# INVESTIGATION OF SOME GREYWACKE AGGREGATES FOR ALKALI-AGGREGATE REACTIVITY

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> Greywackes have a complex mineralogy, and generally include quartz, feldspar and some phyllosilicates. The reaction of aggregates containing amorphous silica and cryptocrystalline quartz has been known as classical alkali-silica reaction (ASR). Because some reactive greywackes found in Canada did not contain the components commonly associated with classical ASR, it was considered that phyllosilicates were involved in the reactions, and the reaction was accordingly termed alkali-silicate reaction.

This work is aimed at characterising a number of greywackes from several countries by using petrographic, X-ray diffraction, chemical analyses, electron microscopy, measurement of expansion of concrete and mortar specimens made with the aggregates, and clarifying the terminology alkali-silica and alkali-silicate reaction as applicable to these rocks.

Based on the results obtained, it has been concluded that the reaction of greywackes is basically the alkali-silica reaction, although chemical attack on some silicates such as feldspars and even phyllosilicates might contribute to the reaction. It appears that the term alkalisilicate reaction in the sense suggested by others to involve exfoliation and expansion of phyllosilicates is redundant.

## **INTRODUCTION**

The two completely distinct types of alkali-aggregate reaction are the alkali-silica reaction (ASR) and the alkali-carbonate reaction (ACR). The latter is outside the scope of this paper and will not be discussed further. The former was reported for the first time by Stanton (1) and was found to occur between amorphous silica (opal) or cryptocrystalline quartz (chert) contained in the sand, used in the concrete, and the alkali component of the concrete derived from the cement. This type of reaction involved rather simple silica components of the aggregate, often monomineralic. The reaction produced certain symptoms in the concrete, e.g. formation of gel, and excessive expansion and cracking, and there was little doubt as to the nature of the reaction and the reactants involved.

In subsequent years, mineralogically complex aggregates were found to cause expansion and cracking of the concrete, and in some cases it was difficult to ascertain which components of the aggregate were involved in the reaction. Such aggregates often contained quartz grains in various forms and shapes, feldspars, mica, chlorite and other phyllosilicates as their major components. Gillot *et al.* (2), studying such aggregates from Nova Scotia, summarised the character of their reaction in concrete and emphasised that there were differences between the nature of the reaction of these and the type of aggregate that caused classical alkali-silica reaction. The rocks under study did not contain opaline material, but did contain microcrystalline and strained quartz,

vermiculite-type and interlayered clay minerals. Because some affected concretes did not contain alkali-silica gel, it was suggested that the observed slow expansion occurred as a result of the removal of the interlayer material by the alkali-hydroxide solution present in the pore space of the concrete, enabling the clay to absorb interlayer water and expand. Gillot (3), pointing out that the rocks he and his colleagues studied contained both fine-grained and strained quartz, and that they may react by a mechanism similar to ASR, stated: 'This may be so, but studies of greywackes, phyllites and argillites from Nova Scotia provided clear evidence that in those rocks the phyllosilicates are at least partly responsible for expansion in the alkali-aggregate reaction'. He stated later: 'Evidently expansion due to alkali-attack upon rock can result from new and previously unsuspected mechanisms. So it is proposed that such cases be placed in a new category termed alkali-silicate reaction'. This was despite the fact that Gillot and Swenson (4) had found that another Canadian aggregate (from Alert) behaved in a similar way to the Nova Scotia aggregates in concrete, although it did not contain the exfoliating type of phyllosilicate (vermiculite-type mineral).

This mechanism of reaction proposed by Gillot (3) has not been demonstrated or accepted by other researchers. Diamond (5) considered the proposed mechanism of ASR unlikely without 'more convincing evidence to the contrary'. Mather (6), in his discussion of the paper by Diamond (5), recommended that, 'there be only one category of alkali-silica reaction, i.e. the reaction of alkalies with thermodynamically metastable silica', and considered that swelling of clay should not have recognition as a category of AAR. The Canadian literature (Rogers (7)) now contains terms such as 'late/slow alkali-silica/silicate reaction', which is uncessarily complicated.

