REPORT 25055/G/4

**REPUBLIC OF CYPRUS
MINISTRY OF AGRICULTURE, NATURAL RESOURCES
AND ENVIRONMENT**

GEOLOGICAL SURVEY DEPARTMENT

**RESEARCH PROGRAMME
INTO POSSIBLE ADVERSE EFFECTS OF AGGREGATE
CONTAINING SULPHIDE MINERALS IN CONCRETE**

FINAL REPORT

Reference : Contract No. GSD/17/2002 dated 29 April 2003.

1.   INTRODUCTION

This report presents the results, evaluation and interpretation of a research programme undertaken by Sandberg LLP on behalf of the Republic of Cyprus, Ministry of Agriculture, Natural Resources and Environment, Geological Survey Department.

A letter of acceptance was received from Mr George Petrides, The Directorate, Geological Survey Department (GSD) dated 31 March 2003.

The contract was duly signed and returned to GSD on 25 April 2003.

The purpose of the research programme was to study the possible adverse effects of diabase aggregates containing sulphide minerals that are used in concrete in regard to the durability and longevity of concrete in Cyprus.

The objectives of the research were defined by GSD as follows ;

1)   To study the adverse effects of concrete aggregates containing sulphide minerals in regard to the longevity and durability of concrete structures.

2)   To enable GSD to apply the conclusions and the methodology derived from the study to future research aimed to establish the relation between the mineral and chemical composition of the various kinds of aggregate available in Cyprus.

3)   To enable GSD to assess the possibility of readjusting the specified limit of 1% for sulphide minerals in Cyprus Standard CYS-64 - Specification for Aggregates from Natural Sources for Concrete.

The criteria delineated as the framework for the research were as follows ;

i)   The content of sulphide minerals (mainly pyrite) in concrete aggregates.

ii)   The content of other deleterious minerals in concrete aggregates.

iii) The significance of the chemistry of mixing water and other parameters of the aggregates or the concrete itself, to the investigation of sulphide reaction(s).

iv)   Other criteria, as applicable.

Based on the defined purpose and objectives of the research programme, a work methodology was developed (Appendix A) along with a work plan (Appendix B).

2. PHASE I - Compilation

2.1 Database

A database was developed and existing data, for aggregates produced in Cyprus retained on file in either electronic form or hard copy by GSD, entered.

2.2 Desk Study

A review into available standards and specifications, articles and published information concerning sulphide minerals in concrete, was undertaken.

A list of standards, references and publications utilised is presented in Appendix C.

2.2.1 Geological Context & Occurrence of Pyrite in Cyprus

Aggregate exploitation can be divided in to three distinct periods in Cyprus, these are ;

(1)   Pre-1974   Crushed limestone (ex. Pentadactylos mountain range)
                  River deposits
                  Beach deposits

(2)   1974 - 1984   River deposits
                      Beach deposits
                      Introduction of ; Crushed diabase
                      Crushed reef limestone

(3)   1984 to date   Crushed diabase
                       Crushed reef limestone
                       Crushed calcarenite (fine sand)

The principal aggregate source (post-occupation of the North) in recent times has been diabase.

Two definitions of diabase are cited which are generally similar and are as follows:

   i.   Slightly metamorphosed medium-grained basic igneous rock in which pyroxene has been altered to amphibole.

   ii.   An altered dolerite in which the original minerals have been replaced by carbonate, albite, chlorite, serpentine etc.

In Cyprus diabase comprises almost the entire Sheeted Dyke Complex of the Troodos Ophiolite (Upper Cretaceous) and has a basaltic to doleritic composition which has been subjected to hydrothermal alteration after emplacement. Localised variations include quartz-diabase, epidote-diabase, amphibole-diabase and albite-diabase.

Primary minerals include plagioclase, pyroxene, olivine and amphibole with accessory ilmenite, magnetite and sphene; whilst secondary minerals resulting from hydrothermal alteration include quartz, epidote, albite, actinolite, chlorite, calcite and zeolites.

Significantly, pyrite and chalcopyrite may be present in small amounts as single grains, grain aggregations or veins.

Currently there are eight active quarry zones of diabase with ten quarries producing coarse and fine aggregate for concrete and road making. The diabase quarries are located two in Nicosia district, five in Limassol district and three in Larnaka district and they produce 57% of the total production of aggregate in Cyprus.
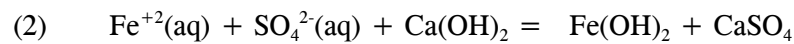
2.2.2   Mechanism of Deterioration

Neville A M (Properties of Concrete, 4th edition)[4] advises that iron pyrites is one of the most common expansive inclusions in aggregate. The mechanism is described in general terms as sulphides reacting with water and oxygen to form ferrous sulphate which subsequently decomposes to form a hydroxide ; and sulphate ions reacting with calcium aluminates in the cement. Sulphuric acid can also form and this can attack the hydrated cement paste. As a consequence, surface staining and disruption may result, particularly under warm and humid conditions.

The process of pyrite degradation was presented in a clear simple form by Grzetic and Pekri (2002)[20] as follows ;

<u>Low oxidising conditions</u>

(1) $FeS_2 + H_2O + 3.5 O_2$ $=$ $Fe^{+2} + 2SO_4^{2-} + 2H^+$
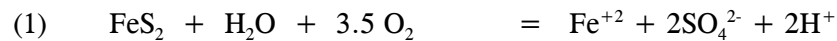
      Pyrite + Water + Oxygen $=$ Ferrous sulphate

(2) $Fe^{+2}(aq) + SO_4^{2-}(aq) + Ca(OH)_2 =$ $Fe(OH)_2 + CaSO_4$

      Ferrous sulphate + Portlandite $=$ Iron hydroxide + Calcium sulphate

<u>High oxidising conditions</u>

(3) $2FeS_2 + 2H_2O + 7O_2$ $=$ $2Fe^{+3} + 4SO_4^{2-} + 4H^+$

      Pyrite + Water + Oxygen $=$ Ferric sulphate

(4) $2Fe+3^{+2}(aq) + 3SO_4^{2-}(aq) + 3Ca(OH)_2 =$ $2Fe(OH)_3 + 3CaSO_4$
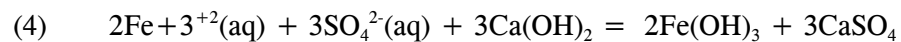
Ferrous sulphate + Portlandite $=$ Ferrous hydroxide + Calcium sulphate

Lea F M (Chemistry of Cement and Concrete, 4th edition)[25] also describes the reactions and discusses the influence of biochemical reactions in soils in the presence of autotrophic bacteria that is they are able to obtain the energy for their growth and proliferation by the oxidation of inorganic compounds in the presence of atmospheric oxygen. In certain circumstances two further stages of reaction can be introduced and breakdown of the pyrite is accelerated.

