Clay Mineralogy of Modified Marginal Aggregates

F.G. Bartley
Bartley Consultants Ltd, Auckland, New Zealand

C.C. Harvey
G. Bignall
Institute of Geological and Nuclear Sciences Ltd., Wairakei, New Zealand

A.B. Christie
A. Reyes
R. Soong
K. Faure
Institute of Geological and Nuclear Sciences Ltd., Lower Hutt, New Zealand

Land Transport New Zealand Research Report No 318

ISBN 0-478-28730-5
ISSN 1177-0600

PO Box 2840, Waterloo Quay, Wellington, New Zealand
Telephone 64-4 931 8700; Facsimile 64-4 931 8701
Email: *research@landtransport.govt.nz*
Website: *www.landtransport.govt.nz*

Bartley, F.G.[1], Bignall, G.[2], Harvey, C.C.[2], Christie, A.B.[3], Reyes, A.[3], Soong, R.[3], Faure, K.[3] 2007. Clay mineralogy of modified marginal aggregates. *Transfund New Zealand Research Report No.318.* 108 pp.

1 Bartley Consultants Ltd, Auckland, New Zealand
2 Institute of Geological and Nuclear Sciences Ltd, Wairakei, New Zealand
3 Institute of Geological and Nuclear Sciences Ltd, Lower Hutt, New Zealand

Keywords: andesite, aggregate, analysis, basalt, CBR, clay minerals, Durabind™, greywacke, marginal aggregate, ,modification, Proctor Needle test, roads, rocks, stabilisation, treatment, weathering

An important note for the reader

Land Transport New Zealand is a crown entity established under the Land Transport Management Act 2003. The objective of Land Transport New Zealand is to allocate resources and to undertake its functions in a way that contributes to an integrated, safe, responsive and sustainable land transport system. Each year, Land Transport New Zealand invests a portion of its funds on research that contributes to this objective.

This report is the final stage of a project commissioned by Transfund New Zealand before 2004, and is published by Land Transport New Zealand.

While this report is believed to be correct at the time of publication, Land Transport New Zealand, and its employees and agents involved in its preparation and publication, cannot accept any liability for its content or for any consequences arising from its use. People using the contents of the document, whether directly or indirectly, should apply and rely on their own skill and judgement. They should not rely on its contents in isolation from other sources of advice and information. If necessary, they should seek appropriate legal or other expert advice in relation to their own circumstances, and to the use of this report.

The material contained in this report is the output of research and should not be construed in any way as policy adopted by Land Transport New Zealand but may be used in the formulation of future policy.

Acknowledgements

The research described in this report was funded by Transfund New Zealand and a grant from Econ Products Ltd. Econ Products Ltd developed and manufacture Durabind™ and market a range of additives used in the modification of roading aggregate including lime, Durabind™ and cement.

The peer reviewers for this report, Dr Phillipa Black (Professor of Geology, University of Auckland) and Mr W.L. (Sam) Cornwell, were involved in the project from the initial stages. Their guidance and advice is gratefully acknowledged.

Winstones Aggregates (Flat Top and Otaika), W. Stevensons & Sons Ltd (Drury), and Fulton Hogan (Poplar Lane) are thanked for access to their quarries and assistance by their staff in sampling.

Abbreviations and acronyms

AP:	All Passing (i.e. all passing through a sieve of width x)
CBR:	California Bearing Ratio
CI:	Clay Index
GNS:	Institute of Geological and Nuclear Sciences Ltd
GP*:	General Purpose (a grade of Portland cement)
KOMB:	Kontinuous [sic] Oxygen Blast Mixture
LOI:	Loss On Ignition
OMC:	Optimum Moisture Content
XRD:	X-Ray Diffraction
XRF:	X-Ray Fluorescence

Contents

Executive summary

The engineering, mineralogical and chemical properties of four marginal aggregates selected from quarries in Northland, Auckland and Bay of Plenty, and treated with three types of chemical additive have been studied. This research was carried out in 2003–2004.

Mineralogical and chemical studies (including petrology, Methylene Blue adsorption, X-ray diffraction and chemical analysis) were used to characterise the raw materials. These determined that their weathering under subtropical conditions was consistent with predicted behaviour.

Samples of partly weathered aggregate from each quarry were treated with lime, cement or Durabind™[1] at concentrations of 1% and 3% by weight. Methylene Blue tests and X-ray diffraction analysis confirmed that the tendency of marginal aggregates to swell was greatly reduced by treatment with the 3% concentration of any of the three additives.

Geochemical studies using mineral stability (activity) diagrams identified trends of changing fluid composition caused by weathering that were reversed by the action of the additives.

Chemical reactions of the additives with the swelling clays in the aggregate include cation exchange and the production of new hydrated calcium aluminosilcate minerals, such as hydrogrossular, through pozzolanic reactions. The formation of hydrogrossular is slow, typically requiring months to develop, and its initial appearance in some treated samples over a 50-day period was confirmed by X-ray diffraction.

The stability of the cements was investigated by suspending crushed samples of the treated aggregates in water. Swelling tendency increased progressively over time, but at a high pH, the various treated aggregates returned to between 30% and 70% of their original swelling values after four days. All three additives create an initial high pH environment which is favourable for maintaining a non-swelling treated aggregate. However, the process can be partially reversed if water is allowed to enter the sample, or if the pH is lowered to create an acidic environment.

The reaction to a particular additive varied from aggregate to aggregate. Generally, cement caused a rapid increase in strength that was enhanced when the samples were soaked for four days in water. However, the lime-based additives caused slower, less dramatic increases in strength in the samples during the curing period. The strength of the andesite and one of the greywackes continued to increase during soaking, while that of the basalt and the other greywacke was maintained or decreased slightly. No clear mineralogical explanation for these differences can be determined. The less resistant test

---

[1] Durabind™is the tradename for a stabilising product manufactured by Econ Products Ltd.

samples may have had higher permeabilities, but this was not tested in the present programme.

The chemical and Methylene Blue adsorption tests used in this research should be considered as a standard test in conjunction with strength tests for defining the addition rates of additives to partly weathered aggregates, to achieve TNZ M/4 specification requirements.

Limitations and constraints

This study was constrained by various factors, including:

- **representative sampling.** Although care was taken to obtain representative samples from the quarries, sampling such large rock volumes and adjusting them for laboratory tests has limits.
- **reaction kinetics.** Cement formation (hydrogrossular etc) using lime and Portland cement is time related. In Portland cement, for example, hydrogrossular may take months to crystallise fully. In this study, the mineralogical and chemical studies were carried out within one to three months after engineering testing.
- **alteration prior to weathering.** Poplar Lane andesite and Flat Top basalt may have been subject to hydrothermal alteration, while Drury greywacke has been extensively sheared. Therefore, even the so-called fresh rocks, which are known to meet TNZ M/4 specifications, contain some alteration minerals (such as zeolites) that were present prior to the present weathering process.
- **kinetics.** The kinetics of the cementing reactions by lime, Durabind™ and Portland cement have not been investigated in this study.

Abstract

This study, undertaken in 2003–2004, aimed to:

1 study changes produced when additives are mixed with roading aggregates containing swelling clay minerals;
2 identify the most suitable chemical to use for a particular rock type and the quantity required to achieve particular effects, namely:
    - conversion of the clay to a better form,
    - establishment of bonds between particles,
    - strength that is insensitive to water content,
    - minimal drying shrinkage, and
    - permanence.

Samples of fresh, partly weathered and weathered rocks of three rock types were taken from four quarries. Cement, lime or Durabind™ was added to the partly weathered samples at two levels.

The untreated and treated samples were analysed. Proctor Needle and CBR testing was performed on the partly weathered samples.

Volcanic rocks contained a higher proportion of more readily weathered minerals than greywacke. Drury greywacke was more intensively sheared than Otaika greywacke. All partly weathered materials treated with 3% of additive had satisfactory CBR values.

Methylene Blue tests and X-ray diffraction analysis confirmed that 3% additive almost eliminated swelling tendencies.

Geochemical studies identified that additives reversed the trends of changing fluid composition caused by weathering.

Cement stability was investigated by suspending crushed treated samples in water. Swelling tendency increased over time, but in alkaline conditions, the aggregates returned to 30–70% of their original values after four days.

1 Introduction

1.1 Marginal aggregate

In New Zealand roading terms, marginal aggregates include those with physical or weathering characteristics that do not comply with Transit New Zealand's (TNZ) M/4 Specification (2000). The very active nature of the New Zealand landscape means that many primary rocks may have been subjected to earthquakes, faulting or perhaps hydrothermal alteration. Subtropical weathering in Northern New Zealand may then have been superimposed. Even the aggregates that comply with TNZ M/4 Specification (2000) may have been subjected to one or more of these processes.

In this study, we have defined marginal aggregates as materials which do not comply with TNZ M/4 Specification (2000) but, when modified with lime or another appropriate chemical additive, may be used to improve the performance characteristics enough to ensure an adequate pavement life.

The introduction of Transit New Zealand Specification TNZ B/3 (1999) permits the use of modified marginal aggregate as a basecourse. Such material has to meet a source property requirement similar to those contained in TNZ M/4, including satisfactory values in terms of the Crushing Resistance, the Weathering Quality Index, and California Bearing Ratio (CBR) tests. In addition, contractors have to take responsibility for the performance of the material and it is important for them to know how to minimise the risk of inadequate performance of an aggregate. Currently, no engineering tests can be used to predict the performance of a modified marginal aggregate.

1.2 Previous research

Earlier work in the field of modified marginal aggregate was described in Bartley (2001). The report defines weathering as the chemical or physical change that occurs when a rock is placed in an environment different from that existing at the time the rock was formed. Little definitive information about the pavement environment is available, but it is possible that a particular rock type will weather during the life of the pavement. Wetting and drying may occur, mechanical abrasion almost certainly occurs, and in some locations, the pavement may undergo temperature changes sufficient to freeze and thaw the pavement on a regular basis. The effect on the aggregate will depend on the type of rock and the severity of the environment.

The change that occurs may not be significant. Commonly, inter-particle abrasion during compaction and trafficking will result in an increase in the proportion of very fine material, but if the fine material is inert, the impact on performance will be negligible. However, if swelling clay minerals are released, the consequences could be very unsatisfactory if pavements are wet.

Swelling smectite clay minerals are often present. The exchangeable cations in the interlayer space of the smectite clays depend on the mineral composition in the purest rock. Most commonly, they are calcium, magnesium or sodium. Sodium smectites are known to have higher swelling properties than calcium or magnesium smectites. They may be inherent in the rock or formed as a product of weathering. They are found within the fines of an aggregate, or are produced as rock particles degrade during compaction or during trafficking of a pavement. Modification of the aggregate with lime cement or Durabind™ causes ion exchange which may change the swelling properties. Exchanging sodium for calcium reduces swelling, whereas if sodium or calcium is replaced by potassium, the clay mineral structure is locked, with potassium bentonite having no swelling properties. Such exchanges, therefore, make the clay minerals and the treated aggregate less sensitive to water. Modification also promotes the formation of cements and inter-molecular bonds.

A number of engineering tests can be used to assess the suitability of an aggregate for roading purposes, but they are all empirically based. The Clay Index (CI) test (also known as the Methylene Blue absorption test) measures the proportion of swelling clay minerals present and can be used to monitor the changes that occur as a result of modification. It provides a measure of the potential instability that exists both before and after the material has been modified. The value of a natural aggregate has been correlated with performance, but little is known how modified materials behave in the long term. Bartley (2001) concluded that further research was necessary to identify the reactions that occur between the rock minerals and the chemicals used more clearly, and to determine the potential for further change once the road is opened to traffic.

1.3 Objectives

The objective of this project was to use clay mineralogy to study the changes that occur when a chemical is mixed with a roading aggregate containing swelling clay minerals. A second objective was to identify a suitable methodology for the design of the stabilisation of an aggregate, i.e. the most suitable chemical to use for a particular rock type, and the quantity of chemical required to achieve particular effects, namely

- conversion of the swelling clay mineral to a more benign form,
- establishment of bonds between particles,
- a level of strength that is insensitive to an increase in water content,
- minimal shrinkage caused by drying, and
- long term permanence of the reaction.

2 Project tasks

The main tasks undertaken to achieve the objectives were:

1. reviewing literature,
2. selecting of aggregate samples,
3. characterising the clay mineralogy of each aggregate,
4. preparing samples of aggregate modified with selected chemicals,
5. performing engineering tests,
6. establishing the permanence of the treatment by exposing treated samples to solutions of various cation composition or by artificial weathering procedures,
7. determining the composition of cements and structure of the clay minerals,
8. preparing a draft report that describes the techniques used in the project and the main factors that determine the modification of aggregates and their long term durability,
9. arranging for the draft report to be reviewed,
10. revising the draft, taking the comments from the reviewers into account, and
11. drafting articles to appear in quarry association and roading contractors' journals, and presenting papers to appropriate conferences.

This research was carried out in 2003–2004.

3 Literature review

3.1 The engineering approach

3.1.1 Weathering of natural rock

Rock is formed under various geological conditions. The potential for a rock to weather depends on such factors as mineral composition, porosity, permeability and the geochemical conditions to which it is exposed. Rocks formed at elevated temperature and pressure are not in equilibrium at the earth's surface and are therefore subject to reaction, i.e. weathering. Weathering is caused by mechanical abrasion, wetting and drying, freezing and thawing, chemical attack, or by a combination of any or all of them. Weathering hydrates previously anhydrous minerals, the end product being clays. In the final analysis, it is the weathering potential and rate of weathering of a rock that will determine its engineering behaviour over time.

The literature review reported in Bartley (2001) indicated that although a lot of information was available about the natural weathering process, little reliable data described the relationship between the weathering characteristics of a particular rock and its performance in the pavement. Fookes (1991), for example, researched failures that were reported to have occurred in aggregate layers of various pavements over the preceding 25 years. The information he provided showed that the most troublesome aggregates were manufactured from igneous rocks and that the cause of degradation was either the presence of secondary minerals derived from alteration or weathering, or the effects of active *in situ* weathering.

3.1.2 Characterisation and quantification of aggregate properties and weathering

The engineering approach to aggregate quality has been to devise mechanical tests to measure characteristics of the rock. Such tests can be grouped under these headings:

- strength (e.g. Point Load Strength test),
- hardness (e.g. Crushing Resistance test),
- performance under freeze/thaw conditions, and
- chemical soundness (e.g. Magnesium Sulphate Soundness).

The type of test used and the acceptable limits are normally based on local experience so that the roading practitioner and the asset manager have confidence that an aggregate will perform satisfactorily in a particular area. This approach is appropriate for all materials that meet or exceed the specified limits, but it provides little guidance as to the use of a material that fails the test. As a consequence, it is likely that a rock type that may be adequate for a particular application is rejected even though it is only slightly outside the specified limit.

The efficient use of marginal aggregates, or the recovery and re-use of existing pavement materials, depends on the practitioner’s ability to understand the inherent characteristics of an aggregate.

Hudec (1997) explained that some rocks are inherently weak while others are weakened as a result of tectonic fracturing or by weathering of their components. The changes in their engineering properties with time and exposure are dependent on their origin and their lack of physical and chemical equilibrium with their current environment. Their durability depends on the rate of response to the effects of the environment.

Various indices have been proposed for forecasting rock durability. For example, petrologic indexes relate ratios of sound to unsound minerals. The indexes change as the ratios change with time and the effects of weathering. Statistical correlation of various engineering tests (e.g. Los Angeles Abrasion, sulphate soundness, point load, uniaxial compressive strength, slaking resistance, freeze-thaw resistance, etc.) have resulted in Rock Durability Indicators (RDI) that predict the changes in engineering properties of weak rock with time and exposure conditions.

Solid density and water absorption are indicators of weathering. The performance characteristics can be expected to decrease as the solid density decreases and the water absorption increases. A Petrographic Number (PN), which was developed by the Ontario Ministry of Transportation (Hudec 1997) and based on the mineralogy, density, softness and degree of weathering, has been used to describe the potential performance of a rock. A secondary mineral rating (Rsm) devised by Cole and Sandy (1982) in Australia is a similar method.

Durability is inversely proportional to the internal surface area of the rock, and adsorption measurements provide a relatively quick, easy and inexpensive method of measuring the internal surface area. Hudec (1989) described experiments that were carried out on carbonate rock types and showed that the rate of absorption is determined by the pore size, which is a function of the grain size. The rate for finer-grained rocks is nearly twice that of coarser-grained rocks, especially in the first few minutes of exposure to water.

Simple tests, e.g. the scratch test or the drying rate when the particle is immersed in water, relate to the degree of weathering. Softer rocks and those that readily absorb water are often weak or weathered.

Two major forces contribute to rock degradation and decay. One is the inner strain which is caused by shrinkage during rapid cooling of volcanic rocks, and the other is the volume change that accompanies phase transformation.

Basalts that produce abundant secondary minerals are considered as rapidly degradable under normal weathering conditions. The durability of Palaeozoic carbonates has been shown by Hudec (1997) to be controlled by their Al_2O_3 content, which reflects the amount of clay present. The isothermal expansion of clay-rich carbonates upon wetting is significantly greater than that of the clay-lean group.

Petrography can be used to estimate both the weatherability and the degree of weathering. Weatherability is determined by the expected response or reaction of the minerals contained in the rock to the environment. High temperature minerals and glasses are the most unstable but even so, the chemical reaction rates are slow in human terms. More importantly, the presence of these minerals may indicate that the rock contains secondary minerals which may break down rapidly in human terms. The susceptibility of rock to the more rapid physical weathering caused by secondary minerals is determined by the ratio of the secondary to primary minerals present in the rock. The Index Petrographic (IP) is the ratio of volume percent of primary minerals in a thin section to the volume percent of secondary minerals derived by weathering, plus pores and cracks.

The more weathered the rock is, the more susceptible it is to additional weathering. All fine-grained (fine-pored) rocks are subject to physical breakdown by freezing and thawing, the forces associated with ice formation, and those generated by the osmotic pore water pressures. All fine-grained, fine-pored rocks are subject to these pressures. The water in small pores can be considered as an osmotic fluid with low vapour pressure. Normal water with higher vapour pressure is enticed osmotically to enter the already filled small pores, creating pressure within the pore and thus causing the rock to expand until the tensile bonds that bind the clay particles together fracture.

Under freezing conditions, the water in the small pores does not freeze; only the water in the larger pores and in cracks solidifies. The ice in the larger pores has a lower vapour pressure than the non-frozen water in the small pores, and the ice continues to grow by vapour transfer, exerting pressure on the pore walls. The presence of dissolved salts increases the osmotic imbalance between pores of different sizes. Repeated cycles cause expansion and contraction of the system until the bonds break down.

3.1.3 Engineering tests

3.1.3.1 Suitable tests

Hudec (1984) used statistical analysis of a variety of tests on 100 samples of aggregates commonly used in Ontario to show that simple tests such as specific gravity, absorption, adsorption, abrasion, impact resistance and freeze-thaw tests are inter-related and can be used to predict performance. Other simulation tests such as sulphate soundness and Los Angeles Abrasion tests were found to bear no relationship to performance.

Hudec (1997) commented that not all rocks weather in the same way and that many engineering tests accelerate the normal weathering process of the rock. Such tests are designed for the 'average' rock and often give inappropriate results for any particular rock type. No single test can be expected to define the behaviour of a rock, and he suggested that some simple tests may be more useful in determining the degree of weathering. He recommended the following tests:

- solid density and water absorption,
- petrographic analysis,
- abrasion, e.g. MicroDuval abrasion,
- slaking or wetting/drying,
- freezing and thawing,
- hardness, and
- pore size.

He also indicated that one or more of the tests may be necessary, depending on the type of rock being evaluated.

Wu et al. (1998) discussed the various engineering tests that have been developed to characterise aggregate empirically, and pointed out that no strong relationship had been established between a particular characteristic and the performance of the aggregate in the road. The objective of their project was to identify and evaluate toughness/abrasion resistance and durability/soundness tests for aggregate used in asphaltic concrete, and to determine those that best correlated with field performance. They associated aggregate toughness and abrasion resistance with mechanical degradation, while durability/ soundness was associated with degradation caused by exposure to the elements, e.g. wetting and drying. They examined the results of tests on sixteen aggregates from throughout the United States with their reported performance rating, and found that the MicroDuval Abrasion test and the Magnesium Sulphate Soundness test were the most suitable for asphaltic concrete.

The material suppliers within the European Economic Area have to meet the requirements of the EU Construction Product Directive (C89/106/EEC 2000) which defines the quality assurance, conformity assessment, factory production control, conformity declaration, and marking of products. Helgason & Fuxen (2002) developed a computer program to predict the performance from the statistical analysis of aggregate test results in terms of the Directive. It is based on the concept that 'it is possible to predict the engineering properties of aggregates if their fundamental properties are known.'

The mechanical, thermal and durability properties of an aggregate are governed by the fundamental properties of the particles and that of the surrounding pore fluid. The fundamental properties are the petrographic composition, size and shape. The software assembles and analyses the experimental data, and produces statistically derived equations that can be used to predict the performance of the material. Engineering test data may also be used.

Kline (1999) describes the evaluation of the various bedrock units of Arkansas and the units' suitability for producing crushed stone construction aggregate. The evaluation was based on the results of Los Angeles Abrasion and Sodium Sulphate Soundness tests, and on Specific Gravity and Absorption values for 423 quarries, test pits and other sites in Arkansas. Alkalia-silica reactivity values were also available for some sites. Each site was located in terms of the geologic bedrock map so that the rock type could be identified. The engineering test data were then compiled according to rock unit in order to compare how products from these units have rated in the past. This provided a measure of the relative quality of aggregate, and particular advantages or disadvantages of the different rock units.

3.1.3.2 Modified aggregate

Bartley (2001) examined the results of the New Zealand standard Weathering Quality Index and the CI test to identify which best reflected the changes that occur when a selection of aggregates was modified with lime or lime based additives. He found that the Weathering Quality Index test was completely insensitive to the changes, while the CI test appeared to respond well to modification and simulated weathering.

Paige-Green (1984) discusses a number of failures of lime stabilised pavement layers that occurred in South Africa. The failures appeared to be caused by carbonisation of the lime causing reversion of the cemented layer to a granular layer. He cured unconfined compression strength specimens under different environments and found that curing in a carbon dioxide atmosphere results in a retardation of strength development in most cases, and a decrease in the strength of partly cured samples. Both lime and the reaction products appeared to be susceptible to reaction with carbon dioxide. This suggests that lime treated materials could be susceptible to attack by groundwater that contains carbonic acid.

3.2 Geological and chemical aspects

3.2.1 Mineral stability and weathering products

The relative stability of various rock minerals to weathering processes and the normal sequence of breakdown and weathering products are summarised in Tables 3.1 and 3.2, and Figure 3.1.

Table 3.1 Relative stability of common rock-forming silicates in chemical weathering (after Goldich 1938).

Increasing stability ↓	Olivine	Calcic plagioclase
	Augite	Calc-alkalic plagioclase
	Hornblende	Alkali-calcic plagioclase
	Biotite	Alkalic plagioclase
	Potash feldspar	
	Muscovite	
	Quartz	

Goldich’s stability diagram (Table 3.1) shows that the order of resistance to weathering is similar to the order of progressive reaction during magmatic crystallisation (Bowen 1922). The minerals that crystallised at the highest temperatures, under the most anhydrous conditions, are more readily weathered than those that crystallised last from lower temperature, more aqueous magmas. As a general rule, the more closely the conditions of crystallisation approximate those now prevailing at the earth’s surface, the more resistant the mineral is to weathering.

A similar sequence based on weathering of fine-grained minerals in soils (Table 3.2) resembles the sequence in Table 3.1 but incorporates a wider range of minerals, including some formed in the surface environment, which are common in sedimentary rocks. The sedimentary minerals originally formed in a surface environment are relatively stable when the sedimentary rock is exposed to weathering.

Table 3.2 Weathering sequence for clay-sized minerals in soils and sedimentary deposits (Jackson et al. 1948).

	Weathering stage	Clay-sized minerals characteristic of different stages in the weathering sequence
Increasing stability	1	Gypsum (halite, etc.)
	2	Calcite (dolomite, aragonite, etc.)
	3	Olivine–hornblende (diopside, etc.)
	4	Biotite (glauconite, chlorite, etc.)
	5	Albite (anorthte, microcline, etc.)
	6	Quartz
	7	Illite (muscovite, sericite, etc.)
	8	Intermediate hydrous micas
	9	Montmorillonite
	10	Kaolinite (halloysite)
	11	Gibbsite (boehmite, etc.)
	12	Hematite (goethite, limonite, etc.)
	13	Anatase (rutile, ilmentite, etc.)

Figure 3.1 illustrates how primary minerals change to successive secondary minerals with increasing intensity and duration of weathering. Kaolinite formation is favoured by an acid environment with free drainage to remove the relatively soluble elements such as sodium, calcium, magnesium and potassium. In contrast, smectite formation is favoured by neutral to alkaline conditions, and by incomplete leaching of sodium, calcium, magnesium and potassium.

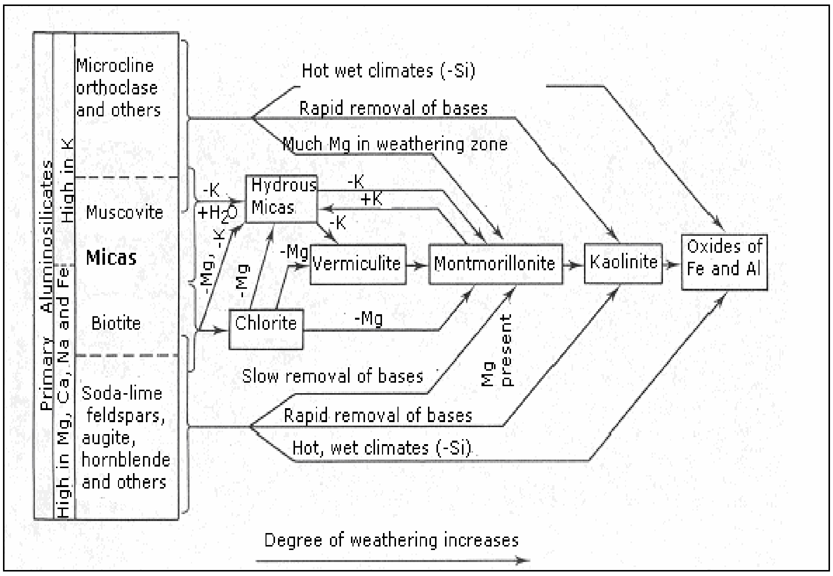

Figure 3.1 Weathering products of primary minerals and sequence of forming clays (after Brady 1974).

3.2.2 Aggregate stabilisation

3.2.2.1 Commonly used stabilisers

Our knowledge of aggregate stabilisation has developed from earlier work in soil stabilisation (Hilt & Davidson 1961, Bhattacharja et al. 2003). The processes involved are very similar because in both cases, the aim is to stabilise clay minerals formed by chemical weathering. A small quantity of literature on experimentation with various stabilisers for aggregate is available, and the most relevant to this study is the work by Sameshima and colleagues (Black & Sameshima 1979, Sameshima 1983, Sameshima & Black 1979, Sameshima & Black 1980, Sameshima & Black 1982). Building on earlier work by others (e.g. Van Aardt & Visser 1977 and 1978), Sameshima & Black (1980) established that mixing lime or cement with clays produce hydrated carbonates and hydrogrossular.