Aggregates, similar to those from Nova Scotia, which have or have not contained the so-called 'exfoliating phyllosilicates' have shown reactivity in concrete and with similar reaction products. The South African greywacke from Mulmsbury contains a type of vermiculite that expands upon exposure to a calcium-containing solution, but also shows crystalline and gel reaction products in concrete affected by AAR (Oberholster *et al.* (8)). The phyllite aggregate that caused AAR in an Australian dam (Cole *et al.* (9)) did not contain the exfoliating type of phyllosilicate, but its reaction products in concrete were the same as those of the South African greywacke. The Australian aggregate was dimensionally unstable and capable of large movements (0.06-0.14%), arising from changes in moisture content, which may be sufficient in itself to cause cracking of concrete. However, Shayan (10) showed that this aggregate was capable of causing deleterious AAR and cracking in concrete regardless of its dimensional instability (isothermal moist curing). Shayan (11) had suggested that an amorphous Si-rich material may have contributed to the observed reactivity of this aggregate, which did not contain any expanding type of clay minerals as shown by X-ray diffraction analysis; quartz, mica and chlorite were the major components of the rock, forming a fine-grained groundmass.

It appears that in the mechanism of ASR proposed by Gillot and co-workers (2, 3), two completely different phenomena have been combined and considered to be one mechanism. The first one is the reaction between the alkali and various forms of silica (and perhaps some forms of feldspars) in which a chemical reaction, ultimately resulting in new products (e.g. gel), is involved. The chemical reaction could be to the extent of diffusion of alkali and hydroxyl ions into the susceptible components, breakage of chemical bonds and swelling of the affected components. This may lead to little-gel formation but could cause significant expansions. The second phenomenon-is basically that of physical instability of the aggregate arising from moisture sensitivity of certain components (usually swelling clay minerals) in the aggregate. Cole and Lancucki (12), Shayan *et al.* (13) and Shayan and Ritchie (14) have shown that rock prisms containing smectite expand on exposure to wet conditions. This involves the uptake of water molecules into the interlayer

space of the swelling clay minerals, and various cations exert different influences on the degree of swelling. Shayan and Ritchie (14) showed that expansion of rock prisms containing swelling clay minerals significantly increased in the presence of Na<sup>+</sup> cations in a dilute NaCl solution. Such cation exchange reactions are very different from the first phenomenon and should not be considered as a category of AAR. If the second phenomenon was the dominant feature of an aggregate, causing problem in concrete, then it should not be called alkali-silicate or alkali-aggregate reaction.

This paper reports on results obtained from the investigation of greywacke aggregates from different countries, and shows that the chemical reactions involved are largely those of alkalisilica reaction.

#### **EXPERIMENTAL**

#### Aggregates

The greywackes examined in this work were obtained from Australia, Canada (Nova Scotia), New Zealand (mixture of Lower Hutt River gravel and Belmont quarry), South Africa (Malmesbury group) and the United Kingdom (North Wales). The Australian greywacke has been assessed as reactive in laboratory tests (Shayan (15)); the Nova Scotia greywacke is well known for its reactivity from the work of Gillot and co-workers (e.g. (2)), and was the reason for introducing the term alkali-silicate reaction; the Malmesbury greywacke has reacted in service and in laboratory tests as shown by the work of Oberholster *et al.* (8, 16); the Welsh greywacke has reacted in Maentwrog dam (B. Blackwell, BRE, England, personal communication); but the New Zealand greywacke was sent to us as a non-reactive aggregate (D. St John, DSIR, New Zealand, personal communication). The greywackes are disignated AST, CAN, NZL, SAF, WLS, corresponding to those from Australia, Canada, New Zealand, South Africa and Wales, respectively.

## Methods

The following experimental methods were used in this investigation:

- 1. conventional petrographic analysis of thin sections;
- X-ray diffraction (XRD) analysis of pulverised (<75 μm) aggregate before and after shaking with a 1M CaCl<sub>2</sub> solution, heating and glycerol treatments;
- determination of exchangeable cations on the pulverised aggregates using a 0.1M LaCl<sub>3</sub> solution at pH 7.7 as the extracting medium, and determination of potential reactivity of the aggregates according to the chemical test (ASTM C289 or AS 1141-39);
- 4. determination of accelerated mortar bar expansions in 1M NaOH solution at 80°C, following the procedure and criteria described by Shayan *et al.* (17);
- determination of expansion of concrete prisms with high cement contents (407 kg/m<sup>3</sup> except for AST aggregate where 500 kg/m<sup>3</sup> was used), at 1.38% cement alkali level (Na<sub>2</sub>0 equivalent);
- 6. scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis of resinimpregnated, polished pieces of aggregate before and after treatment in 1M NaOH solution at 80°C for 28 days. Aggregate particles were also stored in water and 1M NaOH solutions at 80°C for 28 days for examination by SEM and EDX after the treatments.

