

ALKALI-SILICA REACTIVITY IN CONCRETE

Neil Lee, BRANZ Ltd

New Zealand is fortunate to have suffered few problems related to alkali-silica reactions in concrete, despite the widespread use of potentially deleterious aggregate. This is a tribute to the foresight of previous practitioners, both in recognising the problem and taking adequate precautions against it. Future trends within the concrete industry may increase the risk posed by this degradation mechanism. However, methods of mitigation are well-understood and an excellent local guidance document is available from CCANZ.

Origins of alkali-silica reactivity

The aggregate fraction of concrete is often thought of as an essentially inert filler material, extending the active cement paste to more economic volumes. In practice this is an oversimplification, with most aggregates likely to react to some degree with the highly alkaline environment created by hydrating cement. Ordinarily this is beneficial; partial dissolution of the aggregate particles' surface enhances bonding with the cement phase. However, in extreme cases the chemical reactions that can occur are sufficiently disruptive to pose a threat to the structural integrity of the concrete.

The most common damage-causing interaction between cement paste and aggregate is 'alkali-silica reaction' (ASR), the name reflecting the essential interaction between the alkali-rich pore fluid of the concrete and aggregate containing the mineral silica (SiO_2). Susceptible rock types have a mineralogy in which silica is present in either an amorphous phase or a highly-strained or crypto-crystalline form (see Table 1).

The reaction sequence is broadly as follows:

1. Initial depolymerisation and dissociation of reactive silica minerals in the aggregate under highly alkaline conditions.
2. Hydrolysis of the resulting dissolved silica, by sodium and potassium hydroxide derived from the pore fluid, to produce a solid alkali-silicate gel.
3. Hydration of the gel.

The presence of the alkali-silicate gel is not damaging to the concrete *per se*. However, gels of the appropriate formulation have the capacity to absorb large quantities of water. The consequent volume expansion may generate internal tensile stresses in the vicinity of 6–7 MPa, sufficient to crack both the affected aggregate and surrounding cement paste.

ASR typically manifests itself through extensive surface map cracking, although restraint due to structural loading or reinforcement may modify the observed cracking pattern. The progress of the reaction can be extremely slow, and signs of distress may only appear when the concrete is years to decades old. The tensile strength and elastic modulus of the concrete are compromised as the severity of the reaction develops, but compressive strength is usually little affected. This has led to suggestions that ASR problems may be more aesthetic than structural, providing the concrete is well-reinforced, but the potential durability impact must also be borne in mind.

Table 1. Forms of reactive silica that give rise to ASR

Reactive silica type	Physical form	Found in	Comment
Opal Chalcedony	Amorphous Poorly crystalline	Siliceous limestone, chert, flint and shales	Not currently used as concrete aggregate in New Zealand
Glass	Amorphous	Rhyolite, andesite, dacite, tuffs and derived sediments	Principal reactive component of New Zealand aggregate
Tridymite Cristobalite	Crystalline	Rhyolite, dacite	Relatively rare in terrestrial rocks
Quartz	Crystalline	Quartzite, acidic igneous and metamorphic rocks	Very common but only reactive if highly strained

Aggregate reactivity testing

The obvious solution for avoiding problems with ASR is simply to use a non-reactive rock type. Unfortunately there is no single test that can be unreservedly recommended as a fool-proof method for screening potential aggregates for which no historical performance records exist. Consequently a conservative engineering approach is suggested, checking the aggregate performance by more than one technique and taking appropriate measures where the test results indicate caution is justified.

The first step in the evaluation of a new aggregate source should be the commissioning of petrographic examination in accordance with ASTM C 295 (or an equivalent method). This determines whether the rock contains any of the reactive silica phases identified in Table 1, which indicate potentially deleterious performance. The examination should preferably be carried out by a geologist with previous experience in the assessment of the mineral constituents of concrete aggregate, and must also include an inspection of the quarry site to assess variability in the rock's composition.

If the petrologist's report indicates a potentially reactive aggregate then either the aggregate should be treated as deleterious and appropriate mitigation measures taken, as detailed below, or further testing should be undertaken to clarify the significance of the risk posed. A wide variety of test methods have been proposed for determining ASR susceptibility, most of which involve using the suspect aggregate to produce mortar or concrete beams and measuring their eventual expansion under humid conditions. Due to the slow-developing nature of ASR, the test methods necessarily accelerate the reaction by artificial means such as elevated temperature and alkalinity, potentially distorting the result. This, combined with the fact that many tests historically originated as performance discriminators for the aggregates in one particular geographic region, means the potential for generating false positive or false negative results is considerable. Tests recommended for New Zealand, on the basis of both relative speediness and reasonable fidelity to aggregate behaviour observed in the field, include the ASTM C 289 'chemical test' and the ASTM C 1260 'rapid mortar bar method'.

