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Our Ref: M/1991/19/C6
Your Ref.: T2019

6th June 2019

CERTIFICATE OF EXAMINATION AND ANALYSIS OF A SAMPLE OF BANK SLAG

Project Reference	:	North Yorkshire Moors – This Exploited Land of Iron
Sample Location	:	Bank Top Kilns (BTK-Slag)
Sample Description	:	Bank Slag & Ash - Waste Material adjacent to The Bank Top Kilns
Date Received	:	26th March 2019
CMC Sample Ref	:	SR 2709-S1 Bank Slag ex BTK
Date Analysed	:	10th to 18th April and 20th May 2019
Method of Test	:	Determination crystalline and mineralogical composition by X-Ray Diffraction analysis. Particle size distribution by wash grading and the microscopic examination of petrographic thin sections.

Sample

During the examination of mortar samples from a selection of samples from Limestone and Iron processing kilns on the North York Moors, it was identified that many of the samples contained aggregate components that had the properties of a bank slag (waste materials from Iron processing), and, therefore, samples of the materials from the waste piles at one of the kilns was requested. The purpose of this was to permit comparison with the aggregates in the mortars to confirm their origin.

The mortar samples examined were received from Structural and Civil Consultants Ltd., Northallerton, on behalf of the North York Moors National Parks Authority, as part of NPA's "This Exploited Land of Iron" project.

The bank slag material was collected and forwarded by Nigel Copsey of the Earth, Stone and Lime Company, Maltongate, Thornton Dale, North Yorkshire.

The sample was received in CMC's Stirling Laboratory on the 26th March 2019, with the sample details entered into the sample register and the unique sample identification number SR2709 allocated.

Details of the sample received are given below:

CMC Sample Ref.	Client Ref	Location Sampled
SR2709 – S1	BTK-Slag	Waste materials in spoil heap adjacent to Bank Top Kilns – Bank Slag

Method of Test

On receipt in the laboratory the sample was logged, with its mass and the size of the largest piece recorded prior to the sample being photographed, in the as-received condition. The sample was then examined with the aid of a stereo-binocular microscope, at a magnification up to x20 in preparation for a more detailed examination and analysis.

Following the initial examination, a representative sub-sample was obtained, and it's as-received moisture content determined, prior to the dried sample being prepared for determination of particle size distribution and mineralogical composition.

The particle size distribution was determined by wash grading following the methods of BS EN 933-1: 2012 Tests for the Geometrical Properties of Aggregates – Determination of Particle Size Distribution – Sieving Method.

The mineralogical/crystalline composition was determined by X-Ray Diffraction (XRD) with this carried out on each of the variants visually identified in the bulk sample.

Petrographic thin sections were also prepared from each visually different 'aggregate' observed in the sample to permit their examination in the polarised light microscope.

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	Dimensions of Largest piece (mm)	Colour by the Munsell Soil Colour Charts	Moisture Content % by dry mass
SR2709-S1	BTK-Slag	466.6g	77.1 x 58.1 x 54.4	Fines = 5YR 4/2 "Reddish Brown" Slag 1 = 5YR 5/3 "Reddish Brown" Slag 2 = 5YR 4/3 "Reddish Brown" Slag 3 = 10R 5/1 "Reddish Grey" Stone = 10YR 6/4 "Light Yellowish Brown"	7.2

Plates No. 1 & 2: The sample received was a heterogenous material with several materials present. The left plate shows sample, as-received, with the two largest fragments separated from the remainder. The right plate showing a close-up image of the two largest pieces.

It was noted on examination that the lager fragments had the appearance of a metallic slag, with it indicated, on testing with a magnet, that they displayed a magnetic attraction. On separation of the fines for analysis it was also noted that these contained a high proportion of ferromagnetic materials and these could be separated from the mass by passing a magnet over the dried fines.

Plates No. 3 & 4: The left plate shows a portion of the bulk sample after drying with the right plate showing a selection of the different variants apparent after separation, with these selected by visual appearance, variation in weight, texture and property, i.e. magnetic attraction, hardness, density, streak on test tile and response to droplet tests using a range of reagents.

Plates No. 5 & 6: The above plates show freshly sawn surfaces cut through the two largest fragments. These are typical of old iron slags, with the material having been deposited as waste (slag) in the from a partial melt.