In New Zealand, three materials are commonly used as binders in stabilising aggregate: hydrated lime, cement and Durabind™[1].

The typical process of road aggregate stabilisation involves:

1. spreading the additive on top of the laid road aggregate using a truck-mounted mechanical belt spreader,
2. hydrating with a water spreader,
3. pulverising and mixing of the top 150–300 mm with a mechanical stabiliser, and
4. shaping and compacting with a vibrating smooth or padfoot roller.

The stabilised layer may be covered with other aggregate layers or sealed. An additional stage of spreading cement with a pressurised cement spreader may be included following the water spreader stage in the case of Kontinuous [sic] Oxygen Blast Maxiite (KOBM) application (see Chapter 3.2.2.3).

Stabilisation results from three distinct processes caused by the stabilising agent:

- cation exchange,
- agglomeration, and
- pozzolanic and hydration reactions.

The cation exchange and agglomeration effects are immediate, whereas the pozzolanic and hydration effects are longer term reactions. In all cases, the primary ingredient is calcium. In a high pH environment, the solubility of silica and alumina is greatly enhanced and promotes the pozzolanic reaction.

Cation exchange relates to reducing the plasticity of smectite clays. Smectites with monovalent cations (sodium) are more plastic than those containing divalent ions (calcium and magnesium), and therefore a good stabiliser should provide calcium ions in sufficient quantity to exchange with monovalent sodium and reduce plasticity.

---

[1] Durabind™is the tradename for a stabilising product manufactured by Econ Products Ltd.

3.2.2.2 Lime composition and stabilisation

For stabilisation purposes, hydrated lime ($Ca(OH)_2$) with at least 80% CaO is normally used. The addition of hydrated lime to clayey material causes immediate cation exchange with the clay minerals, which effectively reduces the plasticity. Over a longer period of time, the lime sets up a pozzolanic reaction, during which calcium silicate hydrate ($CaSiO_3.nH_2O$) and/or calcium aluminate hydrate ($CaAl_3O_3.nH_2O$) are formed, and the clay minerals are destroyed. The lime may absorb carbon dioxide to form calcite (carbonation) reducing its availability for the clay reaction.

3.2.2.3 Cement composition and stabilisation

The chemical and mineralogical compositions of Portland cement are given in Tables 3.3 and 3.4, respectively. In the typical application of cement to make concrete, mixing water with the Portland cement results in hydration of the various compounds. The main products produced during hydration are calcium silicate hydrate ($CaO\cdot 2SiO_2\cdot 4H_2O$) and calcium hydroxide ($Ca(OH)_2$ or portlandite). Nevertheless, ettringite, or aluminoferrite trisulphate ($C_6AS_3H_{32}$) and monosulphate ($Ca_2(Al,Fe)(OH)_6.X.nH_2O$ (where X is SO_4^{2-}, OH^- or some other anion)) are also produced. Hydrogrossular ($Ca_3Al_2(SiO_4)_3.x(OH)_4$) may form after a curing period of several years. The ultimate cementing agent is an amorphous silica gel (SiO_2).

In aggregate and soil stabilisation, Portland cement reacts like lime with water to release $Ca(OH)_2$, which can cause cation exchange. The main effect of cement, however, is to gel the particles together. The cement reaction with water includes the formation of microscopic needles of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$).

Table 3.3 Chemical analysis of general purpose Portland cement from Golden Bay Cement Ltd. plant, Whangarei (average of 74 analyses between 1/7/03 and 14/6/04 supplied by Warren South, Technical Manager).

	Weight %	**Chemical formula**
	64.73%	CaO
	21.30%	SiO_2
	4.44%	Al_2O_3
	2.15%	Fe_2O_3
	1.05%	MgO
	0.07%	Mn_2O_3
	0.18%	Na_2O
	0.47%	K_2O
LOI[a]	3.62%	
Total	**98.89%**	

Note to Table 3.3

a: LOI= Loss On Ignition

Table 3.4 Mineralogical composition of typical Portland cement.

Cement compound	Weight %	Chemical formula
Tricalcium silicate	50 %	Ca_3SiO_5 or $3CaO{\cdot}SiO_2$
Dicalcium silicate	25 %	Ca_2SiO_4 or $2CaO{\cdot}SiO_2$
Tricalcium aluminate	10 %	$Ca_3Al_2O_6$ or $3CaO{\cdot}Al_2O_3$
Tetracalcium aluminoferrite	10 %	$Ca_4Al_2Fe_{10}$ or $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$
Gypsum	5 %	$CaSO_4{\cdot}2H_2O$

3.2.2.4 KOBM composition and stabilisation

KOBM is a steel foundry slag from the Bluescope Steel Ltd mill in Glenbrook. Lime is added to the smelt to remove impurities from the steel products, some of which is retained in the resulting KOBM. The mineral composition of KOBM slag predominantly consists of four components: dicalcium ferrite ($2CaO.Fe_2O_3$), dicalcium silicate ($2CaO$, SiO_2), wustite (ferrous oxide, FeO) and glassy material. However, Hitching (1981) identified a wide variety of minerals in the slag as listed in Table 3.5; the chemical composition of KOBM is listed in Table 3.6. The slag oxidises and hydrates so that the material used in stabilisation (KOBM Binder) predominantly consists of calcium hydroxide $Ca(OH)_2$, dicalcium ferrite ($2CaO.Fe_2O_3$) and glassy material.

KOBM is usually applied along with cement. The calcium hydroxide provides the initial reaction. Calcium oxide contained within amorphous silicate complexes undergoes slow hydration so that over a period of time, the stabilised material increases in strength as further $Ca(OH)_2$ is released. Even so, carbonation can also occur with KOBM and reduce the quantity of calcium hydroxide available.

Table 3.5 Mineral phases present in NZ Steel refining slag (Hitching 1981).

Mineral	Chemical formula
Armalcolite	$(MgFe)Ti_2O_5$
Brownmillerite	$Ca_4Al_2Fe_2O_{10}$
Calcium oxide	CaO
Coulsonite	FeV_2O_4
Iddingsite	$(FeVMn)_{1.8}Si_{1.2}O_4$
Ilmenite	$(FeMg)TiO$
Iron	Fe
Magnesiowustite	$(FeMg)O$
Melilite	$Ca_2(FeMgAlSi)_3O_7$
MgTiAl-spinel	$MgTi^{3+}AlO_4$
Monticellite	$Ca(FeMg)SiO_4$
Olivine	$(FeMg)_2SiO_4$
Perovskite	$CaTiO_3$
Pyroxene	$Ca(MgFe)Si_2O_6$
Quartz	SiO_2
Rhonite	$Ca_2(FeMgTiAl)_6(SiAl)_6O_{20}$
Rutile	TiO_2
Spinel	$(MgFe)Al_2O_4$
Titanium carbide	TiC
Tricalcium silicate	Ca_3SiO_5
Ulvospinel	$(FeMg)_2TiO_4$
V-maghemite	$Fe^{3+}VO_3$
Wustite	FeO

Note to Table 3.5:

Calcium, iron, manganese, silicone, aluminium oxide and larnite (Ca_2SiO_4) were also present in Pacific Steel scrap slag.

Table 3.6 A typical chemical analysis of KOBM (figures rounded to nearest percent) from Wilson (1999).

Compound	Weight %
CaO	54%
FeO	15%
SiO_2	8%
MgO	8%
V_2O_5	5%
MnO	3%
Al_2O_3	2%
P_2O_5	2%
Other	3%

3.2.2.5 Durabind™ composition and stabilisation

Durabind™ is a proprietary mixture of KOBM and other additives that substitute for the cement commonly used as a mixture in applications of KOBM. Some of these additives slow the binding reactions. Durabind™ contains blended initiators to increase both the hydration products that form on the surface of the aggregate minerals, and the subsequent reactions with the aggregate clay minerals.

4 Sampling

4.1 Source of samples

Rock samples were obtained from four quarries: Otaika (Q07/277014), Flat Top (Q10/496111), Drury (R12/869506), and Poplar Lane (U14/992792). The quarries were selected to provide a range of rock types and rock quality. The general location of each quarry is shown in Figure 4.1. Otaika (Whangarei) and Drury (South Auckland) work greywacke rock, Flat Top (Rodney) is in Tangihua basalt, whereas Poplar Lane (Tauranga) is an andesite quarry. Photographs of the quarry sites are presented in Appendix A.

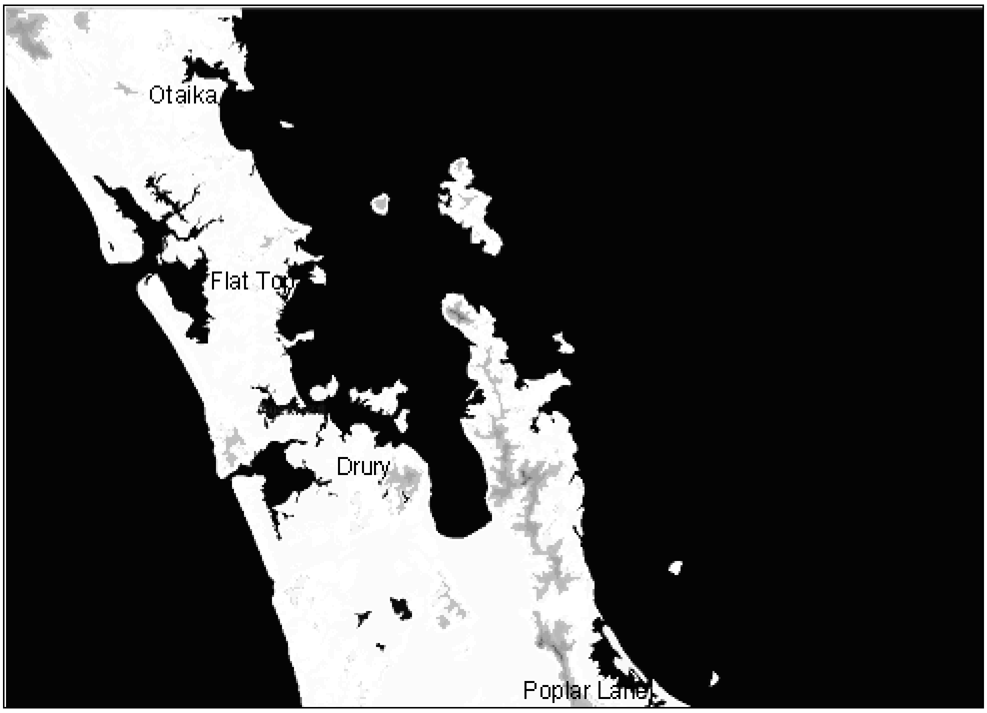

Figure 4.1 Approximate location of quarries which were used to source the samples used in this study.

4.2 Types of samples

Samples of fresh (50 kg), partly weathered (100 kg) and weathered rock (70 kg) were collected from the quarry face or the scree slope below the face from each of the four quarries in August–September 2003 (Appendix A). A bulk sub-sample of the partly weathered rock was crushed so it all passed through a 4.75 mm sieve. These crushed samples were split into sub-samples. The sub-samples, either untreated or mixed with stabilising binders, were initially subjected to simple geotechnical strength tests used to monitor the response of the rock to the additive. On completion of the strength tests in October 2003, the samples were wrapped in plastic and transferred to the Institute of Geological and Nuclear Sciences Ltd (GNS) in Lower Hutt for petrological, moisture, X-ray diffraction (XRD) and geochemical analyses. The 4.75 mm maximum size was selected to suit the penetrometer test and was adequate for most of the other tests.

Poplar Lane and Flat Top have some alteration minerals that were formed by hydrothermal alteration prior to exposure at the surface, where they have been subject to subtropical weathering. In addition, the Drury greywacke is extensively sheared and contains some alteration minerals along fractures.

The samples were referenced as shown in Table 4.1.

Table 4.1 Explanation of the labels used to indicate sample site, weathering and treatment.

Feature	Abbreviation
Quarry	
Otaika	OT
Flat Top	FT
Drury	D
Poplar Land	PL
Degree of weathering	
Fresh rock	F
Partly weathered rock	PW
Weathered rock	W
Additive	
Lime	L
Cement	C
Durabind™	D

4.3 Preparation of stabilised samples

Bulk samples of partly weathered aggregate from each of the four quarries were crushed so all passed through the 4.75 mm (4 mesh) sieve. They were each split into seven sub-samples large enough to fill a mould, and oven dried within a temperature range of 105°C to 110°C.

Each sub-sample was then modified as shown in Table 4.2.

Table 4.2 The sub-samples used in this study, as modified with different proportions of different chemical additives.

Sample	Chemical additive	Proportion by weight (%)
1	Natural (no additive)	–
2	Ordinary Portland cement	1
3	Ordinary Portland cement	3
4	Hydrated lime	1
5	Hydrated lime	3
6	Durabind™	1
7	Durabind™	3

The aggregate and chemical additive was premixed in a plastic bag before water was added to achieve OMC (Optimum Moisture Content) +3%. The OMC was determined using NZS 4402:86 Test 4.1.1: ‘Determination of the dry density/water content relationship (standard compaction)’. The material was then compacted into the moulds (150 mm diameter plastic tubing 150 mm long) in accordance with NZS 4402:86 Test 4.1.1, except 62 blows per layer were used instead of 27 blows per layer as specified.

5 Mineralogical evaluation

5.1 Introduction

Fresh, partly weathered and weathered samples collected from the quarry face from each of the four quarries were analysed by petrography, moisture, XRD, X-ray fluorescence (XRF) and the CI (also called Methylene Blue) methods. These tests were also repeated on most of the 3% stabilised samples described in Chapter 4. In this chapter, the various analytical data are presented and discussed.

5.2 Petrography

5.2.1 Method

Thin polished sections were prepared for the untreated samples and the 3% stabilised samples. These were examined with a polarising microscope and interpreted in conjunction with the XRD data (see below). Petrographic descriptions are presented in Appendix B and summarised below.

5.2.2 Results

5.2.2.1 Untreated samples

Otaika greywacke – Q07/277014

The Otaika greywacke sandstone samples are moderately sorted, medium to coarse-grained feldspathic litharenites containing detrital grains of quartz, feldspar, rock fragments, chlorite, clinopyroxene, hornblende, muscovite, biotite, epidote and tourmaline in a silt-clay matrix of mica–illite, interlayered illite–smectite and chlorite. The rocks are transgressed by thin (up to 0.1 mm wide) veinlets of quartz ± chlorite ± carbonate ± pumpellyite. Some open spaces are rimmed by prehnite and infilled with pumpellyite.

In the fresh rock sample, the feldspars and many of the rock fragments are partly weathered to clays. Progression to the partly weathered and weathered samples is marked by an increase in:

- weathering (clay content) of the feldspars and rock fragments;
- commencement of weathering of the ferromagnesian minerals; and
- a development of brown staining in the matrix, grain boundaries, veins and fractures, and, at a more advanced state, the feldspar and rock fragment grains.

The XRD analyses (see below) showed that the weathering products include smectite and kaolinite.

Flat Top basalt – Q10/496111

The Flat Top basalts are fine-grained porphyritic and hypidiomorphic granular rocks, consisting of phenocrysts of euhedral to subhedral plagioclase (0.5 mm), euhedral to anhedral clinopyroxene (augite?, 0.2 mm) and opaque iron/titanium oxides in a matrix of finer-grained crystals of these minerals. The matrix makes up more than 50% of the rock. The basalts have been hydrothermally altered. They are transgressed by veinlets (<1 mm wide) of quartz and zeolite (chabazite? apophyllite?), and zeolite also fills vesicles and other cavities. In the fresh rock, the plagioclase crystals are fractured, and partly altered or weathered, resulting in a brownish stained appearance. Pyrite was noted in the partly weathered sample, present in thin veinlets and as disseminations.

Weathering results in increasing alteration of the feldspar and progressive alteration of clinopyroxene to clays, and the development of a clay matrix. Alteration of the iron/titanium oxides leaves remnant skeletal grains. The XRD analyses (see below) indicate that the fresh sample contains significant smectite, which increases with increasing weathering. In the most weathered materials, smectite subsequently alters to halloysite and kaolinite in the worst affected parts of the profile.

Drury quarry – R12/869506

The Drury greywacke sandstone samples are well sorted, very fine-grained feldspathic litharenites containing detrital grains of quartz, feldspar, rock fragments, chlorite, opaque iron/titanium oxides, and rare relict hornblende, biotite, zircon and rutile in a silt-clay matrix of mica/illite, interlayered illite–smectite, chlorite, biotite, tourmaline and zircon. Disseminated grains of pyrite are present (up to 1%). The rocks are transgressed by thin (up to 0.12 mm wide) veinlets of quartz, carbonate, prehnite and chlorite. In comparison to the Otaika greywacke samples, the Drury samples are much finer grained, have less quartz, and are notable for the presence of prehnite and pyrite.

In the ‘fresh’ rock, the feldspars and many of the rock fragments are partly weathered to clays. Progression to the partly weathered and weathered samples is marked by:

- an increase in clay alteration of the feldspars and rock fragments;
- clay alteration of the ferromagnesian minerals; and
- a development of brown staining in the matrix, grain boundaries, veins, and fractures, and, in a more advanced state, the feldspar and rock fragment grains.

Like the Otaika samples, the XRD analyses (see below) of the Drury samples showed that weathering develops smectite and kaolinite.

Poplar Lane quarry – U14/992792

The Poplar Lane andesites are fine-grained, glomeroporphyritic and hypidiomorphic granular rocks, with sub-pilotaxitic to sub-trachytic textures. They contain phenocrysts (40%) of euhedral to subhedral plagioclase (0.6 mm), euhedral to anhedral orthopyroxene (hypersthene?, 0.4 mm) and opaque iron/titanium oxides (0.1 mm) in a matrix (60%) of microlite crystals of these minerals (e.g. the plagioclase microlites average 0.07 mm).

The sample of fresh rock has fractures through the groundmass that are flanked by a yellowish-brown staining in the plagioclase microlites. With weathering, the fractures and staining become increasingly common, with goethite and opaques concentrated along their margins. Clay-filled veins also develop. The alteration of plagioclase is well advanced before the orthopyroxene phenocrysts begin to alter. The weathered sample did not exhibit much of an advance of weathering over the partly weathered sample. The XRD analyses (see below) indicated that smectite clays are already present in the fresh sample, and that weathering produces additional smectite along with kaolinite and halloysite.

5.2.2.2 Treated samples

The 3% treated samples are agglomerations of rock particles up to 4.75 mm in size, cemented by additive (Figures 5.1–5.3). The additive coats the grains, and in the case of lime, forms a thin darker layer at the boundary between the lime and the grain. No indication of reaction beyond the rims of the rock minerals was visible and no new mineral products were noted in the thin sections.

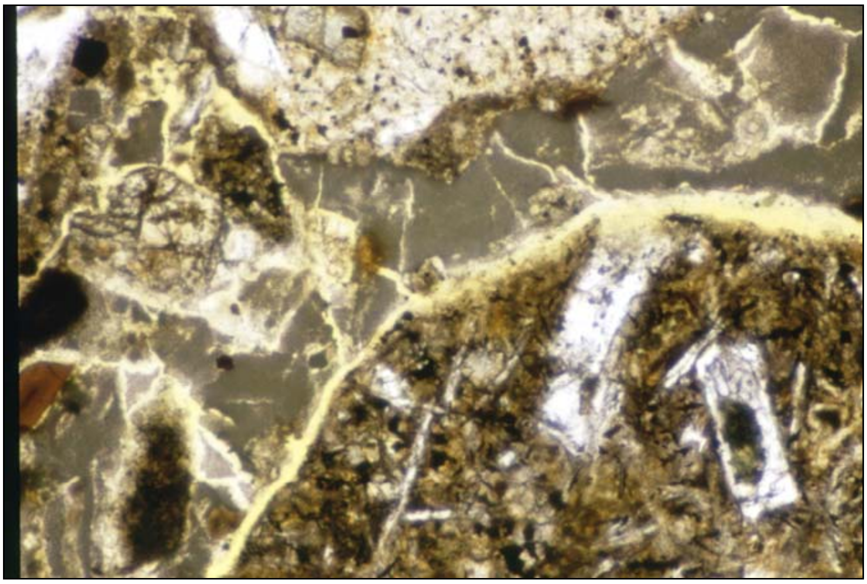

Figure 5.1 Photomicrograph of a thin section showing lime cementing fragments of Flat Top basalt.

Notes to Figure 5.1

(a) Lime appears olive green.

(b) Yellow cement has been used as a mounting medium and invades cracks in the thin section.

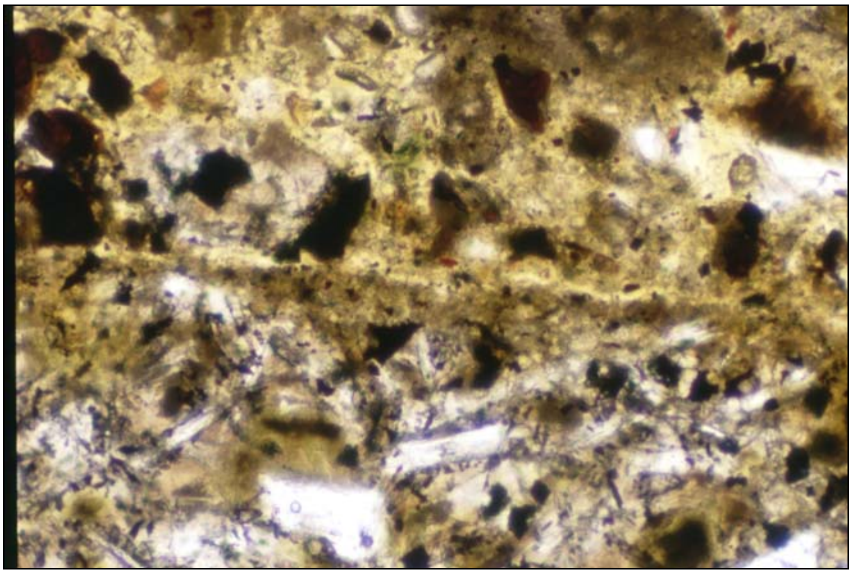

Figure 5.2 Photomicrograph of a thin section showing Durabind™ cementing fragments of Flat Top basalt.

Notes to Figure 5.2:

(a) Durabind™ can be seen as the granular material filling most of the upper half of the photo.

(b) Flat Top basalt appears in the lower half of photo, plus a few isolated grains in the upper half.

(c) Yellow cement has been used as a mounting medium and invades cracks in the thin section.

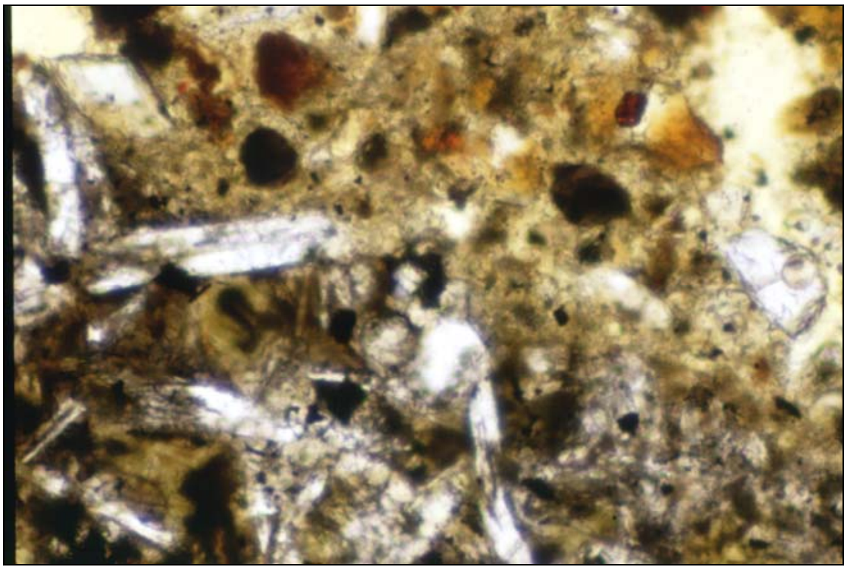

Figure 5.3 Photomicrograph of a thin section showing Durabind™ cementing fragments of Flat Top basalt.

Notes to Figure 5.3:

(a) Durabind™ can be seen as the granular material in the upper right half of photo.

(b) The fragments of Flat Top basalt appear in the lower left half of the photo.

5.2.3 Conclusions

5.2.3.1 Untreated aggregate

The fresh rocks from all four quarries show initial signs of alteration, traces of kaolinite in the greywackes, and smectite in the volcanic rocks, all reflecting the hydrothermal alteration or shearing (discussed previously). The greywacke rocks have a primary clay mineral assemblage of interlayered illite–smectite, illite and chlorite present as a matrix to the larger detrital grains.

The main clay minerals developed by subtropical weathering of greywacke and volcanic rocks are smectite and kaolin (halloysite or kaolinite). With progressive weathering, the smectite alters to other minerals.

The abundance of smectite in the Flat Top basalt is the main reason that this particular rock exhibits such a dramatic improvement in its aggregate quality with stabilisation.

5.2.3.2 Treated samples

Disappointingly, optical examination of the treated samples failed to identify any clear reaction between the additives and minerals in the rock. We conclude that because of the short reaction time, only small quantities of hydrogrossular ($Ca_3Al_2(SiO_4)_3.x(OH)_4$ cement have formed and that this small quantity of hydrogrossular is too finely distributed amongst the clays to be visible with a standard optical microscope. It is recommended that scanning electron microscopy be used in future studies.

5.3 CI testing

5.3.1 Introduction

The presence of expanding clays (smectites and mixed-layer illite-smectite or chlorite-smectite clays) and their approximate abundance can be estimated using the Methylene Blue adsorption (CI) test, which is used to measure the clay cation exchange capacity of fine particles (<75 µm). In this case, powdered rock samples were used; for roading aggregate the test would normally be applied to the natural fines contained within an aggregate sample.

No absolute CI values exist for New Zealand commercial aggregates. However, we would expect the highest quality aggregates to have a CI <1.

CI tests were carried out on crushed powders of all untreated samples, and on the samples treated with 3% chemical additive.

5.3.2 The CI method

The technique used is described in NZS 4407:1991 Test 3.5. The method involves titrating a rock slurry (5 g of powdered rock in 25 ml of distilled water), acidified with three drops of 10% H_2SO_4, with Methylene Blue solution. Spot-checking for the end-point was performed by dropping dye slurry onto filter paper. At the end-point, excess dye migrates beyond the compact clay spot and forms a light blue halo (Phelps & Harris 1968, Jones 1964). The CI increases as the amount of expanding clays increase in a sample, and can therefore be used as an indicator of the degree of weathering.

5.3.3 Results

5.3.3.1 *Untreated samples*

CI measurements are listed in Table 5.1. Samples from all four quarries follow the same trend of increasing CI with increasing weathering. The increase in CI with weathering is strongest in the Flat Top (basalt) series of samples, intermediate for Otaika and Drury (greywackes), and weakest in the Poplar Lane samples (andesite).

Table 5.1 CI values of untreated samples tested in this study.

