Pyrite Testing explained

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For the:

Institute of Geologists of Ireland

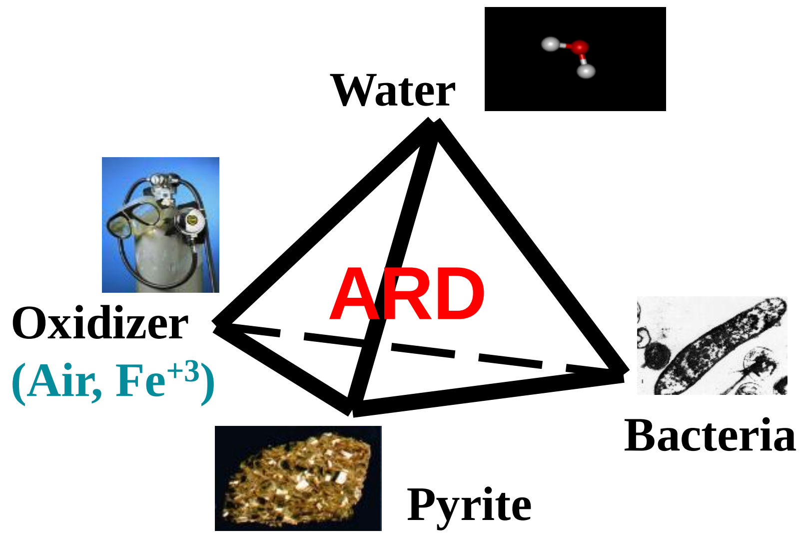
Pyrite CPD Course

4 December 2013

Start at the beginning ….

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

Pyrite, Water, Oxygen, Ferrous sulphate, Sulphuric acid

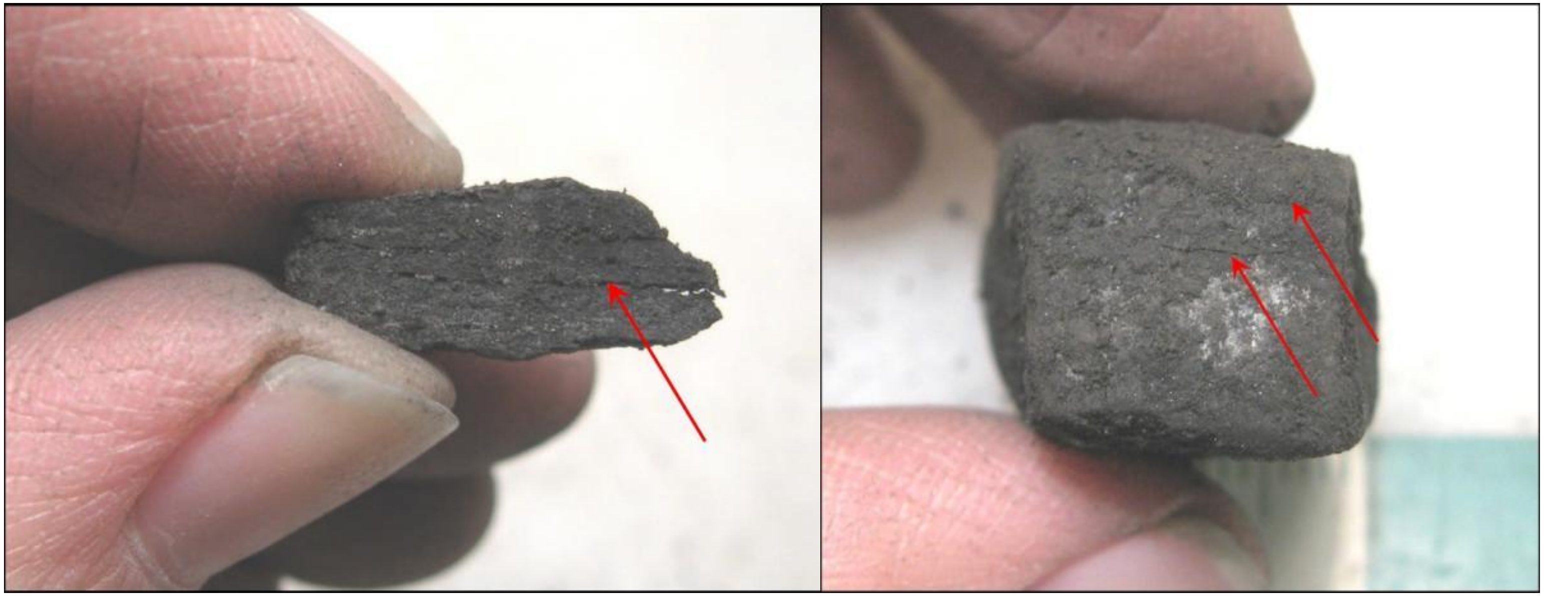


$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 . 2H_2O + CO_2$$

Sulphuric acid, Calcite, Water, Gypsum, Carbon dioxide

Our Goal

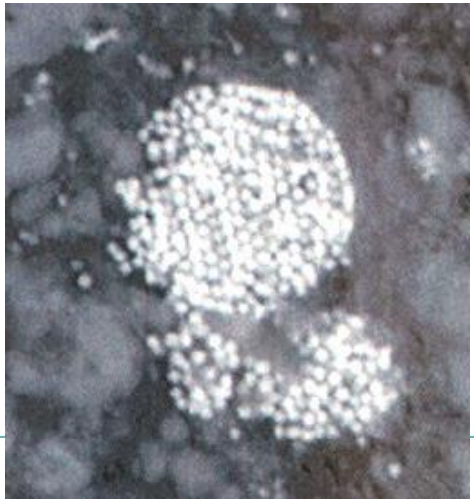
Does the sample contain rock types that are, or have been, associated with pyritic heave?



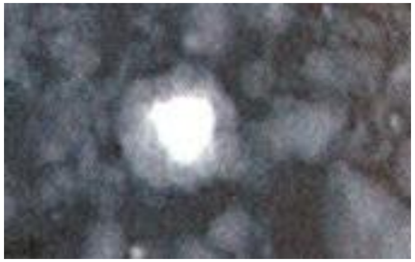
Need to identify the presence of reactive pyrite and secondary minerals that may be associated with heave (e.g. gypsum)

Chemical Reaction

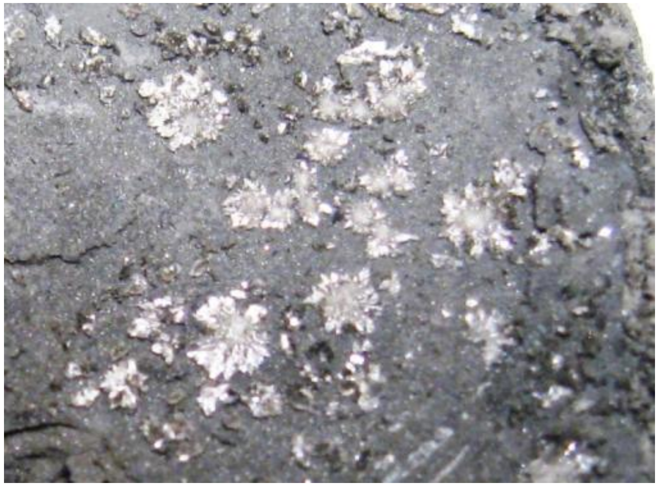
- Pyrite (FeS_2) in framboidal form
- Reacts with moisture and air present in ground – oxidizes the pyrite, releasing sulphuric acid (H_2SO_4)
- These rocks typically have 20 to 30% calcite in them (like the problematic mudstones in Ireland), though only 1-2% calcite needed to feed reaction (Québec Shales). H_2SO_4 dissolves the calcite releasing Ca ions in to solution.
- The solution eventually becomes super saturated
- Crystallization of gypsum ($CaSO_4\ 2H_2O$)



Pyrite framboid, ~20µm fov



Pyrite oxidising, ~20µm fov



Gypsum within opened lamination ~5cm fov

I.S. 398-1 Professional Geologist's Report

Laboratory Test Report

Hardcore Sample Report

Sampling of hardcore, with a visual inspection

Laboratory tests (specific for each test suite)

Overall Classification of hardcore

I.S. 398-1 Test Suites

Selection of a Suite depends on:

- Damage Condition Rating;
- Background information on the house (i.e. location, when built, etc.);
- Results of previous testing (if any);
- A Certificate is required.

Test Suite	Tests
Test Suite 0	Geological inspection
	Chemical testing
Test Suite 1	Geological inspection
	Chemical testing
	Mineralogical analysis (XRD)
Test Suite 2 (following Suite 0 or Suite1)	Thin section petrographic analysis
	Water absorption

Overview of Testing Protocol

- Sample Handling and Preparation
- Visual Inspection and Geologic Description
- Chemical Testing
- Mineralogical Analysis
  - XRD
  - Petrographic microscopy
  - SEM
- Physical Tests
  - Water absorption
  - Abrasion tests
  - Particle size distribution, moisture
  - Etc.

How Much Sample Do you Need?