On testing the surfaces of several fragments, with dilute hydrochloric acid, an effervescent reaction was observed on some of the slag particles, with a strong odour of H_2S evolved. This is not uncommon with iron slags and would infer that there are sulphate minerals present. The limestone fragments, and some small siltstone fragments also reacted with the acid test, and would indicate that the siltstone was also calcareous, at least in part.

The aggregate particles are sub-angular to sub-round and irregular to elongate in shape and contain coal fragments, coke, ironstone, indeterminate ‘slag’ components along with coal clinker and ash, and a low proportion of limestone fragments. The particles ranged from very hard and resistant to breakage under hammer impact, through to well compact and moderately hard to soft and finger friable. With parts of the slag noted to contain vitreous fragments. Small brick fragments were also present along with small slivers of wood and a quantity of fine quartz and indeterminate natural aggregate grains, fine sand, silt and clay.

Results of XRD Analysis

To identify the components in the sample, for comparison with those detected in the mortar samples received from the "This Exploited Land of Iron" project, samples of each variant of the slag materials, excluding the coal, limestone and sandstone fragments, were prepared for analysis by XRD.

A representative sample of each variant was obtained and crushed in an impact mortar, then ground in an agate mortar and pestle until all of the powder passed a 63µm sieve. The powdered samples were then back-packed into proprietary sample holders for presentation in the diffractometer. This technique was employed to ensure, as close as possible, the true random orientation of the components present.

All samples were 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 Figures, in the form of labelled X-ray Diffractograms:

Figure No. 2: SR2709-S1A - Representative sample of the Fines material <0.500mm sieve,
Figure No. 3: SR2709-S1B - Sample of slag – crushed magnetic fragments,
Figure No. 4: SR2709-S1C - Representative sample of the vitreous slag particles,
Figure No. 5: SR2709-S1D - Sample of a stone fragment.

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

- **cc** = Calcite ($CaCO_3$) Calcium Carbonate, found in limestone and due to the carbonation of calcined limestone (lime) in the slag,
- **qz** = Quartz (SiO_2) Silicon Oxide, a component of natural aggregate, also found in some coal ash and slag,
- **he** = Hematite (Fe_2O_3) Iron oxide, from the ironstone and slag also sand/siltstones and some limestones,
- **go** = Goethite (FeO(OH)) Iron Oxide Hydroxide, hydrated iron oxide, corrosion product (rust) present as a component of the slag, also found in some sandstones/siltstones
- **ma** = Magnetite ($FeFe_2O_4$) Iron Oxide, another form of Iron Oxide in iron ore and in the slag,
- **si** = Siderite ($FeCO_3$) Iron Carbonate, Iron ore mineral, present as a component of slag, also found in some sandstones and limestones and other sedimentary rock types,
- **wo** = Wollastonite ($CaSiO_3$) Calcium Silicate, aggregate component, found in thermally altered impure limestone, also associated with iron ore deposits, and as a high temperature mineral in slags,
- **mu** = Mullite ($Al_6Si_2O_{13}$) Aluminium Silicate, high temperature product, in slag and coal ash/clinker,
- **na** = Nacrite ($Al_2Si_2O_5(OH)_4$) Aluminium Silicate Hydroxide, high temperature reaction product component of the slag or in the ash present,
- **mo** = Moissanite (SiC) Silicon Carbide, component of the slag,
- **ar** = Arcanite (K_2SO_4) Potassium Sulphate, component of the slag, sulphate source,
- **ba** = Bassanite ($CaSO_40.5H_2O$) Calcium Sulphate Hemi-Hydrate, component of the slag/ash, probably a dehydrated form of gypsum, formed during drying of the sample in laboratory,
- **mi** = Muscovite Mica, common layer lattice mineral, common mineral found in natural stone/rock,
- **pe** = Penninite, clay mineral of the Chlorite group of minerals, from the alteration of mica, present as alteration product in the stone, or as an adhering weathering product.

The results from the XRD analysis were further processed using Rietveld Refinement, in the MAUD computer program, to permitted quantification of the individual crystalline components present.

