



Alkali Content of Concrete Mix Water and Aggregates

Introduction

Alkali silica reaction (ASR) is a chemical reaction between some types of aggregate and the highly alkaline pore water present in all Portland cement concretes. When the concrete contains sufficient moisture, alkalis and reactive aggregate the reaction produces a gel, which absorbs water and swells. The swelling can create enough pressure to crack the concrete and/or cause significant movement of concrete components. If severe, the damage can affect the performance of the structure.

CCANZ TR3 (2nd edition) describes how to minimise the risk of ASR damage to concrete in new construction. One approach is to control the amount of alkali added to the concrete when it is mixed. For Normal Concrete, as defined by NZS 3104:2003, the concrete producer is required to certify that the total alkali in the concrete, contributed by all constituents of the mix, does not exceed 2.5kg/m³. Control of alkali content is one of several approaches that may be taken for Special Concrete.

Traditionally, Portland cement has been

considered the main source of alkalis, and most concrete manufacturers understand how to manage alkalis contributed by cement. It is now recognised that other mix constituents such as water and aggregates can contribute significant amounts of alkali. These aspects are also discussed in CCANZ TR3 (2nd edition). This Information Bulletin describes how to measure and calculate the alkali contributions from mix water and aggregates. It supports the information and recommendations presented in CCANZ TR3 (2nd edition).



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What is the “Alkali Content” of Concrete?

In general chemistry, the pH scale indicates whether a substance is an alkali or an acid and to what degree. The pH of an alkali is between 14 and 7. The pH of an acid is less than 7. The pH of fresh concrete is around 12.5, so concrete is considered highly alkaline.

In water chemistry, the term “alkalinity” describes the ability of water to maintain its pH when exposed to chemicals, e.g. in the natural environment or during industrial processes. It is largely determined by the presence of carbondioxide, carbonic acid,

and calcium, bicarbonate, carbonate and hydroxide ions. If a water has enough alkalinity, its pH will not change significantly unless a large amount of acid is added to it.

Alkalinity is sometimes referred to as the buffering capacity of water, because the chemicals that contribute to alkalinity neutralise the effect of acids by absorbing hydrogen ions to prevent significant pH change.

In cement and concrete chemistry, “alkali content” refers to the amount of alkali metal

elements (lithium, sodium, potassium, rubidium, cesium, francium) present in the cement or concrete in readily soluble compounds. Although some of these compounds may increase the pH of water when they dissolve, not all of them will. The pH change they produce is too small to be a reliable measure of alkali content in concrete or wash water. Thus ASR is managed by directly controlling the alkali metal content of the concrete, i.e. its “alkali content”, not its pH or its alkalinity.

Most alkali in concrete is supplied as sodium (Na) or potassium (K) ions. The other alkali metals may not contribute significantly to ASR damage. Alkali contents of mix constituents such as cement and water are therefore based on sodium and potassium contents. They are expressed as “alkali equivalent” (Na₂O_{eq}):

$$\text{Na}_2\text{O}_{\text{eq}} (\%) = \text{Na}_2\text{O} (\%) + 0.658 \times \text{K}_2\text{O} (\%)$$

Na₂O and K₂O are the amounts of sodium and potassium oxides measured by chemical

analysis of the sample and expressed as a weight percent of the sample weight. The 0.658 correction factor reflects the relative difference in molecular weight between Na₂O and K₂O.

To calculate the alkali content in kg/m³ of a particular concrete mix, the alkali equivalent of each constituent is first converted to alkali weight in kilograms by multiplying the alkali equivalent by the weight of the constituent per cubic meter of concrete. The alkali weights of all constituents are then added together to give the total alkali content. Appendix C of CCANZ TR3 (2nd edition) explains how to calculate the alkali contributions from individual constituents and the total alkali content of the concrete.

Suppliers of cement, SCMs and chemical admixtures will be able to provide alkali contents of their products. Measurements of the alkali content of water and aggregates, however, may need to be arranged by individual concrete and aggregate producers. The following sections describe how this is done.

Alkali Contribution From Water

When Does It Need to be Measured?

Analyses of water from New Zealand municipal water supplies prior to 1995 can be accessed from the JASPER database held by the Institute for Environmental Science and Research (ESR). Drinking water composition does not vary greatly over time, so old analytical data is generally acceptable unless there has been a major change in the supply since the most recent analysis. Specific chemical analysis of town supplies used for concrete mix water should not be necessary.

Non-potable water supplies, including recycled water, do need to be analysed. Water that has been in contact with cement usually contains significant quantities of alkalis that arise from the initial hydration of cement. Recycled wash water therefore will contain more alkali than potable water and its alkali content must be considered and added to the alkali contributed by other components. This is particularly important if the total concrete

alkali content is close to the maximum specified limit.