(5) $2FeS_2 + 7O_2 + 2H_2O$ $=$ $2FeSO_4 + 2 H_2SO_4$

(6) $4FeSO_4 + O_2 + 2H_2SO_4$ $=$ $2Fe_2(SO_4)_3 + 2H_2O$

(7) $7Fe_2(SO_4)_3 + FeS_2 + 8H_2O$ $=$ $15FeSO_4 + 8H_2SO_4$

The ferric sulphate is an oxidising agent and acts on unaltered pyrite to give ferrous sulphate and sulphuric acid which are the products of the first stage of oxidation (5).

Midgley (1958)[23] refers to surficial brown staining of concrete due to oxidation and hydration of a reactive form of pyrite present as a minor constituent of Thames river aggregate. The brown staining has been identified as goethite, an iron hydroxide and it is formed by the reaction of iron sulphide with water and atmospheric oxygen. The first reaction product is ferrous sulphate which subsequently decomposes to ferric hydroxide releasing sulphate in the solution. The sulphate then reacts with the calcium aluminate hydrate within the concrete paste to form the mineral ettringite (calcium sulphoaluminate hydrate) which can cause expansion. These reactions take place in the presence of lime water (calcium hydroxide).

Reactions with pyrite in concrete mostly occur at the surface zone causing unsightly staining and pop-outs.

The reactivity of pyrite is associated with the "defect" structure of pyrite, the

unreactive forms being "stabilized" by ions of some metal impurity. X-ray powder diffraction failed to differentiate reactive and unreactive forms.

Midgley suggested a simple qualitative test for identifying reactive pyrite. According to the test a crushed particle specimen, to expose as much as possible pyrite, is immersed in saturated lime solution. If the pyrite is of the reactive form a gelatinous blue-green ferrous sulphate precipitate is readily formed which turns to brown ferric hydroxide. The reaction is complete within 30 minutes. If no precipitate is observed the pyrite is considered to be unreactive and unlikely to exhibit any pyritic reaction in concrete.

Casanova et al (1996) refer to initial sulphide oxidation as 'primary expansion' and develop a further expansion model based on the release of sulphate and hydrogen ions into the concrete pore solution which reacts with the cement paste to form additional expansive phases such as gypsum, monosulphoaluminate and eventually ettringite. The latter process is referred to as 'secondary expansion'. The paper concludes that the effects of sulphide oxidation on aggregate expansion and sulphate attack on the cement paste are chiefly controlled by the kinetics of the weathering process. In particular, the rate of the expansive reaction is governed by the change in surface area of the reactants and depends strongly on the original grain size of the sulphides in the aggregate.

2.2.3 Literature and Standards (existing)

2.2.3.1 Selected Papers, Standards and Publications

The weathering of iron sulphide in aggregate in concrete has been recognised extensively within UK as well as internationally.

An exhaustive literature review for the assessment of the sulphate compounds and pyrite in aggregate for concrete, road making and sands for mortars of Cyprus, British, American, German, French and Greek standards and other relevant papers and publications, carried out by Christodoulou E and Loukaidis for the Cyprus Association of Aggregate Producers, February 1997[17], concluded that damage in concrete due to sulphide minerals in aggregate is a minor problem mainly observed as erratic blemishes on concrete surfaces in the form of staining or pop-outs. These blemishes are due to the presence of reactive pyrite which can be detected by the simple lime water test described by Midgley[23]. The unreactive form of pyrite does not pose any danger of reaction with the concrete paste.

An examination of concrete core samples, containing diabase aggregate from Mosfiloti Quarry, from 1987 and 1993 structures in Ready Mix Plant in Nicosia, carried out in July 2000[22] concluded that no damage due to weathering of pyrite was identified and any cracking observed did not relate to the presence of pyrite.

Dougherty and Barsotti (1972)[19] highlighted instances dating back to 1920 in the USA, where the effects of expansive sulfide minerals caused structural damage through ground heave. They reported that the timing and location of the heave due to reacting pyrite could not be predicted.

The reaction of sulphides has also been well recognised in concrete building blocks made from mine tailings, particularly in the south west of England where it is known and defined as the Mundic problem (RICS, 1994)[28].

In the last decade the importance of sulphides in the ground has also been recognised with respect to sulphate attack on buried concrete and has been designated TSA (Thaumasite sulphate attack). This has led to new guidance with respect to the use of concrete in aggressive ground (Report of the Thaumasite Expert Group, 1999[30], and Nixon et al., 2003[26]).

The presence of pyrite in concrete aggregate is referred to in numerous testing standards related to the description and examination of aggregate for concrete.

ASTM C294-98 Standard Descriptive Nomenclature for Constituents of Concrete Aggregates, clause 13 (Iron Sulphide Minerals)[5] notes that pyrite and pyrrhotite can oxidise with the liberation of sulphuric acid and formation of iron oxides, hydroxides and to a much smaller extent sulphates. The standard further notes that pyrite and pyrrhotite are reactive in concrete, producing a brown stain accompanied by a volume increase.

ASTM C295-98 Standard Guide for Petrographic Examination of Aggregates for Concrete, clause 4.5[6], also draws attention to the significance of unstable sulphides in aggregate and reiterates that sulphuric acid may be formed along with distress to concrete where it is exposed to high temperatures during service.

PD 6682-1 : 20038 Aggregates - Part 1[8] : Aggregates for concrete - Guidance on the use of BS EN 12620 : 2002, clause 5 e[9] states that unstable sulphide minerals such as pyrite are reactive and in some circumstances can give rise to problems in concrete.

Concrete Society Technical Report No. 54 (2000) clause 3.6.6[29], notes that pyrite only oxidises in the presence of moisture and atmospheric oxygen and that in extreme cases concrete disruption may occur due to sulphate attack on the cement paste.

2.2.3.2 Standard Limits

The pyrite content in concrete aggregate is currently controlled through Cyprus Standard CYS 64 : 1986 Specification for Aggregates from Natural Sources for Concrete. Clauses 4.1.2 Deleterious substances Table 1 (coarse aggregate) and 4.2.2 Deleterious substances Table 3 (fine aggregate)[1]. Both specify a maximum permissible limit of 1.0% by weight for sulphur in sulphide and or sulphate minerals expressed as SO_3.