The results obtained are shown below:

Component	**Proportion (% by Mass)**			
Sample:	**SR2709-A Fines**	**SR2709-B Metallic Slag**	**SR2709-C Vitreous Slag**	**SR2709-D Stone**
Calcite	12.5	4.0		
Quartz	15.3	2.2	6.6	56.6
Hematite	40.8	41.2	1.5	1.1
Goethite	2.5	1.5	5.7	10.0
Magnetite	11.2	44.7		
Siderite	2.2	1.7	3.8	3.4
Wollastonite	0.1			
Mullite		0.9	82.4	
Nacrite	2.4			
Moissanite	1.8			
Arcanite	6.0			
Bassanite		3.8		
Muscovite Mica	5.2			14.5
Penninite				14.4
Total	**100.0**	**100.0**	**100.0**	**100.0**

From the XRD analysis, it is indicated that all of the components detected, with the exception of sample "D", which is a stone sample, are typical of what could be expected to be found in bank slags, with a number of these components being high temperature minerals, i.e. Wollastonite, Mullite, Nacrite and Moissanite. The presence of these along with the high glass (amorphous) content would confirm that there is an abundance of components present that could act as pozzolans in the lime mortars and impart the strength, observed in some of the mortar samples.

Most of the iron based components will be associated with the feed stock, and the product, of the iron processing carried out at the site. With those detected dominated by Hematite and Magnetite with the hydrated form, Goethite, and the carbonate, Siderite all found in the samples analysed.

The sulphates found to be present in the slag samples examined, are in the form of Arcanite and Bassanite (dehydrated Gypsum), are likely to be the source, in addition to the pyrite observed in some of the siltstones, shales and limestone, of the sulphates responsible for the sulphate reactions observed in the mortar samples.

Aggregate Grading

After drying, and removal of the two large fragments, the sample was reduced by quartering and a representative sub-sampled prepared for determination of its particle size distribution.

The sub-sample was weighed and washed over a 63µm sieve, until the wash water run clear. The retained material was then dried and sieved through a set of British Standard Sieves.

The results of the grading analysis are presented in the following table and in the form of an aggregate filled histogram, see Figure No. 1 appended to this certificate.

Sample Reference	**SR2709– S1 (BTK-Slag) Bank Slag**	
British Standard Sieve Size	**Percentage Retained**	**Percentage Passing**
>8.00mm	34.2	65.8
4.00mm	13.1	52.7
2.00mm	9.3	43.4
1.00mm	7.4	36.0
0.500mm	6.2	29.8
0.250mm	12.5	17.3
0.125mm	7.1	10.2
0.063mm	2.5	7.7
Passing	7.7	

Table No. 1: Results of the grading Bank Slag, less large fragments.

The aggregates in sample are dominated by slag particles, with a proportion of coal, coal clinker, ash with minor limestone and siltstone fragments, with trace proportions of quartz and indeterminate lithic fragments within the fines (silt/clay) fraction.

Microscopic Examination

To permit further clarification of the form of the components in the slag a number of particles were selected for preparation of petrographic thin sections. Observations from the examination of the thin sections are presented below:

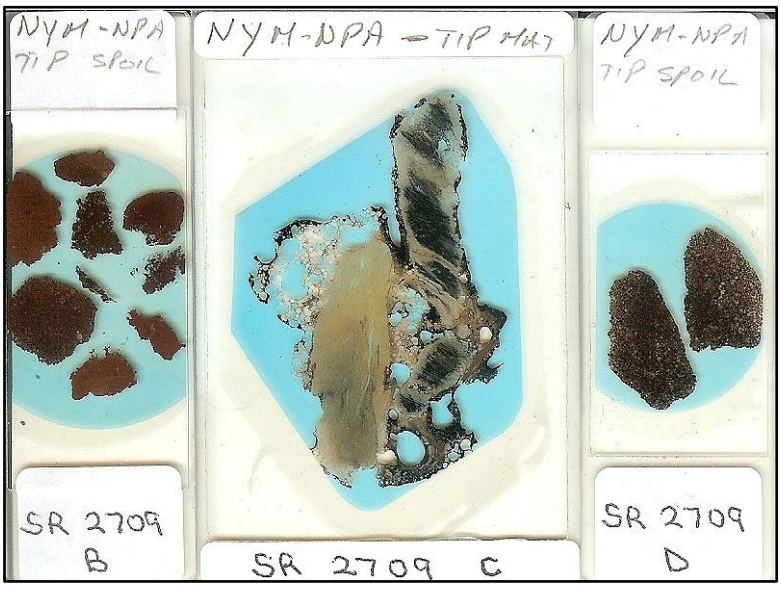

Plate No. 7: Three thin sections were prepared from a selection of particles in the bank slag sample.
B = Magnetic particles (Ironstone) **C** = Large Slag particle **D** = Stone fragments

The particles examined are composed of materials from the slag, with mostly ironstone present, both fresh and heavily burnt, with amorphous materials (glass), along with ash and coal clinker, along with Stoney fragments. Examples of these are shown in the following photomicrographs.