- What tests are going to be performed?
- 5kgs to 500kgs

I.S. 398-1:

- ≥ 500g blinding sand
- ≥ 25kg infill (per sample)
- 250mL standing water (if present)

BS EN 932-1: 1997 Sample Reduction	Sample No.	Original Bulk Mass (kg)	Sample Bag Mass (kg)	Representative Sample Mass (kg)
	Celtic-2	421	25.64	8.86
	Celtic-25	209	26.62	6.56
	Celtic-49	149	29.78	6.32

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Visual Inspection (Field)

Blinding Sand:

- Colour
- Estimated particle size
- Moisture condition *(Dry, damp, wet)*

Infill:

- Colour
- Rock types *(Mudstone, shale, limestone, carbonaceous mudstone, etc.)*
- Particle size
- Particle shape *(Rounded, elongate, tabular, cuboid, sub-rounded, angular)*
- Moisture condition *(Dry, damp, wet)*
- Presence of coatings/crystal growth

Geological Description (Lab)

Does the sample contain rock types associated with pyritic heave ?

i.e. Weak, fine-grained sedimentary (muddy limestone, calcareous mudstone, shale) or metamorphic rocks

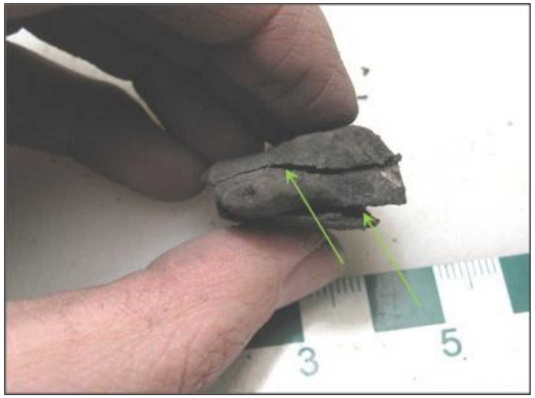
I.S. EN 932-3 (1997) *Tests for general properties of aggregates — Part 3: Procedure and terminology for simplified petrographic description*

Geological Description

Particle size
Particle shape
Rock types (including proportion thereof)

Lithological detail:

Colour
Predominant grain size
Mineralogy
Laminations
Surface coatings
Staining
Hardness / Strength
Carbonates



Chemical Testing

- 'Representative Sub-sample' ….. 1-2 kgs, potentially more!
- Identify and measure concentration and composition of selected sulphur species
- Sample preparation
  - Avoid high heat and extensive milling, which may cause oxidation
- Tests:
  - Total sulphur (TS)
  - Acid-soluble sulphate (AS)
  - Water-soluble sulphate (WS)
- TS and AS allow determination of estimated pyrite content
- WSS indicates aggressiveness of fill to concrete materials

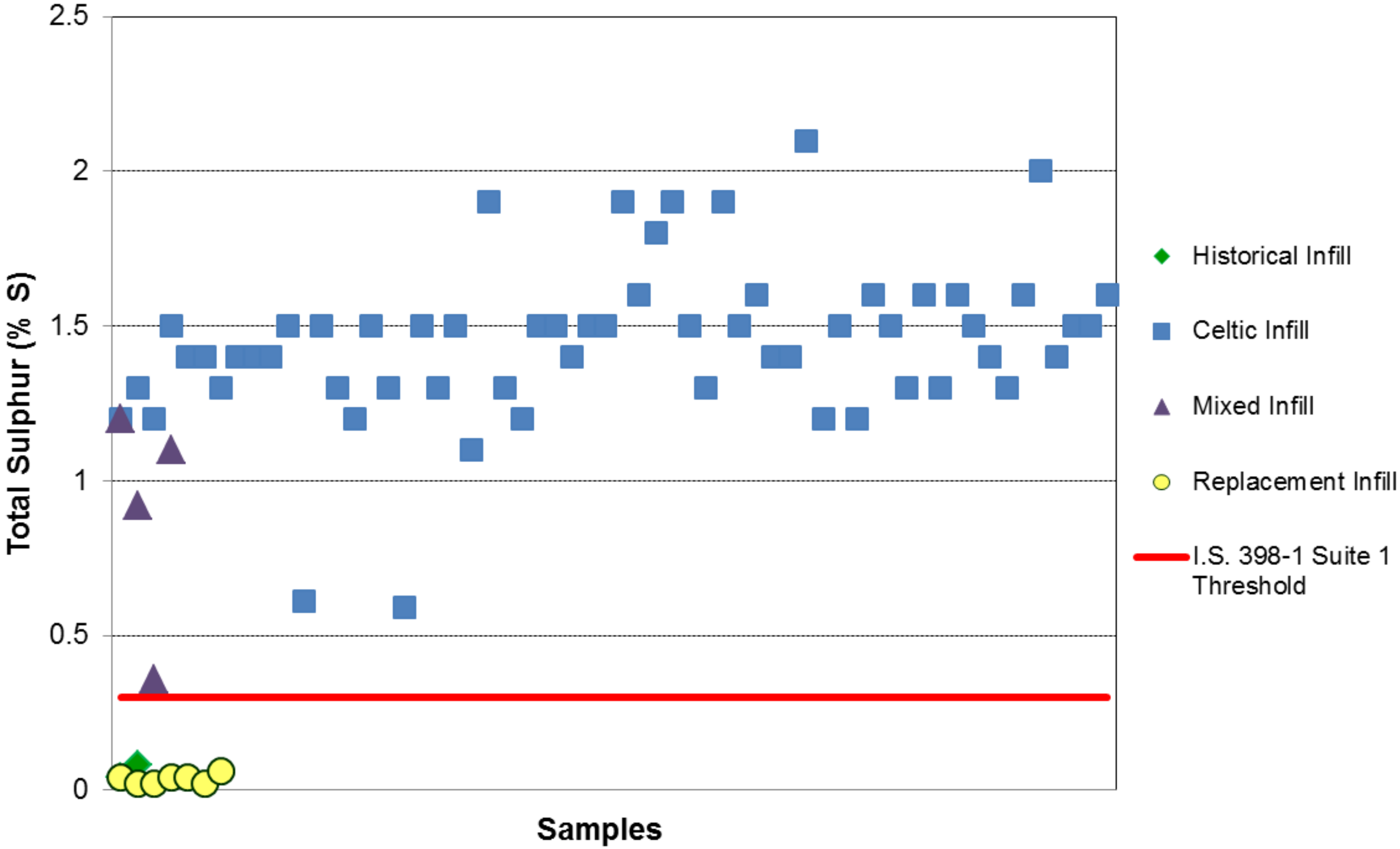
Total Sulphur (TS)

- Includes sulphates, sulphides, monosulphide sulphur, and organic sulphur.
- Allows an estimate of *original* pyrite content:

Original Pyrite (FeS_2) = 1.87 x TS

Method	Description
TRL 447 Method - Test 4	A: Microwave digestion of the sample using aqua regia, with determination of the liberated sulphur in solution using ICP-AES. B: Rapid High Temperature Combustion Analysis (Leco)
Sample Size	**Sample Preparation**
≥500g initially, then 200-300g. Test portion is 300mg.	Dried at 100-105ºC; Sieved to <2mm, Mixed and quartered/riffled to 200-300g; Milled to <212µm

Case Study Example – Total Sulphur



Acid-Soluble Sulphate (AS)

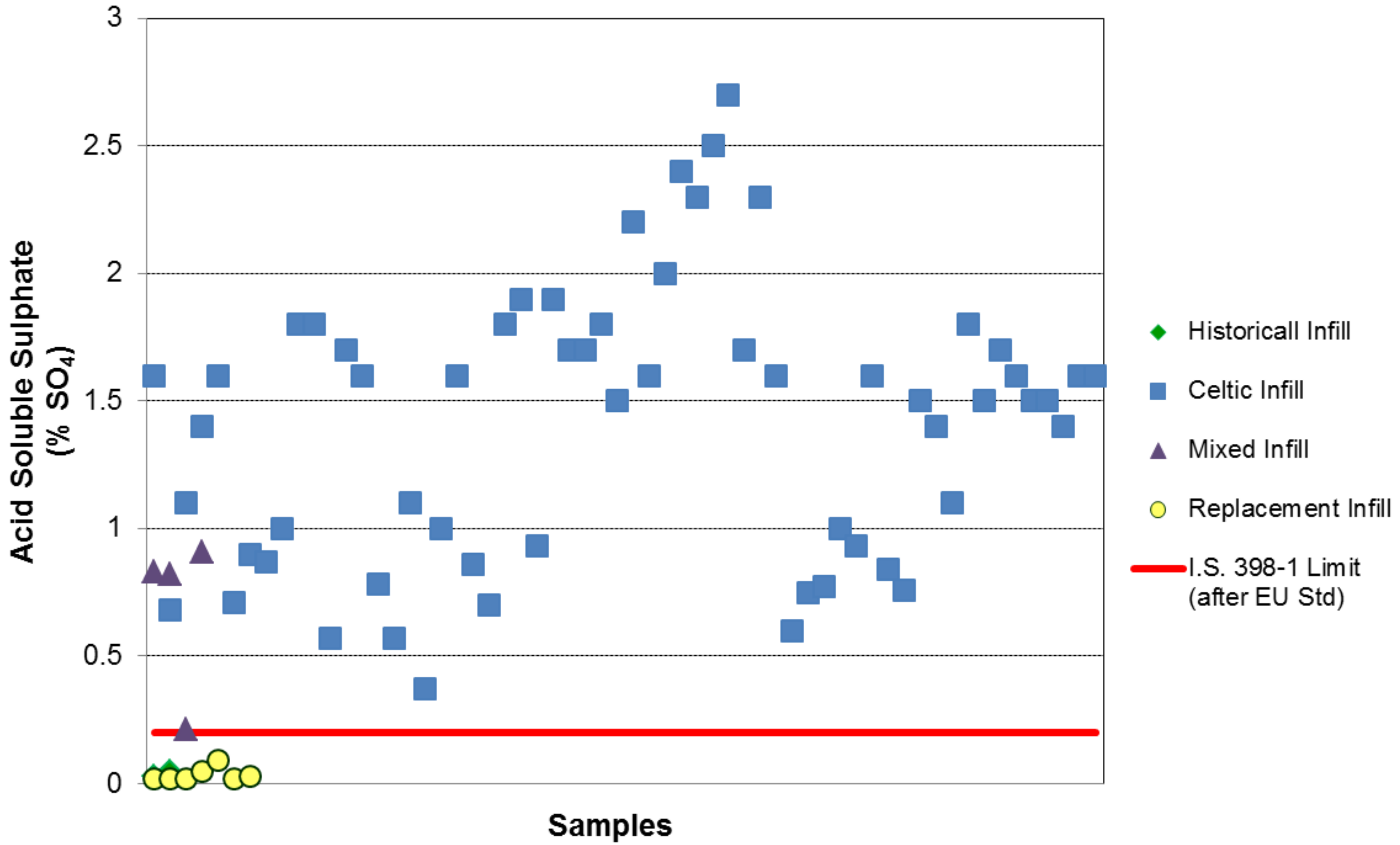
- Acid soluble sulphur measured, with results expressed in %S. Results then converted to acid soluble sulphate by calculation:

AS (%SO_4) = 3 x acid soluble sulphur (as %S)

- Includes sulphur locked up in all sulphate minerals, such as gypsum ($Ca_2SO_4.2H_2O$), anhydrite ($CaSO_4$) and jarosite ($KFe_3(SO_4)_2(OH)_6$).