#### **RESULTS AND DISCUSSION**

#### Petrographic Description

A detailed petrographic description of each aggregate is given in Appendix 1. Features common to all the five greywackes are described below.

Aggregate pieces vary from fine- and coarse-grained greywacke to fine-grained argillite varieties. They are all poorly to moderately sorted. The greywacke clasts are predominately composed of quartz (both mono- and polycrystalline), plagioclase and K-feldspar with subordinate muscovite and biotite. The matrix of the greywackes (~15% by volume) is composed mainly of slightly to moderately recrystallised fine-grained quartz, muscovite, biotite, chlorite and other iron-rich argillaceous material. The matrix minerals are often foliated due to low-grade regional metamorphism. The argillite varieties are predominately composed of muscovite, chlorite and iron-rich argillaceous material, and show a regular schistosity. The quartz grains of all the rock types show variable degrees of undulose extinction.

#### X-ray Diffraction Analysis

X-ray powder diffractograms run in the range of 2-65 degrees 20 confirmed that all greywackes contained large amounts of quartz and lesser amounts of chlorite, muscovite and plagioclase feldspar, AST greywacke contained larger amounts of microcline (K-feldspar) than others, but this phase was not detected in SAF greywacke. A major difference in the argillaceous component was found between CAN and SAF greywackes on the one hand, and the other greywackes on the other hand, Figures 1 shows XRD traces for the various aggregates in the range of 3-13 degrees 20, where information related to the nature of argillaceous materials can be obtained. These traces indicate the presence of chlorite (14 and 7 Å peaks) and mica (10Å peak). The broadness of the mica peak for CAN and SAF indicated that another phase may be present. Shaking of the rock powder in a 1M CaCl<sub>2</sub> solution for three days did not affect the subsequent XRD patterns for WLS, AST and NZL greywackes. In the case of SAF and CAN greywackes, a peak at 14.8Å was observed in the XRD trace (Fig. 2). This phase was more abundant in CAN than SAF greywacke. The shape of the 10Å peak in the XRD trace of SAF aggregate indicates that it reacts with CaCl2 more slowly than CAN greywacke, and the reaction may not have been completed. Figure 3 shows the effect of various treatments on the basal spacing of the 14.8Å phase in CAN greywacke. Glycerol treatment for six days caused expansion of a portion of the 14.8Å phase in the CaCl<sub>2</sub>-treated material to 15.8Å, and heating at 580°C for 1 hour collapsed it to 9.5Å. These indicate the presence of vermiculite-like material.

The chlorite phase remained at about 14Å spacing during the treatments. As expected, the 7Å spacing of chlorite is lost in the XRD trace of the specimen heated at 580°C for 1 hour. The XRD results indicate a type of vermiculite, chlorite and mica in CAN and SAF greywackes, but chlorite and mica in the other greywackes as their argillaceous phases (a minor amount of hornblende was present in AST greywacke, giving the small 8.4Å peak).

An argument Gillot (2) used in support of his alkali-silicate reaction mechanism was that the basal spacing of the vermiculite-like material expanded from 10 to 12.6Å by NaOH treatment. It is shown here that the basal spacing can be expanded to 14.8Å by treatment with CaCl<sub>2</sub> solution, confirming that this is an exchange reaction and not AAR.

## Determination of Exchangeable Cations and Potential Alkali Reactivity

Table 1 shows the amount of exchangeable cations extracted from each greywacke by a 0.1M LaCl<sub>3</sub> solution at pH 7.7, as well as the results of the chemical test for potential alkali reactivity.