Sample B – Magnetic particles:

These particles are dominated by ironstone, see photomicrographs No. 8 and 9.

Plate No. 8 shows ironstone containing both partially altered chamosite ooids. These are yellow to yellow-brown in colour with darker limonite also apparent. Minor calcite cement can be seen in the voids between ooids.

Plate No. 9 shows a heavily burnt ironstone, with some parts showing deformation indicating that it had almost reached sintering temperature, but below melting/liquification temperature.

Sample C – Slag material:

This sample is dominated by opaque material with the material having mostly cooled from a melt, with coal clinker fragments, stone fragments and high temperature minerals trapped within the matrix.

There is an abundance of trapped gas bubbles, some of which are partially infilled with secondary minerals, sulphates, etc.

A high proportion of mullite cenospheres can also be seen within the glassy areas.

Sample D – Stone fragments:

This sample is of a fine siltstone, containing fine quartz grains muscovite mica and clay minerals along with a low proportion of a ferruginous cement.

Some of the particles display partial distortion inferring that they had been raised in temperature.

Photomicrographs:

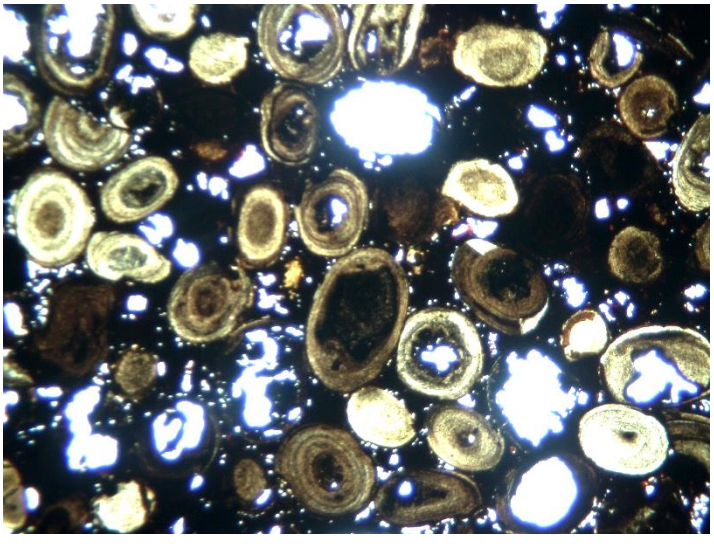

Plate No. 8: Sample "B"

Fresh Ironstone shown in plane polarised light (ppl).

Field of view 2.4mm.

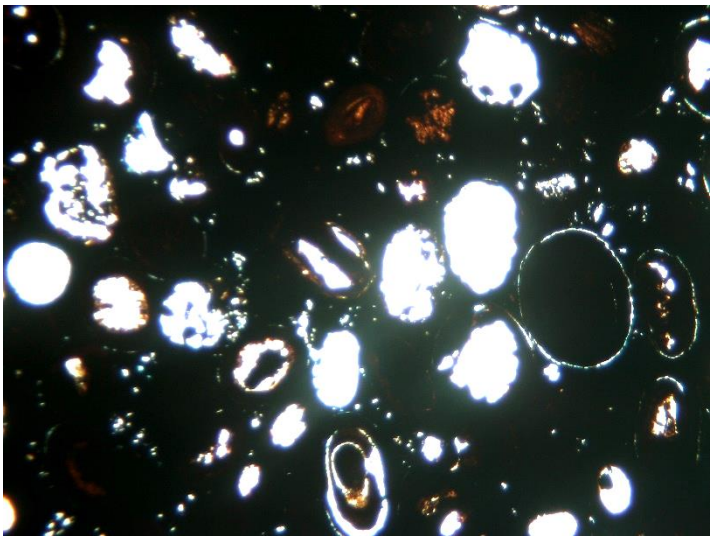

Plate No. 9: Sample "B"

Another view in ppl, of an area of heavily burnt ironstone, but with only limited alteration.

