

ALKALI-AGGREGATE INVESTIGATIONS IN NEW ZEALAND - REPORT ON  
WORK CARRIED OUT SINCE 1989

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Projects investigating AAR for the period 1989-92 are described. Surveying of structures for AAR is now complete. In addition a number of structures with AAR have been identified which contain low-alkali cement and in one case it has been established that an innocuous basalt has contributed alkalis to the concrete. The results of ASTM C227 on two reactive aggregates are given and it was found that in one case the results were strongly affected by the method of storage which caused alkali leaching. Investigations of methods of analysing water reducing admixtures, the development of the chemical identification of cements in hardened concrete and work carried out to correlate I.R. measurement of silica mineral disorder with ASTM C289 are reported. The results of research into AAR have now been incorporated into the publication of a Code of Practice for Minimising AAR to make these available to the construction industry.

INTRODUCTION

The investigations carried out over the last three years by three agencies have covered a range of topics directed at solving some of the remaining problems that AAR presents in New Zealand. With the exception of the Code of Practice and one investigation which will be published shortly the remainder of the work may be found in local reports which are available on request.

AAR in N.Z. Structures

Central Laboratories, Works Consultancy Services, has completed its survey of bridges (1 & 2) and continues to investigate and monitor the bridges affected by AAR, assisted by DSIR Chemistry Division.

Results of Surveys. Adding the results from recent surveys to the total there are now some 420 bridges in the four areas of New Zealand where reactive aggregates are available which have been inspected for signs of AAR. The total of all structures now identified as possibly affected by AAR numbers over 100 with 35 cases confirmed by petrographic examination. This confirms that some 8% of the structures are definitely affected in areas where reactive aggregates are available. This figure could prove to be substantially higher as further petrographic examinations are made of the cases already identified by the surveys. The surveys are now complete and it is not expected that many more cases of AAR will be identified. The results clearly indicate that in areas where reactive materials are available AAR can be a substantial problem unless appropriate measures are taken to limit its occurrence. However, only one structure has required replacement while another four have required major maintenance with the remainder largely requiring minor maintenance only or just constituting an aesthetic problem.

AAR with low-alkali cement. A number of cases of AAR where low alkali cement was used have now been clearly identified. In the case of the pavement at Whenuapai air base the alkali contribution from the cement will not have exceeded  $1.2 \text{ kg/m}^3$ . The measured alkali content of the concrete is about  $5 \text{ kg/m}^3$  and it has been shown (3) that this alkali was derived from leaching of the basalt aggregate present by the pore solution of the concrete. This is the first authenticated case in New Zealand where an innocuous aggregate has contributed alkalis to the concrete to enable the rhyolite also present to react.

In Taranaki 5 structures containing Egmont andesite have been identified with AAR where the contribution of alkali from the low-alkali cement used will not have exceeded  $2.3 \text{ kg/m}^3$ . Analysis for chlorides showed that contribution of alkali from salt spray is not significant in spite of the structures all being very close to the sea. No analyses of the concretes for alkali content have as yet been carried out and possible contributions of alkalis from the aggregates is not known even though these are not expected to be significant. However, petrographic examination of core samples indicates the reaction is only just detectable in thin-section. The results may indicate that extensive laboratory testing of Egmont andesite has failed to detect reactivity at lower alkali levels possibly because of leaching of alkalis from test specimens.

Studies of structures containing Tongariro andesite. Fifty seven bridges were surveyed in the Tongariro area and only 6 cases of AAR were identified petrographically. Three cases are severe. The chloride levels present are so low as to be close to the natural background for the materials used. Further studies among the 57 bridges will be carried out to determine why only these 6 bridges have undergone AAR by identifying cements, aggregates, and determining the alkali content of the concretes. From this study it is hoped to define the parameters that lead to AAR in concretes containing Tongariro andesite. The hot summers and cold winters in the area are more extreme than in many other parts of the country and the effect of this will also be assessed.

#### ASTM C 227 Mortar Bar Tests on Waikato and Rangitikei River Sands

Field evidence has shown that sands from the Waikato and Rangitikei rivers are involved in AAR. Central Laboratories, Works Consultancy Services, tested a range of these sands (4) using ASTM C 227-87 to determine their reactivity and pessimum proportions for commercial usage.

