Further development of new supplementary cementitious materials from processed lithium aluminosilicate materials

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Concrete trials were initially carried out in 2012 on aluminosilicates materials generated from the processing of West Australian spodumene after removal of lithium, with limited test data presented at the 2013 CIA Biennial Conference. Subsequently a more comprehensive testing program was carried out and results presented in 2017 CIA Biennial Conference with the balance of unreported and on-going test results included a paper presented at the 2019 CIA Biennial Conference.

Development of these de-lithiated aluminosilicates has continued into 2020 and 2021 with a view to providing closure for any outstanding test work, such as the potential to mitigate alkali expansion, selection of relevant performance tests, to identify target fineness range to ensure that behaviour was comparable to other SCMs currently in use in Australia, selection of relevant soundness tests and the assessment of durability. Additional testing on pastes was also undertaken to determine the sensitivity of potential expansion to different drying temperatures and the determination of mineralogy by X-ray diffraction both before and after testing.

In parallel with the collection of further data on pozzolanic properties, a draft Australian Standard applicable to de-lithiated aluminosilicates has been under development for these and other processed pozzolans. The results of these investigations confirm these new aluminosilicates are pozzolanic and that they meet acceptable performance requirements for use in typical concretes and therefore the de-lithiated aluminosilicates have potential for use as supplementary cementitious materials in both domestic and structural concretes.

Keywords: de-lithiated aluminosilicates, environmental, recycling, sustainability.

1. Introduction

Previous investigation carried out by BCRC in 2012 and 2013 and reported in a paper by Haigh et al. published at the 26th Biennial Conference in the Gold Coast, October 2013, concluded that Tianqi de-lithiated aluminosilicate (TAS) had pozzolanic properties and could be used as supplementary cementitious materials (SCM) in concretes. Tianqi Lithium Australia Pty Ltd has taken over the development of the TAS products and proposed beneficial use of TAS products from its new processing plant in Kwinana, Western Australia that is expected to be supplying commercial quantities in late 2021.

Another lithium producer, Covalent Lithium Pty Ltd has also joined this development program and proposes to produce de-lithiated aluminosilicates which have pozzolanic properties from their processing plant in Kwinana, Western Australia in the near future. When these plants become operational, Tianqi aluminosilicate and Covalent de-lithiated beta spodumene (DBS) are expected to be available in the southwest of Western Australia for use as SCMs from 2021.

Considering that there has been substantial product development since the earlier trials, the TAS materials were reassessed in a further testing program and partial results were reported in a paper by Munn et al published in the 27th Biennial Conference in Adelaide in October 2017. Results of testing TAS products for use in domestic and structural concretes were reported in the former paper.

The technical paper presented at the 28th Biennial Conference in Sydney in 2019 includes reporting of the basic properties of the TAS products and the properties of domestic concrete and the structural concrete including longer term concrete properties not reported in the 2017 paper. It also reports additional testing carried out on new samples of TAS aluminosilicate subjected to testing for alkali expansion and sensitivity to fineness.

The current paper includes further testing of materials and concrete properties to determine compliance with the requirements of draft AS3582.4 and investigations related to the potential for expansion of the TAS and DBS products subjected to the ASTM C151 Autoclave Expansion test.

2. Compliance with AS 3582.1 and AS3582.4 Specification Requirements

The two new aluminosilicate materials, TAS and DBS have been assessed in order to ascertain compliance with current AS 3582.1 and the new draft AS3582.4 requirements and also to compare their properties with other pozzolans. These products are more correctly described as de-lithiated beta spodumenes and behave as zeolites so assessment as manufactured pozzolans is appropriate. This basic data has been derived from a TAS and DBS samples supplied to a program undertaken by Cement Australia in the Darra Laboratory for the during the development of the draft AS3582.4 in 2020. The data for Collie fly ash shown in Table 1 is from the 2019 CIA Biennial Conference paper.

The key properties and specification limits of the two products assessed are presented in Table 1.