The new Cyprus Standard CYS EN 12620 Specification for Aggregate for Concrete, launched in July 2005, superceded the above CYS 64 :1986. This new Standard specifies in Section 1 that coarse and fine aggregates should not exceed 0.8%AS (acid soluble sulphate) and 1% total S (sulphur).

PD 6682-1 : 2003[8] Aggregates - Part 1 : Aggregates for concrete - Guidance on the use of BS EN 12620, clause 3.4.2.2 and BS EN 12620 : 2002[9], 6.3.2 state that total sulphur is limited to $\leq 1\%$ by mass for aggregate other than air cooled blastfurnace slag. The standard further notes that if pyrrhotite is present in the aggregate, the maximum total sulphur content should be limited to 0.1% by mass.

2.2.4 Research (in respect of limit definition)

RICS (1999)[28] examined concrete blocks made with sulphide containing aggregate with $S_{(total)}$ up to 0.99 (pyrite 1.64). The findings when analysed indicated the following key points ;

- Graphical plotting of calculated pyrite versus total sulphur indicated that in the majority of cases pyrite had suffered very little in situ oxidation.

  Several specific instances did occur however where excess sulphate formed by the oxidation of pyrite.

- Graphical plotting of total sulphur versus SO_4 indicated several anomalous sulphate concentrations ascribed to in situ pyrite oxidation.

  In situ oxidation is calculated on the following basis ;

  (Total sulphate - original sulphate in cement) x (S/SO_4) x $(FeS_2/2S)$
  = oxidised pyrite

- Graphical plotting of calculated pyrite versus SO_4 coupled with statistical analysis showed that ;

  - A limit of 0.6% pyrite (0.4% sulphate ; approx 2σ) could be advised for aggregate blocks where there was no evidence of general concrete deterioration which might be ascribed to in situ pyrite oxidation.

  - A limit of 1.2% pyrite (0.6% sulphate ; approx 3σ) could be advised for aggregate blocks where there was high pyrite concentration but excluding the small number in which there was obvious evidence of sulphide-related concrete deterioration.

Casanova et al (1997) proposed a physico-chemical model of sulfate attack based on the weathering of sulfide-bearing aggregate releasing sulfate ions that can react with cement components. The extent of the attack was identified to be controlled by the composition and size of the aggregate, the kinetics of sulfide oxidation, the composition of the cement and the mix proportions of the concrete.

The model proposed by Casanova et al (1997) was developed further in a paper published by Ayora et al (1998). A conceptual thermodynamic model to predict

the concentration of solutes and the mass transfer to/from the solid phases resulting from the acidic alteration process. The amount of H_2SO_4 is identified as a limiting factor for alteration to progress. Massive alteration of the cement paste is not expected to occur but in the zones where active transport of $SO_4^=$ and H^+ takes place. Therefore the alteration is expected to be limited to cement-aggregate interfaces and fractures. The findings of the research enabled an agreement to be identified between calculations and observations enabling the alteration of cement to be attributed to acidic solutions produced by the oxidation of pyrrhotite.

Investigative work was undertaken by Le Roux et al (2001)[21] to investigate the 1% S (corresponding to 2.5% SO_3) threshold proposed in the European Standard EN 12620. The study utilised iron sulphides present in limestone under accelerated conditions of temperature (38°C) and humidity (100%) over a 12 month period. On completion no swelling due to oxidation of sulphides was observed.

Wakizaka et al[31] undertook an experimental programme of wetting / drying and exposure tests which suggested that concrete durability became poor when the pyrite aggregate content exceeded 6%. Pessima mixing ratio values of pyrite (10% 5-2.5mm ; 5% 0.15mm) were proposed based on relative dynamic modulus of elasticity. It is considered however that further investigation is needed to be carried out to more clearly define this relationship.

2.3 Programme Development

It was agreed that aggregates from five quarries would be used for the research (i.e. four diabase and one reef limestone). The five quarries selected were QS-1, QS-4, QS-6, QS-8 and QS-9. For code identification see Sandberg letter (ref. 25055/G) dated 13 November 2003.

Two of the diabase aggregates were enriched with pyrite rich rock from the respective quarries. These pyrite enriched aggregates were used for the preparation of mortar bar and concrete prism test specimens so that the pyrite content was approximately <0.1%, 1%, 2% and 4% for the four diabase aggregates.

The two enriched aggregates were from QS-1 quarry to achieve 4% and QS-6 to achieve 1% pyrite contents.

The other two diabase aggregates (QS-8 and QS-4) exhibited <0.1% and 2% pyrite contents respectively.

The heavy liquid separation, which would not be an effective method of pyrite content control, was replaced by pyrite enrichment and chemical analysis, of various aggregate combinations and mixes, in the test programme.

3. PHASE II - Application of Methodology

3.1 Field Work & Sampling (aggregate and concrete)

The field work was completed in October 2003. During the field work nine quarries were visited and data were supplied by GSD regarding production figures, type of aggregate produced and physical and chemical properties of the aggregate. The quarries visited were code listed in Sandberg letter (ref. 25055/G) dated 13 November 2003 as QS-1 to QS-9. Also two water samples (from WS-1 & WS-2 suppliers) and small aggregate and rock samples were taken and three concrete core samples from WS-1 supplier were collected for initial examination and analysis.

The aggregate, concrete cores from existing structures, water sample and the cement from two sources (i.e CS-1 & CS-2) used in the mixing of experimental mortar bars and concrete prisms were received on 18 November 2003 and 5 January 2004. The sampling was carried out by GSD.

A schedule of samples received is given in Appendix C.

4. PHASE III - Laboratory Testing of Aggregate and Concrete

4.1 Aggregate

4.1.1 Petrographic Analysis

Three aggregate fractions from each selected quarry source (i.e. 20mm - 10mm, 10mm - 5mm & fine aggregate) and another fine aggregate from quarry QS-2 were subjected to petrographic examination in accordance with the documented UKAS accredited Sandberg Technical Procedure TP/G1/3 which is based upon BS 812 : Part 104 : 1994.

The detailed petrographic examination results of each aggregate fraction from each quarry are presented in Appendix D.

4.1.2 SEM Microprobe Analysis and Elemental Mapping

Scanning electron microscope and microprobe analysis was carried out for the 10mm aggregate fraction from each source (i.e. QS-1, QS-4, QS-6, QS-8 and QS-9), using a Jeol JSM-53 10LV Scanning Electron Microscope with Oxfords Instruments Software ISIS 300 and an accelerating voltage of 20Kv.

