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Our Ref: M/2048/19/C1
Your Ref.: Sandsend Whitby

14th January 2020

CERTIFICATE OF ANALYSIS OF A COATING SAMPLE FOR DETERMINATION OF BINDER TYPE

Project Reference	:	Sandsend Kiln and Milhouse, Whitby, North East Yorkshire
Sample Location	:	Cement Grinding Mill Building
Sample Description	:	Slurry Wash/Lime Wash on exterior of Mill Building
Date Received	:	13th December 2019
CMC Sample Ref	:	SR 2777-S1
Date Analysed	:	13th & 27th December 2019 & 13th & 14th January 2020
Method of Test	:	Determination of Composition by X-Ray Diffraction analysis. With comment on fabric from a thin section examination.

Sample

A sample of a Slurry Coat/Lime Wash was received in CMC's Stirling laboratory on the 13th December 2019. The sample was submitted by Nigel Copsey of the Earth, Stone and Lime Company and was identified as a multi-coat application of a Slurry Coat/Lime Wash that had been applied to the exterior of the grinding mill at Atkinsons (Yorkshire) Cement mill at Sandsend, near Whitby, on the North East Yorkshire coast.

The sample was to be submitted to analysis to determine the composition of the material, to include identification of the form and type of binder used. In addition, a thin section was prepared to assist in identifying if there was any clinker retained in the coatings that may clarify the form of product used.

On receipt in the laboratory, the sample details were entered into the sample register and the unique sample identification number SR2777 allocated.

Details of the sample submitted for examination and analysis is given below:

CMC Sample No.	Description of Sample and Location Sampled
SR2777 – S1	Multi-coat Slurry Coat/Lime Wash applied to the exterior of the Grinding Mill House at Atkinson's (Yorkshire) Cement Mill, Near Whitby.

Method of Test

On receipt in the laboratory the sample was logged, with its mass and size recorded, with the sample photographed, in the as-received condition.

After logging the sample was submitted to an examination with the aid of a stereo-binocular microscope at a magnification up to x20 in preparation for analysis, during which each coat in the sample was exposed to a series of *ad hoc* droplet tests employing a range of reagents and indicator solutions.

Following the initial examination, a sub-sample was obtained from the coating for X-ray Diffraction (XRD) analysis. This was to permit identification of the binder type used in the production of the coating, with this analysis technique used as it would also clarify if there were any crystalline contaminants or reaction products present.

In addition to the above a petrographic thin section was prepared, with this orientated to permit the sample to be examined through the thickness of the coating. This would assist in the clarification of the form in which the binder was used, and confirm if it retained any residual clinker within the individual coats, and if these differed significantly between coats.

Observations from a Macro/Microscopic examination

On receipt in the laboratory the sample was logged with the following determined:

Sample Ref.	Client Ref.	Mass of Sample (gram)	Dimensions of Largest piece (mm)	Colour by the Munsell Soil Colour Charts
SR2777-S1	Coating	66.9	107.3 x 67.7 x 10.3	from 10YR 7/2 "Light Grey" to 10YR 5/2 "Greyish Brown"

This sample consisted of a single piece of a multi-coat wash, or slurry coat. The coating had been applied on to a sandstone substrate with part of the weathered sandstone adhering to the underside of the coating.

The coating was hard and required firm finger pressure to break, and on breaking it was noted to separate along soiled horizons, some which also showed evidence of prolonged water percolation with the leaching and locally the redeposition of hydration components, in the form of calcite or vaterite crstals, within the separated interfaces.

Plates No. 1 & 2: The left plate shows the outer surface of the intact piece of the Coating sample, with the right plate showing the inner masonry wall contact surface, which retained fines from the underlying sandstone masonry along with a fragment of sandstone.

From an examination under the stereo-binocular microscope it was indicated that the coating consisted of at least 16 to 20 applications, that had been applied over an extended period of time, with several horizons of soiling noted within the thickness of the coating.