Method	Description
TRL447 Method - Test 2	HCl digestion, followed by ICP-AES analysis
Sample Size	**Sample Preparation**
≥500g initially, then 200-300g. Test portion is 0.8 - 1.0g	Dried at 100-105ºC; Sieved to <2mm, Mixed and quartered/riffled to 200-300g; Milled to <212µm

Case Study Example – Acid Soluble Sulphur



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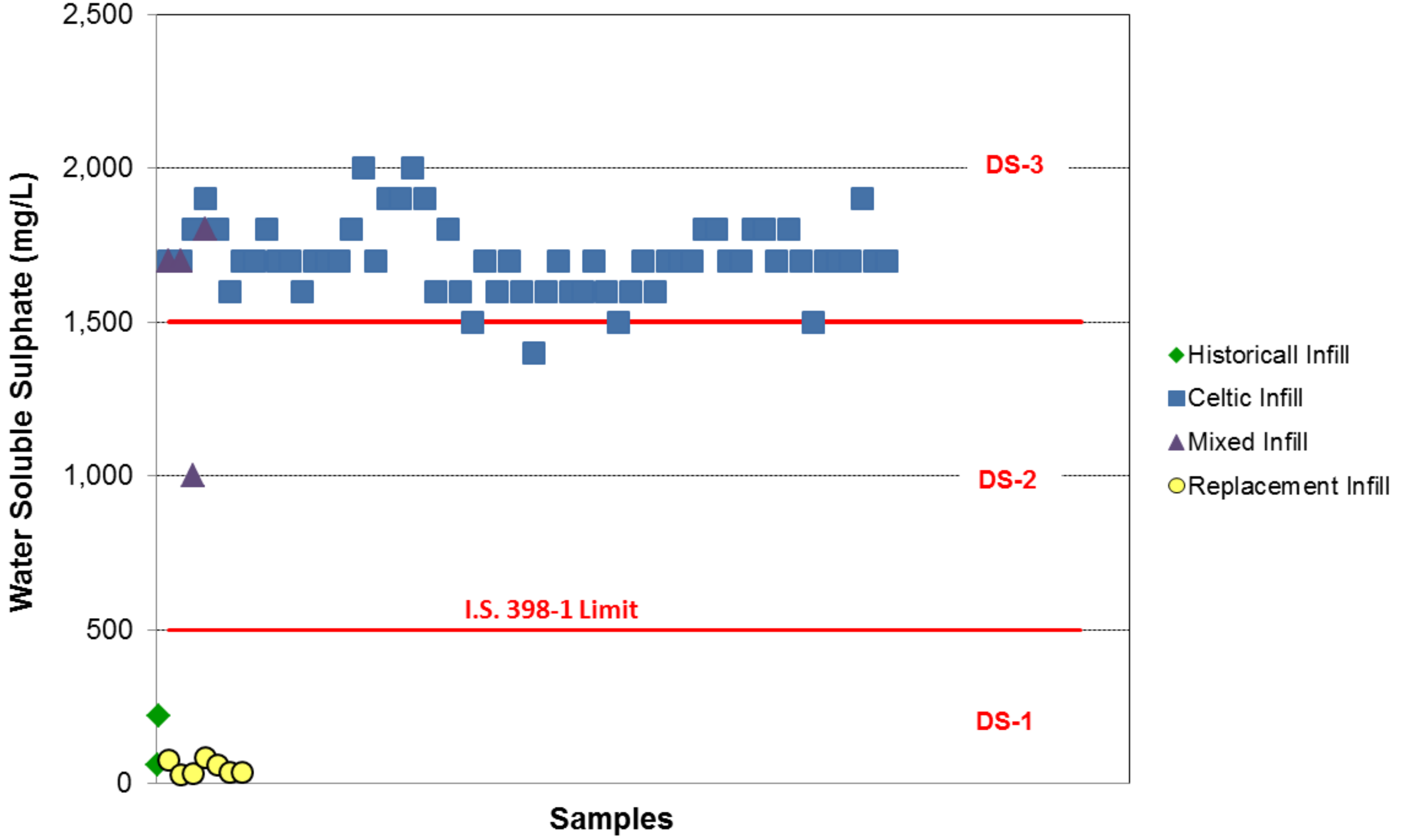
Water Soluble Sulphate (WS)

- Assesses aggressiveness of fill to concrete materials in the presence of water (sulphate attack)
- Water soluble sulphur measured, with results expressed in %S. Results then converted to water soluble sulphate by calculation:

WS (mg/L SO_4) = 15 x 1,000 x water soluble sulphur (as %S)

Method	Description
TRL Report 447, Test 1	Dissolved in distilled water, agitated for 16h then filtered; ICP-AES to determine sulphur content
Sample Size	**Sample Preparation**
Fine-grained soils 100g; Med-grained 500g; Coarse-grained 3kg	Sample passing 2mm sieve; pulverized to pass 425µm

Case Study Example – Water Soluble Sulphate



Estimated Pyrite Content (Current)

Calculate the Oxidisable Sulphide (OS) content:

$$OS = (3.0 \times TS) - AS$$

Where: OS = oxidisable sulphides as % SO_4

TS = Total Sulphur as % S

AS = Acid-Soluble Sulphur as % SO_4

Then assume all oxidisable sulphides are pyrite:

$$\%\ \text{Pyrite}\ (FeS_2) = 0.623 \times OS$$

<u>NOTE:</u> Calculation may overestimate pyrite if barite (barium sulphate) is present

Mineralogical analysis - XRD

- X-Ray Diffraction (XRD) analysis used to detect and quantify gypsum, clay minerals, and sulphur-bearing minerals
- 20g powdered sample
- Detection limits range from 0.5% - 2% depending on minerals present and degree of crystallinity

X-ray Diffraction Analysis

Size Fraction : Whole Rock

Petrolab Sample Ref	Client Sample Ref.	Illite+Mica	Kaolinite	Chlorite	Quartz	K Feldspar	Plagioclase	Calcite	Dolomite	Siderite	Pyrite	Total
MP 1148	DA01	18.5	0.0	5.9	28.7	0.8	3.7	34.9	2.2	1.6	3.9	100

Note: Chlorite composition is Mg-rich
Quantified by Siroquant (semi-quantitative)

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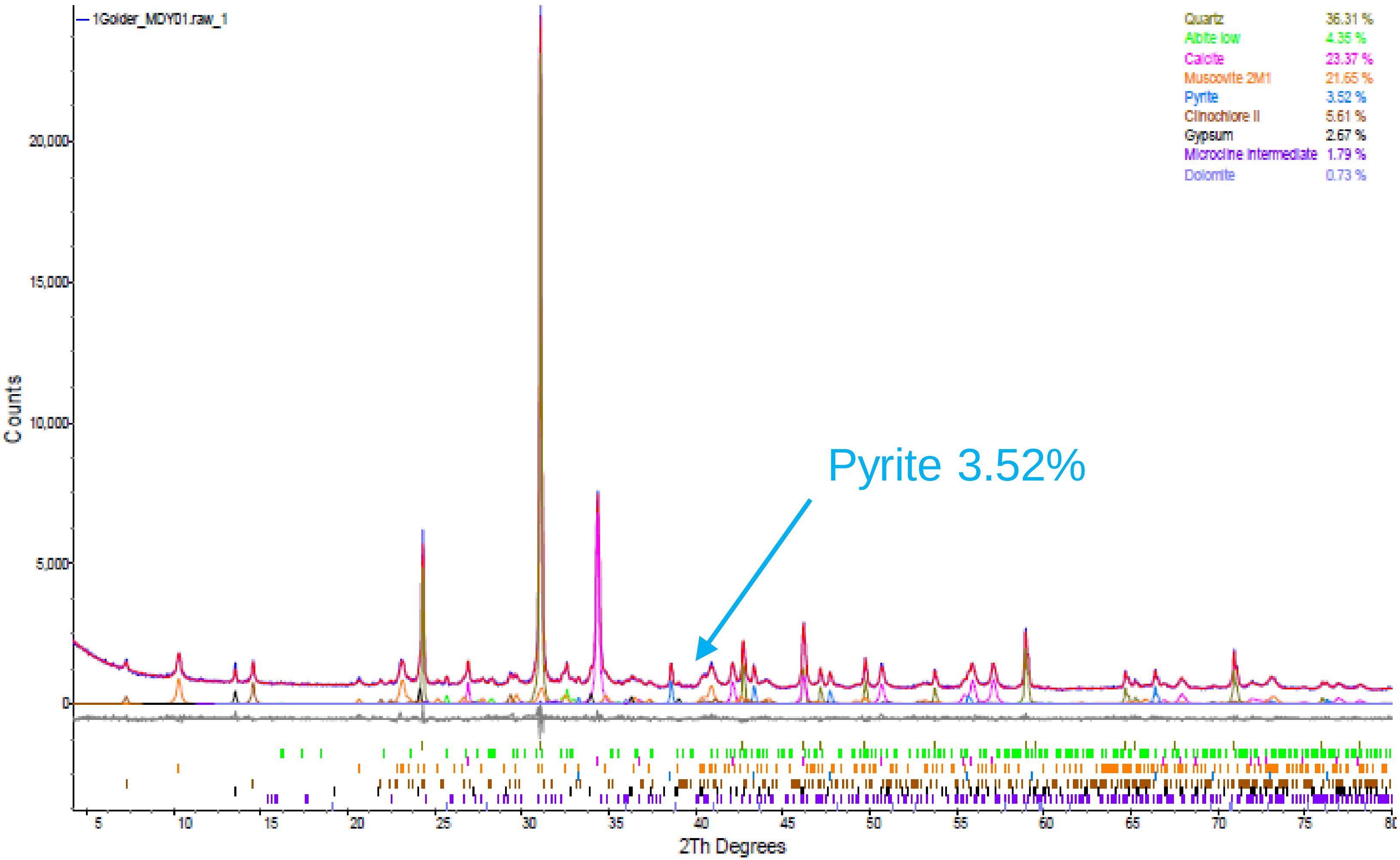
XRD Trace