The scanning electron microscope and microprobe results for the 10mm particle size fraction from each source are given in Appendix E.

4.1.3 Chemical Analysis for Sulphide

The aggregate from five sources (i.e. QS-1, QS-4, QS-6, QS-8, &QS-9) was subjected to chemical analysis to determine pyrite content. Aggregate from QS-1 and QS-6 quarries were enriched with pyrite from each respective quarry.

Determination of total sulphur and acid soluble sulphate in aggregate was made in accordance with the methods given in BS1047:1983, 'Air-cooled aggregate for use in construction'. Sulphide was determined by the method given in BS1881:Part 124:1988. 'Analysis of hardened concrete'.

Pyritic sulphur was calculated as FeS_2 after correcting the total sulphur values for acid soluble sulphate and sulphide.

The chemical analyses results are given in Appendix F.

4.2 Mixing Water

4.2.1 Chemical Analysis

The water samples were analysed in accordance with BS EN 1008 : 2002 and documented in-house methods.
The results are presented in Appendix G.

Water sample (G26746) sampled on 10.10.2003 by GSD was used for mixing the experimental mortar bars and concrete prisms.

4.3 Hardened Concrete From Existing Structures

4.3.1 Visual Examination of Concrete Cores

Twelve samples were received which were advised to represent five different locations. Each core was subjected to a brief visual examination in accordance with the method described in BS1881:Part 120:1983.

The results are presented in Appendix H together with colour record photographs.

4.3.2 Compressive Strength and Density of Concrete Cores

Five cores were prepared and subjected to strength testing in accordance with the method given in BS1881:Parts 120 & 114:1983. The results are given in Appendix I.

Seven cores which were subjected to petrographic examination were also tested for water absorption and density. The samples were oven dried at $105\text{-}110^0C$ for 72hrs and then allowed to cool to room temperature. Each sample was weighed dry before placing into water to a cover depth of 30 to 50mm. After periods of 10mins, 30mins, 1hr, 24hrs and 7 days the samples were surface dried, weighed and water absorption calculated.

The saturated volume was found by the water displacement method and oven dry and saturated densities subsequently calculated.

The results are given below:-

Site Ref:	LAR1	LEM2	DEC2	ATH1	RM93-1	RM87-2	RM98-1
Lab Ref:	G26965 /1	G26966 /2	G26967 /2	G26968	G26969 /1	G26970 /2	G26971
Dry Mass, g	717	627	261	665	1384	349	934
Absorption							
after 10mins	3.9	2.3	4.2	2.4	1.5	4.7	3.6
after 30mins	6.6	4.0	6.1	4.0	2.5	7.6	6.1
after 1hr	8.1	4.9	7.2	5.0	3.2	9.2	7.8
after 24hrs	9.7	8.3	9.7	8.3	6.9	11.6	11.6
after 7 day	10.0	8.9	10.3	8.8	7.2	12.1	12.1
Dry Density, kg/m³	2010	2170	2100	2150	2210	2020	2000
Sat Density, kg/m³	2200	2360	2300	2330	2360	2260	2230

The tests were carried out between 30.3.04 and 8.4.04

4.3.3 Petrographic Examination of Concrete Cores

Ten concrete core samples were subjected to petrographic examination in accordance with the procedures described in ASTM C856-95.

The detailed petrographic examination results are presented in Appendix J.

4.3.4 SEM Microprobe Analysis and Elemental Mapping

The results for the concrete core samples are presented in Appendix K.

4.4 Cements

4.4.1 Chemical Analysis

Two cements (CS-1 & CS-2) were analysed in accordance with Sandberg in-house method 11.1. The chemical analysis of the two cements was used in order to calculate the pyrite content by weight of the aggregate present in the mortar bar and concrete prism mixes (see experimental mortar bar and concrete prism below).

The results are presented in Appendix L.

5. PHASE IV - Laboratory Test Programme (Experimental Concrete)

5.1 Mortar Bar Tests

The aggregate from each quarry source, two of which (i.e. QS-1 & QS-6) were enriched with pyrite were subjected to mortar bar testing using the method given in ASTM C227.

Two sets of mortar bar specimens (4no. specimens per set) were prepared from each aggregate and each cement source. One set of specimens was stored at 38^0C in moist air

whilst the second set was subjected to wetting, in artificial sea water, and air drying cycling at 20^0C +/- 2^0C. Water sample (G26746) sampled on 10.10.2003 was used for mixing.

The aggregate proportion used was that for a typical pavement quality concrete and was 2 : 1 : 2 (20mm : 10mm : sand). The detailed programme is presented in Table 1.

A list of all mortar bar specimens used in the tests is given in Table 4.

Chemical analysis of the mortar bar mixes for sulphide content was carried out. The determined values were first corrected for combined water in the hardened cement paste. The equivalent values for the relevant cement samples (CS-1 & CS-2) were then subtracted to give the sulphur contributed by the aggregate which was converted to FeS_2 as per aggregate sulphide determination.

The results of the mortar bar chemical analysis are given in Appendix M.

5.1.1. Mortar bar test at 38^0C in moist air

One set of mortar bar specimens (i.e. 4no. mortar bars) per aggregate and cement source were stored in moist air (containers over water) at 38^0C and length measurements undertaken with visual examination at 1, 7, 14, 28, 56, 84 days and monthly thereafter up to six months and three monthly thereafter, up to 14 months.

The length measurements with expansion graphs for each set are presented in Appendix N. Visual observations on each specimen (i.e. staining, pop-out, cracking, bending) were also recorded and are given in Appendix O together with selective colour photographs.

A few specimens exhibited faint small rust stains at the end of the 14 months testing period.

It should be noted that the mortar bar test according to the submitted test programme was to be terminated at 6 months testing period. It was decided, however, that the test be carried out up to fourteen months as per the concrete prism test.

5.1.2 Mortar bar test sea water/air dry cycling

One set of mortar bar specimens (i.e. 4no. mortar bars) per aggregate and cement source were subjected to wetting in sea water and drying cycling.

One cycle consisted of immersing the specimens in artificial sea water for one week and air drying for another week at 20^0C +/- 2^0C. Length measurements were undertaken with visual examination after each cycle, up to the 10th cycle and every five cycles thereafter, up to 14 months or 30 cycles.

The length measurements with expansion graphs for each set are presented in Appendix P. Visual observations on each specimen (i.e. staining, pop-out, cracking, bending) were also recorded and are given in Appendix Q together with

selective colour photographs.

A few specimens exhibited minor faint rust stains at the end of the 30th cycle (i.e. the end of the testing period).