Site	Lithology	Weathering status	Field number	CI	LOI
Otaika	Greywacke	Fresh	OT-6	0.6	2.10
		Partly weathered	OT-4a	1.2	2.23
		Partly weathered	OT-4b	2.6	1.67
		Weathered	OT-5	3.4	2.29
Flat Top	Basalt	Fresh	FT-7	1.0	0.85
		Partly weathered	FT-1	4.6	1.35
		Partly weathered	FT-2	3.9	2.04
		Weathered	FT-3	6.9	4.04
Drury	Greywacke	Fresh	D-1	1.0	3.26
		Weathered	D-3	1.3	2.74
		Partly weathered	D-5	2.6	2.87
Poplar Lane	Andesite	Fresh	PL-1	1.2	0.44
		Partly weathered	PL-3	5.4	3.26
		Weathered	PL-2	6.5	3.02

5.3.3.2 *Treated samples*

Results of CI tests on samples treated with 3% chemical additive are presented in Table 5.2. All treated aggregates gave very low CI values, indicating that the expanding clays in the partly weathered samples have been almost entirely fixed by the additives. CI values are slightly higher for the basalt and andesite than they are for the greywackes. The values for the volcanic rocks increase through the series lime, cement and Durabind™, suggesting that lime is the most efficient fixer of the swelling clays, followed by cement and then Durabind™.

Table 5.2 CI values of samples treated with various additives at 3% concentration.

Site	Lithology	Field no	Additive	CI
Otaika	Greywacke	OT-4a	3% lime	0.3
		OT-4a	3% cement	0.8
		OT-4a	3% Durabind™	0.8
Flat Top	Basalt	FT-2	3% lime	0.5
		FT-2	3% cement	0.8
		FT-2	3% Durabind™	1.2
Drury	Greywacke	D-5	3% lime	0.3
		D-5	3% cement	0.3
		D-5	3% Durabind™	0.3
Poplar Lane	Andesite	PL-3	3% lime	0.8
		PL-3	3% cement	1.3
		PL-3	3% Durabind™	1.7

Note to Table 5.2: All samples were partly weathered.

5.4 Changes in the CI of stabilised samples with time – permanence

5.4.1 Method

In order to test the permanence of the cementing process, the various cemented samples were crushed, 5 g were suspended in 25 ml distilled water with a few drops of 10% H_2SO_4 added, and titrated with Methylene Blue (4.5 g/l solution). The samples were left in water for up to 24 hours. CI measurements were made after soaking for 30 minutes, 1 hour, 2 hours, 6 hours and 24 hours.

5.4.2 Results

The results are summarised in Appendix D and an example (for Flat Top basalt) is presented in Figure 5.4. In all cases, some swelling properties recovered with time, as evidenced by small increases in the CI. Of the three stabilising additives used, samples treated with lime showed lower swelling recovery than cement or Durabind™.

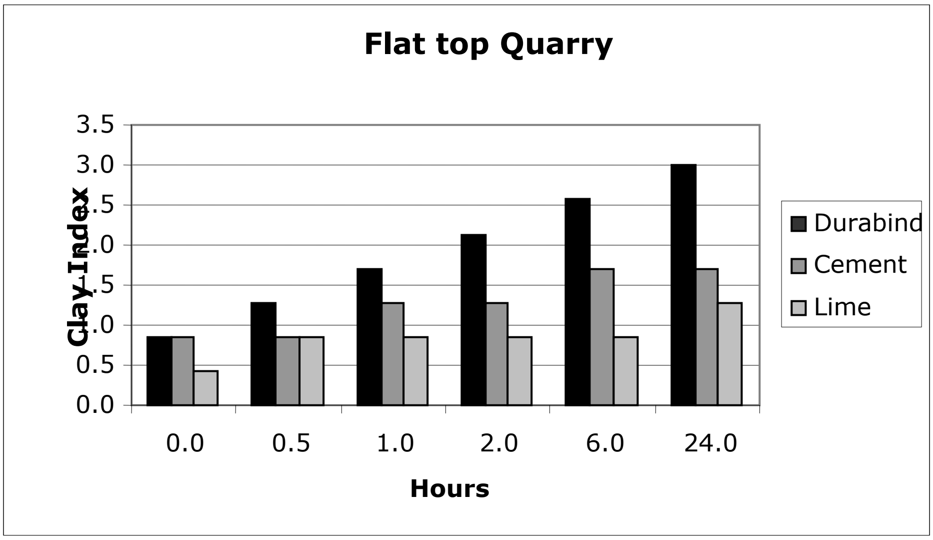

Figure 5.4 **Changes over time in CI for Flat Top basalt treated with 3% additive.**

5.5 Effect of pH on permanence

5.5.1 General

In terms of permanence, as shown in Figure 5.4, when the treated samples were left in water, the pH gradually increased to alkaline pH values between 10 and 11. The CI increased progressively until it reached a stable value. For Flat Top basalt plus 3% Durabind™, this was only 60% of the original value.

The effect of a low pH (<7) on permanence was investigated by adding small amounts of sulphuric acid to ground samples of the treated aggregates. Sulphuric acid was used because the chemical analyses of the treated samples were high in sulphate. The results are presented in Appendix D. In summary, at acid pH values, the CI continued to increase, indicating that the hydrogrossular cement is not stable under acid conditions.

In the stabilised pavement, the high pH environment is likely to persist because of the excess unreacted lime present. Acid conditions are only likely under extreme conditions such as oxidation of pyrite if pyrite is present in partly altered aggregates, or perhaps because of rainwater leaching through unconsolidated stockpiles.

5.5.2 Conclusions

Grinding the aggregate finer than 75 µm and suspending it in water is an extreme case compared to the pavement environment. Nevertheless, it suggests that water flowing through a treated aggregate may cause the clay to become reactive again. However, provided that the pavement is sealed and water cannot move through the aggregate, the treated marginal aggregates should remain stable, maintaining a low CI value. Acid pH values (pH <7) result in a more rapid rate of clay release than an alkaline pH.

Probably, the lime or Durabind™ reacts with the expandable clay to form hydrogrossular, but an excess of unreacted lime still effectively raises the pH in any infiltrating water.

5.6 XRD analyses

5.6.1 Methods

The untreated samples and those treated with 3% additive were analysed by XRD. 'Bulk' and clay separate analyses were made on the stabilised samples, whereas only clay separate analyses were made on the untreated samples.

For bulk analysis, the samples were ground to fine powders using an agate mortar and pestle, and pure ethanol as a grinding medium. The resulting fine powders were packed into stainless steel sample holders as random powder mounts.

For clay fraction (<2 µm) analysis, the samples were carefully crumbled using an agate mortar and pestle. The <2 µm clay fractions were extracted by centrifugation and oriented clay slides were made by a deposition-on-glass-slide method. Separate XRD scans were carried out on untreated, ethylene glycolated and heated clay slides (350^{o}C heating for 2 hours and 550^{o}C heating for 2 hours).

A PANalytical X'Pert Pro X-ray diffractometer with a cobalt radiation source (40 kV and 35 A), a graphite monochromator and a xenon proportional detector was used to record all the XRD scans. Running conditions for both bulk and clay fraction analyses were the same, and consisted of a continuous mode with a step size of 0.02^{o}, a step time of 0.50 seconds and a scanning range of 2^{o} to 80^{o} 2 θ (bulk) and 2^{o} to 45^{o} 2 θ (clay fraction).

Examples of XRD charts for the partly weathered basalt from Flat Top are presented in Appendix E.

5.6.2 XRD results for untreated samples

XRD analyses of untreated samples were only made on the <2 µm clay separates. The results are summarised in Table 5.3.

Table 5.3 XRD Analysis of clay fraction (<2 µm) of untreated samples.

Site	Lithology	Weathering status [a]	Field number	Na-smectite [b]	Na, Ca-smectite	Smectite	Random mixed-layer illite–smectite	Halloysite	Kaolinite	Chlorite	Mica	Zeolite	CI of Bulk sample
Otaika	Greywacke	F	OT-6	–	–	–	M	–	T	A	M	–	0.6
		PW	OT-4(b)	–	–	–	T	–	T	A	M	–	1.2
		PW	OT-4(a)	–	–	–	C	M	–	–	M	–	2.6
Flat Top	Basalt	F	FT-7	A	C	–	–	–	–	T	–	T	1.0
		PW	FT-1	C	A	T	–	M	T	T	–	T	4.6
		PW	FT-2	C	A	T			M	T	T	T	3.9
		W	FT-3	A	–	–	–	–	–	–	T	T	6.9
Drury	Greywacke	F	D-1	–	–	–	T	–	T	C	C	–	1.0
		PW	D-5	–	–	–	–	–	T	C	C	–	1.3
		W	D-3	C	–	–	–		M	T	C	–	2.6
Poplar Lane	Andesite	F	PL-1	A	–	–	–	–	–	–	–	–	2.8
		PW	PL-3	A	–	–	–	M	T	–	–	–	5.4
		W	PL-2	A	–	–	–	M	T	–	–	–	6.5

Notes to Table 5.3:

a

- F= fresh,
- PW= partly weathered, and
- W= weathered

b

- A= abundant (>60%)
- C= common (20–60%)
- M= minor (5–20%)
- T= trace (<5%)

The minerals identified were interlayered smectite, illite-smectite, kaolinite, halloysite, chlorite, mica, and zeolite.

For the Otaika greywacke samples, interlayered illite-smectite and trace kaolinite are identified in the fresh sample. The partly weathered samples exhibit an increase in the proportion of interlayered illite-smectite and the appearance of halloysite. Halloysite has some swelling properties and is a potential deleterious mineral in aggregates.

For Flat Top, Na-smectite and zeolite (heulandite?) are present in all of the basalt samples. Na-Ca-smectite is present in the fresh and partly weathered samples, whereas Na-smectite is present in all samples. Trace chlorite is present in the fresh and partly weathered samples. Kaolinite is present in the two partly weathered samples, whereas halloysite is identified only in one of the partly weathered samples.

The fresh Drury greywacke samples contain trace interlayered illite-smectite and kaolinite. The interlayered illite-smectite is not identified in the partly weathered sample, but kaolinite is present in trace quantities. The weathered sample exhibits increased quantities of kaolinite and a common abundance of Na-smectite.

For Poplar Lane, Na-smectite is abundant in all three andesite samples, whereas kaolinite and halloysite are identified in only the partly weathered and weathered samples.

5.6.3 XRD results for stabilised samples

Sodium smectite has higher swelling properties than calcium smectite. The addition of lime causes ion exchange with calcium replacing sodium. The action of the Durabind™, which has significant potassium that exchanges with sodium, effectively locks the structure together and it does not swell.

The results of XRD analyses of the 3% stabilised samples are summarised in Tables 5.4 (bulk samples) and 5.5 (clay separates). 'New' minerals identified in the stabilised samples are portlandite (calcium hydroxide), hydrogrossular and calcite. In the bulk analyses portlandite was identified in all of the 3% lime treated samples, and also in the 3% cement treated samples from Otaika and Drury (greywacke); whereas in the clay fraction analyses, portlandite was identified in only the Otaika, Drury and Poplar Lane lime samples. Hydrogrossular is also identified in these lime samples.

In the XRD analyses of clay fractions of the 3% stabilised samples (Table 5.5), the smectite decreased dramatically compared to the clay fractions of the untreated samples (Table 5.3) of Flat Top and Poplar Lane, and the weathered sample from Drury. This is explained by the fact that the fine clay-sized particles have been cemented by the additives. The reduction in swelling capacity is also likely to be caused by cation exchange taking place.

Table 5.4 ‘Bulk’ XRD analyses of samples stabilised with 3% additive.

Site	Lithology	Weathering status [a]	Field number	Additive [b]	Quartz [c]	Plagioclase	K-feldspar	Tridymite	Zeolite	Portlandite	Magnetite	Chl/kaolinite	Smectite	Gypsum	Mica	Pyrite
Otaika	Greywacke	PW	OT-4a	L	A	M	T	–	T	M	–	T	T	T	T	T
		PW	OT-4a	C	A	M	T	–	T	T	–	T	T	T	T	T
		PW	OT-4a	D	A	M	T	–	T	–	–	T	T	T	T	T
Flat Top	Basalt	PW	FT-2	L	T	A	T	T	M	M	T	T	M	T	–	T
		PW	FT-2	C	T	A	T	T	M	–	T	T	M	–	–	T
		PW	FT-2	D	T	A	T	T	M	–	T	T	M	–	–	T
Drury	Greywacke	PW	D-5	L	A	M	T	–	–	M	–	T	T	–	T	T
		PW	D-5	C	A	M	T	–	–	T	–	T	T	–	T	T
		PW	D-5	D	A	M	T	–	–	–	–	T	T	–	T	T
Poplar Lane	Andesite	PW	PL-3	L	M	C	M	C	–	M	–	–	T	T	–	–
		PW	PL-3	C	M	C	M	C	–	–	–	–	T	–	–	–
		PW	PL-3	D	M	C	M	C	–	–	–	–	T	–	–	–

Notes to Table 5.4:

a

- PW = partly weathered

b

- L = lime,
- C = cement,
- D = Durabind™

c

- A = abundant (>60%)
- C = common (20–60%)
- M = minor (5–20%)
- T = trace (<5%)

Table 5.5 XRD analysis of clay fraction (<2 µm) of samples stabilised with 3% additive.

Site	Lithology	Weathering status[a]	Field number	Additive [b]	Smectite [c]	Kaolinite	Chlorite	Mica	Zeolite	Calcite	Feldspar	Hydrogrossular	Portlandite
Otaika	Greywacke	PW	OT-4a	L	–	–	T	–	T	M	–	T	T
		PW	OT-4a	C	–	–	T	T	–	–	T	–	–
		PW	OT-4a	D	–	T	T	T	–	–	–	–	–
Flat Top	Basalt	PW	FT-2	L	T	–	–	–	T	–	–	–	–
		PW	FT-2	C	–	–	T	–	–	–	–	–	–
		PW	FT-2	D	M	T	T	–	T	–	T	–	–
Drury	Greywacke	PW	D-5	L	–	–	T	–	–	M	–	T	T
		PW	D-5	C	–	–	T	T	–	–	–	–	–
		PW	D-5	D	–	T	T	T	–	–	T	–	–
Poplar Lane	Andesite	PW	PL-3	L	–	–	–	–	–	–	–	T	T
		PW	PL-3	C	–	–	–	–	–	–	–	–	–
		PW	PL-3	D	T	T	–	–	T	–	–	–	–

See Table 5.4 for key to abbreviations

5.7 XRD analyses of aggregate with a high concentration of stabiliser

5.7.1 Introduction

To characterise the development of hydrogrossular during the stabilisation process, an experiment was carried out using the addition of 10% stabilising binder with aggregate. The partly weathered sample from Flat Top was selected for this experiment because it has a relatively high concentration of smectite clays. Lime was selected as the additive, because it gave the best results of the three different additives tested at a level of 3%. XRD analyses were made at set intervals of time following the reaction of the lime with the aggregate to test the rate of cementation and the development of new minerals.

5.7.2 Method

Two sets of the same mixture were used, one set as 'dry unmoistened' and the other as ‘moistened’. XRD bulk analyses were carried out on both sets of samples using the following schedule:

For the ‘dry unmoistened’ sample, XRD analyses were commenced

- after preparation,
- one week later, and
- every two weeks until cessation of the experiment after a total of 50 days.

For the ‘moistened’ sample, the first XRD analysis commenced about ten minutes after moistening, and then subsequent XRD analyses were made

- 30 minutes after moistening,
- after two hours,
- after four hours,
- after six hours,
- after one day,
- after one week, then
- every two weeks until cessation of the experiment after a total of 50 days from commencement.

A sample mixed with 10% lime was prepared by carefully mixing 9 g of <300 µm Flat Top basalt with 1 g of <300 µm lime in a clean glass beaker. This was labelled as ‘dry unmoistened’ and covered with heavy-duty aluminium foil. A second beaker with a similar mixture, as above, was also prepared and labelled as ‘moistened’. It was then mixed carefully with 2 ml of clean water and covered with heavy-duty aluminium foil. A random powder mount was made with the sample mixture from each beaker, labelled and then X-rayed according to the schedule mentioned above. The X-ray running conditions were the same as with previous XRD bulk analyses. After each XRD scan, the two sample powder mounts were carefully wrapped with heavy-duty metal foil to preserve the initial conditions. To maintain a moist state for the ‘moistened’ sample, it was taken out from the foil wrapping and moistened with a very fine water spray before being X-rayed and then at two to three-day intervals during the longer periods between analyses.

5.7.3 Results

For the ‘dry unmoistened’ sample mix, the following results or observations were noted:

- The main primary minerals such as plagioclase, magnetite, pyroxene and quartz remained stable or unaltered.
- The most noticeable change was the simultaneous increasing presence of calcite with the reduction of portlandite (calcium hydroxide). This was to be expected, as calcium hydroxide readily absorbs carbon dioxide gas from the atmosphere to form calcite.
- Hydrogrossular, which appeared very weakly in the first XRD scan, began to increase in peak intensity as time went on. This confirms that the kinetics of hydrogrossular formation is time-dependent.
- Smectite and zeolite appeared unchanged mineralogically, even though they seem to have a slight reduction in peak intensity after the first XRD scan, but they reverted back to full intensity after the final XRD scan.

For the ‘moistened’ sample mix, the following observations were noted:

- Plagioclase feldspar ‘peaks’ decreased in intensity slowly as time increased.
- Portlandite (calcium hydroxide) had almost reduced to 10% of its original amount by the final XRD scan.
- At the same time, calcite replaced portlandite at an increasing rate, even starting to appear weakly during the second XRD scan (i.e. 30 minutes after moistening) and culminating as the most prominent mineral phase by the final XRD scan at 50 days.
- Other common minerals such as magnetite and pyroxene appeared unaltered with time.
- Hydrogrossular, as in the ‘dry’ sample mix, increased from being weak in the first XRD scan to significant peak size by the final XRD scan.
- Smectite and zeolite peaks appeared to increase in intensity as time elapsed.

5.7.4 Conclusions

The experiment using 10% lime on partly-weathered Flat Top basalt showed that the development of hydrogrossular increased in concentration with time. It was also noticeable that the portlandite ($Ca(OH)_2$) rapidly converted to calcium carbonate ($CaCO_3$) because of interaction with air, confirming the observation by Paige-Green (1984) of carbonation in lime-stabilised materials.

5.8 Chemical analyses

5.8.1 Introduction

The chemical composition of the samples was investigated using X-ray Fluorescence (XRF) and LOI techniques. In some instances, LOI can be used broadly to indicate the quantity of clay minerals and degree of weathering. Chemical composition was also used to examine the significance of the $Na_2O:K_2O$ as a measure of argillite in greywacke rocks. The ratio of $Na_2O:K_2O$ has been noted as a broad indicator of average grain size because of the increased proportion of phyllosilicate minerals in argillites compared with that in greywackes. Other studies have suggested that a ratio of one separates greywacke (>1) from argillite (<1).

5.8.2 Method

Splits were powdered and sent to SpectraChem Analytical Ltd for whole rock geochemical analyses by XRF and LOI by furnace and gravimetric methods.

5.8.3 Results

Results of the XRF and LOI analyses are listed in Appendix F. A pronounced trend of increasing LOI with increasing weathering is exhibited by the Flat Top (basalt) series of samples (Table 5.1). The partly weathered and weathered samples from Poplar Lane (andesite) have similar LOI values, which are substantially higher than those of the fresh samples. These values are consistent with similar CI values and the degree of weathering noted in the petrographic examinations, and show a trend of increasing LOI with increasing weathering. For the greywacke quarries, the Drury samples show a reverse trend and the Otaika samples all have similarly elevated values. Therefore, it appears that LOI does not follow the expected trend in the greywacke samples. This is because of the presence of variable amounts of illite, interlayered illite-smectite, and chlorite in the parent greywacke, and/or vein calcite that would also contribute to elevating LOI.

Samples of greywacke from Otaika and Drury broadly follow the 'Na_2O:K_2O rule', with Drury samples being much finer grained than the Otaika samples, which is reflected by Na_2O:K_2O ratios of 0.78 to 1.14 for the Drury samples versus 1.24:1.5 for the Otaika samples.

5.9 Summary statements

5.9.1 Mineralogical changes caused by weathering

The petrological and chemical data confirm that those minerals most susceptible to weathering are indeed weathered preferentially in the aggregate samples.

5.9.2 Observation on the cementation process

The microscopic studies have indicated that two processes are in stabilisation:

- a simple coating of grains by the additive which seals the grains from reaction with water, and
- the formation of hydrogrossular mineral cement which enhances the seal.

5.9.3 Hydrogrossular and stability of treated aggregates

- Hydrogrossular cement forms when lime, cement or Durabind™ is added to marginal aggregates. In addition, portlandite also forms but may subsequently transform (via carbonation) to calcite.
- Hydrogrossular formation is time-dependent. After 50, days the XRD peak for hydrogrossular was still increasing.
- CI studies of stabilised aggregates ground and soaked in water showed some return of swelling properties, which stabilised after 24 hours. In addition, the pH of the suspensions remained high, reflecting the excess lime present in the suspension.
- Preliminary investigations of stability at acid pH (<7) suggested that the stability of hydrogrossular decreases under acid conditions.

5.9.4 Relative composition of different aggregates

The XRD analysis and CI tests have shown that the rock types evaluated in this study are clearly distinct. The greywacke samples are initially high in mixed-layer clays, while the volcanic rocks have smectite. Smectite increases progressively in all rock types with increased weathering, but in the most highly weathered samples, where leaching dominates, the smectite transforms to kaolinite or halloysite.

5.9.5 Relative performance of different stabilisers (additives)

All treated aggregates gave very low CI values, indicating that the expanding clays in the partly weathered samples have been almost entirely fixed by the additives. CI values are slightly higher for the basalt and andesite than they are for the greywackes. The CIs increase through the series lime, cement and Durabind™, suggesting that lime is the most efficient fixer of the swelling clays, followed by cement and then Durabind™. However, the difference may partly be a function of reaction time. Given a longer reaction period, the difference in performance between the three additives may decrease.

5.10 Geochemistry and activity diagrams

5.10.1 Introduction

In low temperature geochemistry, activity diagrams are frequently used to demonstrate the relationships between fluid chemistry and the alteration minerals with which the fluids are in equilibrium. An example of such a diagram is shown in Figure 5.5. It has been shown experimentally and by observation in nature that in such systems, the fluid composition at equilibrium will plot at the so-called tie line (e.g. kaolinite–albite), or triple point (e.g. kaolinite–calcium smectite–sodium smectite (A in Figure 5.5)) between co-existing phases.

If the solution is not in equilibrium with the assemblage then it will move off the tie line into the stability field of a specific mineral. More extensively weathered materials contain kaolinite. Hence, the weathering trend is towards the kaolinite field (or the origin) of Figure 5.5.

5.10.2 Experimental

In this study, the fresh, partly weathered and weathered samples from Drury, Flat Top and Poplar Lane were ground and suspended in water in the ratio 0.025 g rock powder to 1 ml distilled water. The pH (at 17–18ºC) of the slurries was measured initially and then re-measured at regular intervals. After 39 days, the mixture was centrifuged and the supernatant liquid extracted for analysis of the following components:

- SiO_2,
- sodium,
- potassium,
- calcium,
- magnesium,
- iron,
- rubidium,
- strontium,
- arsenic,
- chlorine,
- total sulphur, and
- bicarbonate.

Results are given in Appendix G.

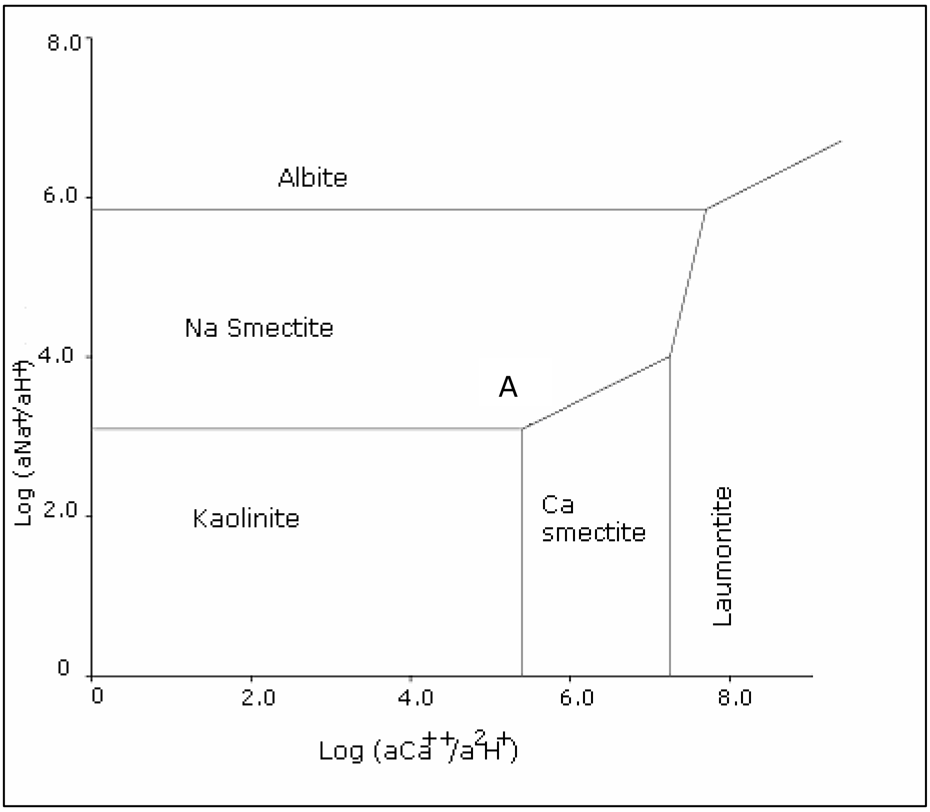

Figure 5.5 Activity diagram for the system log (a Ca $^{++}$/a^{2}H$^+$) versus log (a Na$^+$/aH$^+$) at 25°C and log (a H_4SiO_4 = -2.7 = amorphous silica saturation) (modified after Helgeson et al. 1969).

Using these data, the activities of the sodium, calcium and hydrogen ions were calculated and plotted in the activity diagram shown above (Figure 5.5).

5.10.3 Discussion

The untreated aggregate samples moved progressively away from the triple point (A in Figure 5.5) with increased weathering towards lower ratios of Na/H and Ca/H^2. In this regard, if the pH is lowered, then the hydrogen ion concentration is increased (i.e. a high hydrogen ion activity) and the ratio becomes smaller.

When the samples were treated with Durabind™, lime or cement, similar leaching experiments (Figures 5.6–5.8) showed that the solution chemistry of each was now comparable or slightly above that of the original fresh rock. This is in general agreement with the improvements in the engineering properties.

The most significant change was at Poplar Lane (Figure 5.6), where the treated sample plotted well above the fresh rock (i.e. much higher ratios). Similar trends were observed with Flat Top (Figure 5.7) and Drury (Figure 5.8) samples.

