SELECTIVE DISSOLUTION TECHNIQUES IN AAR INVESTIGATION: APPLICATION TO AN EXAMPLE OF FAILED CONCRETE

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ABSTRACT

Complexing alkaline leachants are used for the determination of aggregate constituents such as sodium, potassium, aluminium and silica, which have been mobilised by reaction of the aggregate with the pore solutions of concrete.

Alkali released to concrete from Auckland basalt in contact with pore solutions from low alkali cement paste over long periods of time creates conditions typical for concretes made up with high alkali cement. This is demonstrated with the help of experimental mortars and old concrete failed due to AAR although prepared with low alkali cement (0.4% Na_2O eq.). It was fortunate for this investigation that only a section of the concrete tarmac showed expansive AAR and this section differed from the rest of the tarmac only in one constituent: the reactive sand. The concrete of the entire tarmac was prepared from the same low alkali cement and the same basalt.

Selective dissolution procedures identified the sources of cement and basalt. The available alkali level, if computed as part of the cement, had been raised by up to 2% Na_2Oeq. during curing. Alkali/aluminium ratios reflect the alkali losses due to environmental leaching during the lifetime of the concrete. Twice the levels of mobilised silica were observed in the leachates of the failed section of the tarmac.

Keywords: *Alkali release, basalt, selective dissolution, chemical identification, pore solution*

INTRODUCTION

The gathering of information relating to AAR from the chemistry of the pore solution in concrete has been limited to analysis of the liquid phase expressed with high pressure equipment. Although this technique gives us proof of the high pH values that provide a reactive environment it does not reflect the magnitude of the mass transfer from the aggregate that has occured over time.

There is a need for the development of selective dissolution methods that leave the mineral phases of the aggregate intact while dissolving the hydrate and gel phases. They would allow the monitoring of chemical modifications of the paste chemistry occuring during the lifetime of the structure.

The commonly used acid dissolution techniques could not be usefully employed particularly for volcanic aggregates such as basalts. Nepheline, which is abundant in intermediate and basic volcanic rocks, is readily dissolved in acid solutions. However, it it has been shown that it resists complexing alkaline solutions based on ethylenediamine tetraacetic acid (EDTA) (Goguel 1995a). Such solutions proved useful in determining unhydrated blast furnace slag (Demoulian *et al.* 1980). Initial results from the use of this method on concretes containing Auckland basalts were reported during the last conference on AAR in concrete (St.John & Goguel 1992). Variation

of the cation associated with the EDTA allows optimisation of the selectivity of the dissolution reagent (Goguel 1995a). Tetramethylammonium (TMA) makes EDTA an effective solvent for cement paste and aggregate reaction products leaving the aluminosilicate phases intact.

Demonstration of the potential of this method based on the study of a severely AAR damaged concrete is the purpose of this paper.

At Whenuapai Air Base, Auckland, New Zealand concrete pavement was placed in 1963. After spectacular signs of disintegration in 1982 due to stress release, engineering (McNamara 1985) and petrographic (St.John 1984) investigations were carried out. This case has been chosen for the present study because it provided two comparable adjoining slabs of the same age where only one suffered AAR due to the presence of reactive Waikato River sand. Initially, the use of high alkali cement was the only available explanation for the failure until preliminary chemical investigations (St.John and Goguel 1992) including chemical cement identification (Goguel & St.John 1993) showed the two slabs were constructed with the same coarse aggregate and the same low alkali cement. This proved that the source of the extra alkali had to be the basalt. Confirmation of the magnitude of alkali release was obtained by laboratory experiments with experimental mortars (Goguel 1995b).

EXPERIMENTAL

100 mm diam. samples were wet cored from the total thickness of the tarmac and then dried at 60°C. All subsequent subsampling was done by dry cutting. The final subsamples were slabs of 100g which were broken up with a hydraulic crusher. Large aggregate chips were isolated. Their coatings of cement paste were removed by treatment with 1M HNO_3 and a stainless steel wire brush. The clean chips were ground and taken up by HF-$HClO_4$ dissolution for analysis by flame- and inductively coupled plasma spectrometry.

Cement rich portions were broken up by hand between tungsten carbide surfaces. Fine material (<125µm) was extracted by sieving and used for selective dissolution of the hardened cement. The residue from cement dissolution consists as part of the sand fraction.