Spot tests with dilute Hydrochloric acid produced a strong effervescent reaction, as would be expected on a carbonated lime or cement type material. With a phenolphthalein indicator tests producing no colour change, on any of the coats, inferring that if they were lime or cement based, they were all fully carbonated.

However, spot tests with an oxidising agent produced a weak effervescent reaction on the outer coatings, over the outer half of the combined coating, which may infer the presence of an organic component, either within the coating, or within the soiling entrapped on the surface of some layers. This would require further analysis if it were necessary to clarify.

Water droplets placed onto the outer surface were supported for an extended period of time prior to slow absorption into the coating around the perimeter of the droplet, but with minimal wetting of the fabric to depth, through the underlying coatings, except where cracks extended to depth. However, droplets placed onto the inner masonry contact surface were rapidly absorbed but only to a depth of three to five coats.

Plates No. 3 & 4: The left plate shows weathered fracture surface through the thickness of the coatings as received, which shows the presence of several delaminations within the coating thickness. The outer surface is shown at the bottom of the plate, with fragments from the sandstone substrate adhering to the inner coat, upper part of plate. The right plate shows a magnified view of a freshly sawn surface through the coating, where, again, the outer coat is shown at the bottom of the plate.

The outer coats appear to be comprised of three thin lighter coloured coats that appear to differ from the inner coats and appear more akin to a paint or modern cement slurry coat, whereas, that within the thickness of the coating have a coarser texture, are harder to the touch, and are more dense, and appear more uniform in both texture but not colour. The colour of the coats alternating from light grey through pinkish grey to reddish brown and dark brown. This inferring a variation in the coating composition.

The coatings do not appear to contain coarse aggregates and it is likely that they were made from a neat binder, mixed with water. Though there may have been other non-crystalline (mineral) material included as an additive, or a contaminant, but if so, the proportions were low.

Results of XRD Analysis for Binder Type

To help clarify the composition of the binder and any mineral components present within the coatings, a representative sample was obtained and prepared for analysis. This was crushed and lightly ground in an agate mortar and pestle in preparation for analysis. During grinding care was taken to minimise the crushing of any aggregate particles that may be in the sample, as if present in abundance, in the analysis sample, they could mask any hydraulic components which may only be present in trace proportions.

The powdered sub-sample was back-packed into a proprietary sample holder for presentation in the diffractometer, with this technique employed to ensure, as close as possible, the true random orientation of the components present.

The sample was analysed in a Diffractometer which was fitted with a single crystal monochromator, set to run over the range 3° to 60° 2θ in steps of 0.1° 2θ at a rate of 1° 2θ/minute using CuKα radiation. With the digital output analysed by a computer program, which matched the peak positions against the JCPDS International Standard Mineral Data-base sub files using a search window of 0.1°.

The results obtained from the analysis are presented in the following attached Figure, in the form of a labelled X-ray Diffractogram:

Figure No. 1: SR2777-S1 – Composite of the coatings from Wall Coating on the Mill Building.

The abbreviations used on the chart, to identify peak positions, are as follows:

- **cc** = Calcite ($CaCO_3$) Calcium Carbonate, carbonated lime from lime binder and any limestone aggregate present in the mortar,
- **va** = Vaterite ($CaCO_3$) another crystalline form of Calcium Carbonate, from carbonated binder present in redeposited leached lime from the binder, or in limestone feedstock/dust,
- **be** = Belite (C_2SiO_4) *di*-Calcium Silicate, clinker component in Natural cement binder,
- **br** = Brownmillerite ($Ca_2(Al,Fe)_2O_5$) Calcium Aluminium Iron Oxide a hydraulic clinker component in Natural cements and some hydraulic limes,
- **ge** = Gehlenite (ca2Al2SiO7) Calcium Aluminium Silicate, clinker component found in Natural cement and in some hydraulic limes,
- **he** = Hematite (Fe_2O_3) Iron oxide, a common component in Natural cements,
- **gy** = Gypsum ($CaSO_42H_2O$) Calcium Sulphate Hydrate, a component of some Natural cements, or present as a reaction product between lime in binder and environmental sulphates,
- **qz** = Quartz (SiO_2) Silicon Oxide, a component of soiling or possibly a component of the binder,
- **fs** = Feldspar, mostly Anorthite of the Plagioclase group of minerals, soiling component,
- **di** = Dickite, a common clay mineral of the Kaolinite group, present as soiling.