Aggregate	Na+	K+	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Total	Chemical Test*		
						S <sub>c</sub> (m/m	R <sub>c</sub> oles/l)	Classification <sup>†</sup>
AST	0.62	0.72	0.46	ND <sup>‡</sup>	1.80	51	21	deleterious
CAN	0.56	0.89	0.87	ND‡	2.33	62	13	deleterious
NZL	1.21	0.97	1.69	ND‡	3.86	47	63	innocuous
SAF	0.44	1.63	1.04	ND‡	3.11	76	41	deleterious
WLS	0.64	0.48	1.34	ND‡	2.46	42	18	deleterious

TABLE 1 - Exchangeable cations (m equiv./100 g) and results of the chemical test

\* Sc = dissolved silica, Rc = reduction in alkalinity.

<sup>†</sup> All results fall near the borderline of innocuous/deleterious regions.

<sup>‡</sup> Mg was not detected in exchangeable form.

The amount of exchangeable cations reflects the quantity and type of clay minerals present in the aggregate, which is an indication of weathering or alteration of the primary minerals. The New Zealand and Australian aggregates seem to be the most and least weathered, respectively, but this was not reflected by the quantity of clay minerals shown in the XRD traces; possibly, some of the cations may have been extracted from sources other than clay minerals.

The results of the chemical test classified all the aggregates except NZL as deleterious, but all including NZL fall close to the borderline, so that a definite decision regarding reactivity cannot be made on the basis of these results.

#### Accelerated Mortar Bar Expansion

Figure 4 shows expansion curves for mortar bars containing the greywackes and subjected to 1M NaOH solution at 80°C, according to the procedure described by Shayan *et al.* (14). All the greywackes expanded more than 0.1% in 10 days, and are considered potentially reactive, i.e. they contain components that have the potential to react with alkali under adverse conditions. The New Zealand greywacke showed the lowest rate of reaction. The arrows show the expansion and age at which cracking was observed in the mortar bars.

## Expansion of Concrete Prisms

Figure 5 shows expansion curves for concrete prisms made with the various aggregates, at a cement content of 500 kg/m<sup>3</sup> for AST and 407 kg/m<sup>3</sup> for the other aggregates. The level of cement alkali was adjusted to 1.38% Na<sub>2</sub>0 equivalent by the addition of appropriate amounts of NaOH to the mix water. The North Wales aggregate was not available for this purpose. Aggregates AST, CAN and SAF caused significant expansions and cracked, as indicated by the arrows. Aggregate NZL did not show significant expansions at this level of alkali content (5.6 kg/m<sup>3</sup>) despite the results of the accelerated mortar bar test which had shown the potential of the aggregate for reaction at higher alkali contents. Concrete prisms made with this aggregate at an alkali content of 7.3 kg/m<sup>3</sup> showed only slightly increased expansions at one year (0.012%), and these specimens are currently being monitored.

#### Scanning Electron Microscopy

Morphological and compositional features of the greywackes have been studied in detail before and after storage with 1M NaOH solution at 80°C. Only a limited amount of representative information can be presented here. Figure 6 gives some features of AST greywacke: Fig. 6a shows the polished surface of quartz grains with fine matrix materials (back-scattered electon image), and Fig. 6b shows details of the matrix in another area in the untreated specimen. The lighter material in the vein in Fig. 6a is chlorite, as indicated by the EDX spectrum in Fig. 7a, and the matrix material in the centre and top of Fig. 6b is mica (muscovite), as indicated in Fig. 7b. After treatment in the NaOH solution, the surfaces of quartz grains became highly etched (Fig. 6c). It appeared that quartz particles, in zones where there was an intergrowth of quartz and K-feldspar, were dissolved to some extent so that a strongly etched surface was obtained (Fig. 6d). The Kfeldspar itself (marker in Fig. 6d) appeared to be unaffected. A new phase was observed in the treated specimen, as shown by round particles in Figs 6c and 6d. Figure 6e shows details of the round particles from another area. These have an octagonal outline and appear to be dodecahedrons. Their composition is given in Fig. 7c and consists of Na, Al, Si with some Fe. The Al and Fe were derived from non-quartz phases, present either as inclusions in the quartz or as separate phases such as feldspar and/or chlorite. The composition and morphology of this material is similar to analcite. In fact, we have identified analcite and tobermorite in the solid suspended materials that form in the NaOH bath at 80°C, after storage of mortar bars for a few weeks. Cole et al. (9) also found that gel-like materials found in AAR-affected concrete were converted to analcite after standing in room conditions for one year.