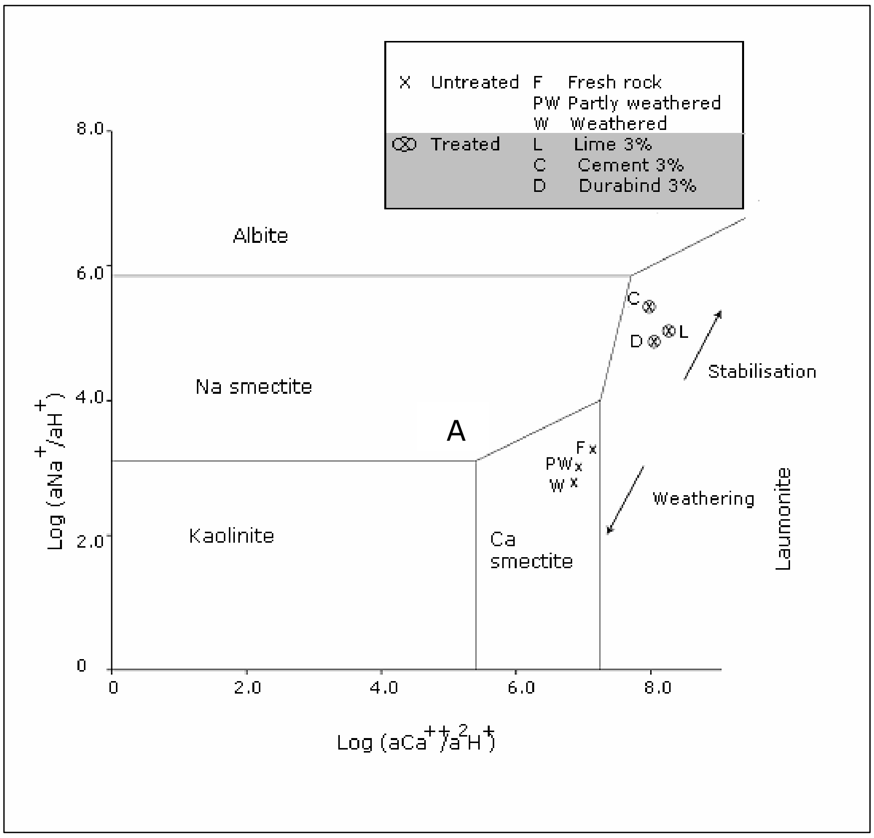

Figure 5.6 Fluid chemistry of Poplar Lane quarry samples (untreated and treated).

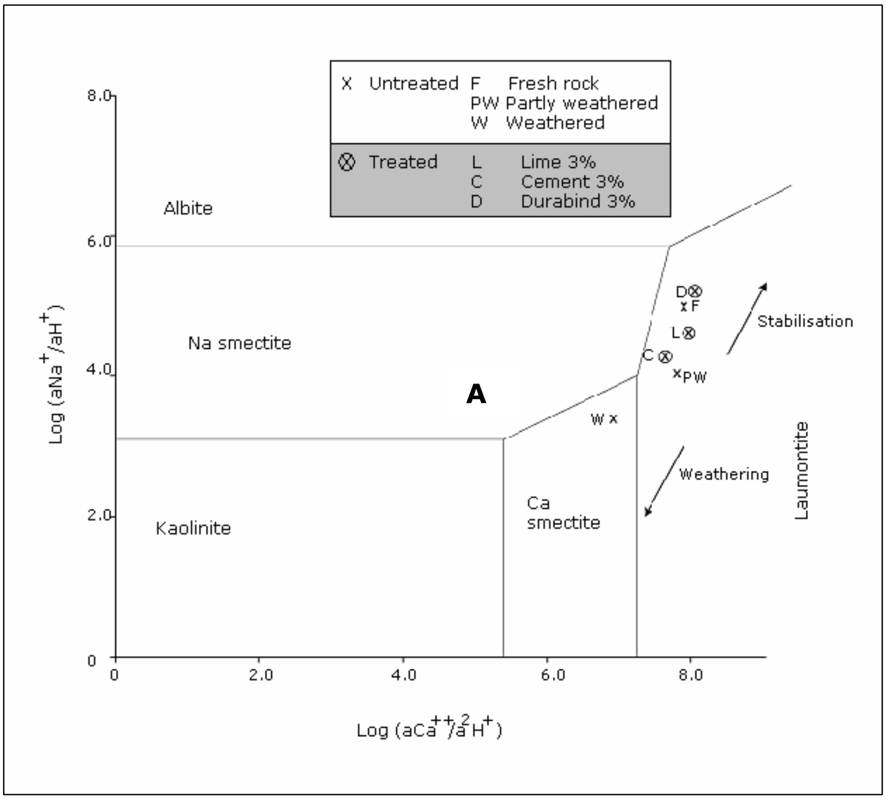

Figure 5.7 Fluid chemistry of Flat Top quarry samples (untreated and treated).

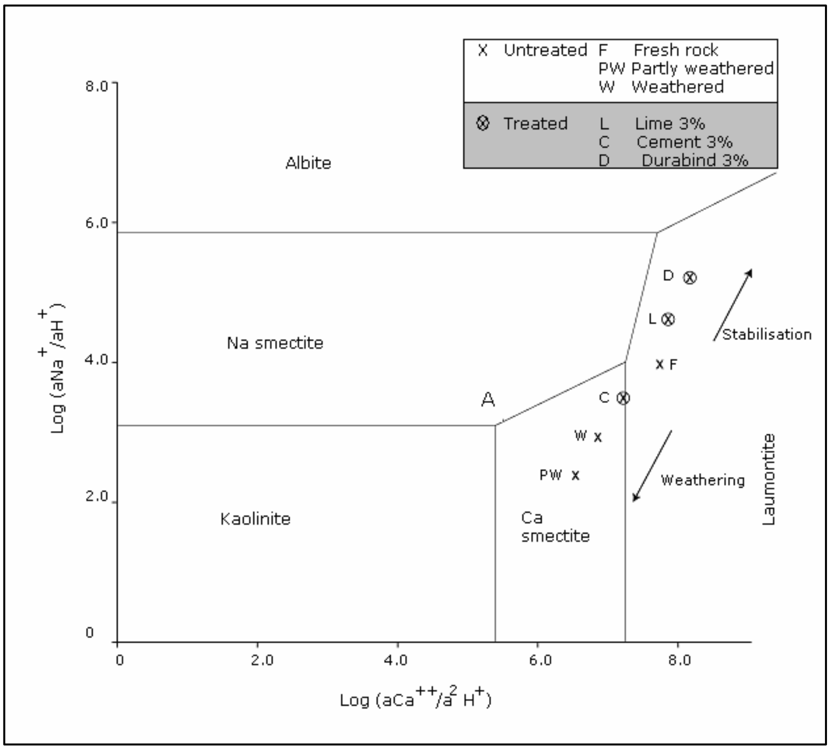

Figure 5.8 Fluid chemistry of Drury greywacke quarry samples (untreated and treated).

5.11 Geochemistry and ternary diagrams

5.11.1 Carbonate, chloride and sulphate ternary diagrams

The carbonate, chloride and sulphate concentrations of the water leaches of fresh, partly weathered and weathered samples (Table G2), and treated partly weathered samples (Table G3) were plotted on ternary diagrams (Figure 5.9), along with the Durabind™ leach water. Leaches of weathered and partly weathered samples are enriched in chloride, whereas leaches of the stabilised samples are enriched in sulphate, reversing the trend induced by weathering. Also, the leaches of samples stabilised with Durabind™ are enriched in bicarbonate, approaching the composition of the leach of pure Durabind™, which contrasts with the relatively lower bicarbonate concentrations in the lime and cement stabilised samples. The relatively high chloride content of the leach of fresh andesite from Poplar Lane suggests that the proximity of this quarry to the ocean may influence the chemistry of its weathering.

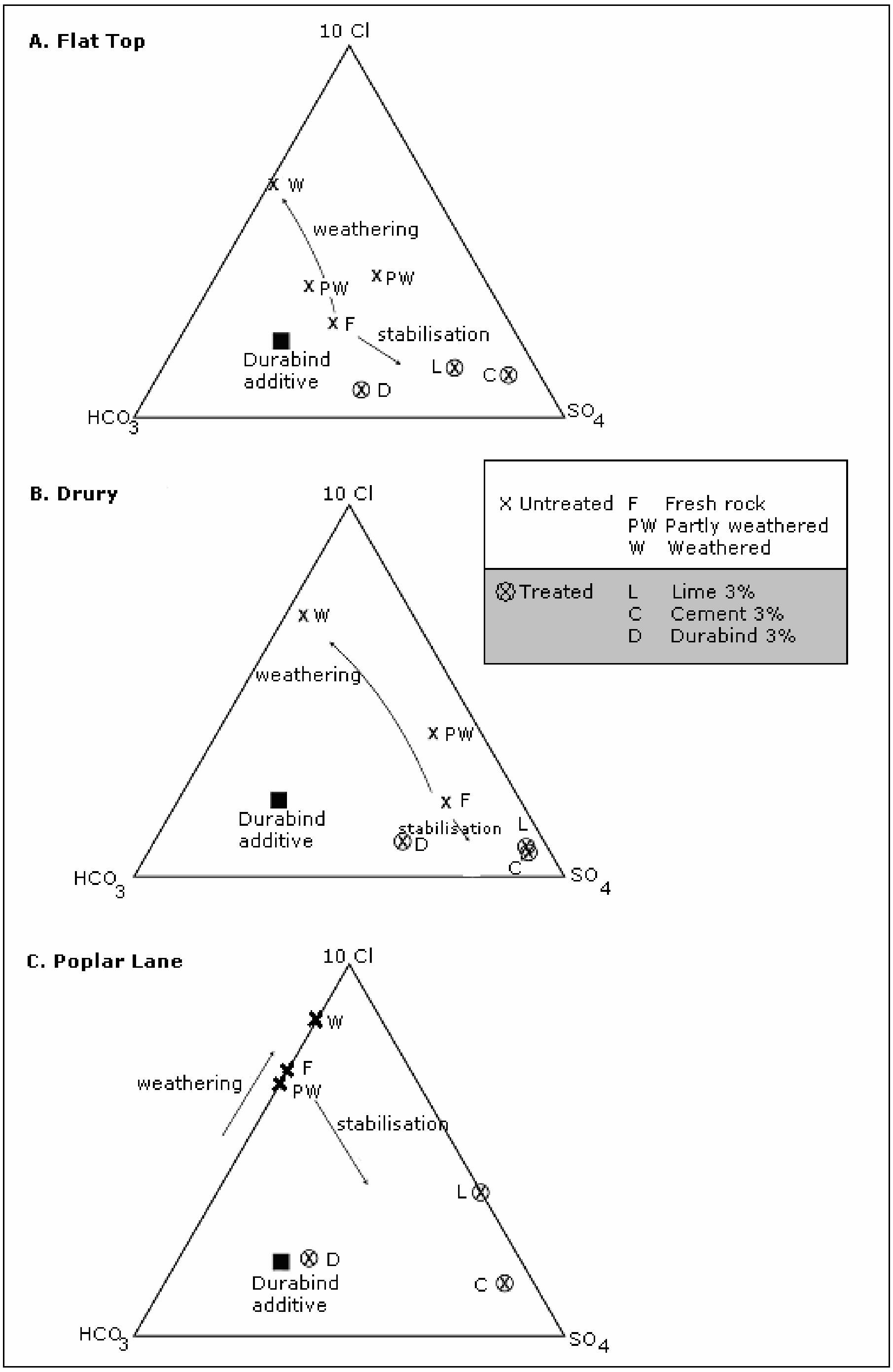

Figure 5.9 Ternary diagrams for bicarbonate, chloride and sulphate in leaches of rock samples from Flat Top, Drury and Poplar Lane.

5.11.2 Alkalis, magnesium and calcium ternary diagrams

In addition to the water leach compositions, the alkalis, magnesium and calcium ternary diagrams (Figure 5.10) include plots of the XRF rock geochemistry from Table F1. The fresh, partly weathered and weathered rock analyses plot in a tight cluster compared to the water leach analyses. Leaches of the weathered rocks are enriched in magnesium compared to leaches of fresh rocks, whereas leaches of the stabilised samples are enriched in calcium, generally in the order lime >cement >Durabind™, as would be expected from the high calcium content in these additives. Progressive weathering and leaching of the rocks yields a leach water composition plot similar to the proportion of alkalis, magnesium and calcium in the original rock. However, the path to get there is different for the different rock types. The leaches of the untreated Drury samples have low total alkalis, and so the trend from fresh rock to weathered rock is simple enrichment of magnesium relative to calcium in the leaches. The leach of fresh Flat Top basalt is relatively high in alkalis compared to all other water leaches except that of pure Durabind™. The trend toward weathered rock is enrichment in magnesium relative to both alkalis and calcium in the leaches. Poplar Lane andesite leaches have very similar proportions of alkalis, magnesium and calcium to the rocks.

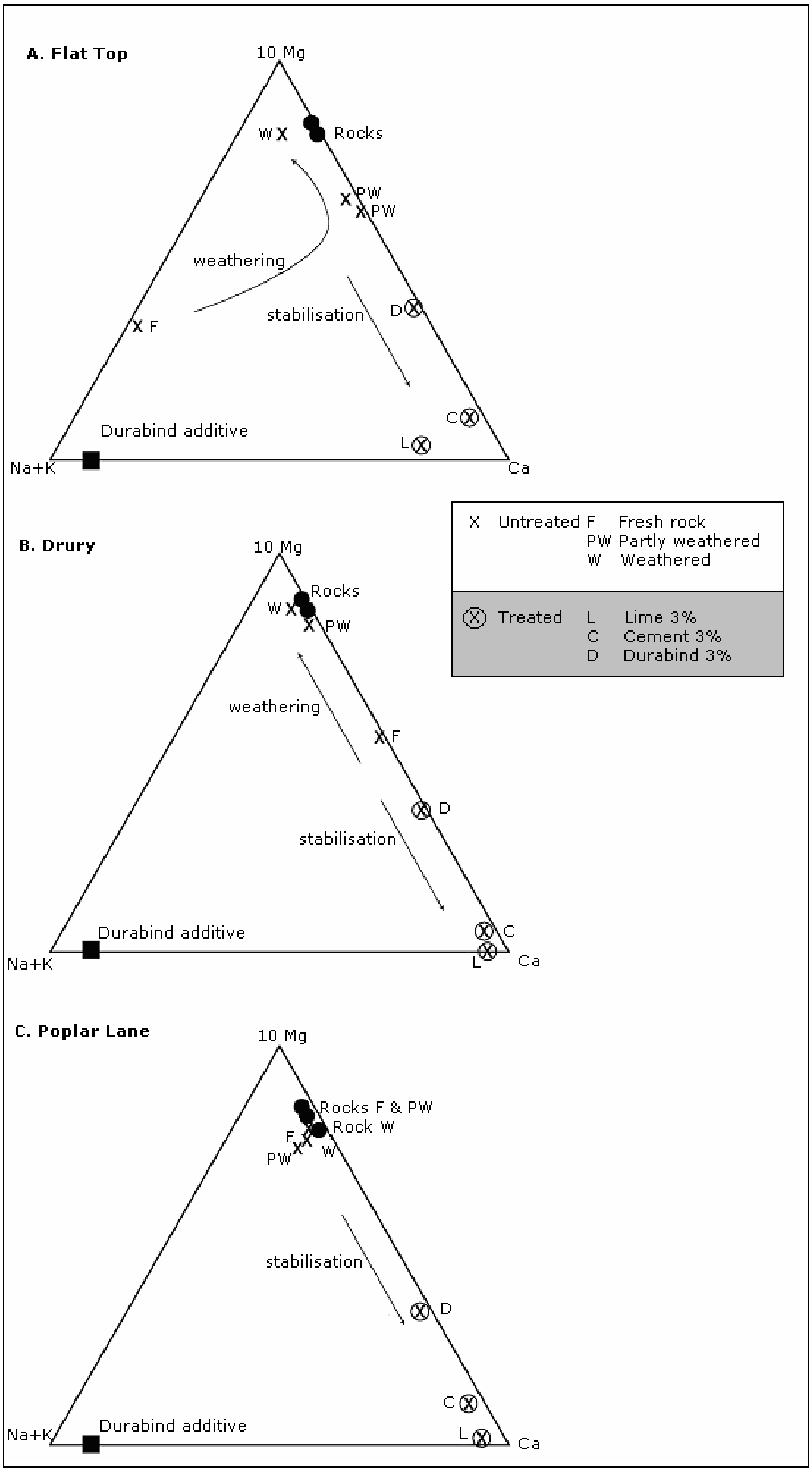

Figure 5.10 Ternary diagrams for alkalis, magnesium and calcium in leaches of rock samples and rocks from Flat Top, Drury and Poplar Lane quarries.

5.12 Mineralogical variation and response to treatment of the different rock types

Four rock types were investigated: a greywacke sandstone (Otaika), a more argillaceous greywacke (Drury), basalt volcanic rock (Flat Top) and an andesite volcanic rock (Poplar Lane). These rocks exhibit distinct differences in mineralogy and chemistry that affect their susceptibility to weathering and potential for stabilisation.

The Flat Top basalt contains the highest proportion of more readily weathered minerals. The high concentrations of FeO and MgO relative to the other rock types (Table F1) are a reflection of the presence of about 25–30% pyroxene (augite?) in the primary mineralogy, which is readily altered. Additionally, the basalt has undergone hydrothermal alteration to clay and zeolite, resulting in some swelling clays even before weathering begins. Weathering initially increases the concentration of smectite before alteration to halloysite and kaolinite at more advanced stages. CI and LOI values increase with increasing weathering. The abundance of Na-smectite suggests that cation exchange is an important factor in the stabilisation process.

The Poplar Lane andesite has a smaller proportion of readily-weathered minerals, being composed of approximately 70–75% plagioclase and 15–20% pyroxene (hypersthene?). However, like Flat Top, some alters to smectite even in the freshest material, leading to relatively high CI values. Weathering produces additional smectite along with kaolinite and halloysite. CI and LOI values increase with increasing weathering. Like Flat Top basalt, the abundance of Na-smectite suggests that cation exchange is an important factor in the stabilisation process.

The Otaika greywacke is composed of approximately 20% quartz, 30% feldspar, 20% rock fragments and 15% of other mineral grains (chlorite, clinopyroexene, hornblende, muscovite, biotite, epidote and tourmaline) and 15% matrix of mica-illite, interlayered illite-smectite and chlorite. In comparison, the Drury samples are much finer grained, have less quartz and slightly different proportions of other minerals, and are notable for the presence of prehnite and pyrite. The presence of K-mica as muscovite and illitic clays gives the greywackes a distinctly higher concentration of K_2O than the volcanic rocks (Table F1). The Drury greywacke is more susceptible to weathering than the Otaka greywacke because of its finer grain size and more fractured nature. Weathering of the greywackes produces smectite and kaolinite, with corresponding increases in CI values. LOI values do not reflect alteration trends, because the primary greywackes contain significant quantities of clays and hydrous minerals in their matrix, as well as some calcite along fractures.

5.13 Conclusions

Based on the results of the chemical and mineralogical testing, the effectiveness and value of the various testing techniques are summarised in Table 5.6. The CI (Methylene Blue) test was the most useful and cost-effective test for determining the amount of swelling clay in the raw material. It was also most effective for assessing the swelling properties of the treated samples.

The mineral stability (activity) diagrams were useful for demonstrating the relationships between the fluid chemistries and mineralogy of the fresh, weathered and treated quarry samples. XRD analysis in conjunction with LOI was of some value in characterising and quantifying the clay mineralogy.

5.14 Recommendations

We recommend that a single profile in a selected quarry which grades from fresh rock to weathered rock be more thoroughly evaluated by a combination of strength and Methylene Blue testing.

The recommended procedure is as follows:

1 Take a series of quarry samples from:
  - fresh rock,
  - partly weathered,
  - moderately weathered, and
  - heavily weathered zones.

2 Crush the samples to a specific size and prepare stabilised samples with a range of additives at 1%, 3%, 5% and possibly higher values.
3 Carry out comparative strength and Methylene Blue tests on the prepared samples.
4 Carry out strength and Methylene Blue tests after soakage tests.
5 Determine if an optimum degree of weathering and addition rate of stabilisers can achieve acceptable strength values.

Table 5.6 Summary assessment of various chemical and mineralogical testing methods.

Measurement	Method or detail	Usefulness	Positive features	Negative features
CI (Methylene Blue)	Untreated material	Useful for identifying raw materials suitable for stabilisation.	Cheap, easy	• Small sample size means that it is difficult to obtain representative samples. • Limited sensitivity for low CI.
	Treated material	Useful for defining effectiveness of stabilisation.		
	Permanence/ swelling recovery	Useful for long-term testing of stabilised pavements.		• Small sample size means that it is difficult to obtain representative samples. • Limited sensitivity for low CI. • Disintegration of sample does not duplicate pavement conditions.
Petrography	Untreated material	Useful for identifying primary minerals.	–	• Expensive. • Magnification insufficient to study clays in detail.
	Treated material	Insufficient magnification to be of value.	–	• Expensive. • Magnification insufficient to recognise hydrogrossular.
Scanning Electron Microscope	Treated material	–	High magnification	• Expensive, but may be useful for identifying cements.
XRD untreated material	Bulk rock	Useful for quantifying primary minerals.	Can be quantitative	• Expensive. • Limited sensitivity to clays.
	Clay separates	Useful for identifying clay minerals.	Useful for clay identification	• Expensive. • Limited sensitivity to clays.
XRD treated material	Bulk rock	Limited value	Can be quantitative	• Expensive. • Limited sensitivity to clays and cements.
	Clay separates	Useful to recognise changes in clay minerals.	Useful for clay identification	• Expensive. • Limited sensitivity to cements.
Chemical methods	Bulk rock analysis	Useful for calculating mineral abundances.	LOI may correlate with clay content	• Expensive.
	Leach analysis & activity diagrams	Useful for assessing additive performance.		• Relatively expensive.

6 Engineering tests

6.1 Introduction

In general, the additives could be expected to reduce the loss in strength of the partly weathered aggregate that commonly occurs when the aggregate becomes saturated.

The additives used in this study were selected to provide a range of reactions. At one end of the scale, the addition of hydrated lime can be expected to reduce the quantity of swelling clay minerals and promote the formation of inter-particle bonds (hydrogrossular and portlandite). The addition of cement, on the other hand, will primarily promote inter-particle bonds and cause only a modest reduction in the swelling clay mineral content. Durabind™ was designed to have properties that fall somewhere between the other two additives, and to have a reaction rate much slower than that of the other two.

The quantity of additive normally used to stabilise aggregate depends primarily on the type of chemical used, but would be expected to be approximately 1.5% by weight for lime or cement. The concentrations of additives used in this study were arbitrarily set at 1 and 3%. As a consequence, it could be expected that Durabind™ would have a lesser effect than either lime or cement, and that cement would generate a much larger change in the strength of the material than the other two additives.

The engineering tests selected for use in this project were primarily intended to measure the changes in strength generated by the different additives. The results were intended to reflect the changes that occurred in the mineralogy of the rocks, particularly with respect to the strength of the inter-particle bonds.

The sample preparation and geotechnical tests were carried out at the laboratory of Geotechnics Ltd, located in Tauranga.

Particle size analysis, compaction, and soaked CBR tests were carried out on samples of partly weathered GAP 65 aggregate, and on some of the fresh basecourse samples collected from the quarry stockpiles. These were intended to provide a benchmark for comparing the normal production from each quarry.

The main strength tests were carried out on crushed (all passing through a 4.75 mm sieve) partly-weathered aggregate obtained from the face of each quarry. A Proctor Needle test was used to monitor the changes that occurred in the initial 24 hours, and after a period of seven days curing and four days soaking. A soaked CBR test was also carried out after the curing and soaking periods had expired. Standard laboratory compaction tests were used to establish the optimum water content for the preparation of strength samples. The samples were oven dried prior to mixing with the chemical additive.

The aggregate and chemical additive were premixed in a plastic bag. Sufficient water was added to achieve optimum moisture content (OMC) +3% water of the dry mass (Calculated from NZS 4402:1986 Test 4.1.1).

The material was then compacted into the moulds using the method specified in NZS 4402:1986 Test 4.1.1 but using 62 blows per layer instead of 27 blows per layer as specified.

6.2 Strength tests

The sample was tested with a Proctor Needle 5 hours and 25 hours after manufacture, again after curing for 7 days, and finally after being soaked for 4 days. The force required to drive the needle to a depth of 25 mm below the surface and the time of the test was recorded. Tests were located no closer than 20 mm from the wall of the mould, and the clear space between any two measurements was not less than 15 mm. The penetration resistance of the material in kilopascals (kPa) was calculated by dividing the vertical force (kN) required to penetrate 25 mm divided by the bearing area of the end of the needle (m^2). The penetration resistance was the mean value of three measurements.

On completion of the test at 25 hours, the sample was wrapped in a plastic bag and allowed to cure at room temperature for a further six days (i.e. a total of 7 days from manufacture). At the completion of the curing period, the penetrometer resistance was measured in a manner similar to that described above. Following this test, the sample was immersed in a water bath for four days. At the end of that time, the sample was taken from the bath and inverted so that the final measurement of penetrometer resistance and CBR (as per NZS 4407:91 Test 3.15) could be determined.

The whole intact sample was then forwarded to Geological and Nuclear Sciences in Wellington.

6.3 Results

6.3.1 Diagrams

The results of the penetrometer and CBR tests are presented in Figures 6.1–6.7. The results of both types of test are compared in Figure 6.8.

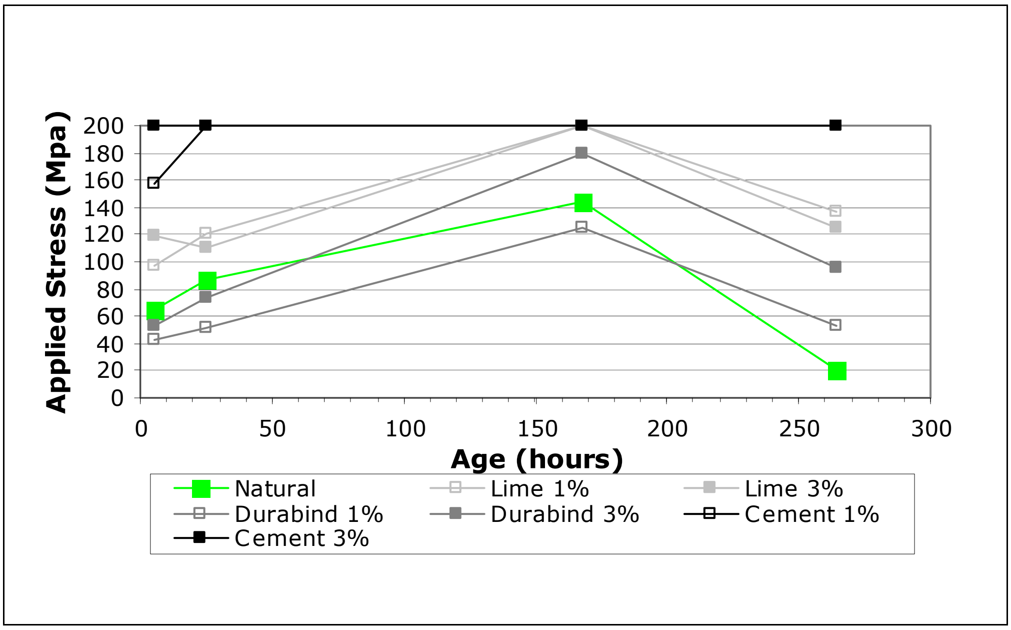

Figure 6.1 Results of the penetrometer test on treated and untreated samples from the Otaika quarry.