The result from the XRD analysis was processed using Rietveld Refinement, in the MAUD computer program, which permitted quantification of the individual crystalline components. The results obtained are shown below:

Sample:	**SR2777-S1**
Coat	**Combined Coats**
Component	**Proportion (% by Mass)**
Calcite	67.2
Vaterite	7.5
Belite (B_2S)	0.6
Brownmillerite	1.1
Gehlenite	1.9
Hematite	0.9
Gypsum	9.4
Quartz	7.8
Feldspar (Anorthite)	2.8
Dickite	0.8
Total	**100.0**

From the XRD analysis, it is indicated that the binder in the coating is a Natural cement, with it likely that, given the variation in the colour and hardness of the individual coats, that the difference was due to the degree of hydration of the binder in each coat being variable, along with varying degrees of calcining at the time of production. The quartz , feldspar and Dickite all appear to be associated with soiling trapped on the individual coat surfcaes.

Microscopic Examination

To permit further clarification of the form in which the binder was used, and permit comparison of the fabric in the coats, a petrographic thin section was prepared for examination in the polarised light microscope. To achieve this a slice was sawn through the intact sample, which was orientated to permit all of the coatings to be included in the section. The slice was dried at 70°C prior to being impregnated with a blue dyed epoxy resin, in preparation for the manufacture of a thin section.

One side of the impregnated sample was cut and polished prior to being mounted on to a glass slide (50mm x 75mm), with the sample orientated to give the maximum area on the slide. The sample was then cut and polished to give a thickness in the region of 30µm, prior to being protected by a cover slip, in preparation for examination in the polarised light microscope.

The thin section was examined in an Olympus BH2 Polarised light microscope, which was fitted with a digital camera to permit the recording of images for record purposes. A selection of the images are included in the report for reference.

Observations from the examination of the thin section is presented below:

Plate No. 5:
Thin section prepared from Coating sample SR2777-S1.
Two slices taken through the thickness of the coating were mounted on a single slide, with the slices orientated so that their outer surfaces were opposite each other, in the centre of the slide.

The coating was noted from the thin section to consist of 19 to 20 coats, with part of the outer coats lost by erosion. In addition, grains from the underlying masonry adhere to the surface of the inner coating, aligned towards the outer edges of the slide.

Within the thickness of the inner 3rd, 4th and 5th coats rare coarse quartz grains, up to 0.5mm in diameter, were observed. These were not observed in any of the other coats and may have been entrapped within the coat at time of application. However concentrations of very fine angular quartz grains, typically <0.05mm are observed in later coatings, which may be a function of the calcining and grinding conditions at the time that cement used in the slurry coat was produced, which, given the variation across the coatings, would infer that quality of production was not necessarily consistent during the early production period.

A number of the interfaces contained patchy deposits of fine grained (<0.04mm) quartz, feldspar and clay minerals, with these commonly observed at the more pronounced interfaces. This suggesting that these represented previous outer coats with, longer periods of exposure, the minerals accumulating from environmental soiling.

Within three of the widest of the disrupted interfaces, coarse crystals of Calcite were observed, along with rare sulphate minerals (acicular shaped crystals) suggesting the redeposition of leached binder components with prolonged water percolation through the discontinuities formed.