Table 1 – Specific product properties and specification limits

Properties		AS 3582.1	AS 3582.4	Eraring Fly Ash, NSW	Collie Fly Ash, WA	TAS	DBS
Fineness passing 45µm, [%]	Grade (1)	min 75	min 65	87	85	--	75
	Grade (2)	min 65	min 50	--	--	54	--
	Grade (3)	min 55		--	--	--	--
Moisture, [%]		max 1	max 0.5	0.1	0.2	0.6	0.4
LOI, [%]		max 4-6	max 6	1.3	0.5	5.4	4.0
Relative Density		--	--	2.11	2.65	2.58	2.51
Relative water [%]		--	< 120	98	--	117	116
Relative strength	7 days	>75	> 85% (1) or >75% (2)	98	--	93	120
	28 days	--		91	--	--	--
SO_3, [%]		max 3	max 3	0.1	0.4	0.3	2.9
Chloride [%]		--	< 0.1	0.002	0.01	0.01	0.002
Magnesia [%]		--	max 5	0.4	1.1	0.1	0.3
Available alkali [%]		--	--	0.3	0.8	<0.1	<0.1
SiO_2 +Al_2O_3 +Fe_2O_3 [%]		--	--	93.8	90.3	93.4	87.4
Autoclave expansion [%]		--	<0.15	<0.me01	--	0.14	0.10

Notes (1) AS 3582.1 allows variations from reference limits if different testing methods are used.

(2) In some areas in Australia, there are limited quantities of reactive fly ash available.

(3) The TAS and DBS samples moisture contents were tested after drying.

(4) Relative water demand and relative strength were determined by comparing the value obtained by testing with relevant values obtained by testing Portland cement mortar only.

(5) After drying, the DBS product was ground minimally in a laboratory ball mill increasing fineness compared with that of the TAS product.

Fineness - Both TAS and DBS products are coarse when compared to AS 3582.1 limits and when they are compared with Eraring fly ash (NSW) and Collie fly ash (WA). The DBS product is finer than the TAS product but both meet AS3582.4 limits and both products are more reactive than fly ash.

LOI – The loss on ignition values for TAS and DBS are less than the AS 3582.1 and AS3582.4 limits but higher than for current fly ash sources. The source of the LOI is mainly bound water that it released in two stages up to 200^0C and above 500^0C.

Relative density – The densities of both TAS and DBS products are in the normal range for fly ash.

Relative water – Both TAS and DBS products exhibit higher water demand when compared with Eraring fly ash, but both are less that the AS3582.4 limit. Differences are likely to result mainly from the differences in fineness, porosity and particle shape. There is no significant difference in water demand between the TAS and DBS products assessed.

Relative strength – The results are also similar to Eraring fly ash relative strength at the same age. At 7days the relative strengths exceed the minimum requirements of AS 3582.4 specification, with higher strength index for the finer DBS product compared with the TAS lithium residue product.

SO_3 – The results for TAS and DBS are below the maximum limit of AS 3582.4. The DBS result test is higher than for TAS test result due to the higher gypsum content of the DBS product.

Chlorides – The test results are low for both TAS and DBS products.

Magnesia – Both TAS and DBS lithium residue products contain low magnesia when compared with Eraring and Collie fly ashes. There is no need for an autoclave expansion test as the MgO content is well below the 5% requirement for the test to be performed.

Available alkali – The test is not mandatory in the AS 3852.4 but may be specified, tested and reported. Both TAS and DBS products exhibit low alkali content.

SiO_2+Al_2O_3+Fe_2O_3 – It is well known that high SiO_2 and Al_2O_3 content in SCM products assist in the strength development and control of the alkali silica reaction (ASR). The TAS and DBS products contain high silica and alumina contents similar to fly ash samples and would be expected to be pozzolanic.

Autoclave expansion – The autoclave expansion test results for both TAS and DBS products of 0.14% and 0.10% respectively are higher than for Eraring fly ash but well below the maximum limit required by ASTM C618 of 0.8% for natural pozzolans. Further research into the cause and consequences of this expansion resulting from accelerated testing to ASTM C151 is required.