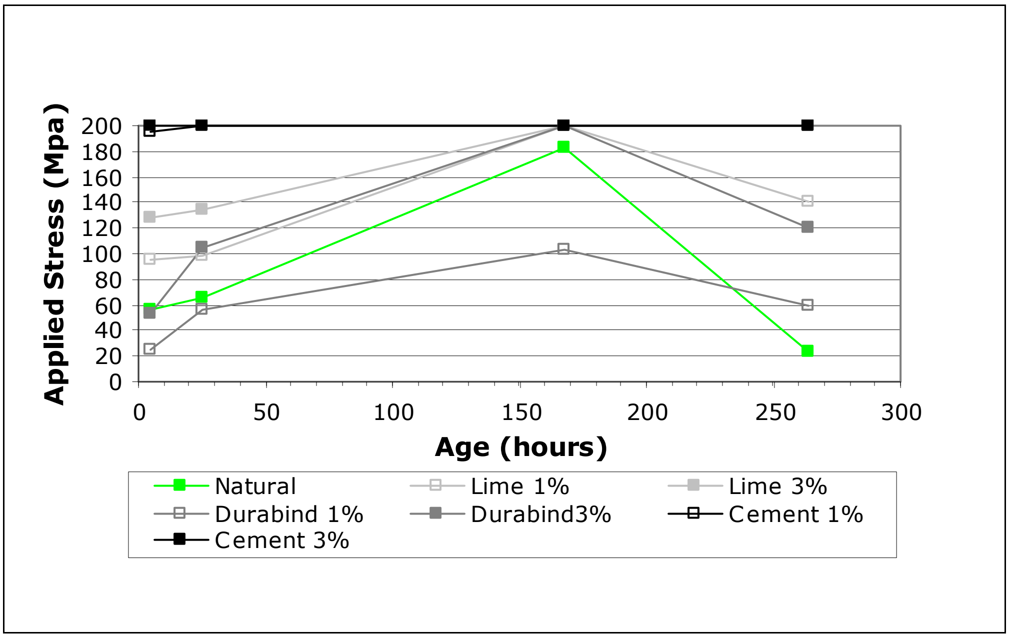

Figure 6.2 Results of the penetrometer test on treated and untreated samples from the Flat Top quarry.

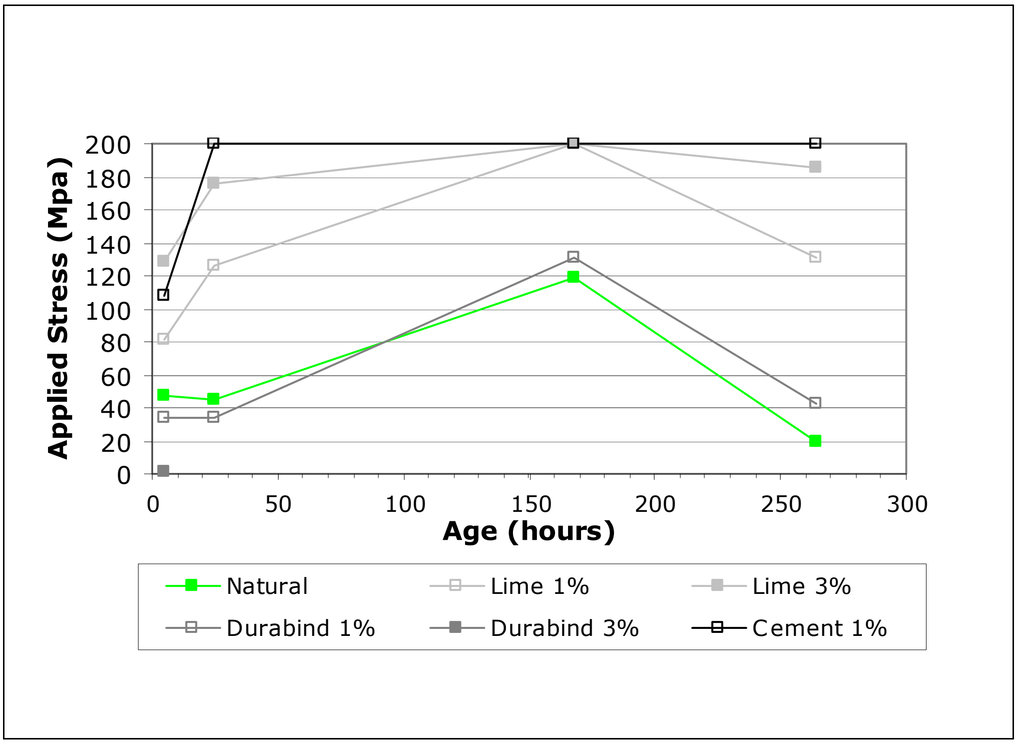

Figure 6.3 Results of the penetrometer test on treated and untreated samples from the Drury quarry.

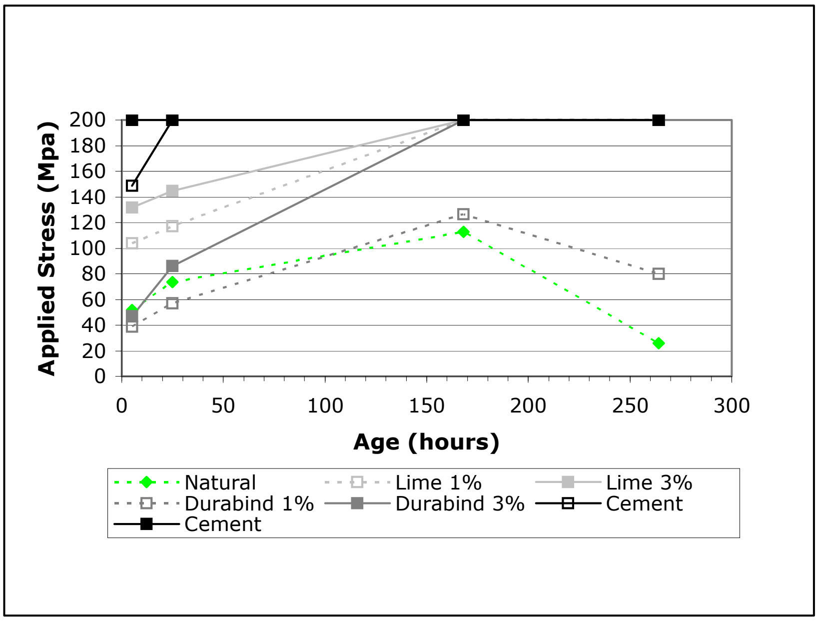

Figure 6.4 Results of the penetrometer test on treated and untreated samples from the Poplar Lane quarry.

In Figures 6.5–6.7, the results are shown for untreated aggregate, aggregate treated with lime, and aggregate treated with Durabind™. Aggregates treated with cement exceeded the capacity of the Proctor Needle soon after manufacture.

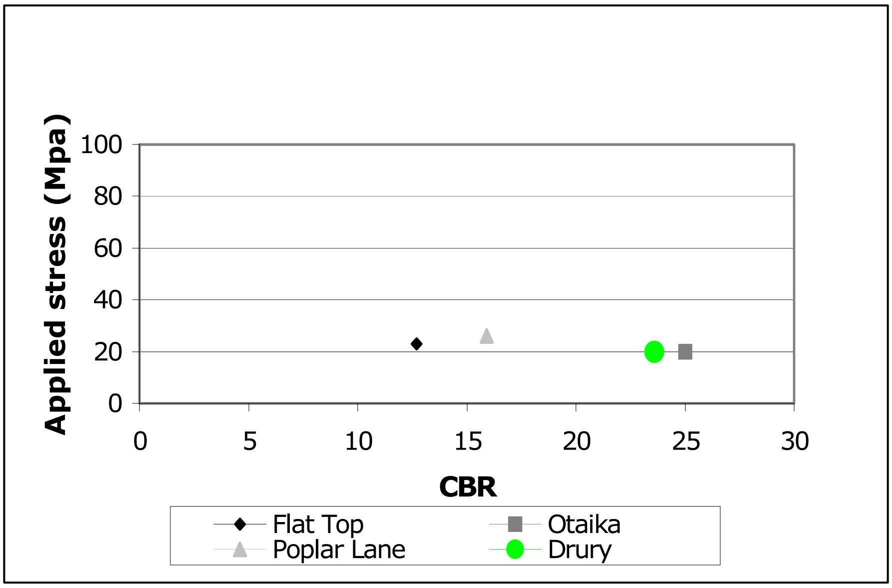

Figure 6.5 **CBR performance of untreated aggregate from all four sites.**

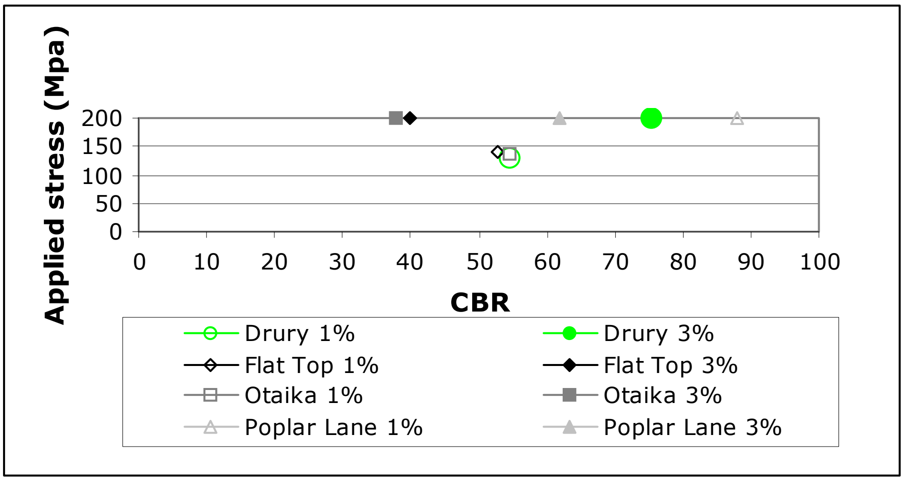

Figure 6.6 **CBR performance of aggregate from all four sites, treated with lime.**

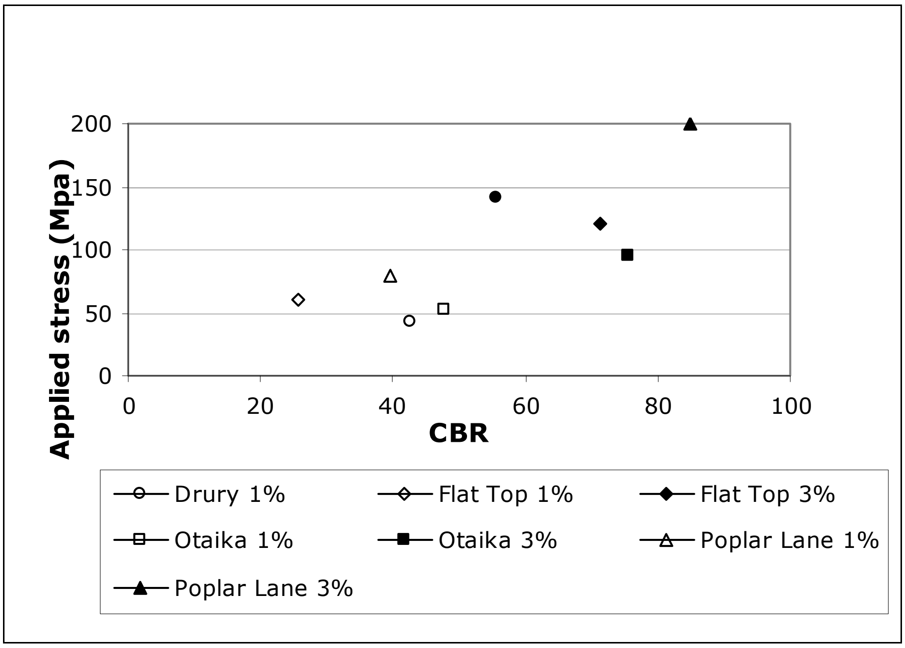

Figure 6.7 CBR performance of aggregate from all four sites, treated with Durabind.

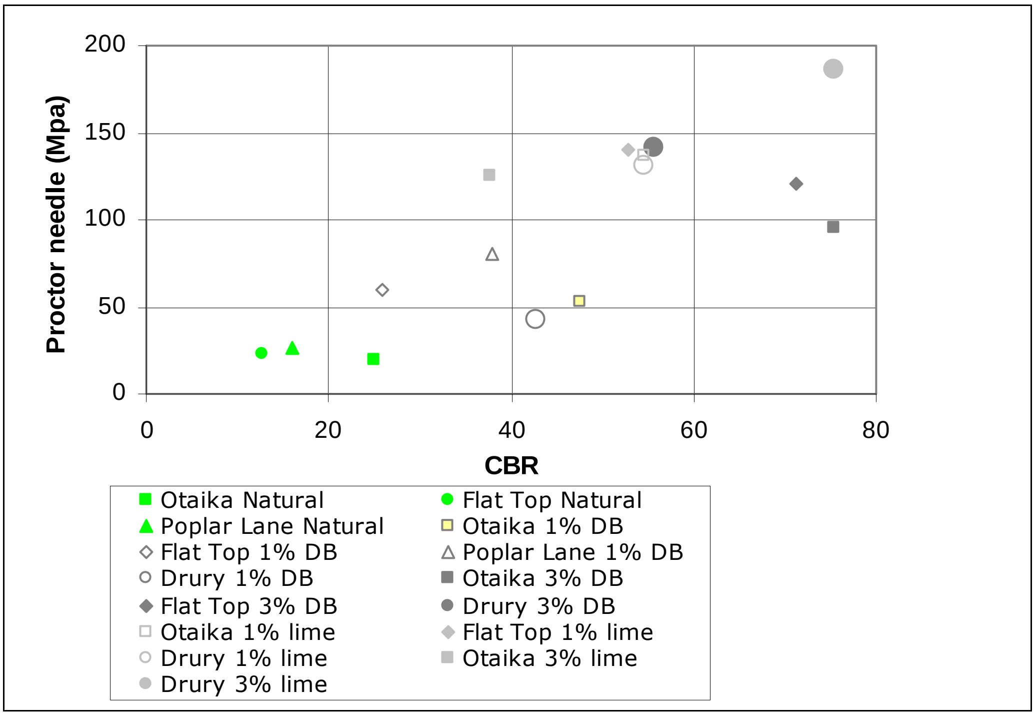

Figure 6.8 CBR values versus Proctor Needle results for treated and untreated samples from all four quarry sites at the end of the testing.

6.3.2 Manufactured aggregate

Typical results of standard engineering tests carried out on samples of manufactured aggregate are set out in Table 6.1.

Table 6.1 Results of standard engineering tests on manufactured aggregate sampled from the four quarries.

Source	Basecourse				GAP 65		
	CBR (%)	Dry density (t/m^3)	Water content (%)		CBR (%)	Dry density (t/m^3)	W/C (%)
Otaika	–	–	–		190–210	2.13	7.0
Flat Top	160–275	2.12	10.0		130–145	2.05	12.7
Drury	80–105	2.13	13.2		125–180	2.10	8.4
Poplar Lane	200	1.94	6.1		235–455	2.09	8.6

It was decided that further testing of the GAP 65 modified with the additives similar to those used in the previous tests would not be relevant, given the high CBR values of the untreated GAP 65, particularly the Otaika and Poplar Lane samples. The results of CBR tests on Flat Top GAP 65 modified with 3% Durabind™ used in another project showed values in the range of 110–240% at seven days and 140–360% at one month. Non-destructive testing of a pavement constructed using this material showed that the stiffness continued to increase for six months.

6.3.3 Strength tests

6.3.3.1 Proctor Needle tests

The diagrams for the results were shown in Chapter 6.3.1 (Figures 6.1–6.4).

The results of all the Proctor Needle tests (also called penetrometer tests) follow a similar pattern. Those in Figure 6.1 are typical, i.e.

- The strength of the untreated aggregate increased with time throughout the curing period. This suggests that the density of the sample was increased by the insertion of the penetrometer. However, the strength decreased rapidly after the sample was soaked for four days.
- The effect of adding 1% of Durabind™ generally had a minimal effect, if any, on the strength.
- The addition of 3% Durabind™ and the lime caused a significant increase in strength, part of which was subsequently lost during soaking.
- The cement had an immediate and substantial effect on strength. It is not possible to say if any deterioration occurred during soaking because the strength was beyond the range of the instrument.

6.3.3.2 CBR tests

The results of the CBR tests after seven days curing and after a further four days soaking are summarised in Table 6.2 and in Figures 6.9–6.12. The final CBR measurement was taken on the undamaged end of the sample.

Table 6.2 Results of CBR tests on cured and soaked AP (all passing) 4.75 aggregate samples from the four quarries.

Source & type	Treatment & additive													
	Cured							Soaked						
	Untreated	Durabind		Lime		Cement		Untreated	Durabind		Lime		Cement	
		1%	3%	1%	3%	1%	3%		1%	3%	1%	3%	1%	3%
Otaika greywacke	38	61	67	37	38	155	–	11	35	85	72	38	210	–
Flat top basalt	18	28	74	53	30	101	297	8	24	68	53	49	179	206
Drury greywacke	16	42	59	54	79	167	–	32	43	52	55	72	223	–
Poplar Lane andesite	23	41	72	65	49	81	264	9	38	99	111	75	205	–

In a number of instances, the CBR after soaking is virtually the same as that prior to soaking. These results have been highlighted in Table 6.2 (pale grey fill).

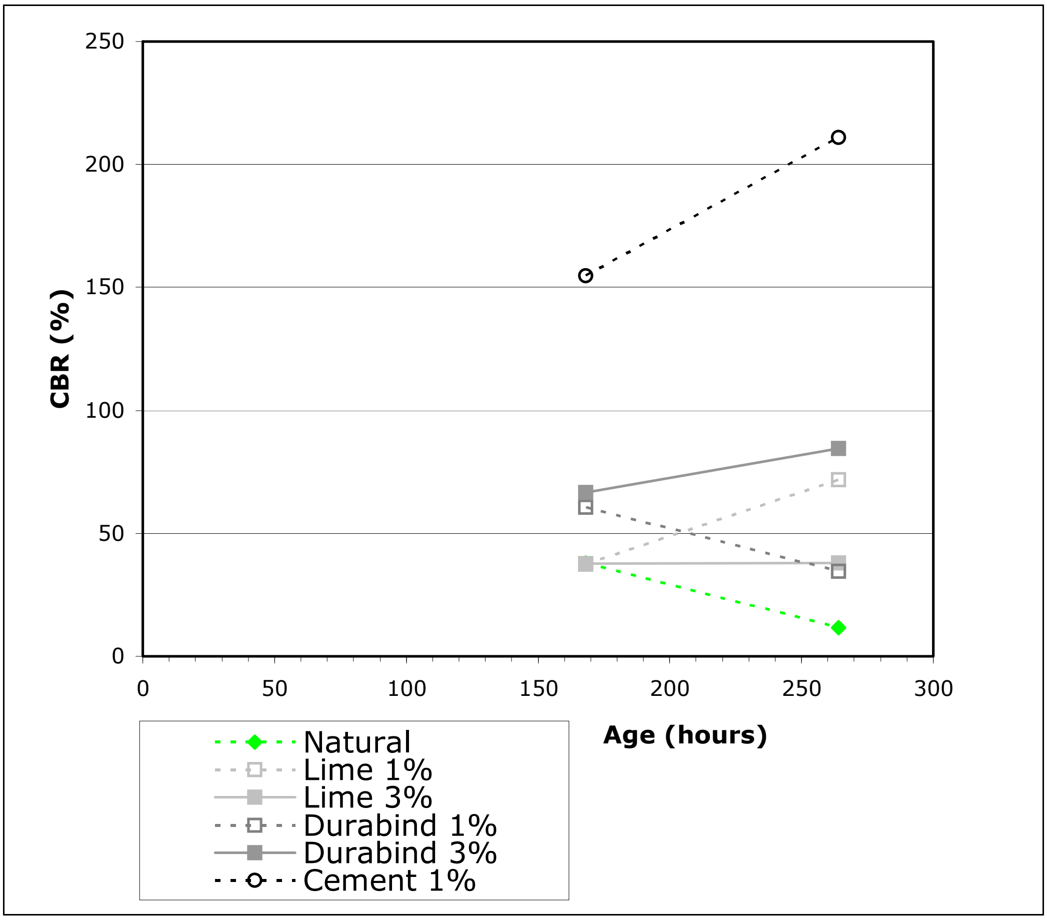

Figure 6.9 **Results of CBR testing over time: Otaika quarry.**

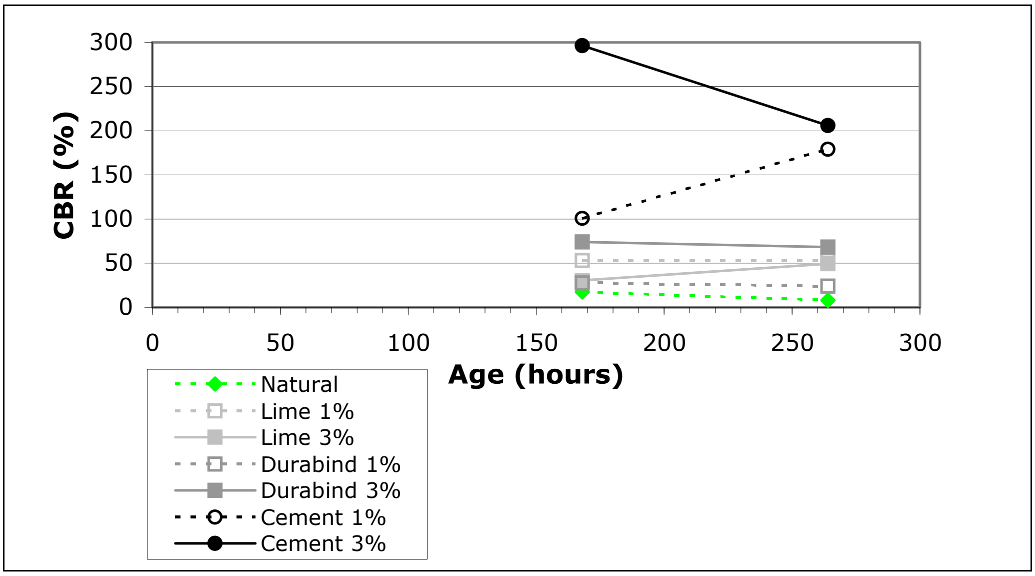

Figure 6.10 **Results of CBR testing over time: Flat Top quarry.**

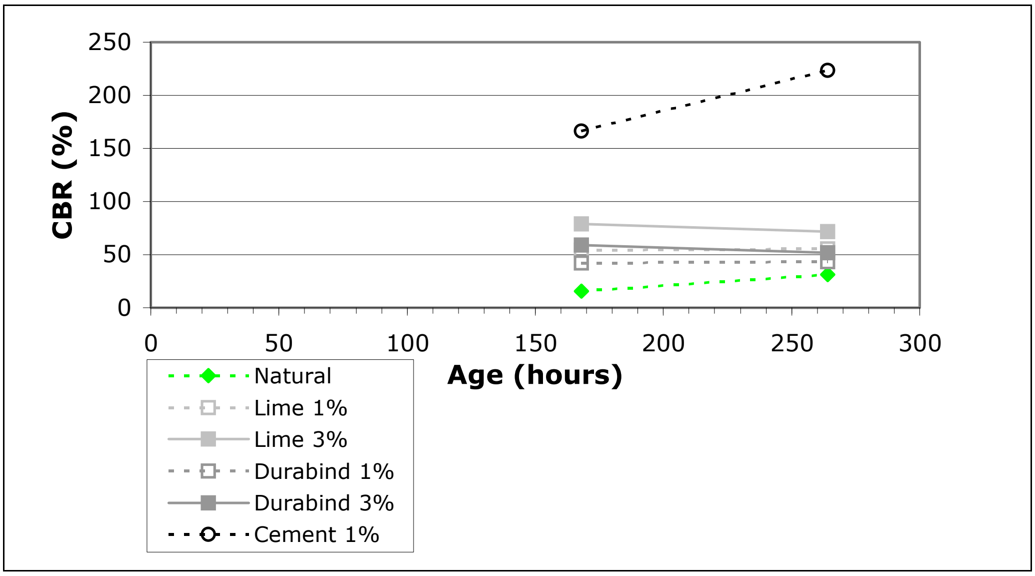

Figure 6.11 Results of CBR testing over time: Drury quarry.

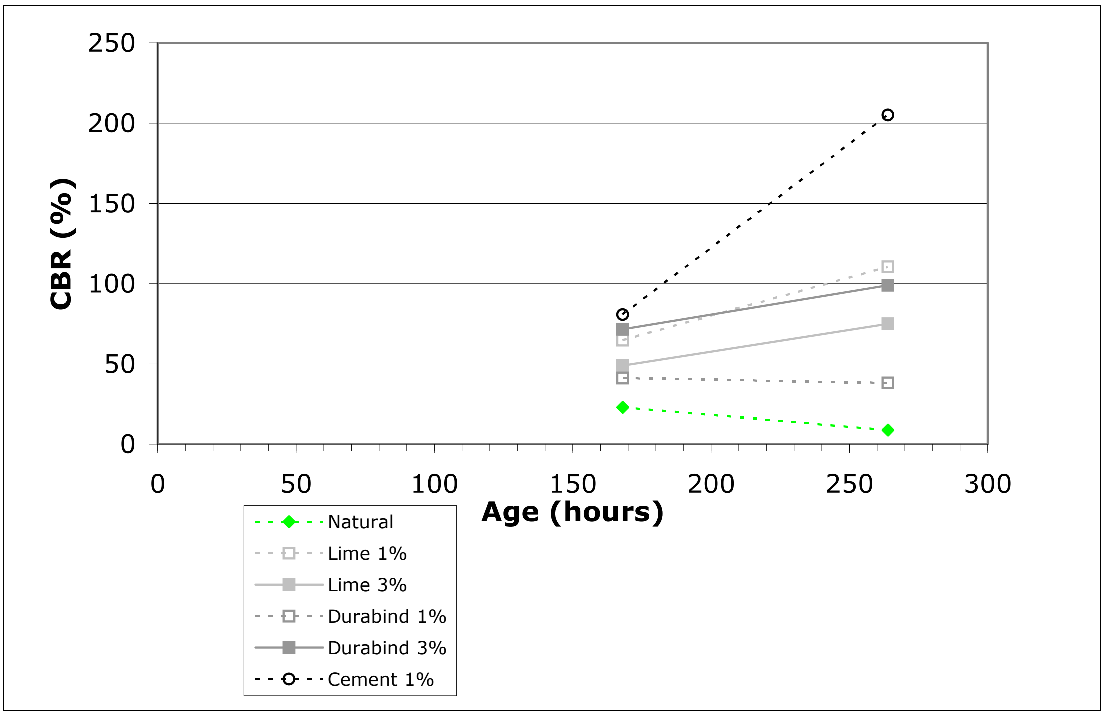

Figure 6.12 Results of CBR testing over time: Poplar Lane quarry.

The results show the following:

- Samples of untreated aggregate usually lost strength as a result of soaking; some lost more than others. The strength of the Drury greywacke sample increased.
- Addition of 1% Durabind™ had little effect on the basalt sample but was effective with the others. It substantially reduced the loss in strength from soaking.
- Samples treated with 3% Durabind™ had similar characteristics to the lime treated samples, except that the Otaika greywacke responded better to Durabind™ than it did to lime.
- Samples treated with cement gained substantially more strength during soaking than all the other samples, except for the Flat Top sample treated with 3% cement.
- The strength of a number of samples treated with Durabind™ or with lime did not change as a result of soaking. The strength of three of the four samples treated with 3% cement exceeded the capacity of the test machine.