ASTM C 289 measures the dissolution of silica and corresponding reduction of alkalinity that occurs when a pulverised sample of the test aggregate is mixed with a 1 mol dm⁻³ solution of sodium hydroxide at 80°C for 24 hours. When plotted graphically, this pair of results can be used to classify the aggregate's likely behaviour as 'innocuous' or 'deleterious' according to boundaries derived from the in-service performance of previously tested aggregates (Figure 1). The method has been criticised for giving misleading results, primarily with aggregates

derived from sedimentary sources, but has been found to correlate well with observed site concrete performance for the volcanic rocks that represent the bulk of New Zealand's potentially reactive aggregate.

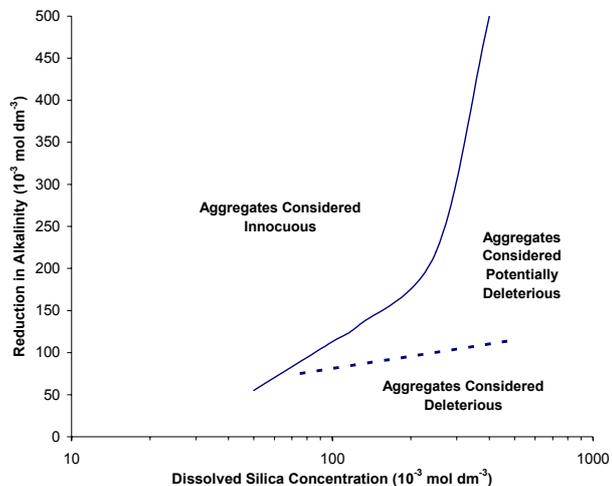


Figure 1. Division between innocuous and deleterious aggregates according to ASTM C 289.

In the ASTM C 1260 test the suspect aggregate, crushed as necessary to achieve the specified grading, is made up as sand-cement mortar bars of a fixed water-to-cement ratio. The bars are stored in a strongly alkaline solution, maintained at 80°C for a minimum of 14 days, and their increase in length is measured periodically. A variety of criteria have been suggested to delineate potentially harmful performance, with a maximum permissible expansion of 0.1% after 14 days testing being the most usual quoted. Some authorities recommend longer testing periods to distinguish between non-reactive and slowly-reactive aggregates. Figure 2 shows expansion curves for various innocuous (greywacke, Auckland basalt) and deleterious (Waikato River sand, Taranaki andesite) aggregates, using results derived from recent BRANZ research.

It is generally accepted that tests of this type may be somewhat over-sensitive, identifying aggregates known to perform acceptably in the field as potentially deleterious. Variations on this method such as ASTM C 1567 are also used to evaluate the effectiveness of SCMs (supplementary cementitious materials) for the suppression of ASR.

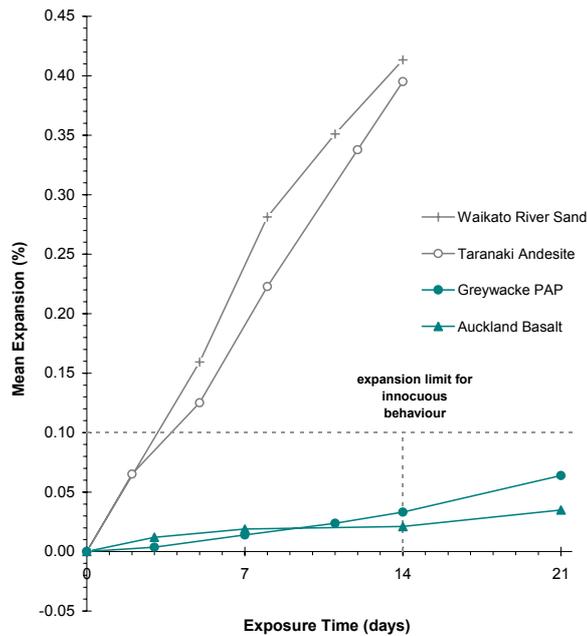


Figure 2. Examples of innocuous and deleterious expansion for different New Zealand rock types under an ASTM C 1260 ‘rapid mortar bar’ test.

Mitigation techniques

Avoidance of susceptible aggregate is not always a practical or economic possibility. An understanding of the chemistry governing ASR allows for the development of approaches that allow potentially reactive aggregate to be safely used. Feasible mitigation techniques broadly encompass:

- decreasing the pH of the concrete’s pore solution to suppress the initial silica solubility
- reducing the free alkali metal ion (sodium and potassium) concentrations present to restrict gel formation
- reducing the permeability of the concrete to restrict water ingress, hence preventing the gel from expanding.