The untreated aggregate particles stored in water at 80°C gave phase compositions similar to those in the untreated polished specimens, but the particles kept in 1M NaOH at 80°C showed new phases. Other than a phase similar to that shown in Fig. 6e, a very Na-rich material was also observed (Fig. 6f). The substrate material in Fig. 6f which appears to have been etched had the composition shown in Fig. 7d (probably chlorite or biotite affected by NaOH), and the rosette-shaped material has the composition shown in Fig. 7e. The high Na in this material may be partly due to sodium silicate and partly due to NaOH from the storage solution retained within the aggregate, because the aggregate particles were only briefly dipped in distilled water to remove the surface NaOH.

In AST greywacke dissolution of quartz was a very common feature, although attack on other phases must also have occurred. No sign of 'exfoliation' of the phyllosilicates (Gillot (3)) was observed.

Some features of the Nova Scotia aggregate (CAN greywacke) are shown in Fig. 8. The untreated polished quartz surfaces (Fig. 8a) were like those in AST greywacke, and the vermiculite phase was observed on the surface of untreated aggregate particles (Fig. 8b). In the treated samples, the etching of quartz surfaces was observed, as well as the formation of some new phases. The roundish particles (Figs 8c and 8d) are similar to those in the treated AST greywacke, and formed in various locations. The vermiculite-like phase in the treated polished specimen (centre of Fig. 8c) has the same features as that in the untreated aggregate particle (Fig. 8b). Some gel-like material (Fig. 8e) and a crystalline platy phase (Fig. 8f) were also observed in some locations, and their compositions (Figs 9a and 9b, respecitvely) were similar to those of AAR products.

These observations indicate that the Nova Scotia aggregate is capable of producing AAR products, regardless of the behaviour of its phyllosilicate content as proposed by Gillot (3).

Figure 10 shows some features of the treated NZL aggregate. The untreated aggregate was similar to AST in features. Figure 10a shows severe etching of a quartz grain by the NaOH, with platy reaction products of the composition shown in Fig. 11a. Microcrystalline quartz at the boundary of coarser quartz also showed similar reaction products (Fig. 10b, bottom). A quartz vein was severely attacked by the alkali (Fig. 10c) and formed platy as well as granular reaction products (Fig. 10d) of the composition shown in Fig. 11b. In other areas some grains (probably amorphous silica) were completely converted to platy AAR products (Fig. 10e) with the same composition as in Fig. 11a. In the polished specimen, severe etching of quartz in the quartz/K-feldspar intergrowth was also observed. Aggregate particles stored in the alkali solution also showed various reaction products, Figure 10f shows a fibrous as well as other morphological forms of reaction products, all with the general composition shown in Fig. 11c. A very fibrous form with elongated strands (not shown due to poor photograph) contained large amounts of K and Ca in addition to the elements indicated in Fig. 11c.

These observations confirm that this aggregate contains reactive components and has potential for reactivity, as indicated by the results of the accelerated test.

Features of the polished untreated SAF aggregate were similar to those already seen for other aggregates. Figures 12a and 12b show surfaces of the untreated aggregate particles with smooth (Fig. 12a) and conchoidal fracture surfaces of quartz grains, together with matrix material containing sheet silicates (mica above quartz grain in Fig. 12a and chlorite/vermiculate to the right of quartz particle in Fig. 12b). Severely etched quartz surfaces and etching of quartz intergrown with K-feldspar in treated polished specimens are shown in Figures 12c and 12d, respectively, with both the dodecahedrons and platy crystals as reaction products. The composition of the former is the same as those already seen for other aggregates, and that of the latter is shown in Fig. 13a which is similar to the composition of some AAR products. The fibrous material formed on the surface of treated aggregate particles (Fig. 12e) has the composition shown in Fig. 13b. Materials shown in Fig. 12f had a very Na-rich composition (Fig. 13c) similar to that in Fig. 7e, but with more Ca and less Fe. In this case also, part of the Na may be present in the form of NaOH and not in the composition of the reaction product itself. Other reaction products observed in the treated aggregate were, firstly, a mixture of fibrous and sheet-like materials (not shown) with a composition (Fig. 13d) suggesting that it was biotite or K-vermiculite attacked by NaOH, and, secondly, materials of the morphology and composition of those shown in Fig. 10f. Those formed on SAF aggregate were made up of densely compacted thin foils, as these were seen to be peeling off in some places. The above observations are consistent with the reactive nature of SAF aggregate.