6.3.3.3 *Comparison of Proctor Needle and CBR results*

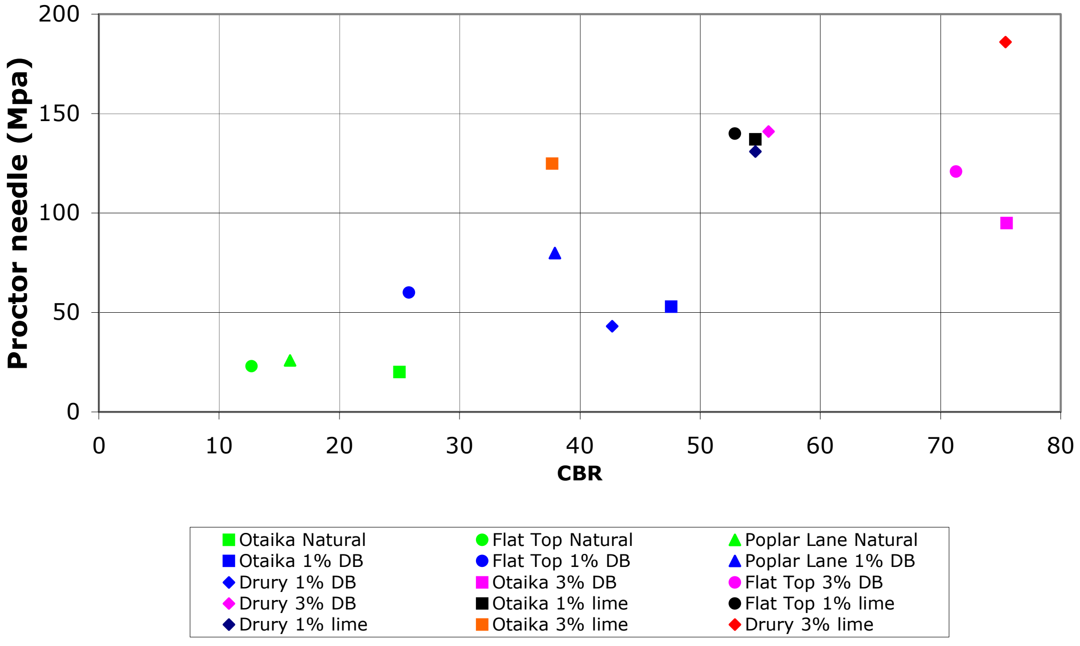

Figure 6.13 Comparison of CBR and Proctor Needle test results for treated and untreated samples from all four quarries.

A comparison of the results of the two methods of strength measurement is presented in Figure 6.13. The approximate relationship between CBR and Proctor Needle measurements is a strength of 100 Mpa measured with the Proctor Needle is equivalent to a CBR of 50%.

6.4 Conclusions

The Proctor Needle test was selected to provide a relatively quick and accurate measure of the changes in strength that were expected to occur during the curing and soaking periods. In fact, it appears that in some samples, the first Proctor Needle tests compacted the aggregate near the top of the sample and possibly may have also caused some other disturbance at the end of the sample the tests were carried out on. It is likely that the opposite end, on which the final Proctor Needle and CBR tests were made, was not affected. This caused the following effects:

- The strength of each sample of untreated aggregate increased 2–3 times during the curing period. It then dropped dramatically following the soaking period. The final strength measurement was 33–50% of the first reading and 15–25% of the maximum reading recorded at the end of the curing period. This suggests that the sample densified with each measurement until it was immersed in water.
- The strength of the cement treated sample, on the other hand, increased rapidly to the extent that it was not possible to push the needle into the sample. Therefore, no densification occurred and the end of the sample suffered little damage.
- The lime and Durabind™ samples have suffered to varying degrees, with the more cemented samples giving more consistent results.

The CBR test provided a range of results that generally met expectations and are considered to be the more reliable, although they are not consistent from one rock type to another. For example, some aggregates (e.g. Otaika) responded better to Durabind™ than to lime.

The change in strength of treated samples during soaking also varied. For example:

- Otaika generally maintained or increased strength,
- Flat Top generally maintained strength,
- Drury generally maintained or slightly decreased strength, and
- Poplar Lane generally increased strength.

The strength of the samples treated with 1% cement all increased substantially on soaking. Generally, the 3% cement samples were beyond the range of the equipment, except for the Poplar Lane sample, which lost strength on soaking.

7 Integration of mineralogical and engineering data

7.1 Composition of samples

The mineralogical studies have confirmed that the fresh greywacke, andesite and basalt contain a proportion of minerals that are highly susceptible to weathering. The basalt has a higher proportion of these minerals, the andesite has slightly less and the greywacke has the least. The partly weathered greywacke, andesite and basalt samples contained a proportion of swelling clays which have been shown previously to be a cause of low strength in pavements.

7.2 Effects of additives

The swelling component of these partly weathered aggregates was significantly reduced by the addition of lime, cement or Durabind™, which led to ion exchange in the interlayer space of the swelling clays, accompanied by the formation of small amounts of hydrogrossular which assisted in cementing the particles together. The decrease in the swelling properties of these clays has been measured using the CI (Methylene Blue Absorption) test. The formation of the hydrogrossular cement is confirmed from XRD analysis.

Treatment with cement promotes different changes in the aggregate than treatment with the predominantly lime based stabilisers. The level of bonding is much stronger. The main products produced during hydration of cement are calcium silicate hydrate ($CaO.2SiO_2.4H_2O$), and calcium hydroxide ($Ca(OH)_2$). However, ettringite or aluminoferrite trisulphate ($C_6AS_3H_{32}$) and monosulphate ($Ca_2(Al,Fe)(OH)_6.X.nH_2O$ (where X is SO_4^{2-}, OH- or another anion)) are also produced. Hydrogrossular may form after a curing period of several years. The ultimate cementing agent is an amorphous silica gel (SiO_2).

In aggregate and soil stabilisation, Portland cement reacts with water to release $Ca(OH)_2$, which can cause cation exchange similar to lime. However, the main effect of cement is to gel the particles together. The cement reaction with water includes the formation of microscopic needles of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$), while amorphous silica gel (SiO_2) may also be a significant cementing agent. Most of these cements have low solubility in water. Therefore even a 3% cement-stabilised pavement will be more resistant to soaking than lime or Durabind™ stabilised pavements.

7.3 Strength and stability

The increase in strength (as evidenced by the engineering tests) is in reasonable agreement with the reduction in swelling (the CI test), but the decrease in strength of some samples after soaking for four days, as measured by the Proctor Needle test, was not expected. The results of the CBR tests, on the other hand, do not show a similar decrease in strength during soaking. It is considered that the CBR results are more reliable than the Proctor Needle results.

The long-term stability of the treated aggregates proved difficult to test using available geological test procedures. In one experiment, finely ground samples of the treated aggregates were immersed in water for up to five days to study the changes that occur. Both pH and CI increased progressively until an equilibrium condition was attained. Also, the rate of return of swelling properties is less if the pH remains above pH 7. The presence of an alkaline material (such as lime or perhaps Durabind™) should ensure that a high pH was maintained to limit the changes that could occur. This experiment indicates that if a stockpile of treated aggregate was exposed to the weather so that water could flow through the aggregate, the swelling properties of the clay minerals may partially return.

Previous literature by Paige-Green (1984) noted that carbonation (the transformation of lime to calcium carbonate) could adversely affect the strength of lime-stabilised pavements. Carbonation was observed in our experiment with a sample of weathered Flat Top aggregate treated with 10% lime. Calcite was also detected in the samples of greywacke treated with 3% lime. However, since vein calcite is present in the untreated greywacke, its significance here is not clear. Further work is needed to evaluate the effects of carbonation.

The results of XRD analysis show that the basalt and andesite samples contained the most smectite minerals (‘common’ to ‘abundant’ levels), while the greywackes had significantly less, being generally in the ‘common’ to ‘minor’ ranges. The addition of lime based materials should be more beneficial on marginal aggregates derived from basalt and andesite rocks than on the greywackes.

8 Conclusions

8.1 The raw materials

- In the four quarries sampled between Whangarei and Tauranga, a significant proportion of partly weathered rock may produce marginal aggregate.
- The partly weathered rocks were composed predominantly of primary minerals, but all rock types (greywacke, andesite and basalt) contained a small proportion of swelling clays.
- The CI (Methylene Blue absorption) test provided a very useful method to determine the amount of swelling clay quantitatively.
- LOI was compared against the CI value. Generally, the CI increased as the LOI increased in the volcanic rocks, but not in one of the greywackes.

8.2 The treated raw materials

- Samples of partly-weathered rock were crushed to AP 4.75 mm and treated with either 1% or 3% of lime, Durabind™ or cement. The treated aggregates were evaluated by various mineralogical and chemical techniques, and their engineering properties were determined.
- The mineralogical tests confirmed the formation of small amounts of hydrogrossular and a decrease in the tendency to swell. However, the kinetics of hydrogrossular formation with the various additives has not been investigated in detail during this study.
- Lime was the most effective chemical for the control of swelling clay minerals.
- The CBR tests confirmed that the treated aggregates increased in strength and had little loss in strength during soaking, if any. Most of the cement-treated samples increased in strength during soaking

8.3 Long term stability of the treated aggregates

- It was not possible to establish the long-term stability of samples of compacted treated aggregate.
- Swelling clay mineral content of ground samples of the treated aggregates increased after soaking for a period of time.
- The tendency to swell was less at higher pH values, but increased when the pH was reduced to <4.
- It is hypothesised that these effects are only relevant to treated aggregate in a loose condition, e.g. in a stockpile.
- Significant carbonation was not detectable in samples treated with 1% or 3% additive. However, carbonation was definitely present in samples treated with 10% of additive.

8.4 Engineering consequences of the study

- Cement is by far the most effective additive for increasing the strength and reducing the effect of water on a marginal aggregate.
- The geological characteristics of the rock determine how it will react to lime-based additives.
- All the lime-based additives had an enduring effect on the strength of the samples. The increase in strength for some of the materials was not large, but the additive generally improved the CBR after soaking.
- Selection of an additive should be based not only on knowledge of the swelling clay content (i.e. CI) of an aggregate but also on its mineralogy.

8.5 Applicability

This project intended to use the skills of chemists and geologists to identify the factors which control ‘weathering’ of stabilised aggregate in a road pavement. This objective has been satisfied to the extent that laboratory tests have demonstrated how the chemical reaction can be reversed to some degree. However, the conditions associated with reversal are unlikely to apply in a compacted pavement except under extreme conditions.

These tests suggest that any significant flow of water through a layer of stabilised material has the potential to reverse the chemical reaction and endanger the stability of the layer. Possible examples are:

- if stockpiling of treated aggregates is considered, then subsequent movement of rainwater through an unconsolidated stockpile could endanger its stabilising properties;
- if a stabilised pavement surface fails, and rainwater or groundwater is allowed to flow through the pavement, then the cements may fail (refer to strength soak tests); and/or
- if an acid groundwater is present around or below the stabilised pavement (perhaps in thermal areas or caused by oxidised pyrite in schists or mineralised areas) then such acid fluids may destabilise the pavement.

However, the density of a compacted stabilised aggregate is normally so high that the permeability probably approaches that of a clayey silt, and any flow of water or air is virtually precluded.

8.6 Limitations

It is acknowledged that this study was constrained by factors including representative sampling, reaction kinetics, and alteration prior to weathering.

Representative sampling.
Although care was taken to obtain representative samples from the quarries, it should be appreciated that sampling such large rock volumes and sizing samples down for laboratory tests has limitations.

Reaction kinetics
It is widely known that cement formation using lime and Portland cement is time related. In Portland cement, for example, hydrogrossular may take months to fully crystallise. In this study, the mineralogical and chemical studies were carried out within one to three months after the engineering testing had been carried out.

Alteration prior to weathering
Poplar Lane andesite and Flat Top basalt may have been subject to hydrothermal alteration, while Drury greywacke has been extensively sheared. Therefore, even the so-called fresh rocks, which are known to meet TNZ M/4 (2000) specifications, contain some alteration minerals (such as zeolites) that were present prior to the present weathering process.

9 References

Bartley, F.G. 2001. Weathering characteristics of modified marginal aggregate. *Transfund New Zealand Research Report No 216. 37pp.*

Bhattacharja, S., Bhatty, J.I., Todres, H.A. 2003. Stabilisation of clay soils by Portland cement or lime – a critical review of literature. *Portland Cement Association Research and Development Information Serial No. 2066*. Portland Cement Association. 60 pp.

Black, P.M., Sameshima, T. 1979. An assessment of basalt and andesite road aggregate resources in the Auckland district. *N.Z. Roading Symposium A4:* 1–4.

Bowen, N.L. 1922. The reaction principle in petrogenesis. *Journal of Geology 30:* 177–198.

Brady, N.C. 1974. *The Nature and Properties of Soils (8th edition)* New York: Macmillan. 639 pp.

Cole, W.F., Sandy, M.J. 1982. The influence of the degree of weathering on hornfels on its physical properties and durability. *Proceedings of the 11th Australian Road Research Board Conference (3):* 80–89.

C89/106/EEC. 2000. *Guide to the implementation of directives based on the new approach.* European Commission.

Fookes, P.G. 1991. Geomaterials. *Geological Society Quarterly Journal of Engineering 24 (01)*: 3–15.

Goldich, S.S. 1938. A study in rock weathering. *Journal of Geology 46:* 17–58.

Helgason, T.S., Fuxen, S. 2002. Testing and conformity assessment of construction aggregates using PM software. *9th Nordic Aggregate Research Conference, Iceland.* 3 pp.

Helgeson, H.C., Brown, T.H., Leeper, R.H. 1969. *Handbook of Theoretical Activity Diagrams Depicting Chemical Equilibria in Geologic Systems Involving an Aqueous Phase at one atm and 0° to 300°C.* San Francisco: Freeman, Cooper & Company. 253 pp.

Hilt, G.H., Davidson, D.T. 1961. Isolation and investigation of a lime-montmorillonite crystalline reaction product. *Bulletin of the Highway Research Board, Washington 304:* 51–64.

Hitching, K.D. 1981. *Investigations into N.Z. Steel Slags.* Unpublished PhD thesis, School of Engineering, University of Auckland.

Hudec, P.P. 1984. Statistical methods of aggregate durability evaluation. *Bulletin of the International Association of Engineering Geology No 29.*

Hudec, P.P. 1989. Durability of rock as function of grain size and rate of capillary absorption of water. *ASCE Materials Engineering Division Vol. 1 No. 1 Feb 1989. 7 pp.*

Hudec, P.P. 1997. Changes in engineering properties of weak and weathered rock with time. Pp 53–71 in *Association of Engineering Geologists Symposium on Characterization of Weak Weathered Rock Masses, Oregon*.

Hudec, P.P. 1998. Rock properties and physical processes of rapid weathering and deterioration. Pp 335–341 in *8th International IAEG Congress. Balkema. Rotterdam.*

Jones, F.O. 1964. New fast accurate test measurement of bentonite drilling mud. *Oil and Gas Journal 1:* 76–78.

Jackson, M.L., Tyler, S.A., Willis, A.L. et al. 1948. Weathering sequence of clay-sized minerals in soils and sediments. *Journal of Physical Chemistry 52:* 1237–1260.

Kline, S.W. 1999. Arkansas resources for crushed-stone construction aggregate. *Contributions to the Geology of Arkansas Volume IV, Arkansas Geological Commission Miscellaneous Publication 18-D.*

NZS 4402. 1986. *Method of Testing Soils for Civil Engineering Purposes.* Standards Association of New Zealand.

NZS 4407. 1991. *Methods of Sampling and Testing Road Aggregates.* Standards Association of New Zealand.

Paige-Green, P. 1984. A laboratory investigation into the influence of carbination on the strength of lime-stabilised materials. Pp 403–406 in *Proceedings of the Eighth Regional Conference for Africa on Soil Mechanics and Foundation Engineering, Harere*.

Phelps, G.W., Harris, D.L. 1968. Specific surface and dry strength by methylene-blue adsorption. *American Ceramic Society Bulletin 47:* 1146–1150.

Sameshima, T. 1983. Chemical stabilisation of roading aggregates – a clay mineralogical approach. *Trans. of the Institution of Professional Engineers New Zealand No 10(2)*: 46–51.

Sameshima, T., Black, P.M. 1979. Clay Index - a simple method of assessing the quality and performance of roading aggregate. *N.Z. Roading Symposium A3:* 1–10.

Sameshima, T., Black, P.M. 1980. Hydrothermal alteration of basecourse aggregates and its effect on basecourse performance. *National Roads Board Pavement Research Project B.C. 23*, 125 pp.

Sameshima, T., Black, P.M., 1982. Stabilization of aggregates with additives and their effects on fines. *National Roads Board Pavement Research Project B.C. 39*. 108 pp.

TNZ B/3. 1999. *Design and Construction of Performance-based Flexible Pavements.* Wellington: Transit New Zealand.
TNZ M/4. 2003. *Specification for Basecourse Aggregate.* Wellington: Transit New Zealand.

Van Aardt, J.H.P., Visser, S. 1977. Calcium hydroxide attack on feldspars and clays: possible relevance to cement-aggregate reactions. *Cement and Concrete Research 7:* 643–648.

Van Aardt, J.H.P., Visser, S. 1978. Reaction of $Ca(OH)_2$ and of $Ca(OH)_2$ + $CaSO_4.2H_2O$ at various temperatures with feldspars in aggregates used for concrete making. *Cement and Concrete Research 8:* 677–682.

Wilson, P. 1999. *KOBM Binder and Durabind™ for successful aggregate modification.* Unpublished report by Stabitec Ltd, Orewa. 35 pp.

Wu, Y., Parker, F., Kandhal, K. 1998. Aggregate toughness/abrasion resistance and durability/soundness tests related to asphalt performance in pavements. *NCAT Report No 98-4 National Cooperative Highway Research Program, United States.* 21 pp.

List of appendices

Appendix A	Photographs
Appendix B	Petrographic analysis
Appendix C	Moisture analyses
Appendix D	Methylene Blue analyses of treated samples
Appendix E	XRD analyses
Appendix F	XRF analyses
Appendix G	Leach water chemical analyses
Appendix H	Engineering tests
Appendix I	Results of tests on manufactured aggregate
Appendix J	Results of Proctor Needle tests
Appendix K	Comparison of CBR and Proctor Needle tests

Appendix A Photographs

One of the authors of this report (A.B. Christie) took the samples and can be seen in these photographs.

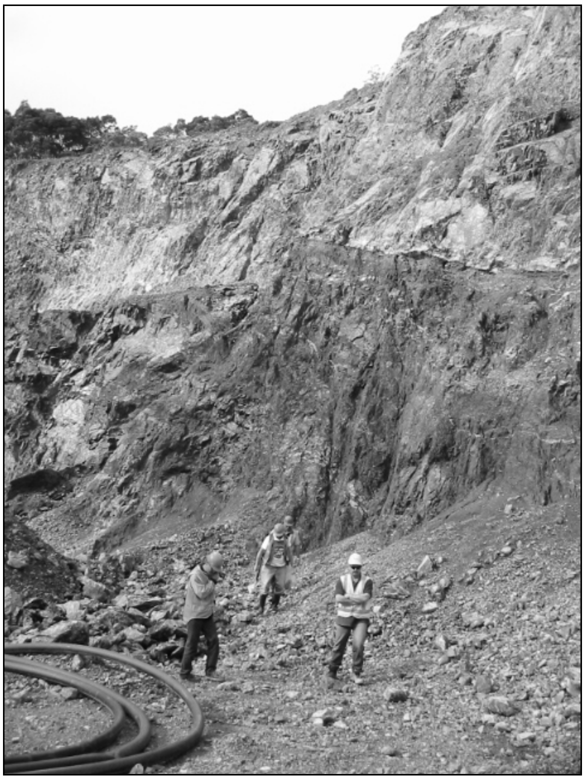

Figure A1 Otaika greywacke quarry: sampling fresh rock on a low bench.

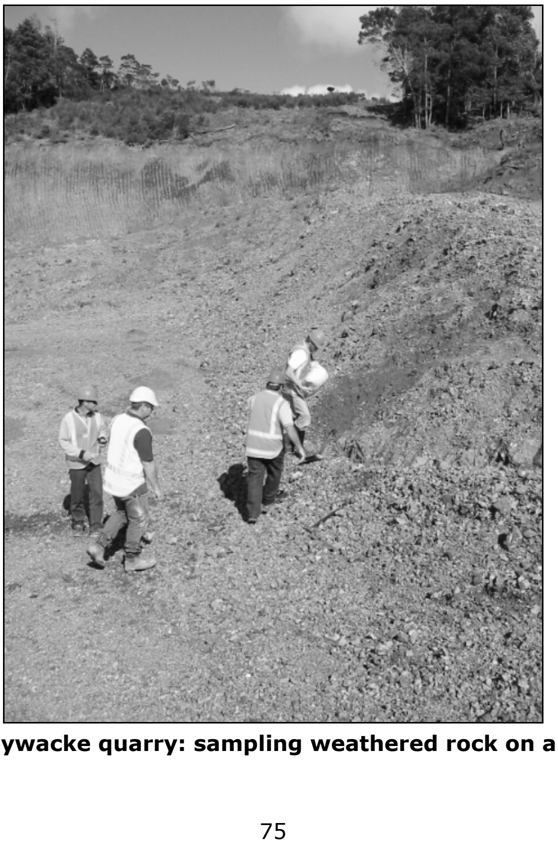

Figure A2 Otaika greywacke quarry: sampling weathered rock on a high bench.

Figure A3 Flat Top basalt quarry: sampling grey partly-weathered rock.

Note: The brown weathered rock (indicated in colour) was also sampled from this location.

Figure A4 Flat Top basalt quarry: sampling grey fresh rock from a boulder stockpile.

Figure A5 Drury greywacke quarry, showing how the rock is strongly jointed and fractured.

Note: the fresh rock (quarry face) samples were taken at the level of the haul road.

Figure A6 Drury greywacke quarry: sampling partly weathered rock.

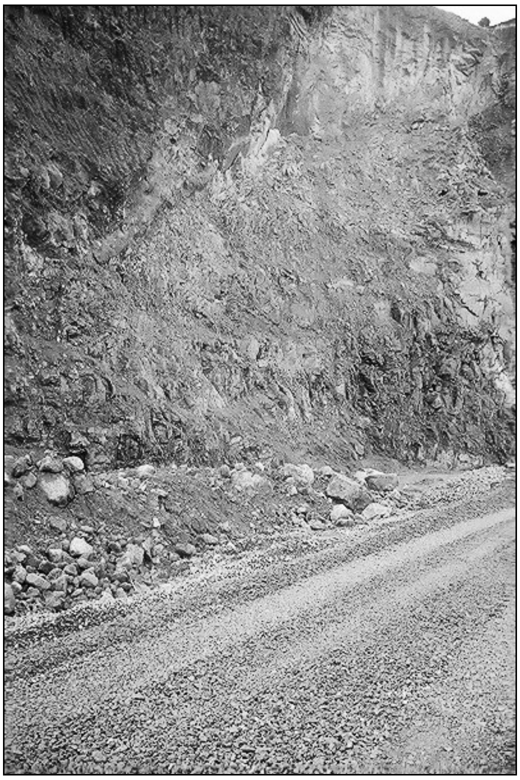

Figure A7 Location of the partly weathered and weathered face samples at the Poplar Lane andesite quarry.

Figure A8 Poplar Lane andesite quarry. The location of the fresh andesite face sample is shown alongside the white sample bags.

Appendix B Petrographic analysis

B1 Otaika greywacke quarry – Q07/277014

B1.1 General comments

All samples from this location were moderately sorted, medium to coarse-grained feldspathic litharenite. The sample number refer to which treatment method the sample was later subject to, as explained in Table B1.

Table B1 Treatment methods and numbering used for the different subsamples.

Sample	Chemical additive	Proportion by weight (%)
1	Natural (no additive)	–
2	Ordinary Portland cement	1
3	Ordinary Portland cement	3
4	Hydrated lime	1
5	Hydrated lime	3
6	Durabind™	1
7	Durabind™	3

B1.2 OT6 P70113 – fresh greywacke

The sample is a clast-filled breccia or conglomerate comprising fragments/clasts of a variety of rocks with different average grain sizes, ranging from argillite to coarse sandstone. The following description is based on two fragments/clasts of the coarsest material because the partly weathered and weathered samples are coarse-grained sandstones.

The coarse-grained sandstone contains detrital grains of quartz, feldspar, rock fragments, lesser clinopyroxene, hornblende, chlorite, muscovite and rare biotite laths, pale yellow epidote and relict tourmaline? in a silt-clay matrix of mica-illite, interlayered illite-smectite and chlorite. The grains of quartz and feldspar, and the rock fragments average 0.3 mm, but range up to 1.2 mm in their longest dimension (feldspar), and are moderately sorted. Quartz makes up about 15% of the greywacke; it is generally clear, but contains dusty trails of fluid inclusions. Feldspar grains are altered to clays (kaolinite? and/or smectite) and are difficult, in places, to distinguish from rock fragments except where they exhibit twinning. Three main types of rock fragments are present, including:

- fragments consisting of a mosaic of fine-grained quartz (mostly recrystallised) and/or mildly altered feldspar crystals;
- mozaics of feldspar, opaques and clay;
- fragments with remnant textures of interlocking, clay-altered feldspar laths (0.08–0.15 mm), characteristic of a trachytic textured volcanic rock?, with some opaques;
- porphyritic volcanics, comprising clay-altered and quartz-altered subhedral plagioclase? pseudomorphs in a groundmass of quartz, chlorite and illite-smectite; and
- well-sorted, tuffaceous-siltstone clasts.

One lithic fragment is cut by a quartz veinlet. Clinopyroxene grains have a non-parallel extinction angle and are high-relief, green, strongly pleochroic, mostly about 015 mm (max 0.22 mm) and are very clear, with no signs of alteration. Chlorite grains (green to brown) were mica grains but they have been altered to chlorite. Chlorite is also present as an alteration product along fractures and some edges of rock fragment and feldspar grains, and in a thin chlorite veinlet cutting the slide. One veinlet is filled with quartz, chlorite and trace amounts of an unidentified carbonate?. Some open spaces are rimmed by low birefringent prehnite, and infilled with pumpellyite?. Rare muscovite and biotite grains, partly altered to chlorite, are also present.

B1.3 OT4(a) P70110 and OT4(b) P70111 – partly weathered greywacke

These samples are lithologically similar to OT6, albeit weathered. Mineralogically, they are similar to OT5 (described below), but coarser (average grain size = 0.6 mm, maximum = 1.8 mm) and subangular to subrounded (some grains are more rounded than OT5). The rock contains quartz fragments with anomalous extinction (up to 0.8 mm diameter) and multiple-twinned plagioclase fragments (up to 1 mm long), as well as other feldspar crystals which have been replaced by quartz, chlorite and weathering products (illite-smectite and/or kaolinite). Overall, the sample exhibits an interlocking grain texture with only a small quantity of matrix. Rock fragments include some consisting of a mosaic of fine recrystallised quartz and/or lesser amounts of altered feldspar; clasts containing clay-altered feldspar laths; and porphyritic volcanics, containing subhedral plagioclase, partly replaced by epidote and quartz in a groundmass of quartz and illite-smectite. Almost no veins were visible, although some lithics may be quartz and/or epidote vein? fragments. The degree of alteration/weathering lies between that of OT6 and OT5.