Samples and methods. Two commercial sand samples from the Waikato River, containing about 30% of reactive volcanic grains, and three sand samples from the Rangitikei River containing 2-15% of reactive volcanic grains were tested as received without further grading. Auckland basalt crusher dust is often blended with the Waikato River sands in commercial practice. In the mixes it was used as the diluent to determine pessimum proportions while the Rangitikei sands were tested without dilution. Alkali contents were adjusted to 0.8% and 1.5%  $\text{Na}_2\text{O}$  equ. by the addition of NaOH to the mixing water. Mortar bars were stored over water at  $38^\circ\text{C}$  in metal containers complying with ASTM C 227 - 87. Length measurements of the mortar bars were terminated at 2 years.

Results. The mortar bars containing sands from the Waikato River gave expansions of about 0.06% and 0.3% at 0.8% and 1.5%  $\text{Na}_2\text{O}$  equ. respectively at 2 years at a pessimum proportion of 40 - 50% of river sand. The Rangitikei sands gave a slow and continuing expansion of up to 0.03% at 2 years at 1.5%  $\text{Na}_2\text{O}$  equ.

Discussion and conclusions. The substantial expansion of the Waikato River sands confirms the reactivity of these materials. Their pessimum proportion differs from the pessimum of 30-35% previously reported (5) but this is probably due to the different locations of the samples used and the fact that in this case commercial sand gradings were used. The use of the ASTM C 227 method of storage (6) undoubtedly leached considerable alkali from the bars and is the probable reason why the Rangitikei River sands failed to show the significant expansion found in some structures. The reactivity of the Rangitikei sands is clearly more sensitive to alkali leaching than the highly reactive sands from the Waikato River.

Detection of future movement. Length changes of cores from many Taranaki structures affected by AAR containing either Egmont andesite or Rangitikei River aggregates have been monitored by sequential immersion in water at 21 °C for 16 weeks, water at 38 °C for 16 weeks and 1M NaOH at 38 °C for 1 year (7). The results indicated that most of the cores contained sufficient alkali-silica gel to significantly expand in water at 21 °C and that further small expansions occurred at 38 °C. All the cores, with one exception, contained sufficient remaining reactive aggregate which only needed further alkali to proceed. In two of the structures the expansion in NaOH is considered significant as these structures are subject to salt spray and brackish water.

Cores from 3 severely damaged bridges in the Tongariro area and 3 bridges in Taranaki with minor cracking are currently being monitored for length change stored in plastic bags at 38 °C. Cracks on the surfaces of the structures which were sampled are being monitored for a qualitative comparison. Useful results are not yet to hand.

The use of surface coatings for the control of AAR. Five precast box beams suffering from severe AAR, were removed from a bridge deck and made available for investigation. Some of the beams were coated with either high molecular weight methacrylate or a silane-siloxane-acrylic coating and expansion of the beams monitored. The experiment has now been running for 2½ years and is being currently evaluated.

### THE ANALYSIS OF HARDENED CONCRETE

As part of ongoing studies DSIR Chemistry is investigating the analysis of concrete obtained from structures in the field. Work has been carried out into the detection and analysis of chemical admixtures and the chemical identification of the origin of cements.

#### Analysis of chemical admixtures

The investigation (8) into the analysis of chemical admixtures was limited to water reducing types in common use in New Zealand as these are the only ones likely to contribute significant alkali to a concrete mix. Compositions claimed by the manufacturers are given in Table 1. The investigation concentrated on applying the methods outlined in references (9) and (10).

Admixtures were freeze dried and analysed by infra-red spectrophotometry. The spectra obtained were similar to those measured previously (11 & 12), and generally confirmed the claimed compositions. Additional peaks were found for Sika BV40 and Sika 1000N because of a modification in their synthesis. Samples of the pure admixtures were analysed according to the chemical methods outlined in references (9) and (10) as follows:-

Extraction with HCl/CHCl<sub>3</sub>. Only naphthalene sulphonate was extracted into CHCl<sub>3</sub>. A precipitate, insoluble in CHCl<sub>3</sub>, was formed on acid addition to the melamine sulphonate and the other admixtures tended to form emulsions. Recovery of the CHCl<sub>3</sub> layer using phase separation papers was made but no extraction into CHCl<sub>3</sub> occurred for other admixtures.