The solvent contained 2.6% EDTA, 1.9% TMA-OH and 6.5 % triethanolamine (TEA) by weight. The pH was adjusted to 12.5 by further addition of EDTA or TMA-OH. About 50 mg of sample was placed in a 50 ml screwcap sealed centrifuge tube and half filled with a weighed amount of solvent at 40°C. The tube was rotated at 30 rpm and 40°C for one hour. The leachate was then decanted after centrifugation and analysed. Further details have been published elsewhere (Goguel 1995a).

RESULTS AND DISCUSSION

Cement identification

Element ratios of 240-320 for Ca/Sr and 600-850 for Ca/Ba in the solutions identify the cement used in the Whenuapai tarmac as originating from the works at Portland/Whangarei. These ratios are unique to these works which have consistently produced cements high in strontium and barium. For other New Zealand cements the

values for Ca/Sr range from 420-2000 while their Ca/Ba values range from 2000-4800. Shifts of these ratios by aggregate contributions of Sr and Ba to the leachate are significant, but too small to lead to misinterpretation (Goguel and St. John 1993). Analytical records for cements from Portland between 1960 and 1966 consistently show low alkali levels between 0.2 and 0.4 % Na$_2$O equivalent.

Aggregate identification

Relatively high concentrations of magnesium and nickel were measured for the aggregate chips separated from the concrete cores of both the failed and the sound portion of the tarmac. Table 1 shows some chemical characteristics of Auckland basalt aggregate. The Mg and Ni concentrations and the K/Rb ratio for coarse aggregate from the Whenuapai tarmac (bottom of Table 1) match the values obtained for the Lunn Ave quarry.

Table 1: Chemical Characteristics of some Auckland basalts

Locality	Position in Flow	%Mg	ppm Ni	ppm Cs	K/Rb
East Tamaki, Milburn	scoria	11.5	250	0.7	670
East Tamaki, Milburn	bottom	10.6	220	0.7	720
East Tamaki, (Pc) Milburn	centre	10.9	230	0.6	700
East Tamaki, (S) Stevenson	bottom	12.1	260	0.5	720
Manukau, Roscommon	at base	10.4	220	0.8	630
Manukau, Roscommon	1 m above base	11.6	240	0.7	650
Lunn Avenue (L1)	at base	13.4	310	0.8	490
Lunn Avenue (L2)	centre	13.6	300	0.8	550
	Position in Concrete				
Whenuapai tarmac	core 2 (AAR)	13.3	320	2.4	510
Whenuapai tarmac	core 5 (sound)	13.0	300	0.6	510

The relatively high cesium concentration in the AAR affected core samples are a proof of migration of cesium from the cement into the coarse aggregate. Waikato River sand contains sorbed cesium of geothermal origin. The three fold rise in cesium concentration in 20 mm size basalt chips indicates both, a high rock permeability and a capacity for cesium sorption.

Release of alkali from basalt

Fig. 1 shows the magnitude of solubilized aggregate constituents. Selective dissolution of the cement from the hardened concrete with alkaline chelates shows up the fraction of alkali that has been mobilised from the basalt. The constituents of the cement have been deducted following Goguel 1995b. The percentage values are referred to the original cement fraction which is set at 100%. When comparing the failed with the