B1.4 OT5 P70112 - weathered greywacke

The sample is a coarse-grained sandstone, averaging about 0.4–0.5 mm, up to a maximum of 2.5 mm. The slide is a mosaic of tightly packed, subrounded-subangular grains with only a very small quantity of fine matrix, resulting in a moderately to well sorted texture (much better sorted than OT6). It is criss-crossed with veinlets of quartz, typically 0.02–0.06 mm wide – but up to 0.1 mm wide – and, less commonly, quartz plus epidote or chlorite, and pumpellyite?, whilst other veinlets contain quartz plus prismatic clinozoisite?. Quartz grains (10% of slide) are prominent because of the contrast of their clear appearance compared with the alteration of the other grains. Some quartz grains have secondary quartz overgrowths. Feldspars are strongly altered to clay and are albitised elsewhere, making them difficult to identify, although a few subhedral twinned grains are present. Rare biotite is evident. Rock fragment types are similar to those of OT6 although additional mudstone fragments can be seen. All are very altered by weathering. The slide contains a strongly altered weathering rind represented by:

- yellow-brown staining of feldspar and rock fragment grains (particularly grain boundaries),
- matrix,
- veins (very dark brown), and
- fine fractures near the veins.

XRD analyses indicate that the clay alteration products are smectite and kaolinite. An unidentified brown carbonate (siderite?) is noted.

B2 Flat Top basalt quarry – Q10/496111

B2.1 General

All these samples were fine-grained basalts. The numbering system is the same as the one used for the Otaika samples (see Table B1).

B2.2 FT7 P70106 – fresh basalt

The sample is a fine-grained hypidiomorphic granular consisting of interlocking crystals of plagioclase, clinopyroxene and opaque iron oxides in a fine-grained groundmass of weathered plagioclase laths, pyroxene, and weathering and alteration products (clay, pyrite). The porphyritic texture in this rock is poorly developed. Plagioclase crystals (comprising ~65% of the rock) are euhedral to subhedral, and average 0.4 mm long with a maximum size of 1.1 mm, with smectite infilling their cleavage cracks. Clinopyroxene (augite, 20–25%) crystals range in size between 0.1 and 0.5 mm, with an average size of 0.16 mm. An unidentified brown material (a mixture of smectite and chlorite) comprises about 10% of the slide. Opaques (3–4%) are 0.06–0.3 mm.

The basalt has been hydrothermally altered. The slide is transgressed by veinlets (<1 mm wide) of quartz and zeolite (<5% of the rock). In places, the zeolite is colourless and has a tabular morphology (chabazite?), whereas other zeolite crystals infilling open spaces have a different appearance, as they are brown and have a fibrous, radiating habit. The plagioclase crystals are fractured and partly altered or weathered to smectite clays (identified by XRD), resulting in a brownish stained appearance, with iron oxides lining the fracture surfaces.

B2.3 FT1 P70103 – partly weathered basalt

The sample is finer-grained than FT7 and is porphyritic. For example, the slide showed two size populations of subhedral to euhderal plagioclase, comprising equant or rectangular phenocrysts (5% of the slide), typically 0.8–1.0 mm in size, and an equigranular, asicular crystalline matrix of crystals averaging 0.3 mm and up to 0.6 mm in size. Clinopyroxene crystals range in size between 0.01 mm and 0.8 mm, and average 0.2 mm long.

Brown clay makes up a significant part of the slide and may be an alteration product of volcanic glass, generally being interstitial to plagioclase and pyroxene crystals. The groundmass also includes minor amounts of opaques (mostly pyrite, but less abundantly than in FT7). The slide is cut by veins filled with brown, fibrous zeolite, and zeolite also fills vesicles and lines cavities. In some cavities, the zeolite is colourless and has a lenticular habit (chabazite?). The XRD analysis indicates that the clay is mostly smectite, with smaller quantities of halloysite and kaolinite. A fracture in the rock is partly filled with calcite and a smaller amount of quartz.

B2.4 FT2 P70104 – partly weathered basalt

A similar porphyritic texture to FT1 is seen in this sample, with rectangular plagioclase phencrysts (5–8% of slide), typically 0.4–0.8 mm in size, in a groundmass of asicular plagioclase crystals (40–50% of slide), mostly 0.2–0.3 mm in size but ranging up to 0.6 mm. Pyroxene (augite) crystals (comprising ~5% of the slide) are euhedral and 0.2–0.5 mm in size. Scattered opaques (4–5% of slide) are 0.02–0.08 mm and average 0.04 mm. Approximately 25–30% of the slide is brown clay and fibrous, radiating zeolite, probably altered volcanic glass. Pyrite is present as veinlets of interlocking grains and as disseminations. The XRD analysis indicates that the clay is mostly smectite, with a smaller amount of kaolinite. Part of the slide has a yellowish-brown iron stain.

B2.5 FT3 P70105 – weathered basalt FT3

This basalt is porphyritic with phenocrysts (15%) of plagioclase, clinopyroxene and opaques in a very altered groundmass of zeolite (translucent, rhombic-shaped chabazite?), brown clay (smectite), chlorite, pyrite and remnant ascicular plagioclase crystals. The slide is traversed by many veinlets of brown fibrous zeolite, rimmed by opaques in places. Plagioclase phenocrysts are generally elongate, 0.1–0.6 mm in size and averaging about 0.3 mm. Pyroxene (augite) phenocrysts are 0.2–1.0 mm, averaging 0.3–0.4 mm, which are partly replaced by chlorite and opaques. The opaque phenocrysts are 0.04–0.23 mm in size and are skeletal aggregates?. The XRD analysis indicates that the groundmass and phenocryst-altering clay is predominantly smectite. Some fractures are filled by iron oxides.

B3 Drury greywacke quarry – R12/869506

B3.1 General

These samples were all very fine-grained feldspathic litharenites. The samples are numbered following Table B1.

B3.2 D1 P70107 – fresh greywacke

This sample is a well sorted, very fine-grained greywacke containing detrital grains of quartz, feldspar, rock fragments, chlorite and opaque iron/titanium oxides in a silt-clay matrix of mica-illite, interlayered illite-smectite and chlorite. The matrix also includes small relict biotite, pleochoric green tourmaline? and zircon? crystal fragments. The average grain size is about 0.08 mm in a coarse-grained part of the slide, but reduces to much smaller in some parts, suggesting grading and banding. The coarsely-grained parts are richer in quartz and feldspar. The grains are angular-subangular and well sorted. Clearish quartz and twinned, anhedral feldspar make up approximately 25% of the slide. Most of the remaining portion of the slide consists of clay-rich rock fragments and illite-sericite altered feldspar grains, and a matrix that is difficult to distinguish. The greenish to brownish detrital chlorite is subhedral to anhedral.

Rare isolated coarse grains of pyrite are present, and consist of a few large grains, one angular 3 x 3 mm grain, and two of about 1 x 1 mm, and another few smaller grains.

The slide is transgressed by thin (up to 0.12 mm wide) veinlets containing microcrystalline quartz, along with one or more of carbonate (calcite), prehnite and chlorite, cut by later cracks filled with low birefrinent clay and iron oxides.

The XRD analysis indicates that the main clay mineral developed by weathering is kaolinite.

B3.3 D5 P70109 – partly weathered greywacke

This slide is similar to the coarse-grained parts of D1, and quartz and feldspar are more prominent because of their clarity, although the degree of weathering evident here is much stronger than in D1. The average grain size of quartz, feldspar and rock fragments is approximately 0.08 mm, with a longest dimension in a quartz grain of 0.32 mm. Twinned plagioclase crystal fragments are up to 0.2 mm long, with most partly replaced by chlorite and quartz. Relict hornblende, biotite, zircon and rutile crystal fragments are evident.

Opaques are more prominent than in D1 and comprise 5% of the slide. The opaque grains are 0.02–0.05 mm in size, but aggregates up to 0.12 mm wide x 1.0 mm long are present. About 1% of the rock? comprises pyrite grains.

Quartz, prehnite and chlorite veinlets are common and range in size from 0.02 to 0.12 mm wide. Some (indistinguishable) rock fragments are completely replaced by chlorite. The XRD analysis, however, indicates that the main clay mineral developed by weathering in the partly weathered greywacke is kaolinite.

B3.4 D3 P70108 – weathered greywacke

The XRD analysis indicates that the main clay minerals developed by weathering are smectite and kaolinite. Some of the constituent plagioclase crystal fragments in this rock are partly replaced by mica/clay and quartz. Pyrite is very rare and occurs as tiny isolated grains. Most has probably been weathered to goethite, which also extends from cracks into the host rock. In places, voids? in the weathered rock are lined by quartz and filled by opaques.

B4 Poplar Lane andesite quarry – U14/992792

B4.1 General

The samples from the Poplar Lane quarry were glomeroporphyritic andesites. They are numbered according to Table B1.

B4.2 PL1 P70114 – fresh andesite

This sample consists of glomeroporphyritic andesite with phenocrysts and aggregates in a fine-grained groundmass of microlites (no glass). About 40% of the sample consists of phenocrysts and 60% consists of groundmass microlites. The largest aggregate of the phenocrysts is 6 mm in diameter. Textures are sub-pilotaxitic to sub-trachytic.

The groundmass microlites are composed of about 70% euhedral plagioclase averaging 0.07 mm in size, 20% consists of brownish and greenish–yellow anhedral orthopyroxene, and 10% consists of anhedral opaque iron oxides (0.005–0.03 mm) which are present as individual grains rather than aggregates.

Plagioclase phenocrysts (22% of slide) are subhedral (one almost euhedral), zoned, twinned and average 0.6 mm in size, with a maximum of 3 mm, and contain abundant fluid inclusions (liquid and vapour), up to 0.02 mm in diameter. Orthopyroxene phenocrysts (hypersthene?, 15% of slide) are anhedral, strongly fractured and average 0.4 mm in size, with a maximum size of 1.2 mm. Two main crystal shapes are evident: equant and elongate (fractures cross-wise). The pleochroic is pale green to pale brownish-yellow when parallel to polarisers, but in between, the interference colours show through, giving purplish and bluish colours. The phenocrysts exhibit parallel extinction under crossed polarisers. Some crystals contain abundant fluid inclusions (liquid and vapour), up to 0.03 mm in diameter. Opaque iron/titanium oxides (about 3% of slide) average 0.1 mm in size, with a maximum size of 0.2 mm, and with parts of the groundmass being iron-stained.

The plagioclase phenocrysts are mostly fresh, although some yellow staining is present as irregular patches in some crystals, and glomeroporphyritic masses have been invaded by clay (smectite). The slide has a series of <0.5 mm wide sinuous fractures spaced 3–5 mm apart. The fractures are developed in the groundmass and partly filled with low birfringent clay, with the adjacent plagioclase microlites stained yellow-brown.

B4.3 PL2 P70115 – partly weathered andesite

The andesite is similar to PL1, but slightly finer grained, and the glomeroporphyritic texture is partly masked by the effects of weathering. Some of the fractures are more obvious with the naked eye, and one edge of the slide is stained yellow-brown over 5 mm depth into the slide from the edge.

Plagioclase pheocrysts (comprising about 20% of the rock) are strongly altered. Patches of plagioclase remain, but most of the sample is now an even grey colour under crossed polarisers, with a loss of twinning and zoning textures. The phenocrysts are fractures and invaded by clay (smectite, plus a smaller amount of kaolinite?) replacing cores and patches, with some albitisation.

Pyroxene phenocrysts in some glomeroporphyritic aggregates are altered to clay, chlorite and pyrite, whereas isolated phenocrysts are generally fresh.

Fractures crossing the slide are better developed than in PL1, with yellow staining developing into goethite. In some parts, opaques are concentrated within and beside the fractures.

The main differences between PL2 and PL1 are:

- more obvious yellow stained fractures, plus developing goethite and concentrations of opaques along the fractures;
- a large number of new fractures invaded by clays;
- the alteration of plagioclase, with almost complete replacement by clays; and
- a very moderate alteration of pyroxene (only in glomeroporphyritic aggregates?).

The XRD analysis indicates that the clay is mostly smectite with smaller amounts of halloysite and kaolinite.

B4.4 PL3 P70116 – weathered andesite

This is very similar to PL2, but possibly slightly more altered. However, some pyroxenes, despite containing opaque inclusions, are still fresh. Plagioclase phenocrysts are up to 1.5 mm long, with most having altered cores. In patches, the andesite contains strongly flow-aligned plagioclase crystals. Like that of PL2, the XRD analysis of PL3 indicates that the clay is mostly smectite with lesser amounts of halloysite and kaolinite. The section contains a quartz veinlet with opaques.

Appendix C Moisture analyses

Table C1: Moisture analyses determined for samples after they had undergone engineering tests.

Quarry	Sample Type	GNS Lab#	Wet weight (g)	Dry weight (g)	Water weight (g)	% Water/ wet sample weight (g)	% Water/ dry sample weight (g)
Otaika	Natural	TFOQ-1	1302.5	1198.2	104.3	8.7	8.0
	Lime 1%	TFOQ-2	1437.7	1275.5	162.2	12.7	11.3
	Cement 1%	TFOQ-3	826.7	745.4	81.3	10.9	9.8
	Durabind™ 1%	TFOQ-4	1124.5	992.5	132	13.3	11.7
	Lime 3%	TFOQ-5	2670.9	2343.6	327.3	14.0	12.3
	Cement 3%	TFOQ-6	2083	1914.5	168.5	8.8	8.1
	Durabind™ 3%	TFOQ-7	2800.7	2513.1	287.6	11.4	10.3
Flat Top	Natural	TFFTQ-1	1133.8	994.1	139.7	14.1	12.3
	Lime 1%	TFFTQ-2	1249.7	1056.2	193.5	18.3	15.5
	Cement 1%	TFFTQ-3	1553.5	1362	191.5	14.1	12.3
	Durabind™ 1%	TFFTQ-4	1052.6	901	151.6	16.8	14.4
	Lime 3%	TFFTQ-5	2525.7	2131.5	394.2	18.5	15.6
	Cement 3%	TFFTQ-6	2544.5	2246	298.5	13.3	11.7
	Durabind™ 3%	TFFTQ-7	2362.3	2019.2	343.1	17.0	14.5
Drury	Natural	TFDQ-1	1048.8	991.2	57.6	5.8	5.5
	Lime 1%	TFDQ-2	1281.5	1151.5	130	11.3	10.1
	Cement 1%	TFDQ-3	1780.7	1640.2	140.5	8.6	7.9
	Durabind™ 1%	TFDQ-4	858.6	774.7	83.9	10.8	9.8
	Lime 3%	TFDQ-5	2631	2374.2	256.8	10.8	9.8
	Cement 3%	TFDQ-6	2616.6	2437.1	179.5	7.4	6.9
	Durabind™ 3%	TFDQ-7	2382.6	2152	230.6	10.7	9.7
Poplar Lane	Natural	TFPLQ-1	834.2	753.9	80.3	10.7	9.6
	Lime 1%	TFPLQ-2	1793.3	1599	194.3	12.2	10.8
	Cement 1%	TFPLQ-3	1735.1	1540.6	194.5	12.6	11.2
	Durabind™ 1%	TFPLQ-4	741.4	660.1	81.3	12.3	11.0
	Lime 3%	TFPLQ-5	2518.3	2175.3	343	15.8	13.6
	Cement 3%	TFPLQ-6	2935.4	2633	302.4	11.5	10.3
	Durabind™ 3%	TFPLQ-7	2520.9	2237.8	283.1	12.7	11.2

Appendix D Methylene Blue analyses of treated samples

D1 Graphs

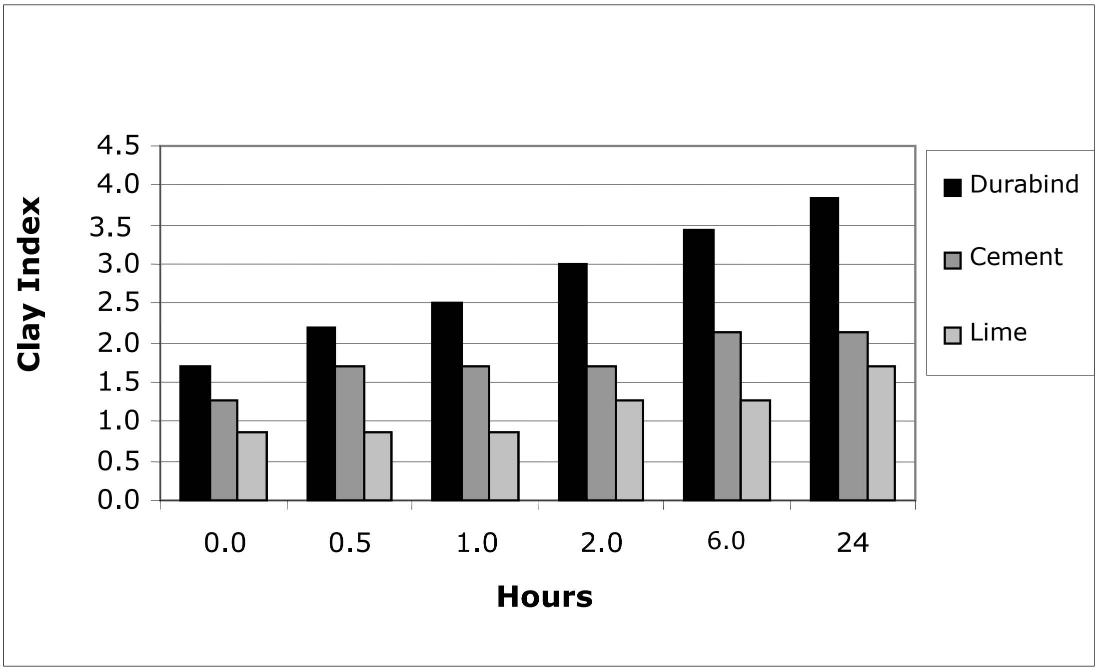

Figure D1 Methylene Blue analysis of how the CI of samples from Poplar Lane, treated with different chemicals, changed over time.

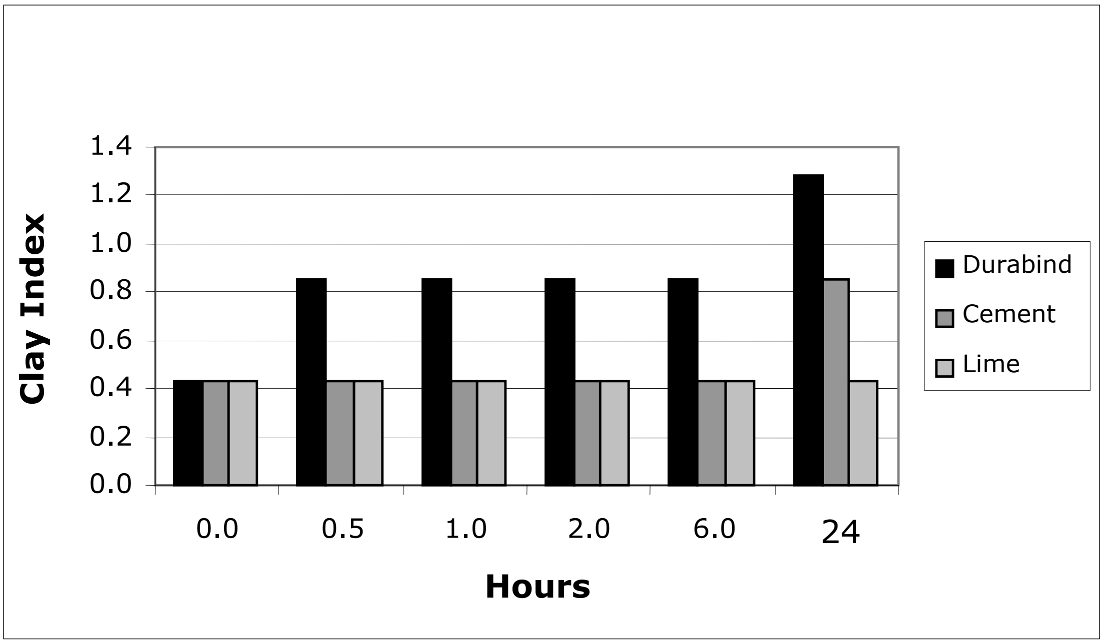

Figure D2 Methylene Blue analysis of how the CI of samples from Drury, treated with different chemicals, changed over time.

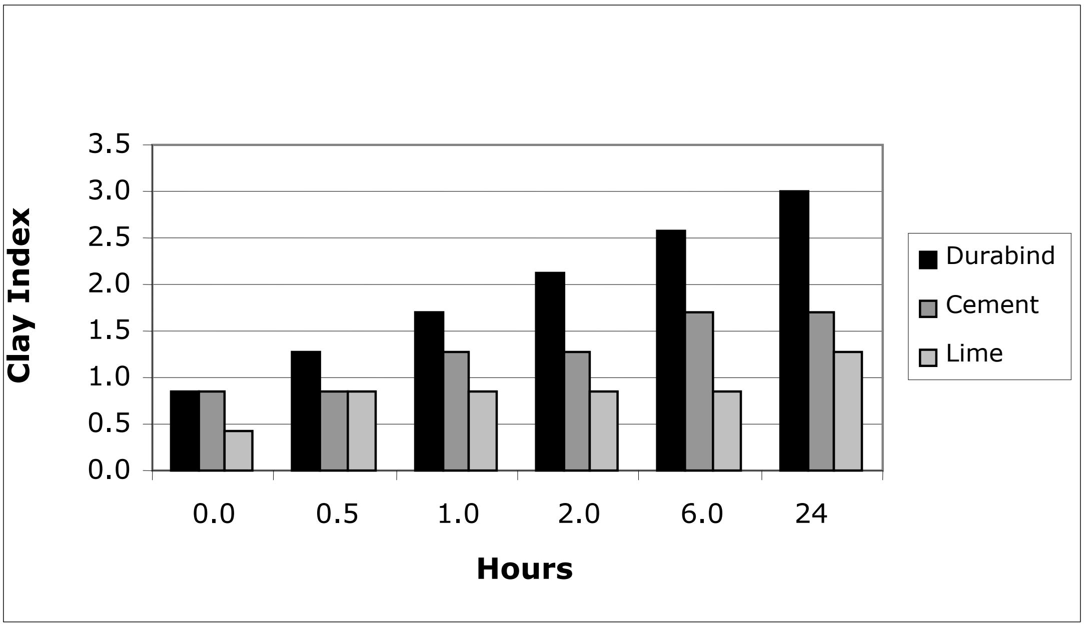

Figure D3 Methylene Blue analysis of how the CI of samples from Flat Top, treated with different chemicals, changed over time.

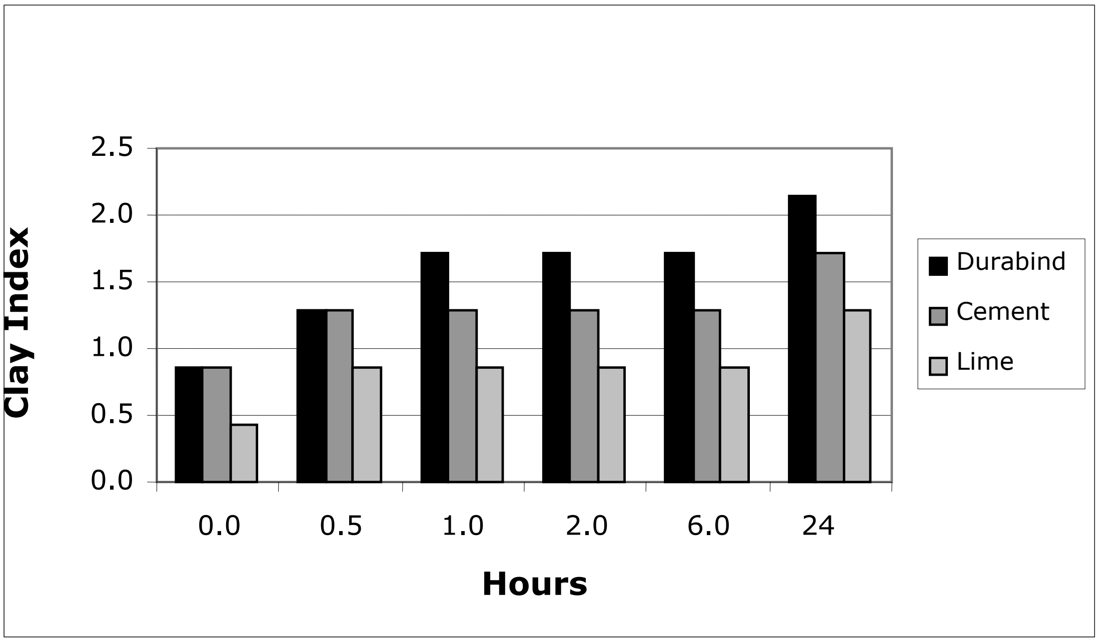

Figure D4 Methylene Blue analysis of how the CI of samples from Otaika, treated with different chemicals, changed over time.

D2 Effect of an acid environment on CI

In order to test the effect of a low (acid) pH on the stabilised samples, a sample of the 3% Durabind™ Flat Top sample was suspended for a Methylene Blue titration and then the pH was adjusted with dilute sulphuric acid.

The initial low CI (<0.5) of the treated sample showed a progressive increase as the pH was reduced. The data are summarised in Table D1 below:

Table D1 CI values for partly weathered Flat Top basalt subjected to acid and treated with 3% Durabind™.

Partly weathered Flat Top + 3% Durabind™		
Description	**Treated pH**	**Treated CI**
Initial pH after Methylene Blue added	pH 6.2	<0.5
Drops of H_2SO_4 added and left to react for 30 min	Initial pH 2.2 increased to pH 7	0.75
Left to react for 3 hrs	pH 9.2	1.5
Left to react for 24 hrs	pH 9.6	1.5
Reduced pH for 1 hr	pH 4	2.0
Held pH 4 for 4 hrs	pH 4	2.5

D3 Discussion:

When the treated samples were ground and in contact with water, the initial addition of the dilute H_2SO_4 resulted in an initial drop in pH accompanied by a small increase in the CI. After a few minutes, the unreacted lime in the Durabind™ caused the pH to gradually increase and the CI to remain stable (at CI 1.5). After 24 hours, the CI did not increase any further and it remained at 1.5.

When the pH was lowered to pH 4 for one hour, the CI increased to 2.0. When the pH was held at 4 for a further four hours, the CI increased to 2.5.