The two inner coats are the thickest of all ranging from 0.85mm to 1.2mm in thickness. These two coats are also the least dense and have the appearance of having been applied as relatively wet pastes, resulting in an open highly porous texture. They also contain the highest proportion of calcite and least clinker content. This may reflect a lower burning temperature during initial production stages.

The following three coats are thicker 0.4mm to 0.85mm in thickness, with the 3rd, 4th and 5th coats, from the masonry interface, containing rare aggregate grains of quartz and incompletely calcined clinker. This may be representative of poor grinding control, or the accumulation of contaminants from the production, or alternatively the use of reject material in the slurry coats.

The remaining coats are relatively uniform in thickness, ranging from 0.2mm to 0.35mm and all appear more dense, with a tight fabric suggesting that they had been applied as a thick paste.

Soiling horizons are most marked by concentrations of fine quartz, with feldspar and clay minerals, with their occurrence being patchy within the thickness of the sample. The heaviest deposits occurring between the 1st and 2nd, 3rd and 4th, 4th and 5th coats and again at the surface of the 9th 12th and 16th coats.

Hydraulic clinker grains, mostly in the form of pseudo-morphs and opaque minerals (Iron oxide – Hematite, with charcoal fragments) is apparent distributed throughout all coats, with these taking the form of Belite clusters, Gehlenite and amorphous angular shards, all typical of the clinker found in the paste in moderate to well hydrated Natural cement binders.

The binder within the inner coats shows evidence of leaching, with little of the clinker remaining, and the binder is now composed essentially of calcite with rare hydration products observed, along with the imprint of past clinker grains, but no clinker. Whereas, in the outer eight to twelve coats the paste is dense and there is a higher proportion of fine clinker grains and pseudo morphs of coarse clinker grains, all bound within a dense hydrated paste.

Photomicrographs:

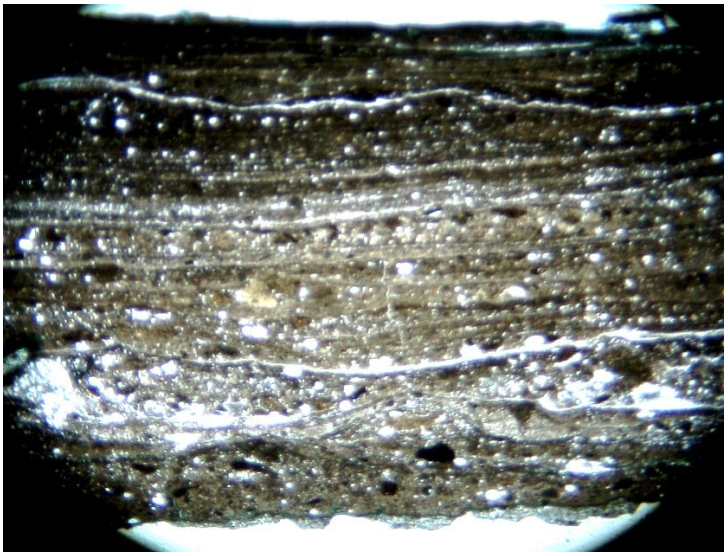

Plate No. 6:

The opposite plate shows a view of the full thickness of the coating, with the inner surface, retaining fines plucked from the surface of the sandstone substrate, shown at the bottom of the plate. Although there appears to be a greater number of layers (32) within the image, than the actual number of coats, this is due to a number of the coats having been applied in several applications, with each application applied prior to the previous application fully drying. The presence of soiling between coats is taken as the delineation between complete individual coatings.

Porosity is highlighted by the blue dyed resin. Field of view 12.0mm.