Porosity and voids are highlighted by the blue dyed resin.

Field of view 2.4mm.

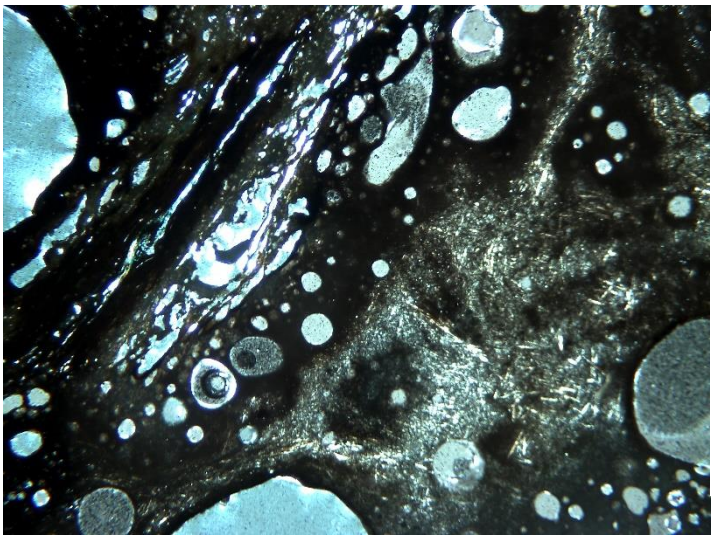

Plate No. 10: Sample "C"

A view in cross polarised light (xpl), of slag with the amorphous material appearing black in the slide. This shows an abundance of spherical and distorted voids (gas bubbles) along with coarsely crystalline acicular crystals see right of centre.

Porosity, the blue impregnating resin and opaque minerals all appear black in xpl. Field of view 2.4mm.

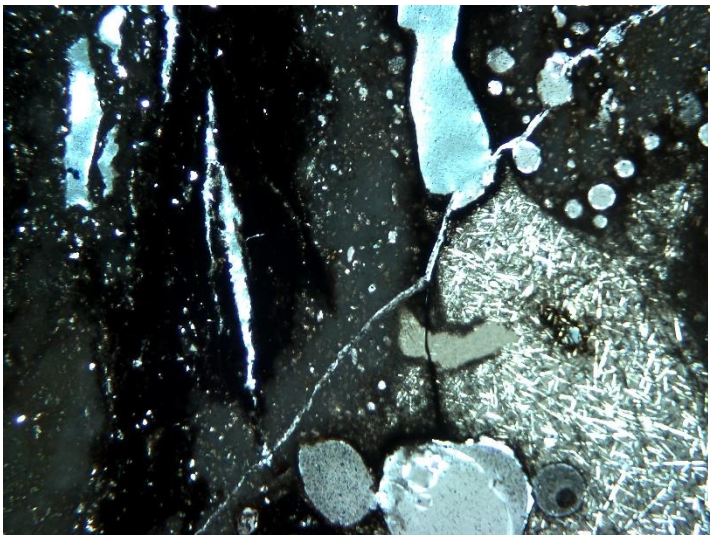

Plate No. 11: Sample "C"

Another view in cross polarised light (xpl).

Here again there are areas of altered minerals shown, with an altered 'aggregate' particle in the lower right quarter, in which there is also a small recrystallised quartz grain in its centre.

Porosity, the blue impregnating resin and opaque minerals all appear black in xpl. Field of view 1.2mm

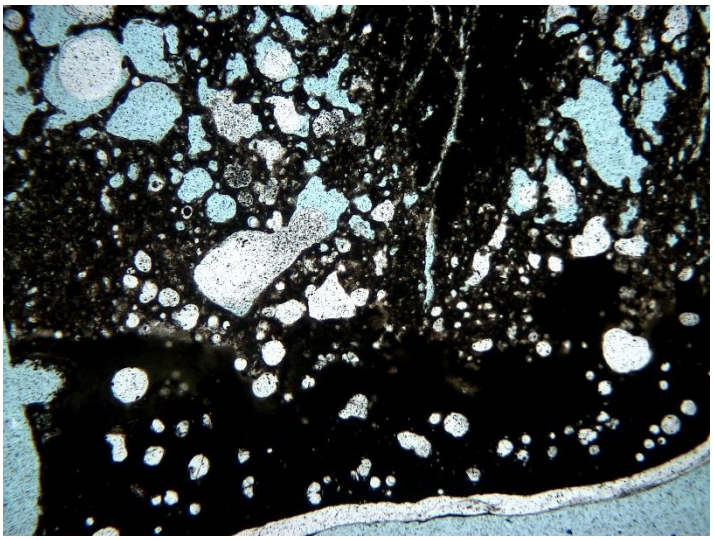

Plate No. 12: Sample "C"