Azeotropic extraction. The ternary azeotrope proposed by Muzzynski (13) using 75% methyl ethyl ketone, 11% water and 14% ethanol was used to extract melamine and naphthalene sulphonates. Refluxing for 4 - 5 hours failed to extract either admixture.

Table 1 - Description of water reducing admixtures analysed

Trade name	Manufacturer's description
Sika Plastiment VZ	Polyhydroxy carbon salts
Sika Plastiment BV40	Modified lignosulphonate
Sika - 1000 N	Modified sulphonated melamine formaldehyde
Daracem FL	Sulphonated naphthalene formaldehyde
WRDA - 20	Polysaccharide
WRDA - Hycol	Lignin-polysaccharide
Melment	Sulphonated melamine formaldehyde

Alkaline oxidation with MnO<sub>2</sub> followed by extraction with CHCl<sub>3</sub>. Once again naphthalene sulphonate was extracted indicating that it was not oxidised. Lignosulphonate was extracted as its oxidation product vanillin. Other admixtures were not extracted.

Detection by reaction with anthrone and β-naphthol. Use of these reagents to detect polysaccharides and polyhydroxy compounds gave inconsistent results, possibly because of the presence of lignosulphonates in some samples.

Detection by reaction with fuschin and methylene blue. After oxidation, the aqueous solutions were reacted with basic fuschin and neutral methylene blue before extraction with CHCl<sub>3</sub>. Basic fuschin failed to extract any admixture sulphonates even though when the test was run with an alkyl sulphonate type washing detergent extraction of the fuschin complex proved satisfactory. Neutral methylene blue (14) will allow extraction of all the sulphonates into CHCl<sub>3</sub> but the extraction procedure is very sensitive to pH. However, only the naphthalene sulphonate extracts after oxidation indicating that the other sulphonates were not stable to oxidation. Even the extraction of naphthalene sulphonate was only successful at high concentrations of the pure admixture. No extraction was detected from hardened mortars containing the low concentrations of admixture that apply in practice.

Detection by U.V. spectroscopic analysis. Good spectra at dilutions of 30 - 50 ng/g were obtained for the sulphonated compounds which were not qualitatively changed in the pH range of 1 - 14. The technique of difference spectra as proposed by Wexler (15) was examined and gave sharper peaks for

lignosulphonates and melamine sulphonates. Naphthalene sulphonates did not provide good difference spectra. Polysaccharides and polyhydroxy compounds do not absorb in the U.V. and so cannot be detected by this method.

Analysis after reaction with slurries of  $\text{Ca}(\text{OH})_2$ . In order to obtain an estimate of admixture lifetime in concrete the admixtures were mixed with slurries of  $\text{Ca}(\text{OH})_2$  and extracted at 1, 3 and 7 days. The slurries were either treated with acid or with  $\text{Na}_2\text{CO}_3$  and then extracted into  $\text{CHCl}_3$ . Naphthalene sulphonate remained intact and could be detected by U.V. and methylene blue. Apart from lignosulphonate the other additives were not detected either intact or as breakdown products and are retained on the  $\text{Ca}(\text{OH})_2$ . Lignosulphonate broke down to vanillin which although it could be smelt at 3 days could not be detected analytically until 7 days reaction with the  $\text{Ca}(\text{OH})_2$ .

General conclusions. In the highly alkaline environment of concrete only naphthalene sulphonate appears to remain intact among the water reducing admixtures investigated. This admixture can be extracted into  $\text{CHCl}_3$  either from an acid solution or with methylene blue. Lignosulphonate admixtures break down rapidly and may be detected as vanillin although oxidation may be necessary to give a quantitative result. All the other admixtures appear to undergo some form of breakdown and further work is required to identify the breakdown products and devise methods for their analysis. Some of the methods detailed in references (9) and (10) do not appear to work with the complex compounds present in many of the water reducing admixtures. There is a need for investigation, using modern analytical techniques, to improve the detection and measurement in concrete of this important group of chemical admixtures which can contribute alkalies to concrete.

#### Chemical identification of the origin of cements

Identification of the origin of the cement present in a structure is important information and often of considerable use in the diagnosis of AAR in a structure. This knowledge allows the use of cement analyses performed by cement works and government agencies to estimate the likely amount of alkalies contributed to the concrete by the cement. An investigation into chemical methods of identification of cements has been completed (16) and successfully applied to a number of structures. Brief details of the investigation are given.