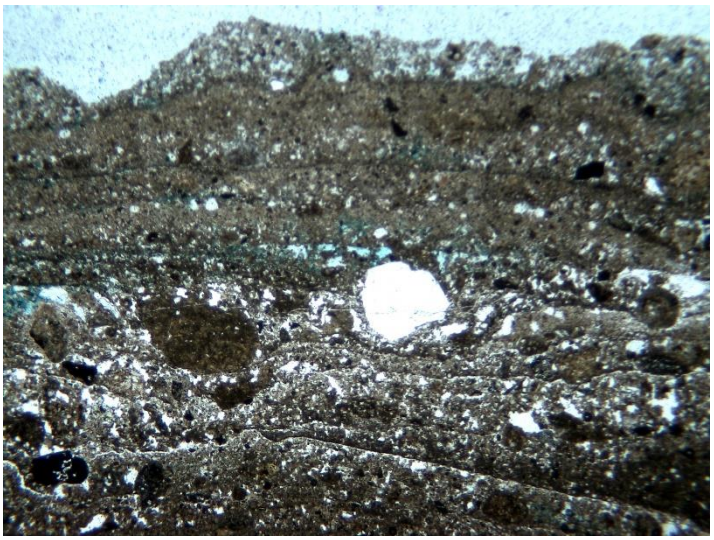

Plate No. 7:

A magnified view in plane polarised light, ppl, of the inner part of the coating, with the stone contact surface shown at the top of the plate. Note the coarse quartz grain (white) embedded in the soiling at the interface between the 2nd and 3rd coats, with coarse incompletely ground fragments of natural cement concentrated in the 3rd, 4th and 5th coats (bottom of plate). Note the presence of soiling in the interfaces between the 2nd and 3rd, 3rd and 4th and 4th and 5th coats. A partial delamination has formed within the interface between the 4th and 5th coats.
Porosity is highlighted by the blue dyed resin. Field of view 2.4mm.

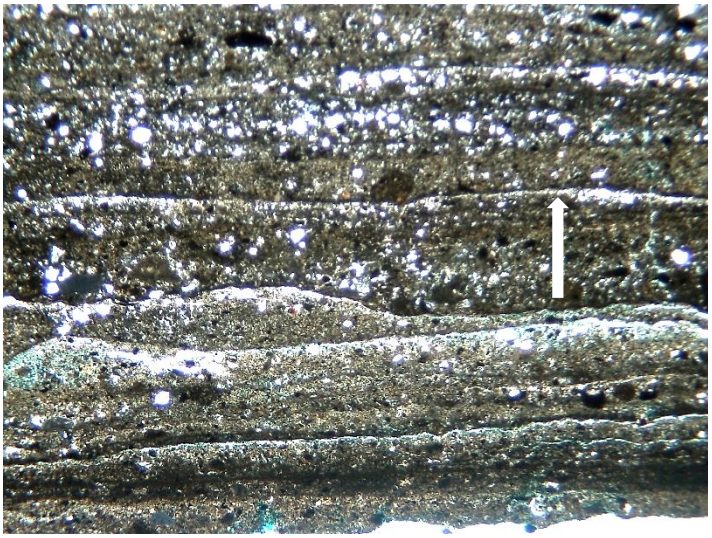

Plate No. 8:

A view in plane polarised light (ppl), of the coats towards the outer surface, which is shown at the bottom of the plate. Note the increased density and the reduced occurrence of fine quartz grains (white in image) in the coats closer to the outside surface, perhaps suggesting that the product produced at the kiln was being better burned and more refined over time.
A fine delamination is forming along a soiled interface between the 6th and 7th coats from the outer surface 13th & 14th from the inner surface), arrowed in plate.
The paste is dense and fully carbonated.
Porosity is highlighted by the blue dyed resin. Field of view 2.4mm.