Figure 14 shows features of the treated WLS aggregate. The untreated one had the same features as the other untreated aggregates. Figures 14a and 14b show the dramatic effect of the alkali on the silica component of the aggregate in the polished specimen. This may have been amorphous or cryptocrystalline silica (chert component) which is very sensitive to alkali hydroxide attack. Figures 14c and 14d show details of the reaction products. The material in Fig. 14c and the background material in Fig. 14d have the composition shown in Figure 15a which is rich in Ca. The Ca could have originated from plagioclase or perhaps calcite found in the aggregate. The crystals shown in Fig. 14d have the same composition as the dodecahedrons in the other cases. Reaction products on the treated aggregate particles included gel (Fig. 14e) with the composition shown in Fig. 15b. In some cases the gel was a pure sodium or potassium silicate. The material shown in Fig. 14f had the same composition as that in Fig. 15a. These observations are consistent with the reactive behaviour of the aggregate in the Welsh dam and in the accelerated test. They have revealed that silica is the major reactive component of the aggregate, although other phases like plagioclase may have been the source of Al and Ca in some of the reaction products.

## CONCLUSIONS

This work has shown that greywackes that contain phyllosilicates with basal spacings susceptible to expansion due to cation exchange with Ca, and those that lack such phyllosilicates, both undergo the same type of reaction with NaOH solution at 80°C, and produce similar reaction products. The products originate largely from silica contained in the greywackes, although chemical attack on silicates such as feldspars and even phyllosilicates may also contribute to the formation of reaction products. However, no SEM evidence has been found in support of the mechanism suggested by Gillot (3) involving the exfoliation of certain phyllosilicates. For all the greywackes studied, including that used by Gillot and co-workers (Nova Scotia greywacke), the alkali-silica reaction mechanism is adequate for explaining their reactivity, and it appears that the term alkali-silicate reaction as intended by Gillot (3) is redundant. It is likely, however, that cation exchange reactions with some phyllosilicates may cause additional stresses due to expansion of the basal spacing of the phyllosilicates, but this cannot be classified as a type of alkali-aggregate reaction. It is suggested that the existing definition of the term alkali-silicate reaction be abandoned or redefined to include cases where both silica and silicate (feldspar, phyllosilicates, etc.) minerals have suffered the same type of chemical attack by alkali and contributed to the formation of the same type of reaction product. A better term may be alkali-silica/silicate reaction for such cases, although the silica components would still be the main cause of reactivity.

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#### **REFERENCES**

- 1. Stanton, A., 1940, Amer. Soc. Civil Eng. Dec., 1781.
- 2. Gillot, J.E., Duncan, M.A.G., and Swenson, E.G., 1973, Cem. Concr. Res. 3, 521.
- 3. Gillot, J.E., 1975, Eng. Geol. 9, 303.
- 4. Gillot, J.E. and Swenson, E.G., 1973, Eng. Geol. 7, 181.
- 5. Diamond, S., 1976, <u>Cem. Concr. Res. 6</u>, 549.
- 6. Mather, B., 1976, Cem. Concr. Res. 6, 813.
- 7. Rogers, C.A., 1990, Ministry of Transportation, Ontario, Report EM-92, p.2.
- 8. Oberholster, R.E., Brandt, M.P., and Weston, A.C., 1978, Civil Eng. in South Africa 7, 161.
- 9. Cole, W.F., Lancucki, C.J., and Sandy, M.J., 1981, Cem. Concr. Res. 11, 443.
- 10. Shayan, A., 1989, Cem. Concr. Res. 19, 434.
- 11. Shayan, A., 1983, Clay Minerals 18, 333.
- Cole, W.F., and Lancucki, C.J., 1976, Clay minerals developed by denteric alteration of basalt, Proc. Int. Clay Conf. (1975), Mexico City, 35.
- 13. Shayan, A., Lancucki, C.J., and Way, S.J., 1984, Bull. Int. Assoc. Eng. Geol. 29, 433.
- 14. Shayan, A., and Ritchie, D.J., 1985, Durability of Building Materials 2, 365.
- 15. Shayan, A., 1992, ACI Materials, J. Jan.-Feb., 13.
- 16. Oberholster, R.E., Brandt, M.P., and Weston, A.C., 1978, Proc. 4th Int. Conf. on AAR, Purdue University, 141.
- 17. Shayan, A., Diggins, R.G., Ivanusec, I., and Westgate, P.L., 1988, Cem. Concr. Res. 18, 843.