1Golder_MDY01.raw_1
Quartz 36.31 %
Albite low 4.35 %
Calcite 23.37 %
Muscovite 2M1 21.65 %
Pyrite 3.52 %
Clinochlore II 5.61 %
Gypsum 2.67 %
Microcline intermediate 1.79 %
Dolomite 0.73 %
Pyrite 3.52%
Counts
20,000
15,000
10,000
5,000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
2Th Degrees

Mineralogical Analysis - Petrography

- Determine the mineralogical characteristics of the sample
- Thin section analysis identifies alteration and weathering features, such as form and distribution of pyrite and presence of derived sulphate minerals (e.g. gypsum)
- Methods:
  - BS 812: Part 104 (1994) *Testing aggregates — Part 104: Method for qualitative and quantitative petrographic examination of aggregates*
  - ASTM C295-03 *Standard Guide for Petrographic Examination of Aggregates for Concrete*
- Select samples of main lithologies for thin section preparation
- Use oil instead of water in sample preparation to preserve soluble minerals, e.g. gypsum
- Use both reflected and transmitted light

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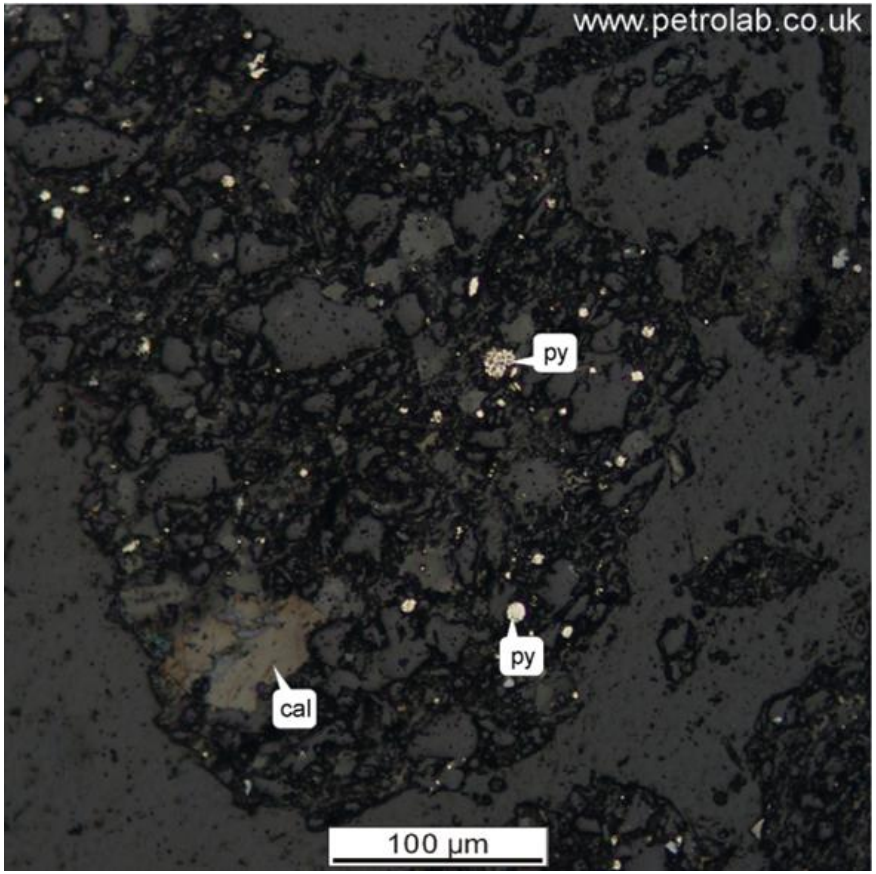
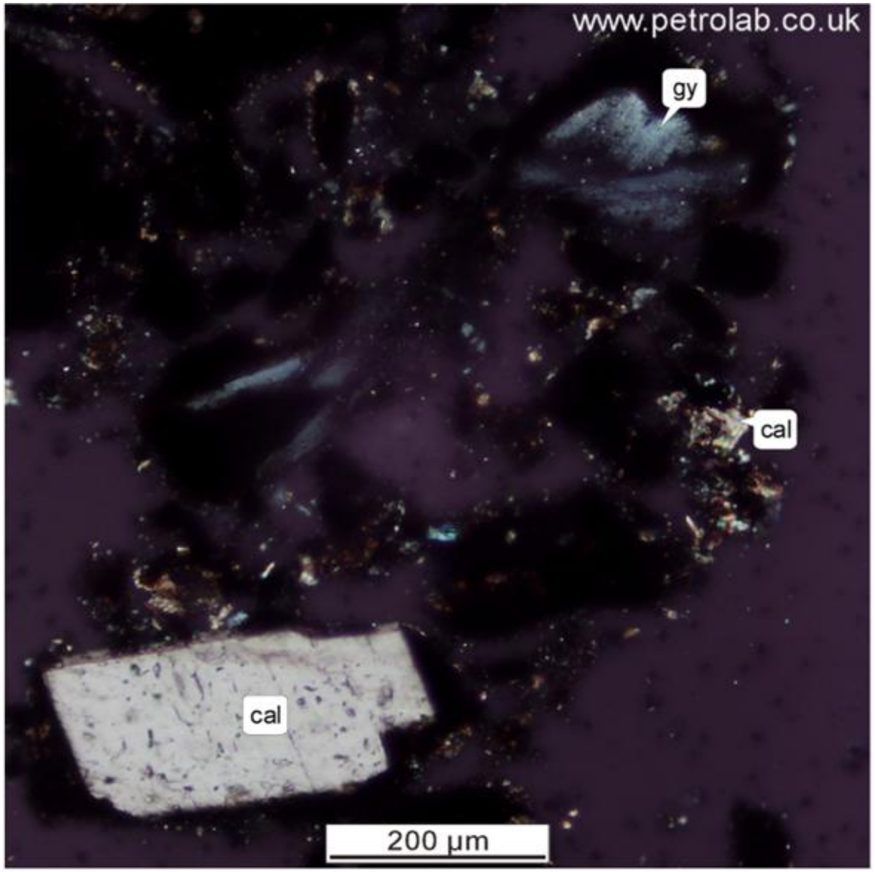
Petrographic Thin Sections

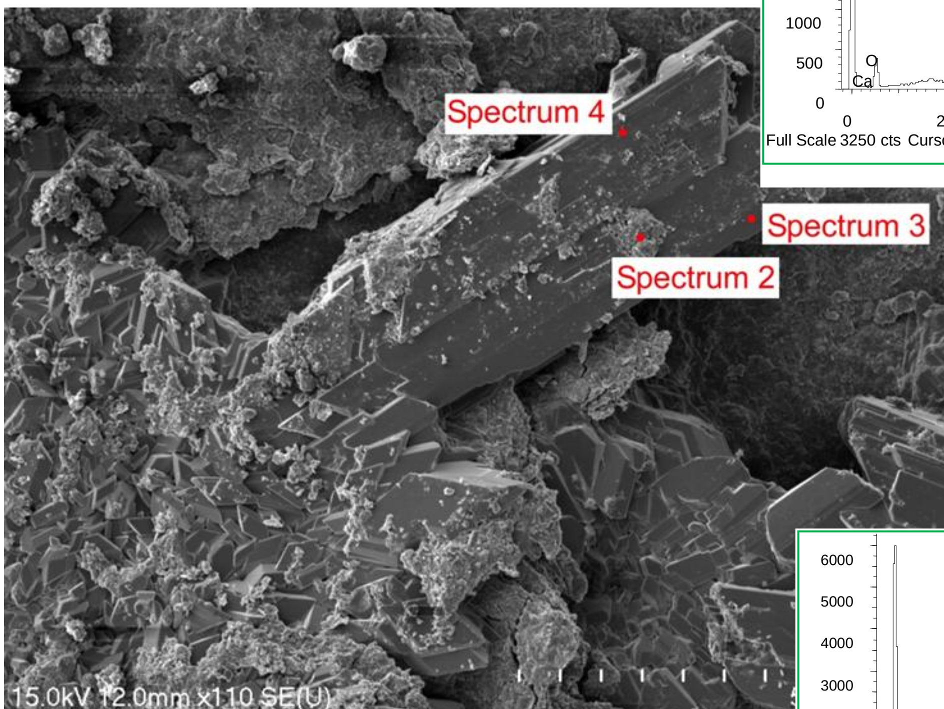


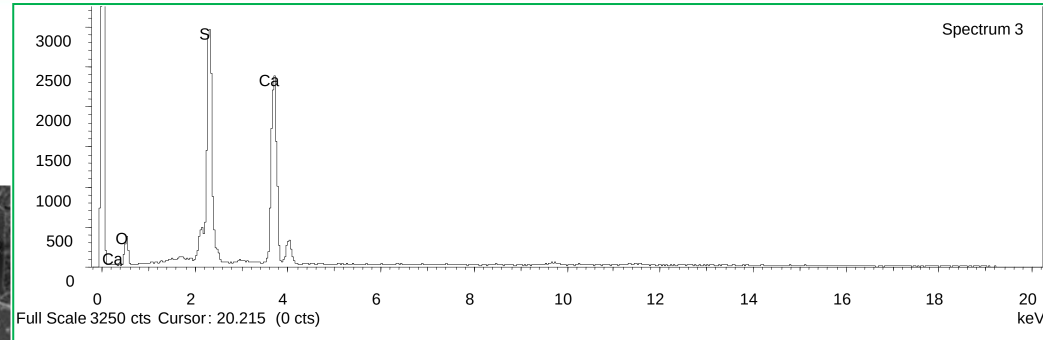


Mineralogical Analysis – SEM

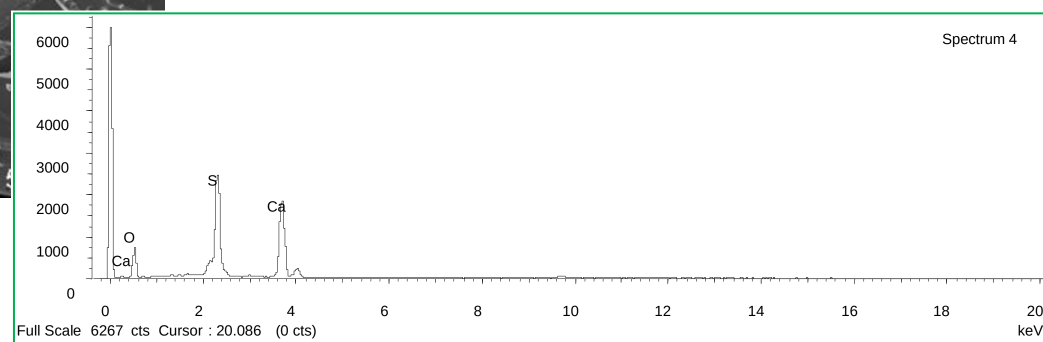
- Scanning Electron Microscopy (SEM)
- Microanalysis uses numerous points of analysis on secondary electron image to produce elemental spectral compositions
- Used to confirm the presence of gypsum and to provide a general chemical analysis of the host material