Appendix E XRD analyses

E1 Visual representations

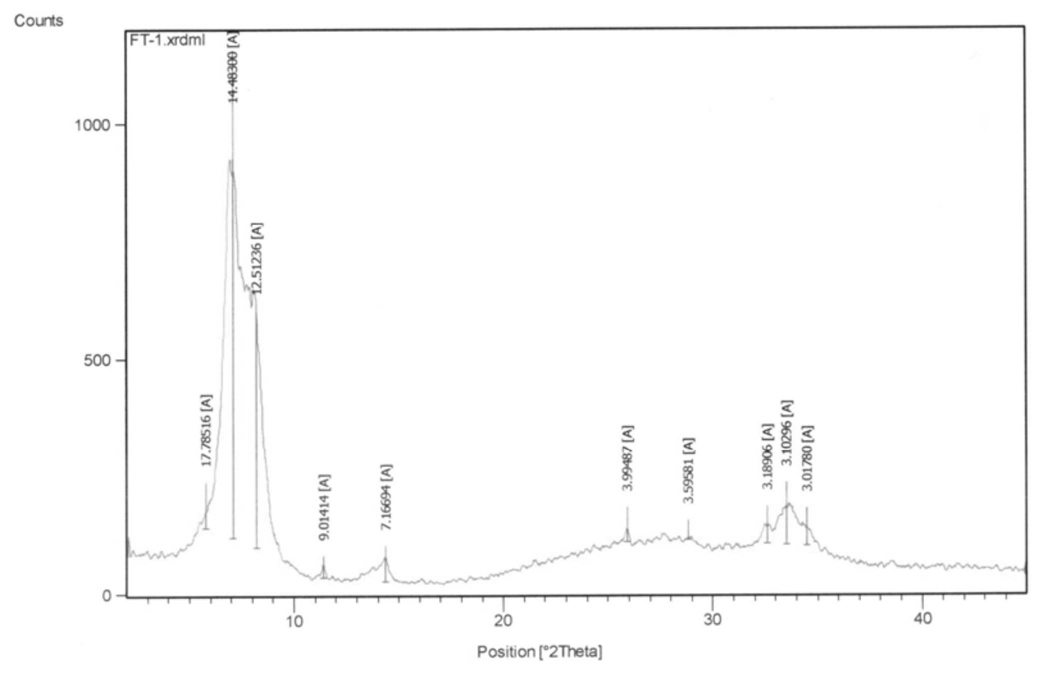

Figure E1 XRD trace for Flat Top partly weathered basalt sample FT-1 air dried.

Note: peaks are:

- 17.9= smectite,
- 15.5= Na, Ca-smectite,
- 12.7= Na-smectite,
- 9.0= smectite,
- 7.2= kaolinite/halloysite/chlorite,
- 4.0= zeolite;
- 3.6=kaolinite/halloysite,
- 3.2= feldspar, and
- 3.1 and 3.0= smectite).

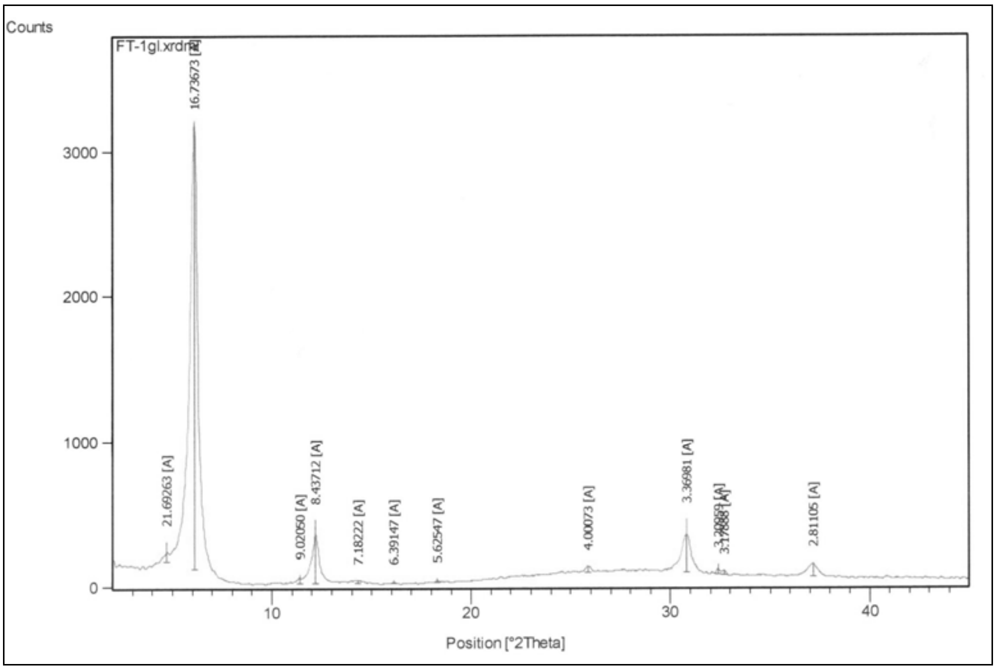

Figure E2 XRD trace for Flat Top partly weathered basalt sample FT-1 glycolated.

Note: peaks are:

- 21.7= smectite,
- 16.8= Na, Ca-smectite and Na-smectite,
- 9.0= zeolite,
- 8.4= smectite,
- 7.2= kaolinite/halloysite,
- 6.4= feldspar,
- 5.6= smectite,
- 4.0= zeolite,
- 3.4= smectite,
- 3.2= feldspar (2), and
- 2.8= smectite.

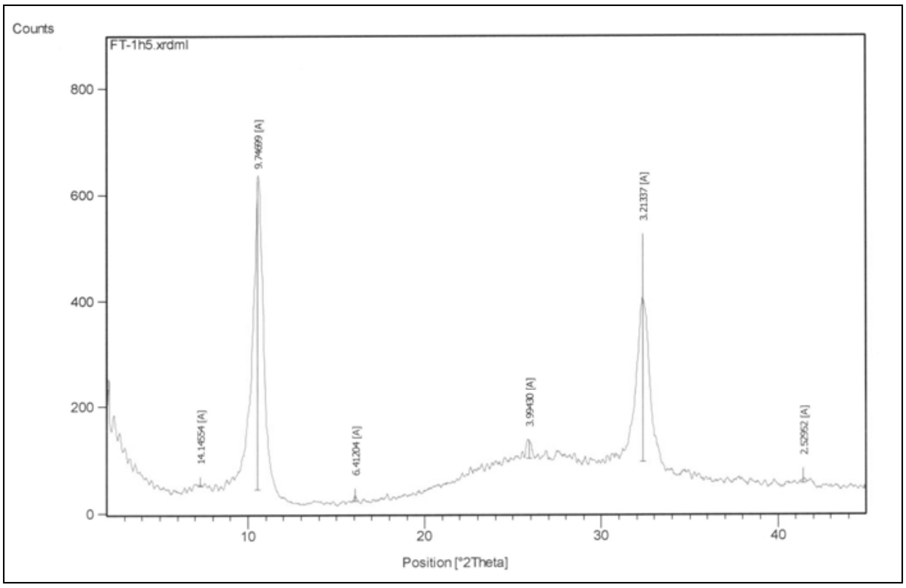

Figure E3 XRD trace for Flat Top partly weathered basalt FT-1 heated to 550°C for two hours.

Note: peaks are:

- 9.7= smectite collapsed,
- 7.2= kaolinite/halloysite, and
- 6.4= feldspar.

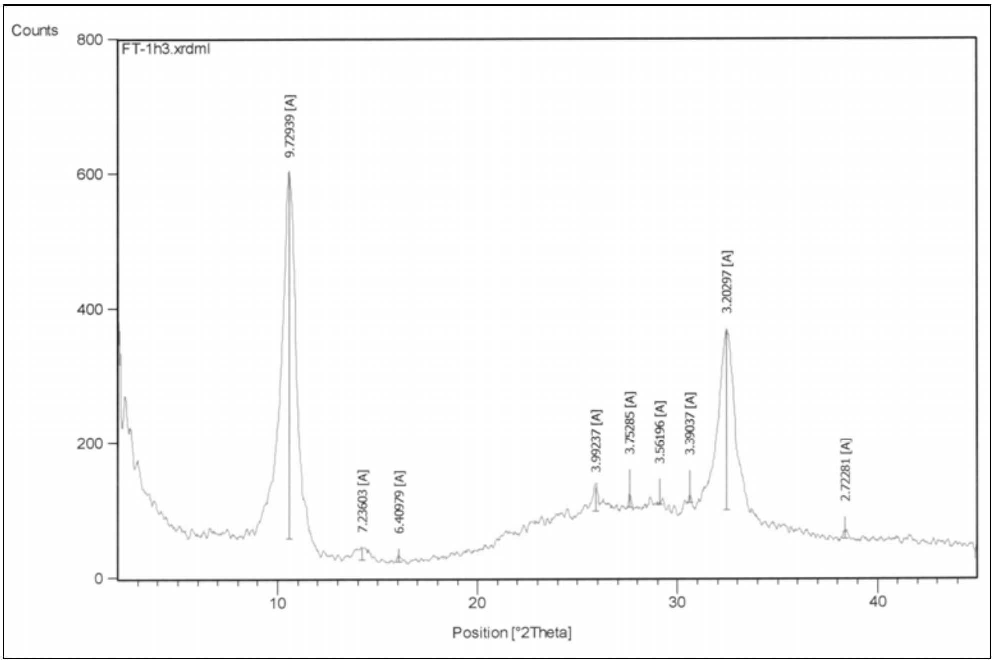

Figure E4 XRD trace for Flat Top partly weathered basalt FT-1 heated to 550°C for two hours.

Note: peaks are:

- 14.1= chlorite,
- 9.7= smectite (collapsed), and
- 6.4= feldspar.

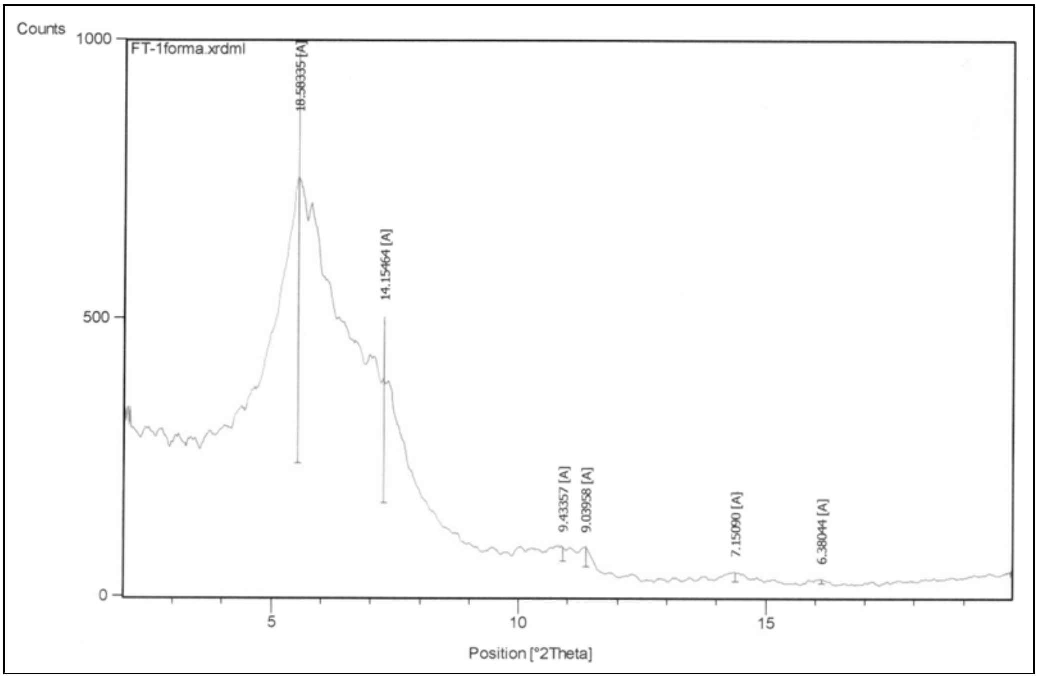

Figure E5 XRD trace for sample FT-1 treated with formamide.

Note: peaks are:

- 18.6= smectite,
- 14.2= chlorite,
- 9.5= halloysite,
- 9.1= zeolite,
- 7.2= kaolinite, and
- 6.4= feldspar.

Appendix F XRF analyses

Table F1 Major oxide element analyses by XRF of untreated quarry face rocks (%).

	Sample number													
	OT6 F (P70113)	OT4a PW (P7110)	OT4b PW (P70111)	OT5 W (P70112)	FT7 F (P70106)	FT1 PW (P70103)	FT2 PW (P70104)	FT3 W (P70105)	D1 F (P70107)	D5 PW (P70109)	D3 W (P70108)	PL1 F (P70114)	PL3 PW (P70116)	PL2 W (P70115)
Major oxides														
SiO_2	61.78	65.39	65.44	65.03	53.56	50.59	50.99	53.81	59.56	60.14	61.85	61.65	62.09	61.50
Al_2O_3	16.78	15.92	15.72	15.12	14.89	15.97	15.60	15.45	16.40	17.23	17.11	16.47	17.44	17.14
Fe_2O_3	6.38	5.15	4.82	5.60	12.83	16.17	12.40	11.59	7.67	5.95	5.94	6.98	7.19	7.59
MnO	0.10	0.07	0.08	0.09	0.18	0.21	0.22	0.19	0.08	0.10	0.08	0.15	0.08	0.12
MgO	2.50	0.69	1.53	1.28	4.02	4.57	4.19	3.10	2.16	2.49	1.74	2.37	1.53	1.64
CaO	1.99	1.38	1.71	1.91	7.79	8.66	8.65	6.34	3.15	3.54	2.37	5.71	2.69	3.03
Na_2O	4.42	4.32	4.69	4.23	3.66	3.29	3.37	3.00	2.92	3.42	3.77	3.34	2.66	2.73
K_2O	3.35	3.48	3.12	3.20	0.52	0.37	0.76	0.73	3.74	3.28	3.31	1.91	2.01	1.96
TiO_2	0.75	0.84	0.84	.081	1.31	1.42	1.37	1.29	0.76	0.75	0.71.	0.80	0.87	0.87
P_2O_5	0.16	0.16	0.15	0.16	0.13	0.14	0.13	0.10	0.17	0.16	0.15	0.16	.015	0.15
LOI	2.10	2.23	1.67	2.29	0.85	1.35	2.04	4.04	3.26	2.87	2.74	0.44	3.26	3.02
Total	**99.84**	**99.63**	**99.76**	**99.72**	**99.73**	**99.75**	**99.72**	**99.64**	**99.88**	**99.92**	**99.77**	**99.97**	**99.96**	**99.75**
Trace elements														
F	<0.01	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	0.01	<0.01	<0.01	<0.01	0.04	0.08	0.06	<0.01	0.62	0.23	<0.01	<0.01	<0.01	<0.01
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table F2 **Trace element analyses by XRF for a range of samples from all quarries.**

Element (ppm*)	**Sample number**												
	OT6 F (P70113)	OT4a PW (P7110)	OT4b PW (P70111)	OT5 W (P70112)	FT7 F (P70106)	FT1 PW (P70103)	FT2 PW (P70104)	FT3 W (P70105)	D1 F (P70107)	D5 PW (P70109)	D3 W (P70108)	PL1 F (P70114)	PL3 PW (P70116)
As	8	6	6	7	<1	<1	<1	<1	41	5	5	1	<1
Ba	813	828	519	438	<1	<1	<1	<1	1294	681	989	509	551
Ce	49	52	54	74	23	25	20	15	75	63	65	35	31
Cr	52	36	35	30	<1	<1	<1	3	41	45	51	11	10
Cs	<1	<1	<1	8	<1	<1	<1	<1	13	6	7	8	<1
Cu	28	24	26	15	56	57	57	57	26	22	28	13	23
Ga	20	18	18	18	18	19	19	18	19	18	18	19	20
La	17	17	19	17	11	<1	<1	<1	28	19	26	16	18
Nb	8	9	9	9	<1	<1	<1	<1	10	10	9	6	6
Ni	22	14	16	18	8	12	10	10	26	16	21	7	8
Pb	16	15	14	17	5	4	3	2	39	20	20	17	20
Rb	107	103	99	104	5	6	7	8	134	135	111	66	76
Sc	17	13	16	14	32	34	33	31	16	15	15	25	23
Sr	356	361	343	335	150	175	177	369	421	407	487	269	176
Th	10	8	9	6	4	2	2	<1	12	12	11	6	8
U	4	2	3	<1	4	<1	<1	<1	4	5	3	1	3
V	133	141	127	105	417	405	387	362	109	115	121	139	115
Y	28	22	25	25	33	33	33	33	29	27	26	24	23
Zn	85	68	93	87	83	93	106	88	95	92	92	68	81
Zr	168	213	211	228	87	86	84	73	196	214	210	145	158

* parts per million

Appendix G Leach water chemical analyses

Table G1 Variation of pH with time in reactions of untreated samples with water leaches.

Date			4/11/03	7/11/03	12/11/03	20/12/03	16/01/04	16/02/04	9/03/04	6/04/04	20/04/04
Day			1	4	9	46	74	106	128	155	201
Solution temperature (°C)			21.5	21.5	23	24.5	25	23.5	22.5	21.4	20.8
Site & Lithology	**Weathering status**	**Field No.**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**	**pH**
Otaika greywacke	F	OT-6	9.5	7.96	8.1	8	7.88	7.88	8.01	8.3	8
	PW	OT-4a	7.49	6.84	8.9	6.87	6.75	6.75	6.95	6.86	6.96
	PW	OT-4b	8.47	7.29	7.37	7.31	7.11	7.11	7.53	7.49	7.26
	W	OT-5	9.95	8.28	8.4	8.3	8.01	8.01	8.42	8.52	8.38
Flat Top basalt	F	FT-7	10.13	8.33	8.32	8.2	8.28	8.28	8.27	8.24	8.16
	PW	FT-1	9.24	8.08	8.12	8.04	7.89	7.89	8.04	8.13	7.96
	PW	FT-2	9.81	8.25	8.31	8.21	8.18	8.18	8.2	8.15	8.1
	W	FT-3	8.49	7.39	7.4	7.45	7.6	7.6	7.54	7.6	7.83
Drury greywacke	F	D-1	9.83	8.5	8.4	8.08	7.82	7.82	8.16	8.2	8.11
	PW	D-5	8.61	7.47	7.45	7.41	7.09	7.09	7.25	7.4	7.07
	W	D-3	8.53	7.88	7.91	7.43	6.81	6.81	7.49	7.38	7.25
Poplar Lane andesite	F	PL-1	8.87	7.47	7.52	7.47	7.19	7.19	7.58	7.51	7.41
	PW	PL-3	8.29	7.32	7.15	7.05	7	7	7.28	7.2	7.29
	W	PL-2	8.19	7.31	7.22	7.19	7.24	7.24	7.35	7.23	7.17

Notes:
- F = fresh
- PW = partly weathered
- W = weathered

See Tables G2–G5 for chemistry of the water leaches at the end of the experiments.

Table G2 Chemical analyses of water leaches from weathering experiments on untreated samples of Otaika greywacke.

Weathering	Fresh	Partly weathered	Partly weathered	Weathered
Field ID	OT6	OT4a	OT4b	OT5
Lab No.	2400765	2400762	2400763	2400764
Ph	7.62	6.32	6.70	8.10
Analysis temperature (°C)	24	23	21	24
HCO_3/date analysed	03/05/04	03/05/04	03/04/05	03/05/04
Element/Compound (in mg/L)				
Bicarbonate (total)	54	40	74	87
Aluminium	0.16	<0.1	0.11	0.14
Calcium	9.1	0.59	1.3	19.9
Chloride	0.56	1.6	0.74	0.68
Iron	<0.02	<0.02	<0.02	<0.02
Magnesium	1.2	0.17	0.74	1.3
Manganese	0.010	0.010	0.011	<0.005
Potassium	2.2	0.82	1.7	1.1
Rubidium	<0.01	<0.01	<0.01	<0.01
Silica (as SiO_2)	10.6	16.5	13.2	9.2
Sodium	2.0	1.3	1.4	0.52
Strontium	0.038	0.007	0.013	0.07
Sulphate	2.0	2.5	2.7	0.29

Table G3 Chemical analyses of water leaches from weathering experiments on untreated samples of Flat Top basalt.

Weathering	Fresh	Partly weathered	Partly weathered	Weathered
Field ID	FT7	FT	FT	FT3
Lab No.	2400761	2400758	2400759	240060
Ph	7.93	7.56	7.65	6.85
Analysis temperature (°C)	22	21	21	20
HCO_3/date analysed	03/05/04	29/04/04	29/04/04	29/04/04
Element/compound (in mg/L)				
Bicarbonate (total)	71	59	98	42
Aluminium	0.25	0.14	0.21	0.10
Calcium	0.11	13.1	20	0.50
Chloride	0.45	0.93	0.84	0.74
Iron	0.49	<0.02	<0.02	0.18
Magnesium	0.15	2.7	3.4	0.42
Manganese	0.006	0.044	0.13	0.005
Potassium	0.09	0.68	0.37	0.06
Rubidium	<0.01	<0.01	<0.01	<0.01
Silica (as SiO_2)	19.3	15.1	13.3	25
Sodium	28.3	9.8	3.0	4.2
Strontium	0.002	0.006	0.006	0.003
Sulphate	5.9	9.1	5.5	0.17

Table G4 Chemical analyses of water leaches from weathering experiments on untreated samples of Drury greywacke.

Weathering	Fresh	Partly weathered	Weathered
Field ID	D1	D5	D3
Lab No.	2400755	2400757	2400756
Ph	7.90	6.42	6.68
Analysis temperature (°C)	21	21	21
HCO_3/date analysed	29/04/04	29/04/04	29/04/04
Element/compound (in mg/L)			
Bicarbonate (total)	75	44	47
Aluminium	0.22	<0.1	<0.1
Calcium	24	3.7	0.76
Chloride	0.84	1.5	1.3
Iron	<0.02	<0.02	<0.02
Magnesium	2.9	2.0	0.64
Manganese	0.013	0.049	0.009
Potassium	3.8	3.0	0.67
Rubidium	0.01	<0.01	<0.01
Silica (as SiO_2)	12.2	12.4	14.5
Sodium	1.6	1.8	2.3
Strontium	0.20	0.02	0.02
Sulphate	27	19.8	0.87

Table G5 Chemical analyses from weathering experiments on untreated samples of Poplar Lane andesite.

Weathering	Fresh	Partly weathered	Weathered
Field ID	PL1	PL3	PL2
Lab No.	2400766	2400768	2400767
Ph	6.89	6.55	6.51
Analysis temperature (°C)	24	24	24
HCO_3/date analysed	03/05/04	03/05/04	03/05/04
Element/compound in (mg/L)			
Bicarbonate (total)	43	51	52
Aluminium	0.20	0.43	0.16
Calcium	1.9	0.63	1.1
Chloride	1.1	1.1	2.9
Iron	<0.02	0.093	<0.02
Magnesium	0.88	0.28	0.48
Manganese	0.017	<0.005	<0.005
Potassium	1.5	0.77	1.4
Rubidium	<0.01	<0.01	<0.01
Silica (as SiO_2)	18.7	19.7	20.0
Sodium	1.8	2.4	2.1
Strontium	0.015	0.005	0.011
Sulphate	0.10	0.10	0.10

Table G6 Variation of pH with time in reactions of treated samples and Durabind™ with water leaches.

Date			28/02/04	29/02/04	6/03/ 04	19/03/04	2/04/04
Day			1	2	8	21	24
		Mixture	**repeat experiment (initial)**				
Solution Temperature (°C)			19.3	19.3	19.1	18.2	18
Site	**Lithology**	**Additive**	pH	pH	pH	pH	pH
Flat Top	Basalt	3% Lime	12.08	12.11	12.38	11.65	10.35
		3% Cement	10.95	11.24	10.86	10.1	9.57
		3% Durabind™	10.84	11.25	10.06	9.38	8.89
Drury	Greywacke	3% Lime	11.92	12.06	12.35	11.89	11.14
		3% Cement	10.92	11.24	11.24	10.31	9.73
		3% Durabind™	11.29	11.85	10.4	9.14	8.67
Poplar Lane	Andesite	3% Lime	12.06	12.14	11.95	10.94	10.15
		3% Cement	10.59	10.69	10.66	9.92	9.56
		3% Durabind™	10.19	10.18	9.38	8.92	8.2
Lime			12.38	12.48	12.91	13.03	12.51
Cement, Portland, GP*			12.13	12.38	12.65	12.87	12.17
Durabind™			12.19	12.3	12.53	12.34	11.43

Notes:

- See Tables G7–9 for chemistry of the water leaches at the end of the experiments.
- * General Purpose (trade grade of Portland Cement)

Table G7 Chemical analyses of water leaches from weathering experiments on treated samples of Flat Top basalt.

Additive	**3% lime**	**3% cement**	**3% Durabind™**
Lab No.	2400753	2400752	2400751
Ph	7.97	7.52	8.50
Analysis temperature	21	22	21
HCO_3/date analysed	29/04/04	29/04/04	29/04/04
Element/compound (in mg/L)			
Bicarbonate (total)	48	53*	193*
Aluminium	0.58	0.17	<0.1
Calcium	5.7	28	51
Chloride	0.36	0.93	0.35
Iron	<0.02	<0.02	<0.02
Magnesium	0.027	0.35	3.3
Manganese	<0.005	<0.005	<0.005
Potassium	0.80	0.80	0.36
Rubidium	<0.01	<0.01	<0.01
Silica (as SiO_2)	7.9	21	32
Sodium	11.6	9.7	13.6
Strontium	0.02	0.13	0.04
Sulphate	17.5	65	22

Table G8 Chemical analyses of water leaches from weathering experiments on treated samples of Drury basalt.

Additive	**3% lime**	**3% cement**	**3% Durabind™**
Lab No.	2400750	2400749	2400748
Ph	7.93	7.00	8.52
Analysis temperature	21	22	20
HCO_3/date analysed	29/04/04	03/05/04	29/04/04
Element/compound (in mg/L)			
Bicarbonate (total)	32*	49*	175*
Aluminium	0.86	0.22	0.11
Calcium	24	37	59
Chloride	0.53	0.67	0.50
Iron	<0.002	<0.02	<0.02
Magnesium	0.014	0.20	3.3
Manganese	<0.0056	<0.005	<0.005
Potassium	4.0	6.3	1.8
Rubidium	<0.01	<0.01	<0.01
Silica (as SiO_2)	<0.05	12.8	23
Sodium	5.7	5.2	10.4
Strontium	0.14	0.28	0.12
Sulphate	59	89	31

Table G9 Chemical analyses of water leaches from weathering experiments on treated samples of Poplar Lane andesite and Durabind™.

Additive	**3% lime**	**3% cement**	**3% Durabind**	**Durabind™**
Lab No.	2400747	2400746	2400745	2400754
Ph	8.44	8.66	8.56	10.16
Analysis temperature	20	20	19	21
HCO_3/date analysed	29/04/04	29/04/04	29/04/04	29/04/04
Element/compound (in mg/L)				
Bicarbonate (total)	<20	41	189*	296
Aluminium	4.4	0.17	<0.1	0.14
Calcium	12.9	25	56	1.6
Chloride	0.84	0.81	0.81	1.1
Iron	<0.02	<0.02	<0.02	0.028
Magnesium	0.019	0.29	2.9	<0.01
Manganese	<0.005	<0.005	<0.005	<0.005
Potassium	3.33	4.7	2.2	1.5
Rubidium	0.012	0.010	<0.01	<0.01
Silica (as SiO_2)	1.2	19.1	15.5	58
Sodium	3.5	4.4	11.8	158
Strontium	0.04	0.20	0.10	0.007
Sulphate	13.4	44	11.7	12.8

Clay Mineralogy of Modified Marginal Aggregates

Land Transport New Zealand
Research Report 318