## APPENDIX 1 PETROGRAPHIC DESCRIPTION OF GREYWACKE AGGREGATES

#### AST Greywacke

This greenish-grey poorly sorted greywacke varies from 0.2–0.5 mm in clast size and displays a slightly recrystallised fabric. It is composed predominantly of clasts of sub-angular quartz and subordinate plagioclase feldspar, microcline feldspar, and lesser amounts of chloritised lithic argillaceous fragments and very fine-grained lithic siltstones set in a fine-grained matrix (15–20% vol.) of silt-sized quartz, muscovite, iron oxides and chlorite. Accessory amounts of zircon and pyrite are also present. Undulose extinction in the quartz clasts is common. The feldspar clasts are strongly sericitised and show a perthitic nature. Small veinlets of polycrystalline quartz cross-cut the original bedding. Undulose extinction of the quartz in these veins is similar to that of the matrix, indicating that the rock underwent in situ deformation. The bedding is often defined by the fine bands of dark argillaceous materials which is often chloritised or replaced by iron-rich phases.

## CAN Greywacke

Aggregate pieces are dark grey and vary from coarser greywacke varieties to very finegrained argillite varieties, and occasionally both varieties appear in the same aggregate piece. Both varieties appear fissile as a result of metamorphism.

The greywacke is poorly sorted with clasts that range in size from 0.1–0.5 mm and display a moderately recrystallised fabric. The rock is composed predominantly of sub-angular monocrystalline quartz and plagioclase feldspar, with subordinate K-feldspar, relict biotite, muscovite, and minor amounts of pyroxene, lithic slates, very fine-grained quartzites and calcite. There are also accessory amounts of zircon and sphene. The matrix makes up about 10% of the rock and is composed predominantly of recrystallised muscovite and quartz with minor biotite and other iron-rich argillaceous material. Some of the biotite has been altered to chlorite. Many of the larger quartz clasts have been stretched by deformation and, together with the presence of recrystallised muscovite in the matrix, define a microschistose structure to the rock. These larger stretched quartz clasts also display irregular rough outlines probably due to dissolution of the quartz during metamorphism. Some of the smaller quartz clasts show recrystallisation to more equant mosaics (tending toward triple-point junction grain boundaries). Further evidence of metamorphism is displayed by the feldspars that show inclusions of quartz. Undulose extinction angles in the quartz clasts are variable. The larger stretched quartz clasts generally have higher extinction angles.

The argillite variety is predominantly composed of very fine-grained foliated muscovite, quartz, chlorite, plagioclase feldspar with the occasional chloritised mud fragments. Some spotting is evident (up to 0.4 mm); the spots are probably porphyroblasts of chloritised cordierite due to a local thermal metamorphic event.

#### NZL Greywacke

This dark grey moderately sorted greywacke varies from 0.1–0.6 mm in grain size and displays a slightly recrystallised fabric. It is composed mainly of sub-angular quartz clasts with subordinate plagioclase feldspar, perthitic K-feldspar and relict (crinkled) muscovite and biotite, devitrified volcanogenic glassy fragments, and minor amounts of iron-rich chert fragments, slaty

fragments, fine-grained quartzites and volcanic (basaltic) fragments. Accessory minerals include zircon, titaniferous augite, chlorite and iron oxides. The matrix makes up 10–15% of the rock and is mainly composed of iron oxides, fine-grained muscovite, chlorite and biotite. The quartz clasts occur as both mono- and polycrystalline fragments. An occasional quartz clast shows recrystallisation into smaller, more equant internal crystal boundaries – probably due to a meta-morphic source. The feldspars are moderately sericitised. Some feldspars show a graphic intergrowth with quartz. Some of the plagioclase clasts show concentric zoning, the cores being more heavily sericitised than the rims (igneous source). Undulose extinction angle in the quartz clasts is quite variable; an indication of a mixed source and not in situ deformation.