The sea water solution was prepared using a proprietary sea water concentrate (ref. F59549) containing pharmaceutical grade sea salt and trace elements found in natural sea water. A fresh solution was used every three months.

It should be noted that the mortar bar test, according to the submitted test programme, was to be terminated at 6 months testing period. It was decided however the test be carried out up to 14 months as per the concrete prism test.

5.1.3   Petrographic Examination

One mortar bar from each set, stored at 38^0C moist conditions and sea water immersion/drying at 20^0C cycling, was selected and used to prepare a large area thin section which was then examined in accordance with the procedure given in ASTM C856 -95 and scanning electron microscope analysis. A list of the mortar bar specimens used for petrographic examination is given Table 2.

The results are presented in Appendix R together with selected photomicrographs.

5.1.4   SEM Microprobe Analysis and Elemental Mapping

A list of the mortar bar specimens used for SEM analysis is given Table 2.

The results for the mortar bars stored at 38^0C moist conditions and sea water immersion/drying at 20^0C cycling are presented in Appendix S.

5.2   Concrete Prism Tests

The aggregate from two quarry sources (i.e. QS-1 & QS-6), each of which was enriched with pyrite from the respective source, was subjected to concrete prism testing based on the method given in BS812 : Part 123 : 1999. Two sets of concrete prism specimens were prepared from each of two aggregate and each cement source. One set of specimens (3 no. specimens per set) was stored at 38^0C in moist air whilst the second set (2 no. specimens per set) was subjected to wetting, in artificial sea water, and air drying cycling at 20^0C +/- 2^0C. Water sample (G26746) sampled on 10.10.2003 was used for mixing.

The aggregate proportion used was that for a typical pavement quality concrete and was 2 : 1 : 2 (20mm : 10mm : sand). The detailed programme is presented in Table 1.

A list of all concrete prism specimens used in the tests is given in Table 4.

Chemical analysis of the concrete prism mixes for sulphide content was carried out. The determined values were first corrected for combined water in the hardened cement paste. The equivalent values for the relevant cement samples (CS-1 & CS-2) were then subtracted to give the sulphur contributed by the aggregate which was converted to FeS_2 as per aggregate sulphide determination.

The results of the concrete prism chemical analysis are given in Appendix T.

5.2.1   Concrete prism test at 38^{0}C in moist air

One set of concrete prism specimens (i.e. 3no. concrete prisms) were prepared and tested from two aggregate (i.e. QS-1 & QS-6) and cement (i.e. CS-1 & CS-2) sources.

The specimens were stored in moist air (containers over water) at 38^{0}C and length measurements were undertaken with visual examination at 1, 7, 14, 28, 56, 84 days and monthly up to 6 months and every 3 months thereafter, up to 14 months.

The length measurements with expansion graphs for each set are presented in Appendix U. Visual observations on each specimen (i.e. staining, pop-out, cracking, bending), were also recorded and are given in Appendix V together with selective colour photographs.

All prism specimens exhibited faint small rust stains in places at the end of the testing period.

5.2.2   Concrete Prism Test Sea Water/air Dry Cycling

One set of concrete prism specimens (i.e. 2no. concrete prisms) were prepared and tested for each of two aggregate (i.e. QS-1 & QS-6) and cement (i.e. CS-1 & CS-2) sources.

The specimens were subjected to wetting and drying cycling. One cycle consisted of immersing the specimens in artificial sea water for one week and air drying for another week at 20^{0}C +/- 2^{0}C. Length measurements were undertaken with visual examination after each cycle, up to 10 cycles.

After 10 cycles, length measurements were conducted every five cycles.

The length measurements with expansion graphs for each set are presented in Appendix W. Visual observations on each specimen (i.e. staining, pop-out, cracking, bending) were also recorded and are given in Appendix X together with selective colour photographs.

Concrete prism specimens (except those in T1M set i.e. QS-1 & CS-1) exhibited small rust stains at the end of the 30th cycle of the testing period.

The sea water solution was prepared using a proprietary sea water concentrate (ref. F59549) containing pharmaceutical grade sea salt and trace elements found in natural sea water. A fresh solution was used every three months.

5.2.3   Petrographic Examination

One prism from each set, stored at 38^{0}C moist conditions and sea water immersion/drying at 20^{0}C cycling, was selected and used to prepare a large area thin section which was then examined in accordance with the procedure given in ASTM C856 -95. A list of the prisms used for petrographic examination is given Table 3.

The results of the petrographic examination are presented in Appendix Y.

5.2.4   SEM Microprobe Analysis and Elemental Mapping

A list of the prism specimens used for SEM analysis is given Table 2.

The results for the concrete prisms stored at 38^0C moist conditions and sea water immersion/drying at 20^0C cycling are presented in Appendix Z.

6.   PHASE V - Evaluation and Interpretation

6.1   Aggregate

The diabase aggregates (QS-1, QS-4, QS-6 & QS-8) examined were found to be fresh containing frequent opaque grains which were generally iron pyrite, although chalcopyrite, ilmenite, magnetite and or haematite were occasionally observed. Galena and other sulphide minerals were sporadically present. The aggregate from QS-8 source was found to contain minor proportions of pyrite and sparse chalcopyrite and ilmenite.
The reef limestone from QS-9 quarry was found to contain traces of iron oxide, possibly haematite and ilmenite (iron titanium oxide).

The pyrite and in general the opaque minerals in the aggregate were found to be in a crystalline form and fresh although the rock appeared altered (diabase is an altered basic rock) with an assemblage of secondary minerals; amphibole, chlorite, calcite, quartz, microgranulated and microcrystalline quartz, sporadic serpentine and epidote. Some iron containing minerals, possibly amphibole and chlorite, occasionally exhibited some oxidation imparting to the mineral a brown/rusty colour discolouration.

The aggregate from each source was combined in proportions 20 : 10 : fines (Zone 2), which are the proportions of a pavement quality concrete, and the pyrite content was determined for each source.

Pyrite rich material from QS-1 and QS-6 was first crushed to 20-10mm, 10-5mm and fine aggregate (Zone 2) and used to enrich the normal production aggregate to 4% and 1% approximately. The enriched aggregate from each source was then used in the same ratio for the experimental mortar bar and concrete prism tests.