Initial survey of elements. Initially it was considered that data from Ce and Eu anomalies, La/Y ratios and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were potentially of use in cement identification. On this basis a semi-quantitative survey of minor and trace elements in New Zealand cements was determined by inductively coupled plasma mass spectrometry. Some of this data was further refined for the alkaline earths, some transition metals and the lanthanide series.

Choice of leaching methods. Previous work (17) indicated that dilute  $\text{HNO}_3$  was a useful concrete leachant and extracted less from aggregates than picric acid/methanol mixtures. It was considered that acid leaching would be necessary for the complete recovery of constituents such as Mg, Al and  $\text{SiO}_2$  from the hardened cement paste. However, leaching with neutral or alkaline EDTA to selectively extract Ca and Sr would be necessary if Ca/Sr ratios were to be used. After some investigation 1 hour leaching with 1 M  $\text{HNO}_3$  or 0.2 M  $\text{NH}_4\text{EDTA}$  was selected.

**Sample preparation.** Initially small diamond drilled cores intended to give a defined surface area were used as sample for leaching. However, these were found to give less reproducible results than crushed samples of concrete. It was established that hand crushing and selection of fragments 0.5 - 1.0 mm in size, to be as rich as possible in cement, gave satisfactory results. Later work showed that the 0.065 - 0.125 mm fraction gave even better results.

**Effect of leachants on aggregates.** The two leaching methods were applied to the common rock types found in New Zealand aggregates prepared as described above. These rock types are greywacke, basalt, andesite and rhyolite. It is to be noted that calcareous aggregates are not used and that contamination with these materials is minimal. The leaching experiments confirmed previous work (17) which showed that substantial acid leaching of basalt aggregates occurs. It also found that substantial acid leaching of lanthanides from aggregates occurs and this precludes their use for cement identification. This lanthanide leaching was less with EDTA but still significant.

**Choice of chemical parameters for identification.** Evaluation of a wide range of analytical results indicated that ratios of Mn and Sr to Ca determined by acid leaching were the best identifiers of cement origin and could be used without correction for aggregate contamination. Ratios of Ba to Ca are also of use. The results of applying Mn/Sr/Ca ratios to cements and concretes are shown in the ternary diagrams given in Fig.1. The method clearly distinguishes the four major cement works F, B, T and P. Two minor works W and S, now out of production for over twenty years, are less distinguishable but further refinement of the Ca/Sr ratios by EDTA leaching is likely to better distinguish these two cements.

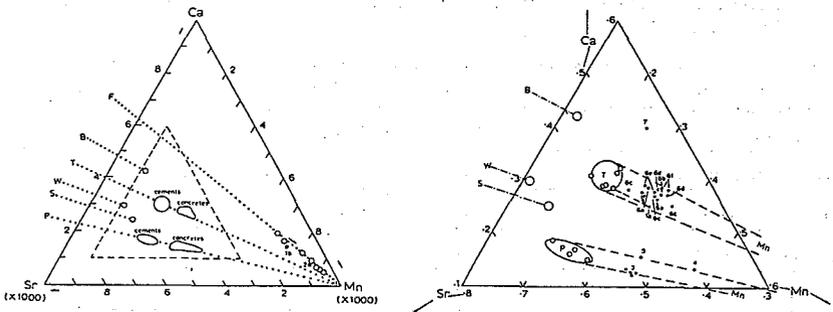


Fig.1 The Ca-Mn-Sr plots used to identify N.Z. cements. The ternary diagram to the right is an expanded portion of the diagram to the left. Results for cements are shown as open circles and results derived from concrete are shown as filled small circles. (16).

**$^{87}\text{Sr}/^{86}\text{Sr}$  ratios.** A separate investigation (18) of this isotope ratio in New Zealand cements showed that it was not as effective as the Mn/Sr/Ca ratios in distinguishing the cements. This is because New Zealand limestones used in cement production only range from 10 - 30 million years in age. However, the technique is of potential use where the limestones used are from a greater age range.