sound slab, the high level of mobilised silica from AAR is the most pronounced feature. In the absence of reactive aggregate the silica/alumina molecular ratio leached from aggregate is only about 2. This suggests that the feldspar crystals in the basalts are attacked by the pore solutions in preference to the glass phase in the basalt which has a typically higher Si/Al ratio.
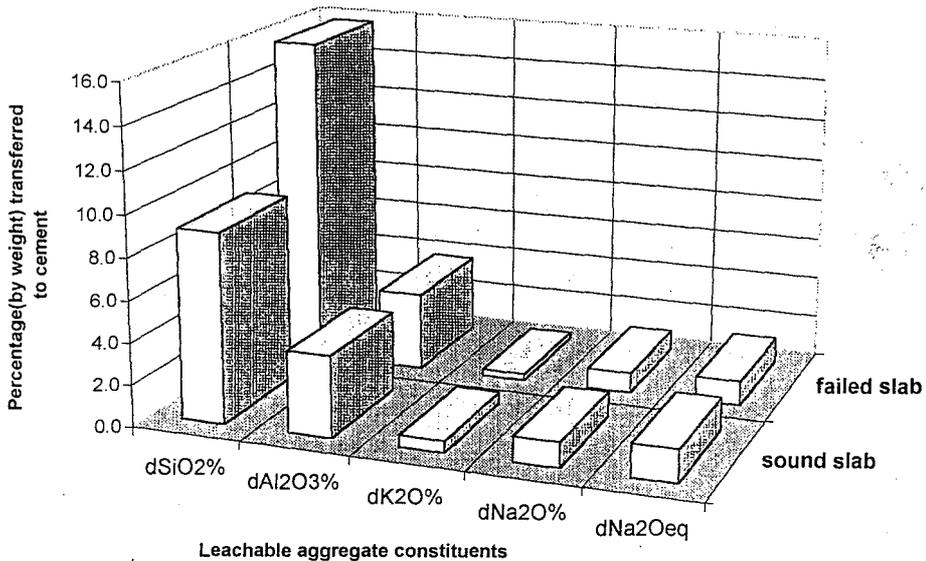

Fig. 1 Solubilized aggregate constituents in 30 years old concrete at Whenuapai, New Zealand

At first sight it might be surprising that the sound slab produces a substantially higher level of leachable alkali than the failed slab. The reason is that the sound slab could better retain the mobilised alkali than the disintegrating portion of the tarmac. Environmental leaching after 30 years of exposure in the Auckland climate, which has a high rainfall, will have removed alkali from the concrete at a greatly enhanced rate once it had started to disintegrate. The remaining leachable alkali in the failed slab only amounts to 4 kg Na_2Oeq/m^3 which reflects this relative loss when compared with the value of 6.2 kg Na_2Oeq/m^3 remaining in the sound slab after environmental leaching (Table 2).

Table 2   Contribution of alkali in Whenuapai tarmac as Na_2Oeq:
(Mix design: 1300kg basalt/m^3, 325kg cement/m^3, W/C=0.5.

	Basalt	Cement	Hardened Paste: Sound Slab
kg/m^3 alkali as mixed	52	1.3	1.3
kg/m^3 alkali released	>4.9	1.3	>6.2

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An approximate measure of the alkali losses due to environmental leaching is available from the ratios of the environmentally mobile alkali ions relative to the immobile aluminium (Fig. 2).
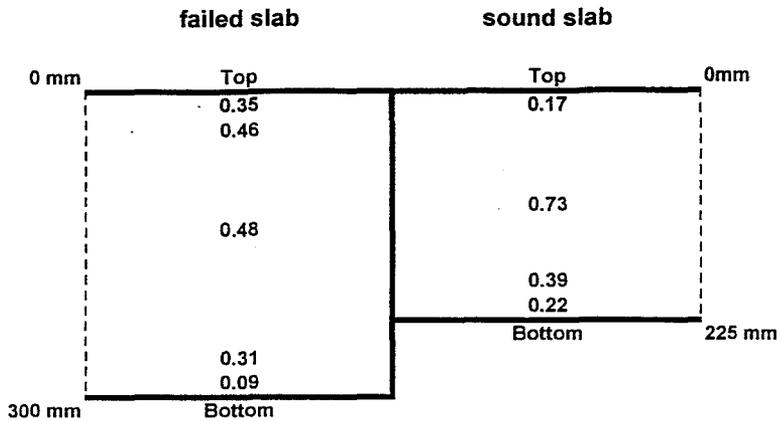
failed slab　　　　**sound slab**

0 mm	Top	Top	0mm

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0 mm            Top                    Top              0mm
            0.35                     0.17
            0.46

                                     0.73
            0.48

                                     0.39
                                     0.22
                                    Bottom           225 mm

            0.31
            0.09
300 mm          Bottom
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Fig. 2 Leachable alkali-aluminium atomic ratio in Whenuapai tarmac. (cement constituents deducted)

The atomic ratio of the sum of the sodium and potassium ions and aluminium released from the Lunn Avenue basalt in experimental mortars is 1 ± 0.1. The values measured in the centre of the sound slab (0.73) and the failed slab (0.48) of Whenuapai pavement indicate an alkali loss of about ¼ for the sound concrete and ½ for the failed concrete. Consequently the the basalt aggregate released about 12 % of its alkali transferring near 2 %Na_2Oeq to the cement, or 6.5 kg Na_2Oeq/m^3 to the concrete.