6.2   Concrete from Existing Structures

The concrete represented by the concrete cores, we were advised to exhibit various ages ranging from 1987 to a few years old. All cores were taken from concrete exposed to elements and some of them (see Appendix J) were next to the sea exposed to sea water wetting or spray. The 100mm diameter concrete cores (ref. G26969, G26970 & G26971) and the 45mm diameter cores (ref. G26229a, G26229b & G26230), were advised to be from a floor slab which was exposed to wet conditions and lorry traffic. The cores were found to contain pyrite grains which predominantly appeared fresh and unoxidised with

sporadic evidence of some faintly oxidised pyrite grains and occasional other grains of iron containing minerals i.e. amphibole, pyroxene, and chlorite which sporadically exhibited brown/rusty discolouration.

No evidence of associated damage due to oxidation or deleterious pyrite reaction was identified in the samples examined.

The concrete, of samples examined petrographically, was found to be sound and in good condition. The microporosity of the concrete samples ranged generally from moderately low to moderately high which is indicative of normal water : cement ratios. The concrete exhibited occasional residual unhydrated and hemihydrated cement grains which is normal for sound concretes.

A.M. Neville 1995[24] "Properties of Concrete" states regarding hydration of the cement in concrete "…19% of the original mass of cement has remained unhydrated and can never hydrate because the gel (hydration products) occupies all the space available i.e. the gel/space ratio of the hydrated cement paste is 1.0." and goes on to state "It may be added that unhydrated cement is not detrimental to strength and, in fact, among cement pastes all with a gel space of 1.0 those with a higher proportion of unhydrated cement (i.e. a lower w/c ratio) have a higher strength, possibly because in such pastes the layers of hydrated paste surrounding the unhydrated cement grains are thinner."

Alkali silica reaction was identified in one concrete core sample (G26966/LEM 2) and in one occasion only and was associated with one cherty limestone particle. No definitive evidence of deleterious alkali silica reaction was identified in this sample. Also possible incipient alkali silica reaction associated with a microcrack was observed in sample G26967/DEK 2F but no alkali silica gel was present.

Scanning electron probe microanalysis (SEM) did not show any consistent pattern of sulphate and iron concentrations at the vicinity of the iron pyrite or any pyritic grain. Fluctuation of sulphur and iron concentration within the cement paste and with regard to the vicinity of pyrite were generally within the expected range. Iron concentrations in the vicinity of pyrite grains and within the cement matrix away from pyrite grains were in a few cases higher than expected for iron content from the cement paste but it was sporadically observed and might be attributed to very fine iron oxide grains within the cement paste. It should be noted however that some incipient pyrite oxidation may have taken place but was isolated and not definitively detected.

Cracks and microcracks in the concrete core samples examined were possibly due to shrinkage effects from cement paste and/or aggregate particles. Some fine cracks and microcracks were seen to run along the borders of some pyrite grains but they did not apparently originate from these grains.

6.3   Experimental Mortar Bar and Concrete Prism Tests

A summary of the mortar bar and concrete prism test programme is given in Table 1 and a list of all mortar bars and concrete prism specimens used in the test is given in Table 4.

6.3.1   Mortar bar test at 38°C in moist air

The expansion test results for the mortar bars stored at 38^0C moist air showed

very small expansion values with a maximum expansion mean value of 0.022%
after 14 months of testing. A summary of the final mean expansion values is
given in Table 5 and are plotted versus the aggregate pyrite contents in Figure 1.

It should be noted that for expansion to be considered significant it should exceed
0.1% at six months.

The final expansion values for all mortar bar sets stored at 38°C moist air after
14 months were much lower than 0.1%. In particular the mortar bars containing
diabase aggregate and cement from CS-2 source exhibited final expansion values
which were lower (almost by 50%) than in those containing cement from CS-1
source.

The mortar bars containing limestone aggregate exhibited relatively higher
expansion values than those with diabase aggregate and were identical,
irrespective of the cement used. The expansion values of the limestone containing
mortar bar sets however were still very low and the relatively higher expansion
may be due to the high porosity of the aggregate.

The expansion values of the mortar bars made using diabase aggregate showed
some minor differences with regard to the pyrite content (see Table 5). Mortar
bar sets made using cement from CS-1 source showed slight consistency in
expansion values with respect to pyrite content i.e. M4M (4.8% pyrite)
0.015% expansion, M1M (1.4% pyrite) 0.012% expansion, M5M (0.9%
pyrite) 0.012% expansion and M2M (pyrite not detected) 0.010% expansion.
The mortar bar sets made using cement from CS-2 source generally exhibited
similar trend in expansion values but with the exception of set M5V. In
particular M4V (4.3% pyrite) 0.007% expansion, M1V (1.3% pyrite) 0.007%
expansion, M5V (0.6% pyrite) 0.004% expansion and M2V (pyrite not
detected) 0.006% expansion.

Two mortar bar specimens made using limestone aggregate and CS-1 cement
exhibited small stains at the 12th month to the end of testing. No stains were
observed in the set made with CS-2 cement. The limestone was used as a
control aggregate because it did not contain detectable pyrite.

A few mortar bar specimens made using diabase aggregate exhibited sporadic
small stains, generally less the 2mm and in very few occasions up to 5mm
across, due to oxidation of probably pyrite. Two specimens from M4V set
(4.3% pyrite) and CS-2 cement showed staining at the 5th month until the end
of testing by which time one stain had increased in size up to 5mm across. No
staining was observed in set M4M (4.8 pyrite) made with CS-1 cement. Also
M2V test with no detectable pyrite and CS-2 cement exhibited a 2mm stain, at
12 months, which increased to 4mm at the end of the testing period.

In general the staining observed in the few mortar bar specimens could not be
reliably associated with the source of cement used or pyrite content. No visible
deleterious reaction (i.e. cracking, spalling, pop-outs or reaction products) was
observed in any specimen.

Mortar bar specimens exhibiting stains were selected for petrographic examination
and SEM and microprobe analysis. Suspected pyrite reaction was seen in two
pyrite grains (see mortar bar 9373 M4V, QS-4+CS-2, Appendix R pp 13 & 14)
but no features indicative of deleterious reaction were associated with these

grains. No other features indicative of pyrite reaction were observed in the mortar bars examined.

The probe microanalysis determined in some cases within the cement paste in the vicinity of pyrite grains, which appeared fresh, higher sulphur and iron contents than would normally be expected. The sulphur and iron content increase is likely to be due to dissemination of ions released, by a possible incipient reaction, which concentrate in zones in the vicinity (50μm) of the ion source. This concentration of ions was waning to normal levels as far as 150μm from the pyrite grains. No features indicative of deterioration due to pyrite reaction were observed in the mortar bars examined.