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It is strongly recommended that recycled water be sampled and analysed over several weeks to obtain a range of typical operating alkali contents. The maximum value obtained should be used in concrete alkali calculations, in the same way as the maximum cement alkali content reported by the cement supplier would normally be used.

How to Measure It

Water should be analysed by a commercial chemistry laboratory that is IANZ accredited for analysing drinking water. A list of these laboratories is available on the IANZ website's Directory page. A laboratory that is specifically accredited for sodium analysis should also be capable of measuring potassium although it will probably not be accredited specifically for potassium.

The alkali contents measured will be determined by the way the water is sampled, particularly for recycled water. It is important that the sample taken for analysis represents the water as it is delivered to the concrete mixer. For recycled water this means including suspended solids. All sampling equipment and containers must be clean, and should be rinsed with the water before collecting the sample. The chemistry laboratory will be able to advise how much water should be sampled, and how it should be stored and delivered to the laboratory.

Analyses should be performed according to an internationally recognised Standard, such as those published by the American Public Health Association (APHA) or similar organisations. Analytical techniques commonly used include atomic absorption (AA), inductively coupled plasma spectroscopy (ICP), and titration.

The laboratory must be instructed to analyse the water sample for sodium and potassium. If the water sample contains suspended solids (e.g. a if it is a recycled wash water) the laboratory must include the solids in the analysis. This means the laboratory must dissolve the solids and analyse the resulting solution along with the liquid fraction of the sample. An acid digestion is considered satisfactory for this purpose. Acid digestion will also dissolve any non-cementitious minerals in the slurry, i.e. minerals that are not soluble in alkaline pore solutions, and may therefore give a slightly higher result than if only the cement solids are included. Results based on a digestion process that selectively dissolves only cementitious particles may be used if analysis (e.g. by XRD) shows that the suspended solids consist largely of aggregate particles rather than cementitious materials.

How to Calculate Water Alkali Contribution from the Analytical Results

Results from water analyses are usually reported as the concentration of sodium and potassium ions (Na and K) expressed as milligrams per litre (mg/l) or parts per million (ppm), rather than as weight percent of sodium and potassium oxide. If specifically requested, the laboratory may be willing to express the results as alkali equivalent as described below. There may be a small extra fee for doing this.

The sodium and potassium ion contents Na and K in mg/L (or ppm) are converted to alkali equivalent by the formula:

$$\text{Na}_2\text{Oeq} = \frac{(\text{Na} \times 1.35) + (0.658 \times \text{K} \times 1.20)}{10,000}$$

The correction factor 1.35 reflects the relative difference in molecular weight between sodium and sodium oxide. The correction factor 1.20 reflects the relative difference in molecular weight between potassium and potassium oxide. The 10,000 converts mg/L (ppm) to a percentage.

If the equivalent alkali is less than 0.02% (190 mg/L (ppm)) it shall be treated as nil and not included in the calculation of concrete alkali content. If it is 0.02% or greater it must be included in the calculation. ASTM C94 has an optional maximum limit for alkali equivalent in wash water of 600 ppm (0.06%).

The total alkali contributed to the concrete by the mixing water is calculated from the alkali equivalent by the formulae:

$$W = \frac{\text{Na}_2\text{Oeq} \times C \times W/C}{100} \quad \text{or}$$

$$W = \frac{\text{Na}_2\text{Oeq} \times \text{water content}}{100}$$

where W = equivalent alkali contributions made to the concrete by the alkali ions sodium and potassium present in the water in kg/m³.

C = Portland cement or Portland-limestone cement content of the concrete in kg/m³.

W/C = the water cement ratio.

Water content = water content of the concrete in kg/m³.

The alkali content of the water already present in the aggregate when batched is included in the alkali contribution from the aggregate.

Alkali Contribution from Aggregates

Where it Comes From

Aggregates can contribute alkalis from two sources: release from minerals within the rock, and marine salt contamination on the external surfaces of aggregate particles.

The contribution of alkalis by the minerals is described in CCANZ TR3 (2nd edition) Section 7.6. The phenomenon is limited to release of alkali by the minerals nepheline and leucite. The amount of alkali that will be released from an aggregate in this way over the lifetime of a structure is difficult to predict, so TR3 recommends not combining in the same concrete alkali reactive aggregates and aggregates containing nepheline and leucite. Therefore alkalis contributed by nepheline and leucite are not included in the calculation of concrete alkali content.

Aggregates may be contaminated with sea salts, especially if they are derived from a marine source or stockpiled near the coast. The sodium chloride in the salt contributes reactive alkali to the fresh concrete. This alkali must be determined by chemical analysis and included in the calculation of concrete alkali content.