The rate of alkali release from basalt and the effect of grain size.

The increased cesium concentration observed in the coarse aggregate of the failed concrete but derived from the sand fraction is due to permeation. This indicates that the reverse movement, the release of alkali from basalt, is not dependent on the presence of a fine fraction such as crusher dust. It is dependent on factors such as the water permeability of the basalt matrix, and the grain size of feldspar crystals and residual glass. Lunn Avenue basalt can be distinguished from basalt Pc by its fine grained groundmass of feldspars attributed to its cooling history being substantially different. Slower cooling typically develops larger crystals. When L1 and Pc results for sodium release are compared (Fig. 3), Lunn avenue aggregate shows a substantially higher release. However, as the basalts are crushed to a powder approaching the size of the feldspar crystals, the differences in alkali release become negligible.

After 6 months curing the experimental mortars prepared at the same W/C-level as the concrete solubilize between 4 and 10 percent of the alkali content of the Lunn Ave basalt aggregate (Figs. 3 and 4). This range is relatively narrow compared with the corresponding 12 fold increase in specific surface area or mean grain size (0.056 - 0.7 mm). Extrapolated to the specific surface area of the basalt aggregate in the pavement
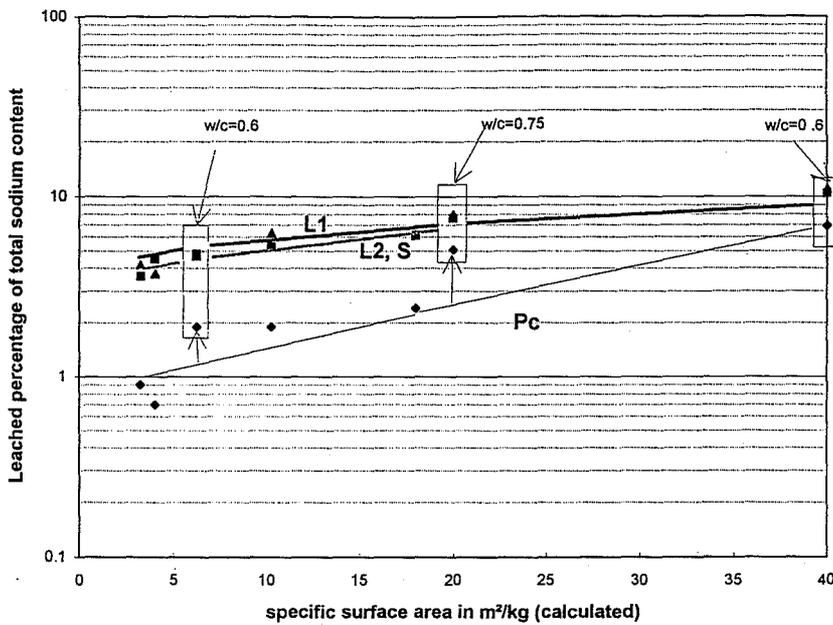
Fig. 3   Experimental mortar curing for 6 months at 21°C;   Comparison of sodium release characteristics of three basalts (w/c=0.47 except values in rectangles).
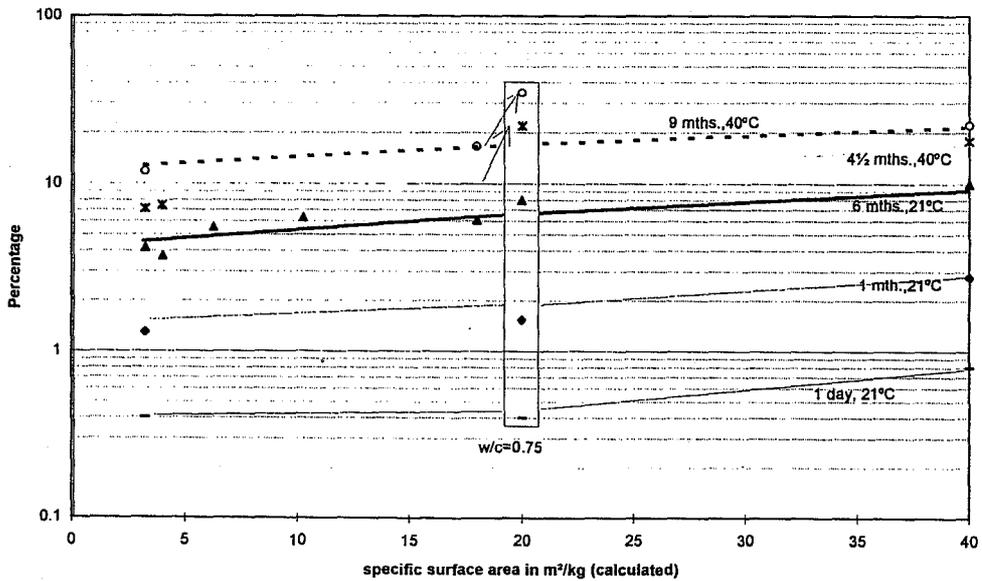