New Zealand has followed a de facto route of controlling the alkali content of concrete, courtesy of an informal agreement amongst local cement manufacturers to restrict the free alkali content of their cement to less than 0.60% Na₂O equivalent. Figure 3 demonstrates just how sensitive the development of ASR can be to this parameter. Note that cement is not the only source of soluble alkalis in concrete, however, and contributions from the aggregate, mix water and chemical admixtures also need to be assessed. Normal concrete, as defined by NZS 3104: 2003, made with a potentially reactive aggregate, can be expected to be durable for 50 years, suffering only cosmetic damage if a maximum concrete alkali limit of 2.5 kg/m³ is observed.

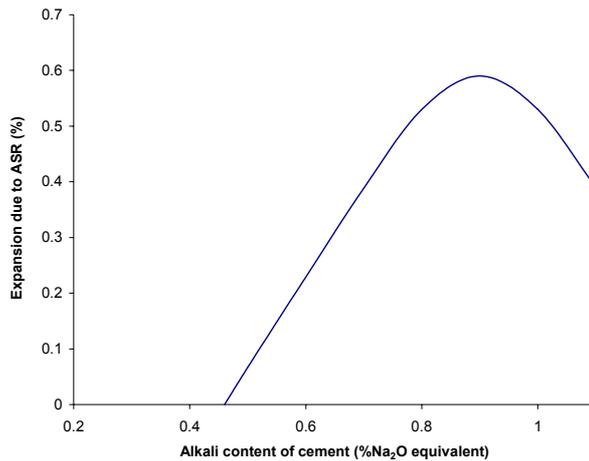


Figure 3. Effect of alkali content of cement on ASR expansion with a reactive aggregate (after Mindess and Young).

Where alkali limits of less than 2.5 kg/m³ are not achievable, or the concrete performance requirements are particularly demanding, SCMs can be used to successfully suppress damaging levels of expansion. Table 2 highlights the approximate dosage levels necessary to protect against ASR for some of the more familiar SCMs.

Table 2. Approximate SCM dosages for ASR suppression (excerpted from CCANZ TR3)

SCM	Approximate dosages (% replacement of GP cement)
Silica fume / sinter	10% +
Metakaolin	15% +
Fly-ash	25% + (Class C ash may require larger dosages)
Blast-furnace slag	50% +

SCMs can be dramatically effective at controlling ASR. BRANZ has recently completed research that evaluated various SCMs for the purpose of mitigating ASR caused by Waikato River sand. This is an alluvial rhyolite-derived sand and is highly reactive, representing somewhat of a ‘worst-case’ scenario. As Figure 4 demonstrates, the measured expansion in an ASTM C 1567 test greatly exceeds the 0.1% limit for innocuous behaviour when a mortar containing the sand is made with straight GP cement. However, mortars incorporating Duracem, Microsilica and Genesis (Huntly) fly-ash clearly suppress the damaging expansion.

Quantities of the SCMs found to be necessary were similar to those given in Table 2. Specific technical advice should be sought from the suppliers of these materials where their use is contemplated for use with potentially reactive aggregate.