On the basis of the results of the microprobe analyses there was slightly more frequent occurrence and sulphur and iron concentrations in the 50μm zone from pyrite grains in the mortar bar specimens made using CS-2 cement. No reliable correlation could be made with regard to the pyrite content and the frequency of occurrence of sulphur and iron concentrations. In the mortar bar sets with higher pyrite contents (M4M & M4V 4.8%& 4.3% respectively) there was no observed increased frequency of occurrence of sulphur and iron ions concentrations in the vicinity of the pyrite grains when compared with those with lower pyrite contents.
Cracks and microcracks in the mortar bars examined were possibly due to shrinkage effect from cement paste and/or aggregate particles. Some fine cracks and microcracks were seen to run along the borders of some pyrite grains but they did not apparently originate from these grains.

6.3.2   Mortar bar test sea water/air dry cycling

The mortar bars in sea water/air dry cycling exhibited a shrinkage mean value up to 0.036% at the end of 30 cycle testing period (i.e. 14 month period). A summary of the final mean expansion values is given in Table 5 and are plotted versus the aggregate pyrite contents in Figure 2.

It should be noted that shrinkage values below 0.06% (i.e negative expansion absolute value) are considered acceptable.

The final shrinkage values for all mortar bar sets subjected to sea water immersion and air dry cycling after 14 months were much lower than 0.06%. In particular the mortar bars containing diabase aggregate and cement from CS-1 source exhibited final shrinkage values which were generally slightly lower than those containing cement from CS-2 source with the exception of sets made using QS-8 aggregate which showed approximately similar shrinkage values with the two cement sources.

The shrinkage values of the two limestone containing mortar bar sets (i.e. containing CS-1 & CS-2 cement respectively) were low and almost identical.

The shrinkage of the mortar bar sets made using CS-1 cement generally exhibited a reverse trend to that in the 38°C sets with respect to the pyrite content i.e the highest pyrite content M4M (4.8% pyrite) showed the lowest shrinkage (0.015%) and the lowest pyrite content set M2M (pyrite not detected) exhibited the highest shrinkage (0.027%).

The shrinkage of the mortar bar sets made using CS-2 cement showed somewhat mixed results with the sets M1V and M5V (1.3% & 0.6% pyrite content) exhibiting almost similar shrinkage values (0.036% & 0.035% respectively) and the set M4V with the highest pyrite content (4.3%) and that M2V with the lowest pyrite content (not detected) exhibiting almost similar shrinkage values (0.026% & 0.025%).
A few mortar bar specimens exhibited a small number of some localised brown/rusty staining of sand size spots possibly due to surficial oxidation of pyrite.

Mortar bars from sets made using CS-2 cement appeared to exhibit slightly more frequently rusty stains than those made using CS-1 cement. The staining in the sets of the sea water/air dry cycling appeared at earlier ages than those stored at 38°C, but the stains slightly increased in number and size at later stages. No visible deleterious reaction (i.e. cracking, spalling, pop-outs or reaction products) however was observed in any specimen.

On the basis of the results of the microprobe analyses there was slightly more frequent occurrence of sulphur and iron concentrations in the 50μm zone from pyrite grains in the mortar bar specimens made using CS-2 cement. No reliable correlation could be made with regard to the pyrite content and the frequency of occurrence of sulphur and iron concentrations. In the mortar bar sets with higher pyrite contents (M4M & M4V with 4.8% & 4.3% respectively) there was no observed increased frequency of occurrence of sulphur and iron ions concentrations in the vicinity of the pyrite grains when compared with those with lower pyrite contents.

Cracks and microcracks in the mortar bars examined from the sea water/air drying cycling were more abundant that those store at 38°C and were mainly due to shrinkage effects from cement paste and/or aggregate particles. Some fine cracks and microcracks were seen to possibly originate from sporadic pyrite grains but due to the abundance of microcracks present and the sparsity of these grains it could be not reliably concluded that this cracking/microcracking was definitely stemming from those grains. Some small scale incipient reaction may have sporadically occurred but it was not apparent at this stage.

6.3.3 Concrete prism test at 38°C in moist air

The expansion test results for the concrete prisms stored at 38°C moist air showed very small expansion values with a maximum final expansion mean value of 0.008% after 14 months of testing. A summary of the final mean expansion values is given in Table 6 and are plotted versus the aggregate pyrite contents in Figure 3.

It should be noted that for expansion to be considered significant it should exceed 0.03% at one year.

The final expansion values for all concrete prism sets stored at 38°C moist air after 14 months were much lower than 0.03%. The concrete prisms containing high pyrite contents (T1M & T1V with 4% & 5% respectively) exhibited final expansion values (0.004% & 0.003%) which were lower than those (i.e. containing lower pyrite contents (i.e. T2M & T2V with 1% pyrite each & 0.008% & 0.004% expansion respectively).

The prisms made using CS-2 cement exhibited slightly lower expansion values compared to those of prisms made using CS-1 cement.

All concrete prism specimens exhibited localised brown/rusty staining of sand size spots possibly due to surficial oxidation of pyrite. Small scale spreading of rust discolouring the surrounding cement paste was observed in some occasions.

No visible deleterious reaction (i.e. cracking, spalling, pop-outs or reaction products) was observed in any specimen.

The microprobe analyses results showed that there was slightly more frequent occurrence of sulphur and iron concentrations in the 50μm zone from pyrite grains in the concrete prism specimens made using CS-2 cement. No reliable correlation could be made with regard to the pyrite content and the frequency of occurrence of sulphur and iron concentrations. In the prism sets with higher pyrite contents (T1M & T42V with 4% & 5% respectively) there was no observed increased frequency of occurrence of sulphur and iron ions concentrations in the vicinity of the pyrite grains when compared with those with lower pyrite contents (i.e. T2M & T2V with 1% each).

Cracks and microcracks in the concrete prism specimens examined were mainly due to shrinkage effects from cement paste and/or aggregate particles. Some fine cracks and microcracks were seen to possibly originate from sporadic pyrite grains but due to the abundance of microcracks present and the sparsity of these occurrences it could be not reliably concluded that this cracking/microcracking was definitively stemming from those grains. Small scale incipient reaction may have sporadically occurred but it was not apparent at this stage.

6.3.4   Concrete prism test sea water/air dry cycling

The concrete prisms in sea water/air dry cycling exhibited a shrinkage mean value up to 0.017% at the end of 30 cycle testing period (i.e. 14 month period). A summary of the final mean expansion values is given in Table 6 and are plotted versus the aggregate pyrite contents in Figure 4.

It should be noted that shrinkage values below 0.06% (i.e negative expansion absolute value) are considered acceptable.