3. Assessment of the TAS aluminosilicates in domestic and structural, high durability concretes

Domestic concrete - Domestic concrete applications represent the majority of concrete used in Western Australia. In 2020 to determine whether consistent performance was demonstrated over a longer time period, properties of domestic concrete were evaluated using strength grade 20MPa with 90 slump and 20mm aggregate concrete with TAS replacing 20% of the cement content. A control concrete was also cast using 20% of the cement content replaced by Eraring fly ash with all concrete prepared in the Boral Testing Services Laboratory. The mix designs were similar to those used and reported in the CIA Biennial Conference paper in 2017 with lower cement content.

Additional properties were tested than previously included for domestic concretes which were slump, density, air content, bleeding, setting time, AVPV, compressive strength and drying shrinkage. The plastic and hardened state properties of these concretes are shown in Table 2 and Table 3 respectively.

High durability concrete - High durability concretes play an important role in the WA concrete industry and in particular the mining industry, gas and port projects, railway, bridges, etc. The assessment of the TAS products in high durability, structural concrete was carried out as required for a typical bridge concrete mix in NSW as per B80-B2 Class exposure. The design strength grade was 40 MPa, with 20 mm maximum sized aggregate and nominal slump of 100 mm. The TAS was used at 24% replacement of cement content. The results for fresh concrete properties are presented in Table 2 and for hardened concrete properties presented in Table 3.

Additional properties were tested than previously included for high strength concretes which were slump, density, air content, setting time, AVPV, compressive strength and drying shrinkage. The plastic and hardened state properties of these concretes are shown in Table 2 and Table 3 respectively. In the case of high strength concrete, tests for sorptivity and chloride diffusion were also carried out and results presented below.

Table 2 – Fresh Concrete Properties for 20MPa and 40MPa mixes

Concrete Properties	**20MPa - 20% Fly ash**	**20MPa - 20%TAS**	**40MPa – 24% Fly ash**	**40MPa – 24% TAS**
Slump [mm]	90	90	100	100
Water/cement	0.81	0.81	0.51	0.51
Density {kg/m3}	2360	2340	2350	2350
Bleeding [%]	1.9	1.1	0.9	0.1
Air Content [%]	1.5	.2.4	1.7	2.6
Setting time [min]	309/434	312/427	--	--

Table 3 – Hardened Concrete Properties for 20MPa and 40MPa mixes

Concrete Properties		**20MPa-20% Fly ash**	**20MPa-20%TAS**	**40MPa - 24% Fly ash**	**40MPA-24% TAS**
Compressive Strength [MPa]	3 days	10.0	10.5	26.5	27-0
	7 days	14.0	16.0	32.5	37.0
	28 days	21.0	30.0	45.5	55.0
	90 days	26.5	34.0	57.5	64.0
Drying Shrinkage [µm]	21 days	410	530	580	580
	56 days	550	650	720	670
	90 days	570	680	770	720
Sorptivity at 7 days [mm]	wet	--	--	22.9	14.9
	bagged	--	--	25.4	15.7
	waxed	--	--	27.9	17.8
AVPV %		15.7	16.4	14.2	15.9
NT443 Chloride Diffusion [E-12m2/sec]		--	--	6.20	6.38

3.1 Comments on fresh properties of domestic and structural, high durability concretes

- **Slump** - No difficulty was experienced in mixes containing TAS achieving the slump requirements of the mix design (120 ±20mm).
- **Water/Cement** - The TAS mixes are not significantly different from control concretes.
- **Bleeding** - There is no negative impact and the TAS mixes show reduced bleeding.
- **Air content** -TAS mixes are slightly higher than the respective control concretes.

As a general comment, there are no negative impacts on fresh concrete properties when TAS is used as SCMs (20% - 24%) replacing fly ash in the mix designs.

3.2 Comments on hardened concrete properties of structural, high durability concretes

Compressive strength

Age 3 days - TAS and control mixes have similar test results.

Age 7 days - TAS test results are higher than control results.

Age 28 days - The compressive strengths of the TAS mix increased significantly and is 20% greater than the control concrete.