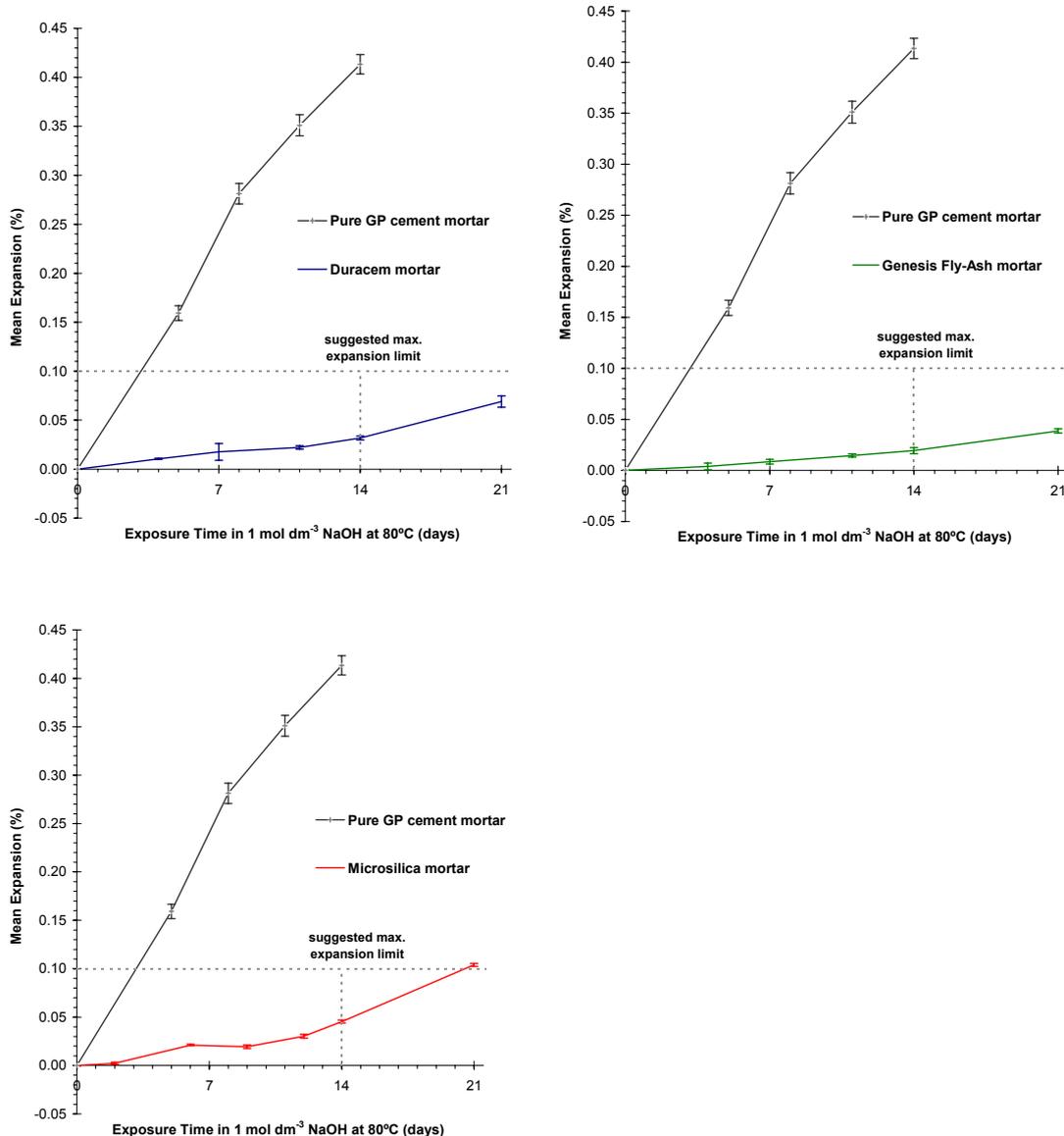


Figure 4. Effectiveness of SCMs commonly available in New Zealand for mitigating ASR due to highly reactive Waikato River sand (measured using ASTM C 1567).

SCMs function via a number of beneficial modes: all typically reduce the permeability of the concrete, limiting its capacity to imbibe water. By replacing cement, they also physically dilute the amount of free alkali metal ions available in the concrete. SCMs with true pozzolanic characteristics react with the calcium hydroxide produced by the cement hydration reaction, helping lower the alkalinity of the concrete below that of the pH needed to support the formation of the alkali-silicate gels. It is also believed that these gels can only be formed in the presence of calcium ions, whose concentration is reduced by the pozzolanic reaction. Paradoxically, finely divided and highly-reactive amorphous silica in the form of silica fume or equivalent natural silica sinter is one of the most effective means for reducing the risk of ASR. This can be explained by the fact that where reactive silica contents are initially low, adding additional silica, e.g. in the form of a reactive aggregate, ordinarily increases the potential for gel formation. However, if the silica addition is great enough, and the particles' size fine enough, the ratio of free alkali metal ions to the surface area of the reactive silica

becomes unfavourable, suppressing the formation reaction. This mechanism is also assumed responsible for the phenomenon of 'pessimum' proportions observed with certain aggregates, whereby the severity of the ASR developed has a clear maximum which is not found to correspond with a ratio of reactive to unreactive aggregate in the concrete equal to 100%.

CCANZ TR3

For more information on this subject, interested readers should consult the Cement and Concrete Association's publication *TR3 Alkali Silica Reaction*. This document provides a comprehensive review of New Zealand and international research and practical experience and canvases the topics presented here in greater depth. It also includes a detailed Recommended Practice for minimising the risk of ASR damage with both Normal and Special Concretes, and model specification clauses covering concrete supply suitable for inclusion in tender documents.

The future

A combination of currently identifiable trends will likely increase the need for concrete suppliers and specifiers to take precautions against ASR damage in the immediate future. These trends include: economic and environmental pressures encouraging reduction of the kiln temperatures used for the manufacture of cement, thereby increasing its alkali content; depletion of aggregate sources in urban areas requiring the use of potentially deleterious material (e.g. Taranaki andesites); and routine recycling of wash-water in ready-mix plants allowing alkali levels in mix water to exceed those normally encountered in potable town supplies. However, the industry is fortunate to have access to a wide range of SCMs capable of both enhancing the fresh and hardened properties of concrete and reducing the risk of ASR.

REFERENCES

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