The final shrinkage values for all concrete prism sets subjected to sea water immersion and air dry cycling after 14 months were much lower than 0.06%. The concrete prisms containing cement from CS-1 source exhibited final shrinkage values which were generally higher than those containing cement from CS-2 source.

The shrinkage of the prism sets made using CS-2 cement exhibited generally a reverse trend with respect to the pyrite content i.e the highest pyrite content T1V (5% pyrite) showed the lowest shrinkage (0.004%) and the lowest pyrite content set T2V (1% pyrite) exhibited higher shrinkage (0.008%).

Some prism specimens with the exception of those of set T1M (4% pyrite content) exhibited a small number of localised brown/rusty staining of sand size spots possibly due to surficial oxidation of pyrite.

Concrete prisms from sets made using CS-2 cement appeared to exhibit slightly

more frequently rusty stains than those made using CS-1 cement. The staining in the sets of the sea water/air dry cycling appeared at slightly earlier ages than those stored at 38°C. The stains slightly increased in number and size at later stages.

No visible deleterious reaction (i.e. cracking, spalling, pop-outs or reaction products) however was observed in any specimen.

It should be noted that all specimens in sets stored at 38°C moist air exhibited rust spots whilst in the prism specimens subjected to sea water immersion/air dry cycling some only exhibited rusty spots. This is not as it was expected because chloride in sea water should promote the reaction with pyrite.

On the basis of the results of the microprobe analyses there was slightly more frequent occurrence of sulphur and iron concentrations in the 50μm zone from pyrite grains in the prism specimens made using CS-2 cement. No reliable correlation could be made with regard to the pyrite content and frequency of occurrence of sulphur and iron concentrations. In the prism sets with higher pyrite contents (T1M & T2V with 4% & 5% respectively) an increased frequency of occurrence of sulphur and iron ions concentrations was not observed in the vicinity of the pyrite grains when compared with those with lower pyrite contents (i.e. T2M & T2V with 1% each).

Cracks and microcracks in the concrete prisms examined from the sea water/air drying cycling were apparently similar in frequency of occurrence to those stored at 38°C and were mainly due to shrinkage effects from cement paste and/or aggregate particles. Some fine cracks and microcracks were seen to possibly originate from sporadic pyrite grains but due to the abundance of microcracks present and the sparsity of these occurrences it could not be reliably concluded that this cracking/microcracking was definitively stemming from those grains. Small scale incipient reaction may have sporadically occurred but it was not apparent at this stage.

7.   CONCLUSION

In the present research programme experimental pavement quality concretes were tested employing different grain size of the aggregate (i.e. utilising finely crushed aggregate in the mortar bar test in order to increase the surface area of the aggregate and pyrite), normal concrete aggregate sizes (i.e. 20mm, 10mm and sand in the concrete prisms) and accelerating conditions of elevated temperature and moisture and saline water immersion and air drying conditions which are known to promote reactions and oxidation.

Two types of cements were employed for the experimental mortar bars and concrete prisms testing. The period of testing for the mortar bars was extended to 14 months (as for concrete prism test), which was longer than that specified in the contract, in order to obtain more reliable results.

In addition in-service dense concretes from advised exposed to elements structures of ages up to 15 years old and not less than 5 years old were examined.

On the basis of the experimental testing programme, examination and analyses, carried out, including the in-service concrete samples, no deleterious pyrite reaction was definitively identified. Some incipient and sporadic reaction may have taken place but it did not appear to have been

manifested to a detrimental level.

The two cements used exhibited minor differences in the expansion tests (given the very small expansion values) and frequency of pyrite surficial reactions (staining) and no reliable conclusion can be drawn.

It appears that the pyrite oxidation and concomitant expansion is a reaction which takes time to manifest especially in dense concretes. The reaction is dependent on factors such as moisture, temperature, pH of the environment, oxidising and alkaline conditions (in that oxidising and alkaline conditions can operate synergistically), amount and grain size of pyrite and probably degree of crystallinity and chemical composition of pyrite (i.e. if other elements are present in the crystal lattice). It should be noted that the pyrite observed within the aggregate was in crystalline form and occasionally contained other metals such as copper and lead.

Although the amount of pyrite content did not reliably correlate with the highest expansion values (in that expansion values were very much smaller than those considered to have a detrimental effect) or frequency and amount of sulphur and iron concentrations within the cement paste of the experimental mortar bar and concrete prism specimens, it is considered reasonable that the maximum limit of acid soluble sulphate content of aggregate (as specified within Cyprus Standards) for concrete, expressed as SO_3, be re-affirmed as 0.8% maximum and total sulphur (S) as 1% maximum. Consideration should be given, however, to an on-going test programme to further investigate, assess and monitor the potential for pyrite deleterious reaction in concrete. Some minor surficial oxidation of sand size pyrite has taken place in the experimental concrete prisms and mortar bars, after 14 months conditioning, but it was not damaging. Surficial reaction has been frequently reported in the literature including pop-outs and spalling. But major damage can occur in time when pyrite reactions proceed to cause expansion and reaction products react with the cement paste of the concrete.

The testing period of 14 months and the age of the in-service concretes indicate that for pyrite damaging reaction to occur longer exposure or testing periods are required. A survey of concrete structures under different regimes of exposure as foundations or buried structures and otherwise exposed concrete, and additional testing of in-service concrete and experimental concrete under conditions promoting pyrite oxidation and reaction in conjunction with different aggregate combinations (i.e. diabase with limestone and/or calcarenite in different proportions) and pyrite proportions and possibly crystallinity, using the two cement types (CS-1 & CS-2), should be carried out in order to further investigate the effect of pyrite in aggregate for concrete. Other parameters such as concrete compaction and density, cement content, water : cement ratio, mixing water chloride content may be employed in this research.

These results and comments conclude the programme of testing and examination requested to date. Please do not hesitate to contact us if we can be of any further assistance in this matter.

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REPORT 25055/G/4

**REPUBLIC OF CYPRUS
MINISTRY OF AGRICULTURE, NATURAL RESOURCES
AND ENVIRONMENT**

GEOLOGICAL SURVEY DEPARTMENT

**RESEARCH PROGRAMME
INTO POSSIBLE ADVERSE EFFECTS OF AGGREGATE
CONTAINING SULPHIDE MINERALS IN CONCRETE**

FINAL REPORT

Ministry of Agriculture, Natural Resources and Environment
Geological Survey Department
1415 Nicosia
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For the attention of Director and Mr Ch. Hadjigeorgiou

22 November 2005

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