View of the outer edge of the slag particle, in plane polarised light (ppl). The outer margin, lower part of plate, had cooled quickly and has a very fine glassy texture. With the inner, upper part in plate, containing an abundance of gas bubbles. Fragments of incompletely melted material which also, locally, displays a coarser glassy texture, and appears to have formed at a slower rate.

Porosity and voids are highlighted by the blue dyed resin. Field of view 2.4mm.

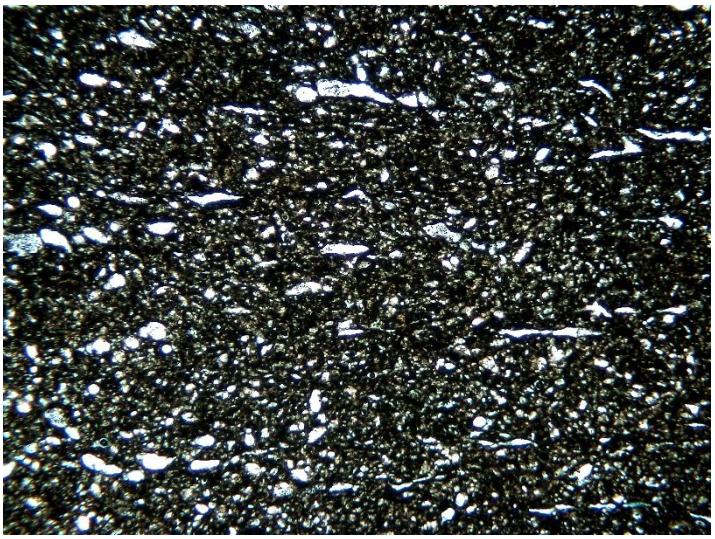

Plate No. 12: Sample "D"

A view in plane polarised light (ppl), of an area within a relatively fresh siltstone fragment.
The elongated minerals are muscovite mica. Quartz shows as small sub-round to sub-angular white grains.

Porosity and voids are highlighted by the blue dyed resin. Field of view 1.2mm.

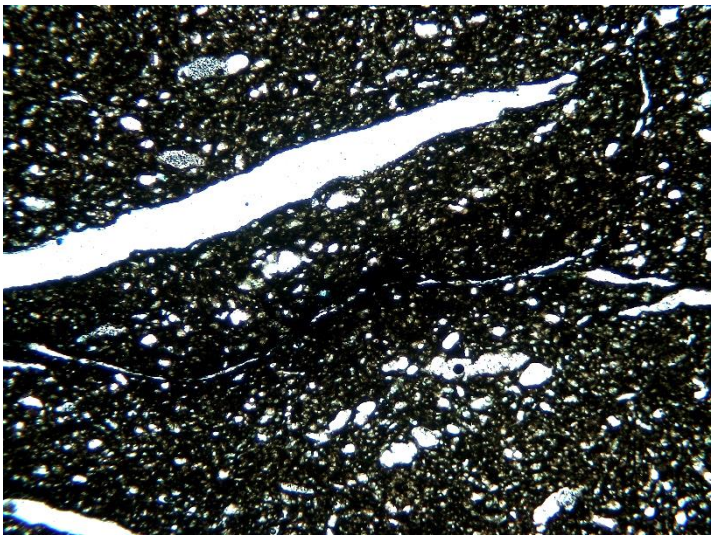

Plate No. 13: Sample "D"

Another view in plane polarised light (ppl), of an area within a siltstone fragment that has undergone the impact of a high temperature, with partial delamination and distortion, along faint depositional features.

Porosity and voids are highlighted by the blue dyed resin. Field of view 1.2mm.