Age 90 days - The compressive strengths of the TAS mix increased significantly and is 12% greater than the control concrete.

Testing of the domestic and structural concretes confirms that TAS concretes exhibit good pozzolanic activity. The strength growth profile indicates that, due to the coarser particle size distribution of both products compared with fine grade fly ash, the pozzolanic activity takes some time to take effect which can be improved with greater fineness.

- **Drying shrinkage** - The test results at 21, 56 and 90 days for the TAS concretes are not significantly different when compared with respective control concretes.
- **Sorptivity** - The results for TAS lithium residue concrete are much lower than control concrete. All results for TAS concretes are well below the specifications requirements of maximum 25 mm and so TAS contribute to better concrete durability.
- **AVPV** - 20MPa and 40MPa concretes containing TAS showed similar AVPV to respective control concretes.
- **Chloride ion diffusion** - The Nordtest Method NT Build 443 was used to assess chloride ion diffusion coefficients after 35days immersion of concrete samples in 16.5% sodium chloride solution. When compared with the control concrete containing 25% Eraring fly ash in the binder, the concrete containing 24% TAS exhibited a similar chloride ion diffusion coefficient.
- **General** - These test results show that concretes containing TAS products have generally superior performance in strength, serviceability and durability related properties when used in similar proportions and comparable concretes made with well recognised fly ash.

4. Potential expansion of lithium residues (TAS and DBS) when tested to ASTM C151.

The testing program undertaken by Cement Australia confirmed many of the properties of the testing previously available for TAS and DBS but also included additional testing and analysis for mineral composition, paste properties, pozzolanic activity, and the testing of both mortars and concretes containing TAS and DBS. Test carried out on pastes included soundness to AS3583.4 (autoclave) and to AS2350.5 (Le Chatelier) and whilst the tests to the latter standard test method indicated expansion of 1mm to 3mm which are similar to test results on Portland cement and fly ash obtained from the same testing program, the autoclave expansion tests to AS3583.4, indicated expansions of 0.10% to 0.14% which are significantly greater than the corresponding values for Portland cement and fly ash.

The authors understand that two soundness tests were included in this testing program because the autoclave test to ASTM C151 is included in ASTM C618 as a soundness test however the AS2350.5 test method is more commonly used Australia for cement and pozzolan testing. The autoclave testing methods AS3583.4 and ASTM C151 are very similar and comparable test results would be expected. The expansion reported of 0.10% to 0.14% in the Cement Australia testing program is much lower than the maximum of 0.8% permitted in ASTM C618 for natural pozzolans which has been in place for decades in the USA so if a similar limit was set in the draft AS3582.4 to ASTM C151, the expansions recorded would be acceptable however a more cautious approach was taken by the AS3582.4 drafting committee.

The autoclave expansion test, ASTM C151, has been used for decades as an accelerated test to determine the potential for long term expansion in cement pastes. The principal purpose of this test has been to detect the potential expansion caused by the presence of periclase and free lime In portland cement. This test was included in as a criterion for soundness in ASTM C618 which includes natural pozzolans and fly ash. The expansion limits have changed several times with the initial maximum value of 1.0% permitted for portland cements. The maximum value was decreased to 0.5% in 1940 when ASTM C151 as formulated and subsequently increased to 0.8% in 1963 and adopted in ASTM C151 and ASTM C618 and hence applied to assessment of natural and calcined pozzolans.

The ASTM C151 is an accelerated test which is carried out on small cement paste prisms (25mm side) which are cured for 24 hours than placed in an artificial environment with pressures of 2.1 to 2.2 bar and temperatures up to 216^{0}C. As result of this environment minerals are formed in the prisms which are completely different to any which are formed in normal concrete and even those subjected to accelerated curing under atmospheric pressure. The relevance of this test to general concrete is therefore questionable.