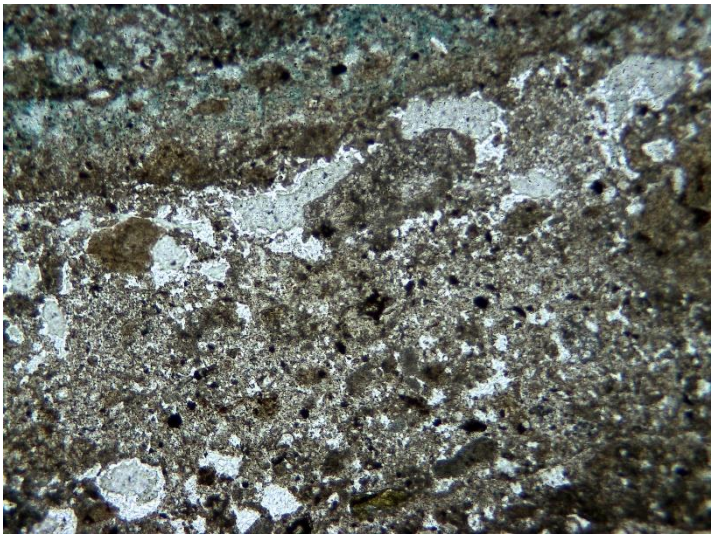

Plate No. 9:

Another view in plane polarised light (ppl), of an area adjacent to a delamination through which water has percolated, with partial leaching of the paste along with the redeposition of calcite as void linings, seen as white crystal deposits in the hand specimen.
The paste within the adjacent coats are well compacted and contain fine quartz grains, with amorphous (black) particles and clinker grains, containing both Belite and Gehlenite present. The paste near the lower interface, at the base of the plate also contains fine entrained air bubbles, from the application procedure (brushing). Porosity is highlighted by the blue dyed resin. Field of view 1.2mm.

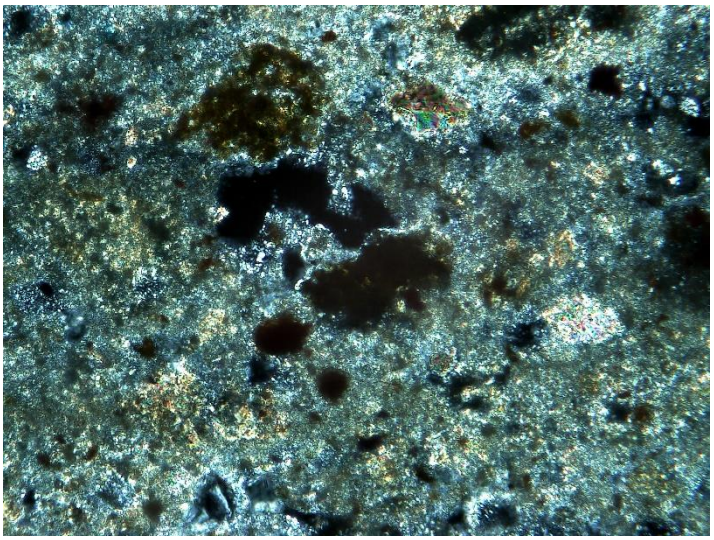

Plate No. 10:

A view in cross polarised light (xpl), of a dense area of the paste within the centre of the Slurry coat, at an interface between two well bonded coats. The interface is highlighted by the paste in the earlier coat, top of plate, displaying a well carbonated paste with intergranular redeposited binder in the form of calcite and Vaterite present. Note several coarse clinker grains apparent within this coat (brown in colour).
There is an abundance of clinker grains, amorphous fragments and partially hydrated clinker throughout the thickness of the coating filling the remainder of the field of view. Porosity, amorphous particles and impregnating resin all appear dark in xpl. Field of view 0.6mm.

Quality Statement

We confirm that in the preparation of this report we have exercised reasonable skill and care.

The results presented, and comments offered relate only to the sample of Multi-coat Slurry or Lime Wash received in CMC's laboratory on the 13th December 2019 from the Earth, Stone & Lime Company. With the sample identified as a surface coating on the exterior of the grinding/mill building at Atkinson's (Yorkshire) Cement Mill, Near Whitby, North East Yorkshire.