Summary

From the examination and bank slag sample it is confirmed that this, or a similar, source of waste material from the Iron processing kilns had been used as aggregate in a number of the samples submitted for examined from the North Yorkshire National Parks "This Exploited Land of Iron" project.

The bank slag material represented by the sample contains an abundance of material that would act as a pozzolan when added to a lime mortar. Provided that it was screened to remove the abundance of fines present, and was then crushed, as was indicated in the mortar samples examined, it would provide a very effective pozzolan.

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 slag material received in CMC's laboratory on the 26th March 2019 from Nigel Copsey of the Earth, Stone and Lime Company. Which was identified as bank slag from the spoil heaps adjacent to the Bank Top Kilns, in the North Yorkshire National Park.

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For CMC Ltd.

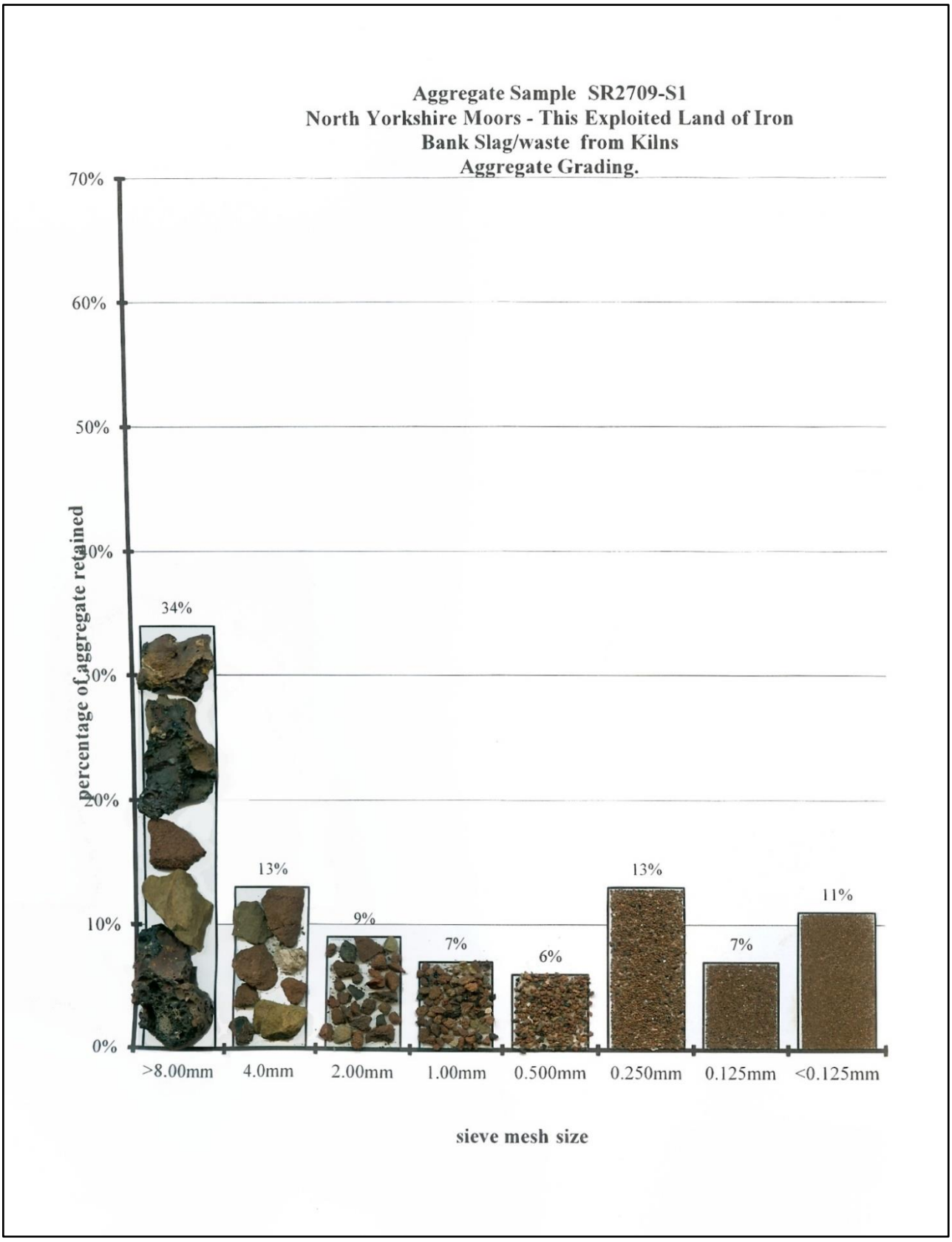

Figure No. 1: Aggregate Grading on Bank Slag sample from Bank Top Kilns.