## SAF Greywacke

Aggregate pieces are black and vary from coarser greywacke varieties to very fine-grained argillites. Some aggregate pieces show interbedding of both varieties. Both varieties are marginally fissile as a result of regional metamorphism.

The greywacke is poorly sorted with clasts that range in size from 0.05–0.3 mm and displays a moderately recrystallised fabric. The rock is composed predominantly of both mono- and polycrystalline quartz, which commonly show angular outlines. Other clasts present include plagioclase feldspar, pyroxene, very fine-grained quartzite, primary muscovite, biotite, and the occasional small fragments of pyrite and magnetite. The matrix makes up about 15% of the rock and is composed of former argillaceous material which has now been recrystallised into foliated muscovite and minor chlorite. Many of the quartz clasts display irregular cracking (stress fractures). Recrystallised muscovite intergrowths are common between the matrix and some quartz clasts. Undulose extinction angle of the quartz clasts is variable.

The argillite variety is predominantly composed of very fine-grained schistose muscovite, with the occasional silt-sized clast of quartz, pyrite and magnetite.

#### WLS Greywacke

The aggregate pieces are greenish-grey and vary from coarser greywacke varieties of finegrained argillites. The argillites are marginally fissile due to metamorphism.

The greywacke is poorly sorted with clasts that range in size from 0.2-3.0 mm and displays a slightly recrystallised fabric. It is predominantly composed of sub-angular to angular mono- and polycrystalline quartz and plagioclase feldspar. Small amounts of microcline feldspar and lithic fragments of chert, fine-grained quartzite, basic volcanics, siltstones and slates are also present. The matrix varies from 10-20% of the rock and is composed of silt-sized quartz, plagioclase, muscovite, magnetite and other iron-rich argillaceous material which has altered to a strongly pleochroic green chlorite. Together, the chlorite and muscovite display a microschistosity. The polycrystalline quartz grains often show inherent sutured grain boundaries (metamorphic origin). Many of the quartz grains are also coated with iron oxide. Many of the feldspars are sericitised. Undulose extinction is common in the larger quartz clasts.

The argillite variety is moderately sorted and is predominantly composed of very finegrained quartz (0.05–0.1 mm), chlorite, foliated muscovite and minor amounts of plagioclase feldspar, sericitised K-feldspar, magnetite, pyrite and accessory calcite and sphene. Undulose extinction angles of the larger quartz clasts are minimal.



Figure 1 XRD traces of the untreated greywackes.



Figure 3 XRD traces of CAN greywacke samples subjected to various treatments.



Figure 2 XRD traces of CAN and SAF greywackes after treatment with  $CaCl_2$  solution.



Figure 4 Expansion curves for mortar bars made with the various greywackes and stored in 1M NaOH at 80°C.



Figure 5 Expansion curves for concrete prisms made with the various greywackes at a cement alkali level of 1.38% and stored at 40°C, 100% RH.



Figure 6 SEM of AST greywacke: a and b = untreated, c-f = stored in 1M NaOH at 80°C for 28 d (see text).







Figure 8 SEM of CAN greywacke: a and b = untreated, c-f = stored in 1M NaOH at 80°C for 28 d (see text).



Figure 9 Compositions of the various phases shown in Fig. 8, as indicated by EDX spectra (see text).







Figure 10 SEM of NZL greywacke stored in 1M NaOH at 80°C for 28 d (see text).











Figure 12 SEM of SAF greywacke: a and b = untreated, c-f = stored in 1M NaOH at 80°C for 28 d (see text).







Figure 14 SEM of WLS greywacke stored in 1M NaOH at 80°C for 28 d (see text).



Figure 15 Compositions of the various phases shown in Fig. 14, as indicated by EDXL spectra (see text).