Fig. 4 Leaching of sodium content from basalt L1 during experimental mortar curing (w/c=0.47 except values in rectangle)

(0.5 m²/kg) the expected alkali release after 6 months curing at 21°C is between 1 and 2 % or 0.5 - 1 kg Na_2Oeq/m^3. This brings the total available alkali to about 2 kg Na_2Oeq/m^3. Therefore after 6 months no AAR will have occurred. However, after several years alkali levels are expected to rise to the high levels observed in the cores obtained from the tarmac. Ideally, it would be desirable to collect data for decades of curing time at 21°C but at present data are available only from relatively short curing times up to one year from earlier work (Goguel 1995b) and up to 9 months at 40°C plotted in Fig. 4.

The results from curing at 40°C may be regarded as a measure of alkali release during much (~ 4 times) longer periods of curing time at 21°C and indicate that alkali release is an ongoing process. The results obtained for a mean grain size of 0.7 mm (specific surface area 3 m²/kg) after 9 months, probably representing 3 years curing at 21°C, approximate the chemistry of the selective alkaline leaches of the Whenuapai tarmac.

Alkali release at the level of 10 % is in agreement with Tab.2 . Considering the larger average grain size of the aggregate at Whenuapai, 3 years is considered a minimum time interval to bring about the observed levels of alkali release.

Surface cracking and minor damage required frequent small repairs after ten years until after twenty years the stresses due to AAR became so high that the concrete slab suddenly broke up by moving upwards. At this stage at least 1.5% Na_2Oeq referred to the cement have been mobilised. The combined level of available alkali in the tarmac exceeds 6 kg Na_2Oeq/m^3 (Table 2).

CONCLUSIONS

Selective dissolution of the cement paste matrix with a complexing alkaline solvent at pH 12.5, provides information on the elements mobilised from the aggregate during curing.

Chemical analysis of the resulting solutions provides a useful tool in investigation of concrete failures as follows:

- Identification of cement source
- Identification of aggregate source
- Determination of available alkali
- Estimation of alkali loss due to environmental leaching

Application of this technique to experimental mortars in a closed system confirmed that Auckland basalts release alkali in contact with the pore solutions of cement paste. The alkalis (Na+K) are released together with Al in a characteristic ratio. This atomic ratio approximates unity in the case of Lunn Avenue basalt. The alkali losses due to environmental leaching of a concrete slab during its lifetime can be estimated by evaluation of downwards shifts of (Na+K)/Al ratios.

The magnitude of alkali released by the aggregates depends on the following variables: the type of basalt, including alkali content and cooling history, the water/cement ratio, the grain size distribution of the aggregate, and the time and average temperature of

freedom from AAR in concretes as demonstrated by this study. Both slabs contain low alkali cement from the Portland cement works and Lunn Avenue basalt as coarse aggregate. It is assumed that the same quarry also provided the crusher dust which has been added to improve the workability of the sand fraction.

During two decades of curing, sufficient alkali was released (6 kg Na_2Oeq/m^3) to cause severe AAR in the slab that contained reactive Waikato River sand.

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