Mineralogical Analysis - SEM





Spectrum 3
Gypsum

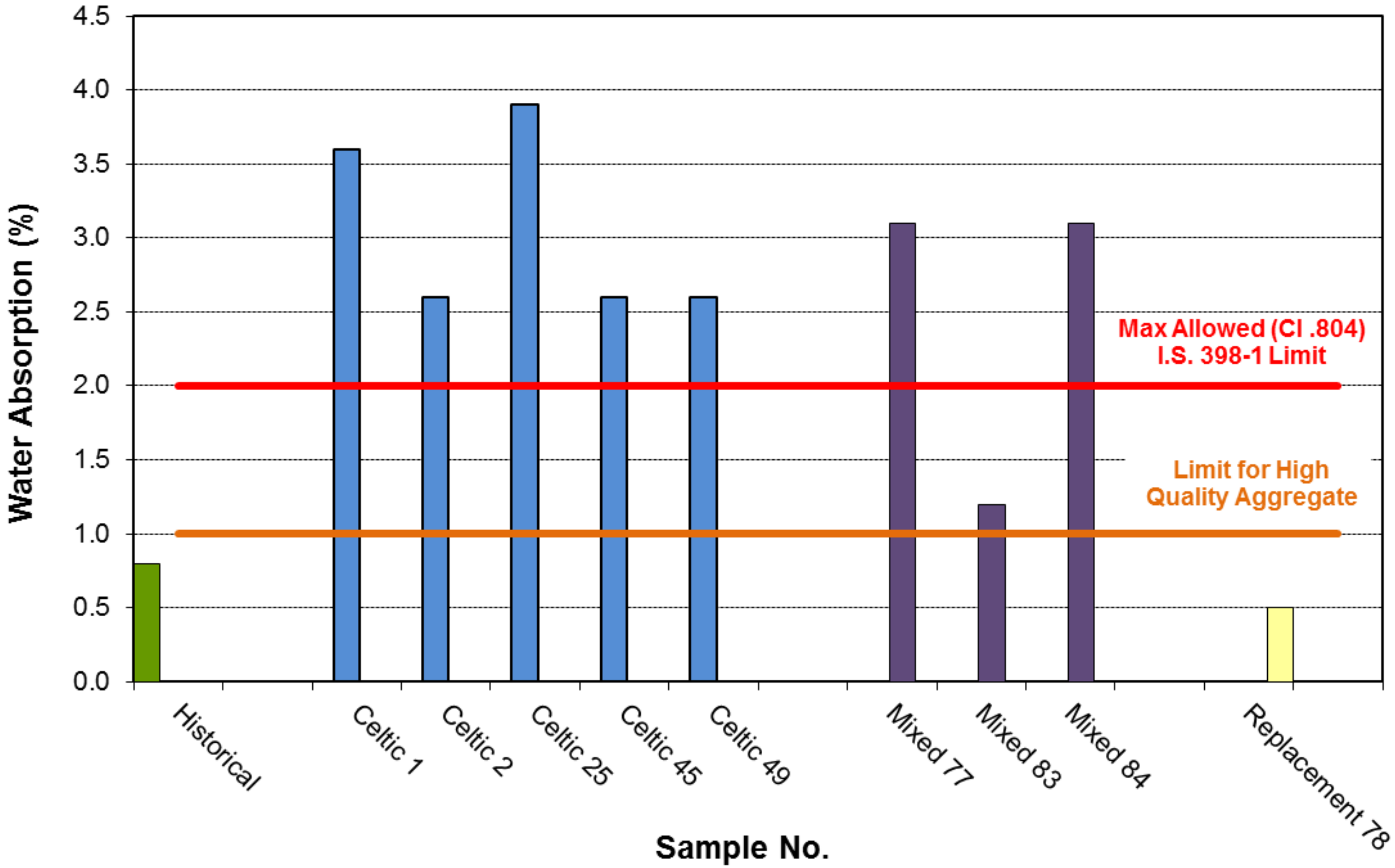


Spectrum 4
Gypsum

Physical Tests - Water Absorption

- Indicator of the ease which any contained pyrite will oxidise
- Determined by measuring the increase in mass of an aggregate due to water being absorbed into pores
- I.S. EN 1097-6 (2000) *Tests for mechanical and physical properties of aggregates — Part 6: Determination of particle density and water absorption*
- Representative sub-sample of bulk sample
- Sample size: 2kg minimum
- Results are expressed as a percentage of the dry mass of a sample
- High absorption values are indicative of high porosity and lower durability
- Values for the coarse fraction above 2% are of concern

Example – Water Absorption

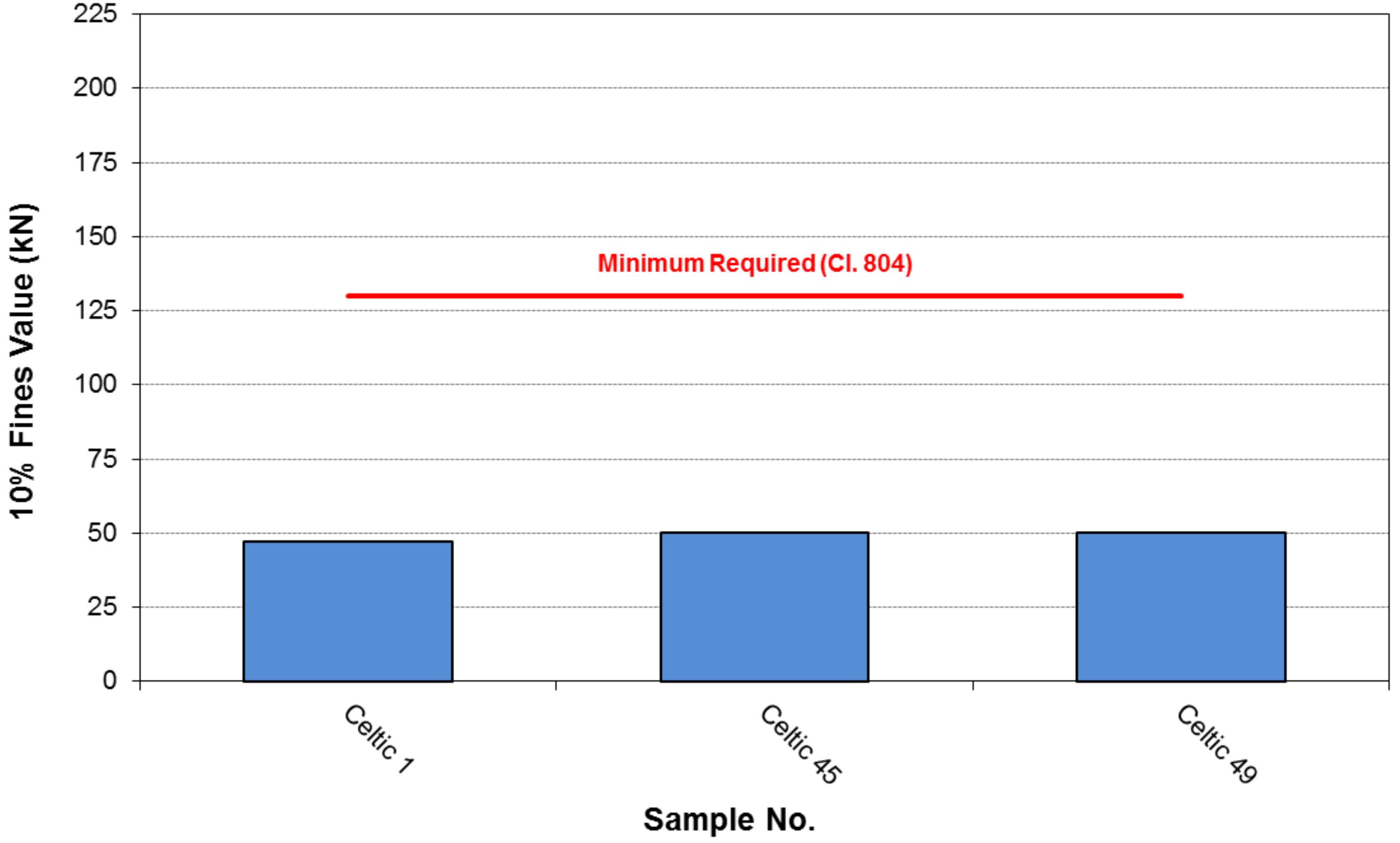


Physical Tests - Crushing

Ten Per Cent Fines Value (TFV) Test

- Measure of resistance to crushing
- *BS 812-111: 1990 Testing aggregates - Methods for determination of ten per cent fines value (TFV)*
- 15 - 60kg of particles in the 10 mm to 14 mm size range
- Low TFV are indicative of weak aggregates, and confirm low quality
- NRA specification for Clause 804 (March 2000) sets a minimum TFV of 130kN

Example – Ten Percent Fines Value



Physical Tests - Crushing

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Removed from Cl. 804 specification