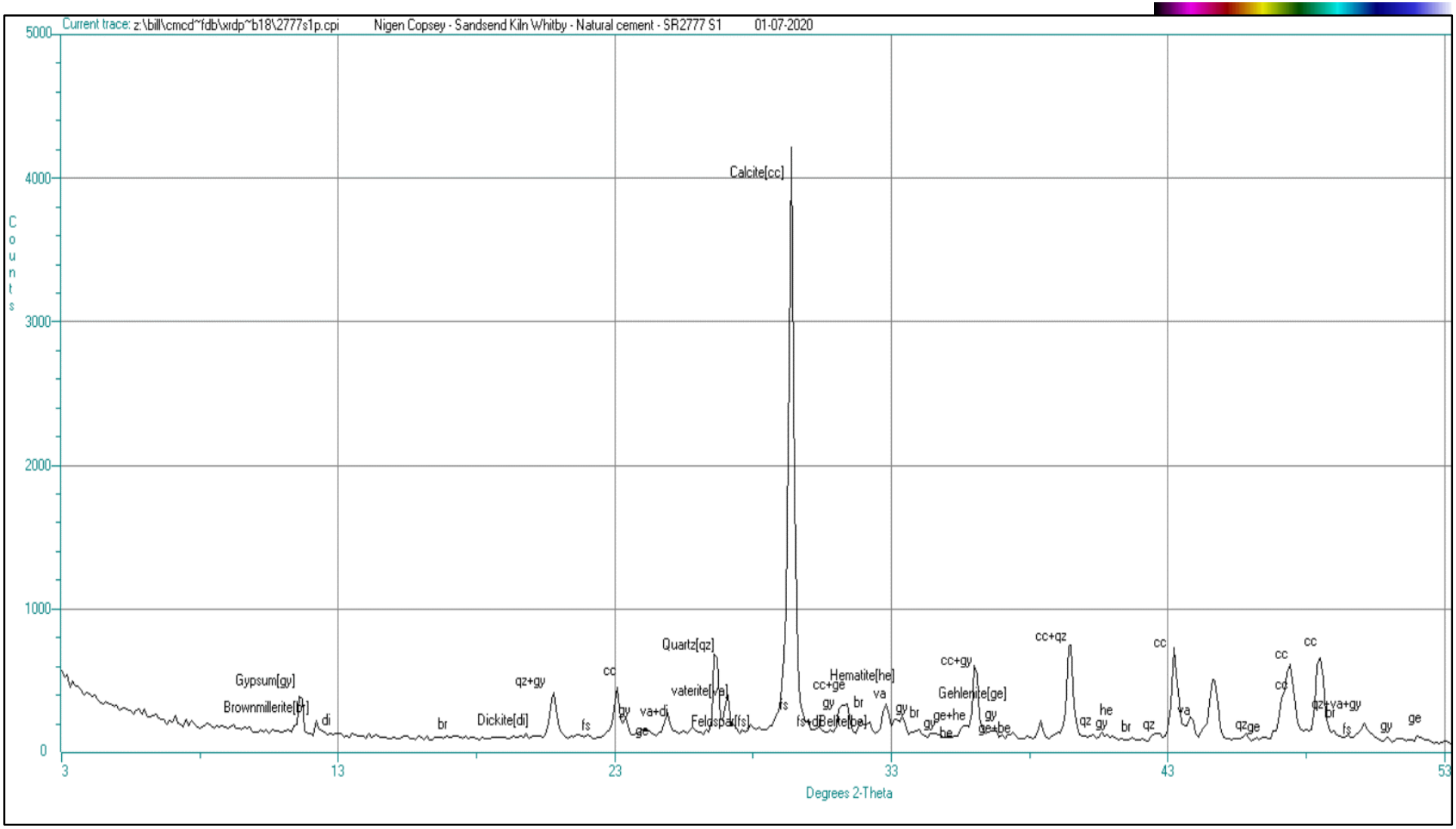

Figure No. **1**: SR2777-S1 – Composite of the coatings from Wall Coating on the Mill Building.