent or exceedingly slow, lithium dosage will not be proportional to the equivalent soda content of the concrete and perhaps more work is required to establish a rule of thumb for determining dosage rates.

The compatibility of lithium with some widely used concrete admixtures was investigated by Wang and Stokes (14). Water reducing and superplasticising agents of both the plain and retarding varieties were tested in combination with a Vinsol resin air entraining agent in lithium charged concretes and lithium-free controls. The authors concluded that no significant effect of lithium admixture on concrete workability, strength development, or air entrainment was found. This was a global view as variations were evident between the four Type I cements used in the programme.

It is, perhaps, relevant to mention that attempts have been made to suppress further expansion in asr afflicted concrete by treatment with aqueous solutions of lithium salts. Manissero (15) reported that penetration of the solution into the concrete can be slow, but where successful, expansion is arrested.

Conclusions

The asr expansion tests described in this report used calcined flint cristobalite as the reactive aggregate in concrete moist stored at 20°C. The results agree with other published data in finding that an Li_2O : Na_2O ratio of 0.3 : 1 by mass in concrete is close to that required to almost totally inhibit asr expansion. The ratio would probably be different for mixes outside typical mix proportions and will also vary with actual equivalent soda content of the cement.

In common with other work the tests indicate that the threshold dosage of compound which just starts to reduce asr expansion is roughly half that of the fully effective dose which therefore cannot be significantly reduced with impunity. This effect was found in other laboratories and is explained by the pore solution work of Diamond and Ong (11).

Tests have been running for 6 years to-date, with no sign of the suppression effect ageing.

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