- 15 - 60kg of particles in the 10 mm to 14 mm size range

in 2004 and replaced with LAA

- Low TFV are indicative of weak aggregates, and confirm low quality
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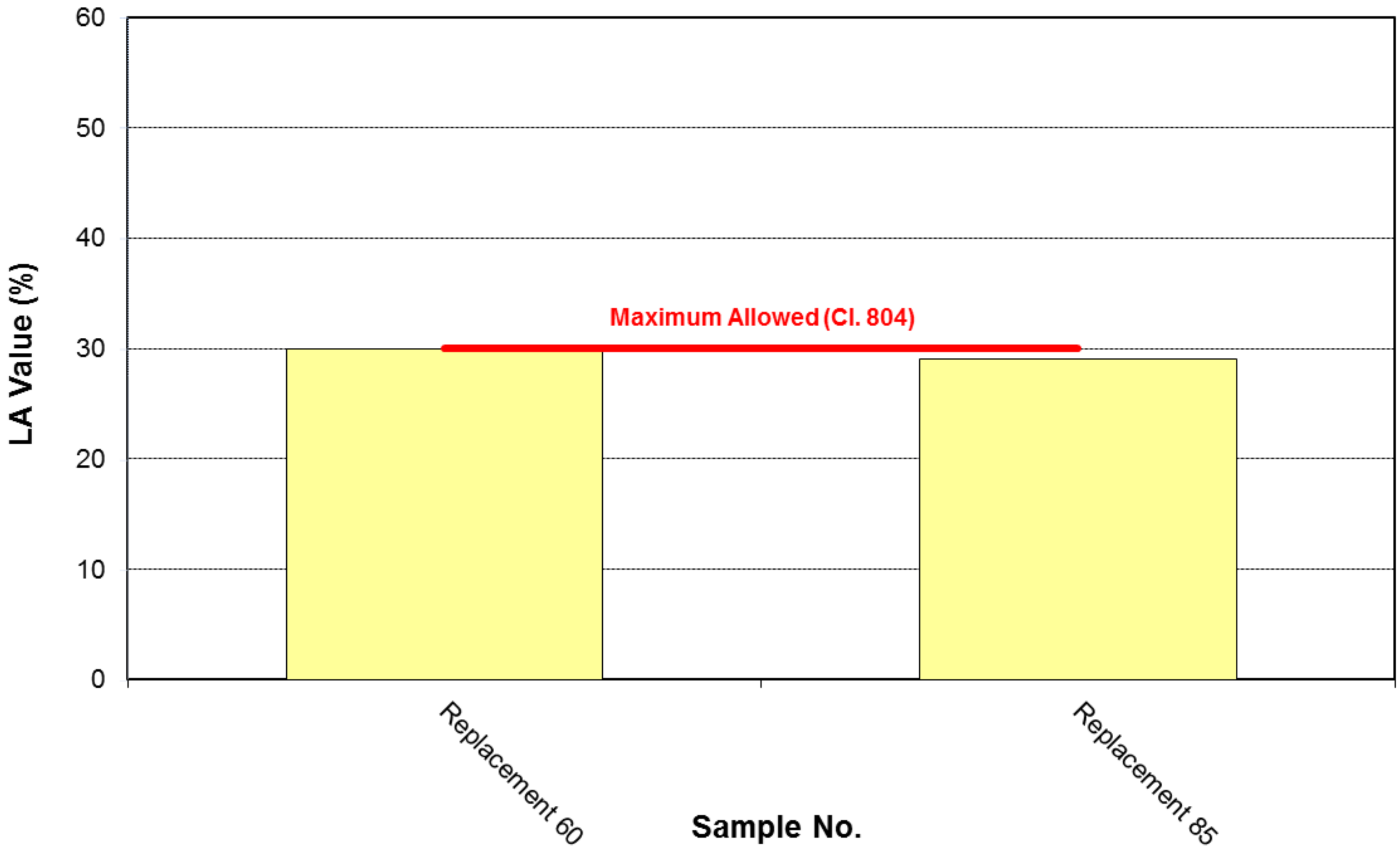
Physical Tests – Abrasion / Impact

Los Angeles (LA) Abrasion Test

- Impact and abrasion resistance of coarse aggregate
- *BS 1097-2: 1998 Tests for mechanical and physical properties of aggregates - Methods for the determination of resistance to fragmentation*
- 15kg of particles in the 10 to 14 mm size range
- The higher the LA coefficient, the poorer the infill material
- NRA specification for Clause 804 (May 2000) sets a maximum LA of 30%

Example – Los Angeles Abrasion



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Poor correlation with field performance

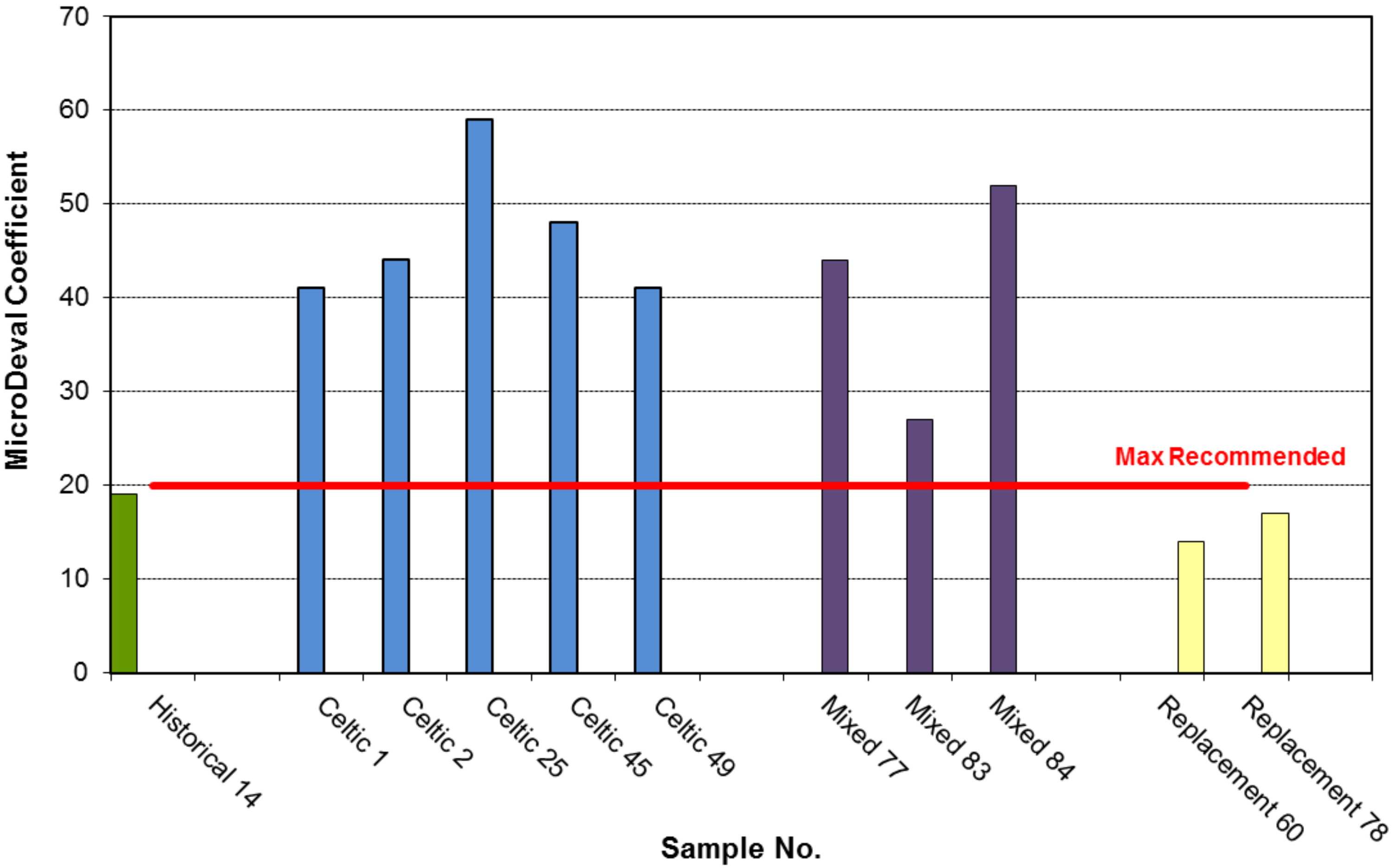
Test performed on dry aggregates

Physical Tests - Abrasion

Micro-Deval Test

- Wet test for abrasion resistance and durability
- Provides a good indication of aggregate's durability when exposed to weather and moisture
- *BS 1097-1: 1996 Determination of Resistance to Wear*
- 2kg of particles in the 10mm to 14mm size range
- Generally accepted upper limit for micro-Deval coefficient is 20 (Typical standards specify maximum values of 18 to 25)