As is the case with ASR expansion, it is important to note that autoclave expansion in a cement paste does not reliably indicate expansion in concrete will occur and several authors in North America, where this test is most commonly used, have argued that this autoclave test is not a reliable indicator of unsoundness. In particular, a report prepared for the American Coal Ash Association by Ella Shkolnik of Wiss, Janney, Elsner Associates Inc. found this test has never been incorporated in major standards outside North America because European concrete experts believe "The autoclave test is not relevant to practical application of concrete since they have not experienced any concrete failure in practice due to MgO unsoundness as long as MgO content is limited".

Recent investigations into the relevance of the autoclave expansion testing of cements have been published by Kabir, Hooton and Popoff that found that the ASTM C151 test does not correctly predict the-long-term expansion of cements and whilst it is desirable to have an accelerated cement soundness test, the result must reflect the long-term behaviour. In this study, paste, mortar and concrete prisms were stored at different temperatures, measured and it was found that the autoclave test provides an unrealistic basis for assessing volume stability as well as for rejecting portland cement for concrete use.

With this background, the authors decided to embark on a program to determine whether the autoclave test is a relevant test to indicate potential expansion of concrete.

5. Testing program to determine factors influencing autoclave test results on TAS and DBS

5.1 Methodology

BCRC sourced both TAS and DBS samples and prepared these by screening across 90um sieve to remove coarse particles prior to preparation. Three paste prisms were prepared for autoclave testing using 25% GP cement replacement by drying samples at four different temperatures, 65^{0}C, 85^{0}C, 105^{0}C and 125^{0}C. Samples were also prepared with the reference cement and a blended cement made with 25% fly ash replacing the reference cement. Samples prisms were retained for each product prior to autoclaving and ground so that the minerals present could be determined by XRD analysis.

Representative samples of each cement blend were subjected to autoclave testing to AS3583.4 and the change in samples length measured and recorded. Representative samples were cooled and ground so that minerals present after autoclaving could also be determined by XRD analysis. The results of the expansion following autoclaving and the minerals present in samples subject to XRD analysis were recorded with some test results shown in Tables 4, 5 & 6.

5.2 Test Results

Following drying of prisms at different temperatures and testing of TAS and DBS blended cement prisms in the autoclave, the expansions were recorded and are presented in Table 4.

Table 4 – Mean autoclave expansion of TAS and DBS paste prisms (ue)

Drying oven temperature	GP 75% +TAS 25%	GP 75% + DBS 25%
65^0C	1500	1100
85^0C	1500	1200
105^0C	1400	1100
125^0C	1400	1100

The minerals detected by analysis of the paste prisms used in the autoclave testing prior to and after testing were determined by XRD following drying at each of the four temperatures but for brevity only test results are reported for two drying temperatures of 65^0C in Table 5 and 105^0C in Table 6**.**

Table 5- Composition of autoclaved TAS and DBS pastes post drying at 65^0C (% by mass)

Phase name	TAS ambient	TAS autoclaved	DBS ambient	DBS autoclaved
Portlandite	23	1	13	ND
C_3S	24	7	35	39
C_2S	16	36	14	11
C_4AF	7	7	4	4
Ettringite	6	ND	7	ND
Calcite	16	26	15	21
Quartz	3	Trace	8	4
B-spodumene	5	2	3	1
Garnet	ND	21	Trace	15
Erionite	ND	ND	ND	5

Table 6 – Composition of autoclaved TAS and DBS pastes post drying at 105^0C (% by mass)

Phase name	TAS ambient	TAS autoclaved	DBS ambient	DBS autoclaved
Portlandite	19	ND	13	ND
C_3S	20	47	32	41
C_2S	21	9	16	13
C_4AF	7	5	5	4
Ettringite	5	ND	9	Trace
Calcite	19	24	15	16
Quartz	3	2	7	5
B-spodumene	5	2	3	1
Garnet	ND	15	Trace	15
Erionite	ND	ND	ND	5