The alkali content of the coarse and fine aggregates used in the concrete should be determined at agreed intervals.

How to Measure It

Although the sodium and potassium contents of aggregate can be readily determined by chemical analysis of a rock sample, the sodium and potassium in the rock itself generally does not take part in ASR. Thus direct determination of the alkali content of a rock sample by techniques such as X-ray fluorescence (XRF) is not appropriate for determining alkalis that will contribute to ASR. Instead, any of the following three approaches may be used:

1. *By Acid-soluble Chloride*

Aggregates susceptible to chloride contamination from sea salt should be tested for acid-soluble chlorides to ensure that the chloride content of the concrete does not exceed NZS 3101:1995 requirements. Rather than analysing these aggregates both for water-soluble alkalis and for acid-soluble chlorides, the reactive alkali content of the aggregate can be estimated from the analysis of acid soluble chlorides. New Zealand aggregates do not contain significant amounts of chloride other than as sea salt contamination, so this approach will give a reasonable estimate of the water-soluble alkalis.

The standard methods for analysis of concrete for acid soluble chlorides are ASTM C1152 and BS 1881:Part 124:1988. These may also be applied to aggregates. Both these methods involve preparing acid extracts from the aggregate and analysing the extracts by wet chemical techniques. Instrumental techniques such as XRF are more convenient than wet chemical techniques because the aggregate itself can be analysed. Where the chlorides are predominantly in the form of sea salt contamination, results from XRF do not differ significantly from wet chemical analyses of acid soluble or water-soluble chlorides. Testing laboratories offering XRF analysis will prepare the sample.

Because of its convenience, XRF analysis of the chloride content of the aggregate sample is the recommended method for determining alkalis that will contribute to ASR.

2. *By Water Soluble Chloride*

The reactive alkali present in the aggregate can be estimated from its water

soluble chloride content determined by BS 812: Part 117. This test method involves washing the aggregate in water to dissolve the salt, then analysing the chloride content of the aggregate wash water. Two laboratories may be needed for this process: an aggregate testing laboratory to wash the aggregate, and an analytical chemistry laboratory to analyse the chloride content of the wash water. XRF is a suitable method of analysis. The results must be expressed as chloride content as a percentage of aggregate weight.

3. *By Water-soluble Alkali*

An alternative approach is to wash the aggregate in water as described in BS 812: Part 117 and then measure the alkali equivalent of the aggregate wash water (as described in the previous section) instead of the chloride content. The alkali equivalent of the aggregate wash water is then converted to alkali equivalent of the aggregate.

An IANZ-accredited chemistry laboratory with experience in chemical analysis of rocks and minerals or water (as appropriate to the approach taken) should perform the analysis. A list of these laboratories is available on the IANZ website's Directory page. The laboratory should be instructed to analyse the sample for total chlorine or for sodium and potassium as appropriate.

How to Calculate Aggregate Alkali Contribution from Analyses of the Chlorine Content of Aggregate

Results from XRF analyses for chlorine are usually quoted as total chlorine in weight percent. This approximates the total chloride content. When the total chloride ion level in the aggregates is less than 0.005% it shall be regarded as nil. Otherwise, the reactive alkali contributed by sodium chloride contamination of the aggregates is calculated from the formula:

$$H = \frac{0.76 \times [(NF \times MF) + (NC \times MC)]}{100}$$

where H = reactive alkali contribution made to the concrete by the sodium chloride present in the aggregates expressed as kg/m³ sodium oxide equivalent.

NF = chloride ion content of the fine aggregates as a percentage by mass of dry aggregate.

MF = fine aggregate content in kg/m³.

NC = chloride ion content of the coarse aggregate as a percentage by mass of dry aggregate.

MC = coarse aggregate content in kg/m³.

The correction factor 0.76 is the product of correction factors that reflect the relative difference between the concentrations of sodium and chloride ions in seawater and the relative difference in molecular weight between the sodium ion and its oxide.

How to Calculate Aggregate Alkali Contribution from Analyses of the Water-soluble Alkali Content of Aggregate

The reactive alkali contributed the aggregates is calculated from the formula:

$$H = \frac{(NF \times MF) + (NC \times MC)}{100}$$

where H = reactive alkali contribution made to the concrete by the soluble alkalis present in the aggregates expressed as kg/m³ sodium oxide equivalent.

NF = Na₂O_{eq} of the fine aggregate as a percentage by mass of dry aggregate.

MF = fine aggregate content in kg/m³.

NC = Na₂O_{eq} of the coarse aggregate as a percentage by mass of dry aggregate.

MC = coarse aggregate content in kg/m³.



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