Example - Micro-Deval



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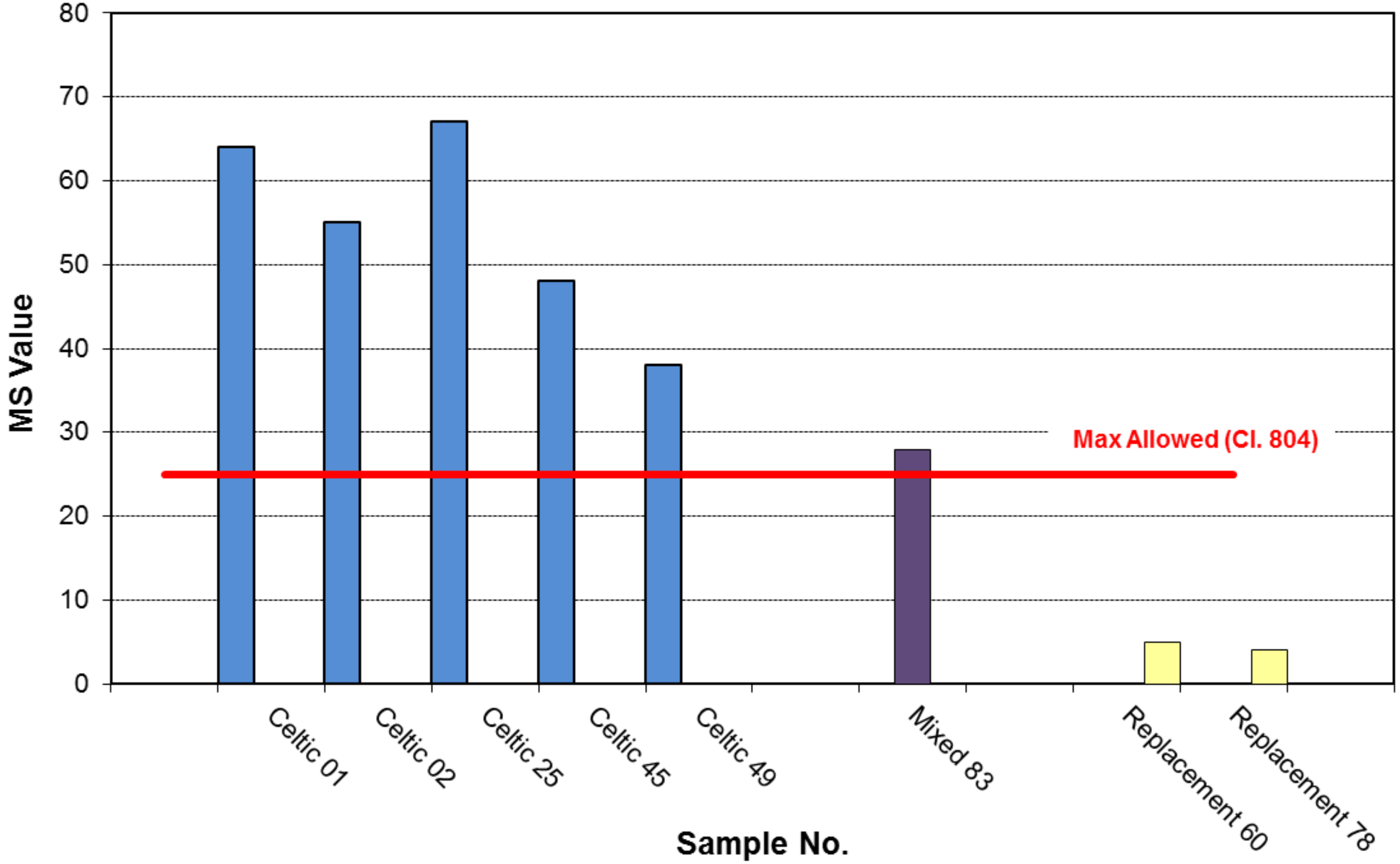
Physical Tests – Magnesium Sulphate Soundness

- Degree of degradation resulting from repeated crystallisation and rehydration of $MgSO_4$ within the materials pores depends on soundness of aggregate
- *BS EN 1367-2: 1998 Tests for thermal and weathering properties of aggregates. Magnesium sulphate test*
- 500g of particles in the 10mm to 14mm range
- Higher the MS value, the less durable the aggregate
- NRA specification for Clause 804 (May 2004) sets a maximum MS value of 25%
- Test is mainly used to determine susceptibility of an aggregate to degradation by exposure to freeze-thaw cycles

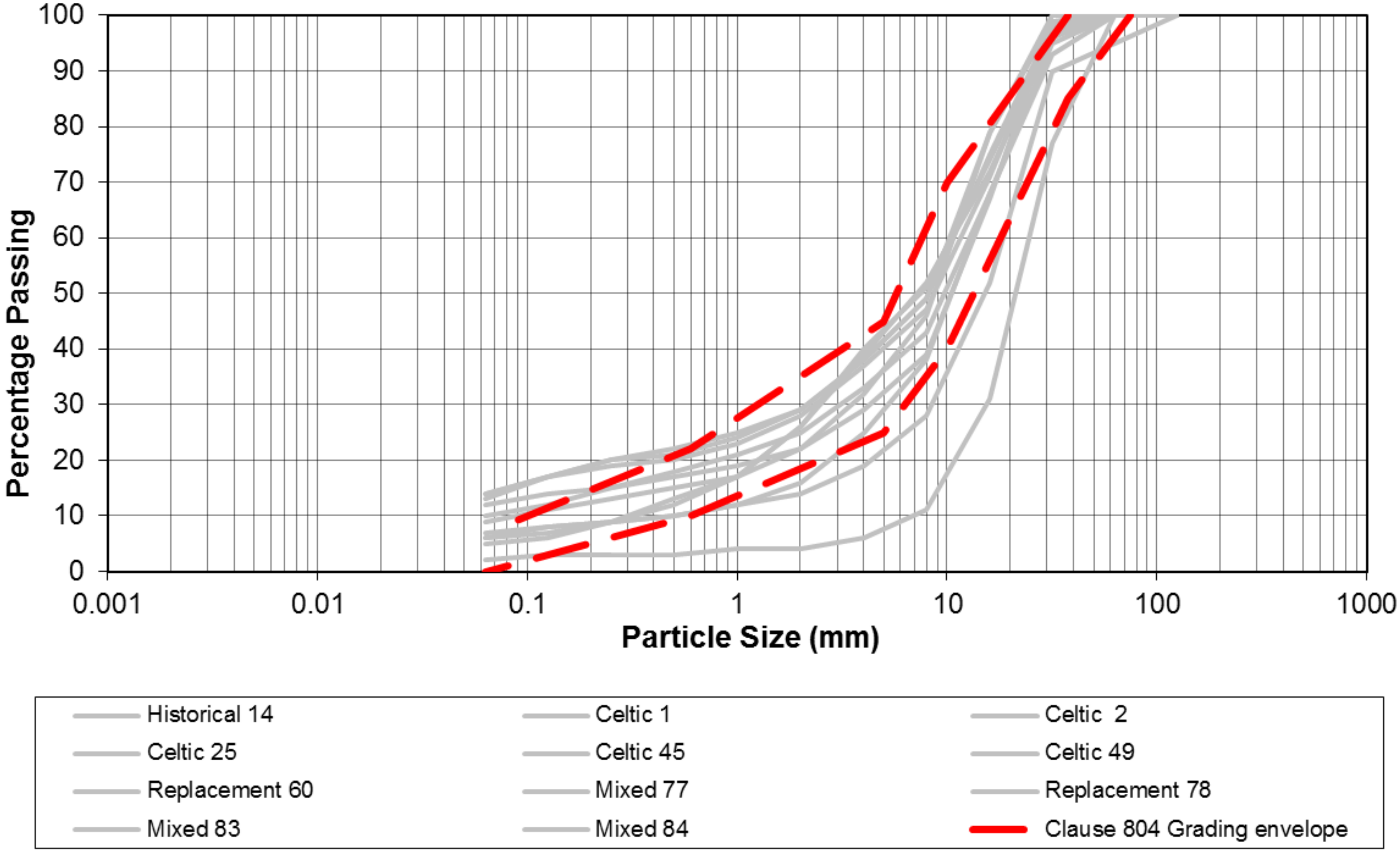
Example – Magnesium Sulphate Soundness



Physical Tests - PSD

- Measures the grading of an aggregate sample with respect to different size fractions over the range of particle sizes
- Primary aggregate classification test
- Shape of grading curve and % of silt and clay fraction have large influence on aggregate performance
- *BS EN 933-1:1997 Tests for geometrical properties of aggregates - Determination of particle size distribution. Sieving method*
- Sample size dependent on particle size (60g to 80kg)
- Comparisons made with Clause 804 requirements
- High fines content (>8%) are of concern in high quality aggregate
    - Fines retain moisture which feeds oxidation of pyrite
    - Consistent with high clay content indicating a non-durable rock
    - Fines contents of up to 12% are common

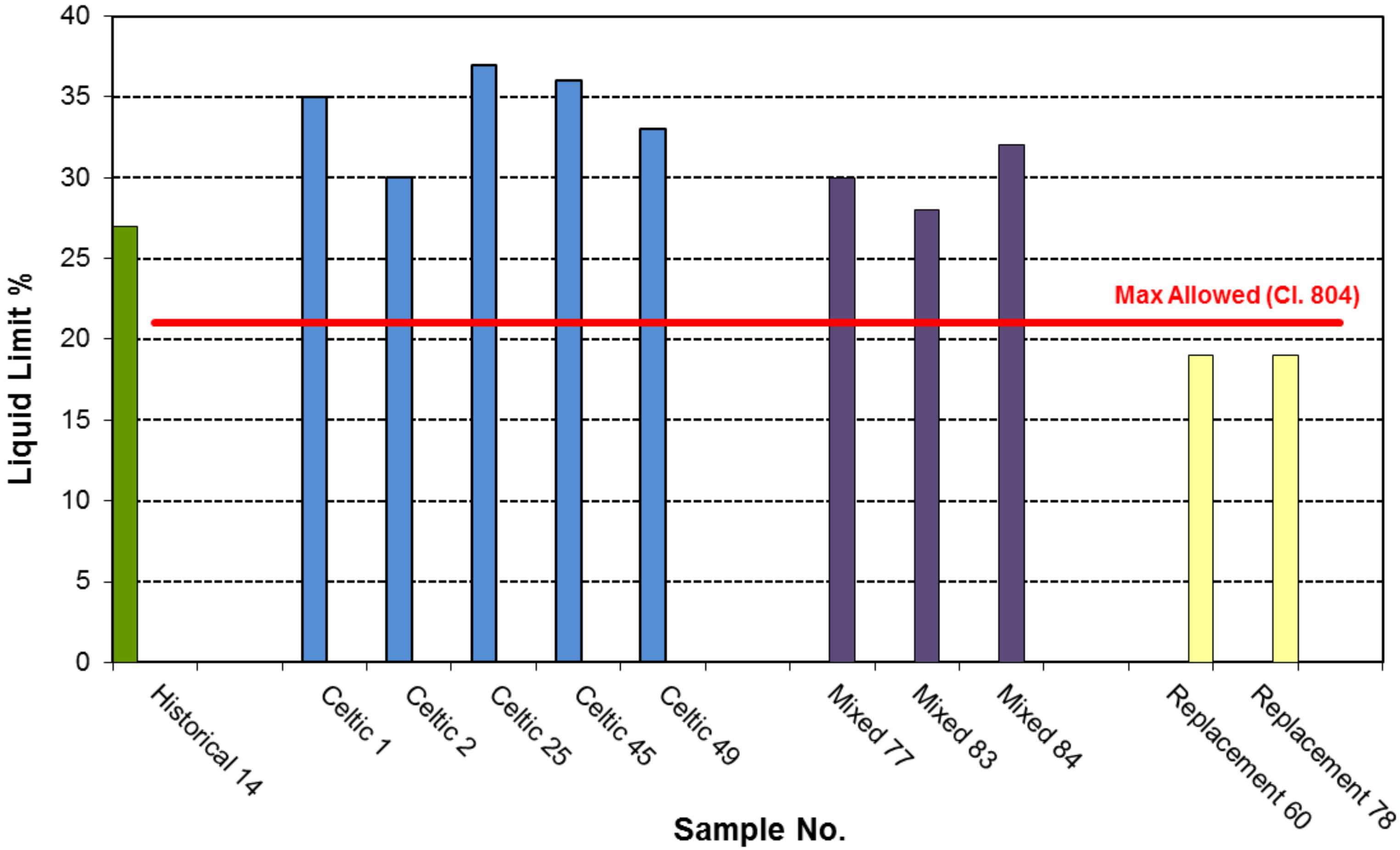
Example – Particle Size Distribution



Physical Tests – Atterberg Limits

- Atterberg Limits testing evaluates the nature of the fine grained fraction in relation to the water content at which the state changes from liquid to plastic to semi-solid
- *BS 1377-2: 1990 Methods of test for soils for civil engineering purposes - Classification tests*
- 500g of sample in natural state (not dried)
- Fines in crushed rock aggregates should be non-plastic
- High liquid limits in crushed rock indicate low quality and the presence of fines with undesirable characteristics and potentially prone to volume change with changes in moisture content
- The NRA specification for Clause 804 sets a maximum limit of 20% for the liquid limit for limestone aggregates, and 21% for other rock types