5.3 Comments on autoclave test results

- Differences in expansion following autoclaving were found in all samples but expansion measured was greater in the TAS and DBS paste prisms compared to GP cement and fly ash blended cements
- Small differences in expansion following autoclaving between TAS prisms and DBS prisms were noted at each drying temperature
- Differences in expansion of samples subjected to different drying temperatures confirmed that samples should be dried at temperatures at or above 105^0C
- The mean expansion of all samples was less than 0.15%
- The features observed by XRD analysis confirmed pozzolanic activity in autoclaved TAS and DBS prisms with significant reduction of portlandite presence
- In reference cement prisms, the presence of portlandite increased significantly following autoclaving with limited garnet formed
- Ettringite was significantly reduced in all samples following autoclaving
- No free lime presence was identified in the analyses
- No minerals containing significant magnesium were detected by XRD
- No traditional minerals causing expansion following autoclaving appear to be present
- Portlandite and β-spodumene appear to have reacted to form garnet in the autoclave
- Garnet is easily synthesised from any aluminosilicate and lime at high temperature and pressure and explains the disappearance of portlandite and appearance of garnet
- The likely cause of expansion in TAS and DBS samples following autoclaving is conversion of zeolitic minerals present into garnet occupying a greater volume in the paste
- The autoclave test is a very severe test and it is no longer used for testing soundness for other Australian SCM's. The test method used to establish soundness is AS2350.5 (Le Chatelier) and this test should also be used for manufactured pozzolans in AS3582.4.
- Considering that no recognised expansive minerals were identified it is recommended that autoclave expansion to the AS3583.4 test method be made a reportable property rather than a mandatory property until more information is available.
- The authors recommend that a note should be included in AS3582.4 to the effect that manufactured pozzolans with autoclave expansion greater than 0.20% be used with caution in concrete and concrete products subject to autoclaved curing.

6. Accelerated expansion testing using concrete test prisms

6.1 Test Method

Accelerated expansion testing was carried out on standard drying shrinkage prisms (section dimensions 75mm x 75mm) made with domestic concretes from testing program for TAS and DBS discussed in Section 3 above, following wet curing for 1 day and then stored in lime saturated water at 23^0C. Testing for expansion was subsequently undertaken periodically on these prisms according to the AS1012.13 method used for measurement of the change in length of shrinkage specimens in the Boral Technical Services Laboratory. In addition to the above freshly cast prisms of the same concretes containing TAS and DBS were subjected to a typical steam curing cycle with initial length measurements made after 24 hours. Prisms were then stored in lime saturated water and then measured for change in length periodically following the above methodology.

6.2 Results of accelerated prism testing

Table 6 sets out the average length change of the concrete prisms for each concrete mix at ages of 7, 28, 56 days following initial curing and thereafter storage in lime saturated water. Concretes used in this testing program were as reported in the 2017 CIA Biennial Conference paper for 25MPa concrete except that the reference portland cement used was Goliath GP and DBS product was also included in the testing program. Measurement of length change of test prisms is scheduled to continue beyond 56 days with periodic measurements to age of 1 year.

Table 6 – Accelerated shrinkage prism test results for length change

Concrete Type/Age	TAS prisms cured at 23^0C	TAS prisms steam cured	DBS prisms cured at 23^0C	DBS prisms steam cured
Length change (+/-)	Expansion-με	Contraction-με	Expansion-με	Contraction-με
1 day	0	0	0	0
7 days	50	-70	110	-60
21 days	70	-60	120	-30
56 days	60	-60	120	-40

The measured expansion and contraction of shrinkage prisms after 56 days storage in lime water appear to have stabilised and were an order of magnitude less than the autoclave test results and insufficient magnitude to result in cracking in unreinforced concrete despite curing under conditions most pessimistic for promotion of expansion. The expansion of concrete prisms stored in water is so small and contraction following steam curing was such that neither is not likely to cause cracking in unreinforced or reinforced concrete.

7. Conclusions

Both TAS and DBS products show good pozzolanic activity with positive effects on fresh and hardened concrete properties and so could be used as partial GP cement, or fly ash replacement in concrete mixes, despite being coarser than typical fly ash. The two products were assessed for their basic properties and performances to draft AS 3852.4 “Supplementary Cementitious Materials for Manufactured Pozzolans”.