**General conclusions.** Mn/Sr/Ca ratios determined by extraction with 1 M HNO<sub>3</sub> are able to identify New Zealand cements in hardened concrete. Where doubt exists extraction with 0.2 M NH<sub>4</sub>EDTA to accurately determine Sr for the Ca/Sr ratio may be used to refine the identification. Any method of identification must take into account unwanted contributions from the aggregates and assess whether they unduly interfere with the results obtained from the acid extraction. Leaching with HNO<sub>3</sub> extracts significant amounts of lanthanides from the aggregates and precludes the use of lanthanides for cement identification in concrete.

**CORRELATION OF I.R. MEASUREMENT OF SILICA MINERAL DISORDER TO ASTM C 289.**

The relationship between the co-efficient of disorder (C<sub>d</sub>) of silica minerals as measured by I.R. analysis and the reactivity of aggregates as determined by ASTM C 289 and field data is being investigated (19).

**Samples.** Commercial samples of 11 alluvial sands from the Waikato river (containing substantial proportions of rhyolite), 8 basalts, 9 marine sands (primarily quartz and feldspars with some mafics) and 9 greywackes from formations in the Wellington and Auckland districts were tested.

**Methods.** The samples were prepared and the I.R. spectra measured following the protocol described by Bachiorrini (20). Samples were tested according to ASTM C 289 and the total analyses performed using X-ray fluorescence spectrometry.

**Results.** The results are given in Table 2.

**Table 2 - Coefficient of disorder C<sub>d</sub> measured for aggregate types together with typical SiO<sub>2</sub> contents and results for ASTM C 289.**

Aggregate type	SiO <sub>2</sub> %	ASTM C 289	C <sub>d</sub>
River sands (rhyolite)	c.67	Reactive	280-520
Quartz rich marine sands	66-76	Innocuous	100-215
Wellington greywacke	70-75*	Innocuous	100-135
Auckland greywacke	62-64	Innocuous	250-520
Auckland basalt	43-45	Innocuous	-

\* Results from literature

**Discussion and conclusions.** For the alluvial sands in which reactive rhyolite predominates, the C<sub>d</sub> values ranged from 280 to 520. With the exception of the Auckland greywackes all the innocuous samples have C<sub>d</sub> values that range from 100 to 215. In the case of the basalt aggregates there was insufficient silica present to give measurable peaks in the IR spectra. Thus the disorder co-efficient is clearly distinguishing between the sands containing the reactive rhyolite and the innocuous materials with the exception of the Auckland greywacke. These Auckland greywackes, which are albitised siltstones, are innocuous both by laboratory testing and field experience and the reasons for the apparently anomalous results obtained require further investigation. The results indicate that use of the C<sub>d</sub> co-efficient may offer a more rapid method than ASTM C289 for classifying the reactivity of siliceous volcanic rocks.

CODE OF PRACTICE FOR MINIMISING AAR

A working party, representing the New Zealand government and the construction industry, has prepared a code of practice for minimising AAR (21). The publication of this code represents the culmination of many years of research and investigation. The principle embodied in the code is that where reactive aggregates are used in concrete it is the specifier's responsibility to limit the alkali content of the concrete to a maximum of 2.5 kg/m<sup>3</sup> Na<sub>2</sub>O equ. irrespective of its source or alternatively use methods that allow the aggregates to be safely used where this limit is exceeded. The code also makes it the specifier's responsibility to identify reactive aggregates.

The procedures recommended for identifying reactive aggregates are petrographic examination, ASTM C289 - 87 and field data. Alkalies in the concrete are calculated as the sum of the total alkali in the cement, chemical admixture and water, alkali from NaCl in the aggregates, and available alkali in mineral admixture or blast furnace slag as determined by reaction with Ca(OH)<sub>2</sub>. The acceptability of mineral admixtures is evaluated by ASTM C441.

The alkali limit of 2.5 kg/m<sup>3</sup> was set on the basis that in practice New Zealand cements do not exceed 0.6% Na<sub>2</sub>O equ. and most concretes rarely exceed a cement content of 380 kg/m<sup>3</sup>. These figures give a total alkali content in the concrete of 2.3 kg/m<sup>3</sup> which allows 0.2 kg/m<sup>3</sup> alkali from sources other than the cement. While this procedure may appear arbitrary it is firmly based on local construction practices and the experience that damage due to AAR is minimal where low-alkali cements are used with reactive New Zealand aggregates.

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