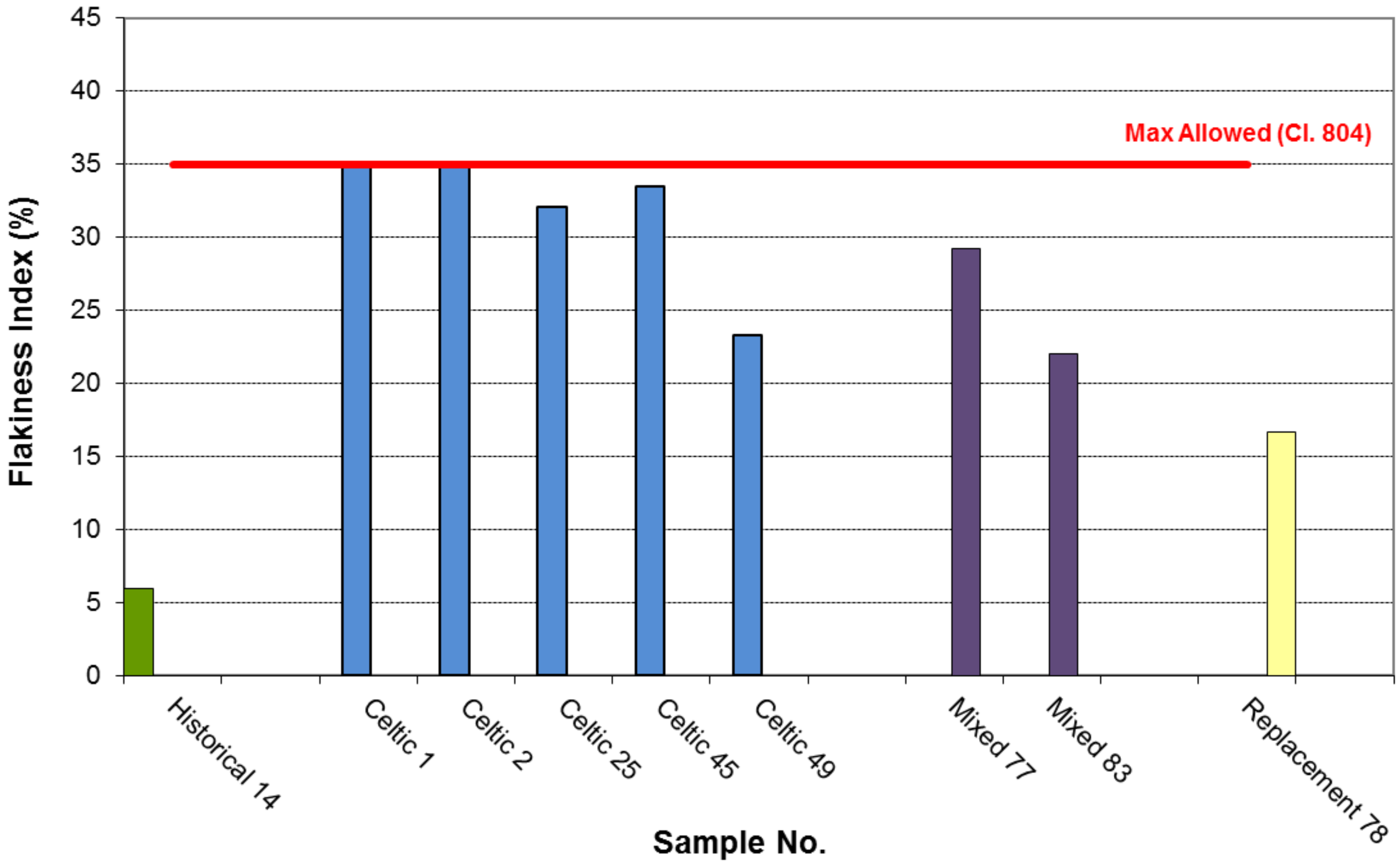
Example – Liquid Limit



Physical Tests – Flakiness Index

- Laminated fine-grained sedimentary rocks usually produce flat and elongated or highly flaky particles
- Test measures the percentage of particles passing a slot width specified for that particular size fraction … flaky particles are those which pass through slots
- *BS EN 933-3 1997: Tests for geometrical properties of aggregates - Determination of particle shape. Flakiness index*
- Sample size dependent on particle dimensions and proportions
- NRA specification for Clause 804 (May 2004) sets a maximum Flakiness Index of 35%

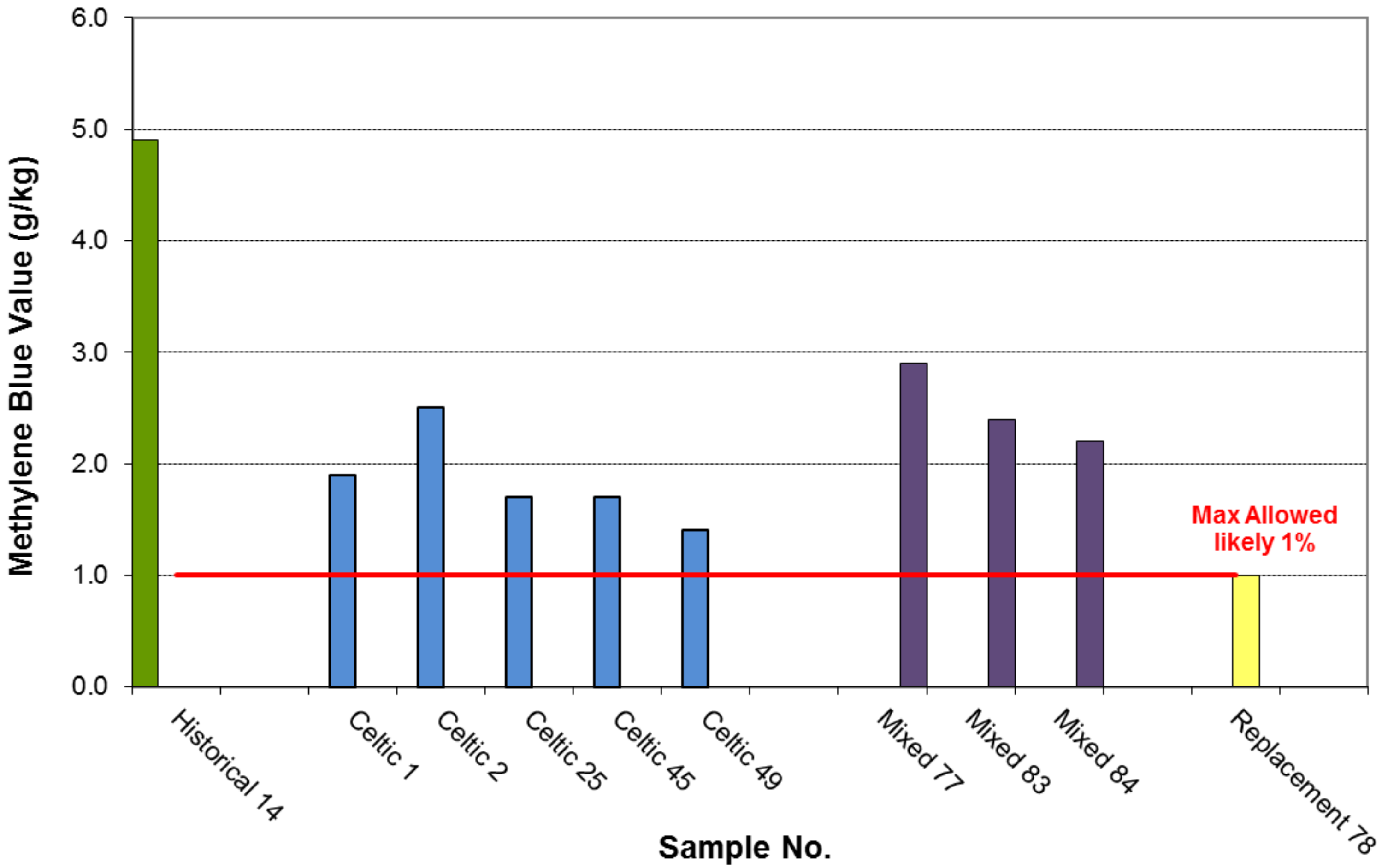
Example - Flakiness Index



Physical Tests – Methylene Blue Absorption

- Test used to quantify the effect of clay minerals in an aggregate … and hence to indicate soundness
- *BS EN 993 – 9: 1999 Tests for geometrical properties of aggregates - Assessment of fines. Methylene blue test*
- 200g minimum in the 0mm to 2mm size range
- Included in NRA specification for Cl 804, but <u>no</u> upper limit set yet
    - Values above 1.0g/kg would be cause for concern
- High MBA would be consistent with high Liquid Limit values as indicators of unsuitable construction aggregates

Example – Methylene Blue Absorption



CONCLUSION

PASS *or* FAIL *or* INCONCLUSIVE?

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Questions?