The testing program undertaken by Cement Australia confirmed many of the properties of the testing previously available for TAS and DBS but also included additional testing and analysis for mineral composition, paste properties, pozzolanic activity, and the testing of mortars and concretes containing TAS and DBS. The reported expansion of 0.10% to 0.14% in the Cement Australia testing program is much lower than the maximum of 0.8% permitted in ASTM C618 for natural pozzolans which has been in place for decades in the USA so if a similar limit was set in the draft AS3582.4 to ASTM C151, the expansions recorded would be acceptable however a more cautious approach was taken by the AS3582.4 drafting committee.

BCRC sourced samples from of TAS and DBS and prepared the samples by screening across 90um sieve to remove coarse particles prior to preparation of samples of 3 paste prisms for autoclave testing using 25% GP cement replacement by drying samples at four different temperatures, 65^0C, 85^0C, 105^0C and 125^0C. Samples were also prepared with the reference cement and a blended cement made with 25% fly ash replacing the reference cement. Samples prisms were retained of each product prior to autoclaving and ground so that the minerals present could be determined by XRD analysis.

This investigation has confirmed that the drying conditions prior to autoclaving influence the expansion and samples should be dried at temperatures no less than 105^0C. The XRD analyses carried out prior to and after autoclaving showed that, none of the traditional minerals that typically cause expansion following autoclaving appear to be present. The likely cause of expansion in TAS and DBS samples following autoclaving is conversion of zeolitic minerals and lime present into garnet. The magnitude of this expansion is considered to be much greater than will occur in practice at lower temperatures and pressures to which typical concretes are subjected to in service.

The autoclave test is a very severe test and it is no longer used for testing soundness for other Australian SCM's. The test method used to establish soundness is AS2350.5 (Le Chatelier) and this test should also be used for manufactured pozzolans in AS3582.4. Considering that no recognised expansive minerals were identified it is recommended that autoclave expansion to the AS3583.4 test method be made a reportable property rather than a mandatory property until more information is available.

The measured expansion and contraction of concrete shrinkage prisms after 56 days storage in lime water appear to have stabilised and were an order of magnitude less than the autoclave test results and insufficient magnitude to result in cracking in unreinforced concrete despite curing under conditions most pessimistic for promotion of expansion.

Both TAS and DBS aluminosilicates have been found to be good SCMs in concretes with improved strength, serviceability and durability compared with good quality fly ash. These aluminosilicate products are a new class of pozzolan that have the potential to improve compressive strength, mitigate ASR expansion, reduce sorptivity, reduce chloride diffusion and the potential for widespread use to partly replace GP cement and replace other SCMs in both domestic and structural concretes.

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9. References

1. Haigh M, Dumitru I, Munn R and Papworth F, "Development of New High Performance Supplementary Cementitious Material – A Lithium Production By-product", Proceedings of the CIA Biennial Conference, Understanding Concrete, Gold Coast, October, 2013.

2. Bob Munn, Ion Dumitru and David Maree, "Assessment of the performance of new supplementary cementitious materials from lithium production residues", Proceedings of the CIA Biennial Conference, Adelaide, October, 2017.

3. Bob Munn, Ion Dumitru and Suzanne Maree, "Continuing development of new supplementary cementitious materials from lithium production residues", Proceedings of the CIA Biennial Conference, Sydney, September, 2019.

4. American Society for Testing Materials, ASTM C151, "Test Method for Autoclave Expansion of Hydraulic Cement Paste".

5. American Society for Testing Materials, ASTM C618, "Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as Mineral Admixture in Portland Cement Concrete".

6. Cement Australia, "Interim Summary of Pozzolan Testing Program", Cement Australia Darra Laboratory, August, 2020.

7. Ella Shkolnik, "Evaluation of Autoclave Expansion Test for Fly Ashes", Final Report prepared for American Coal Ash Association, July 21, 2020.

8. Kabir H., Hooton R.D., Popoff N.J., "Evaluation of cement soundness using the ASTM C151 autoclave expansion test", Cement and Concrete Research Vol.136, October, 2020.