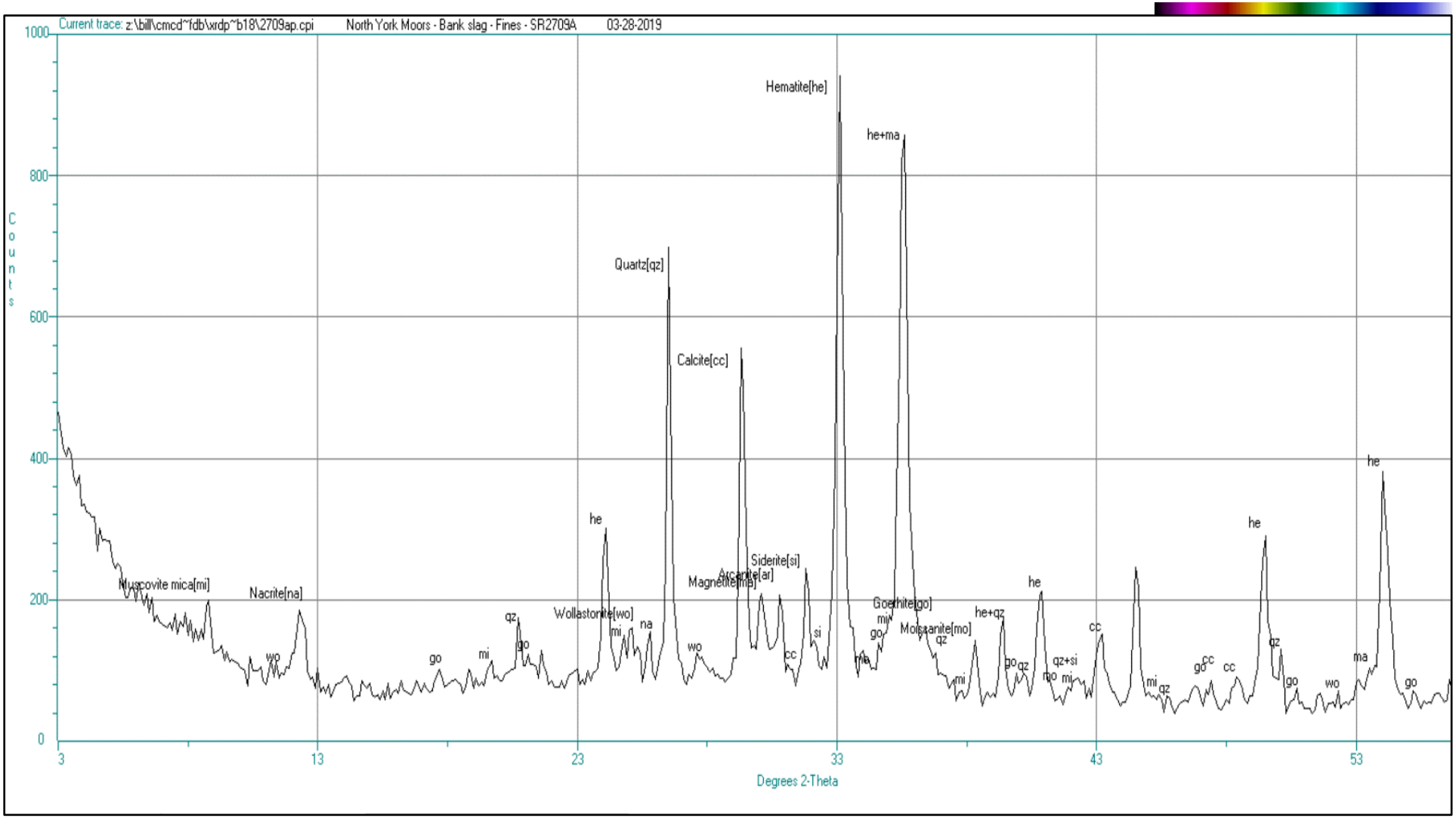

Figure No. **2**: SR2709-S1A Representative sample of the Fines material <0.500mm sieve.

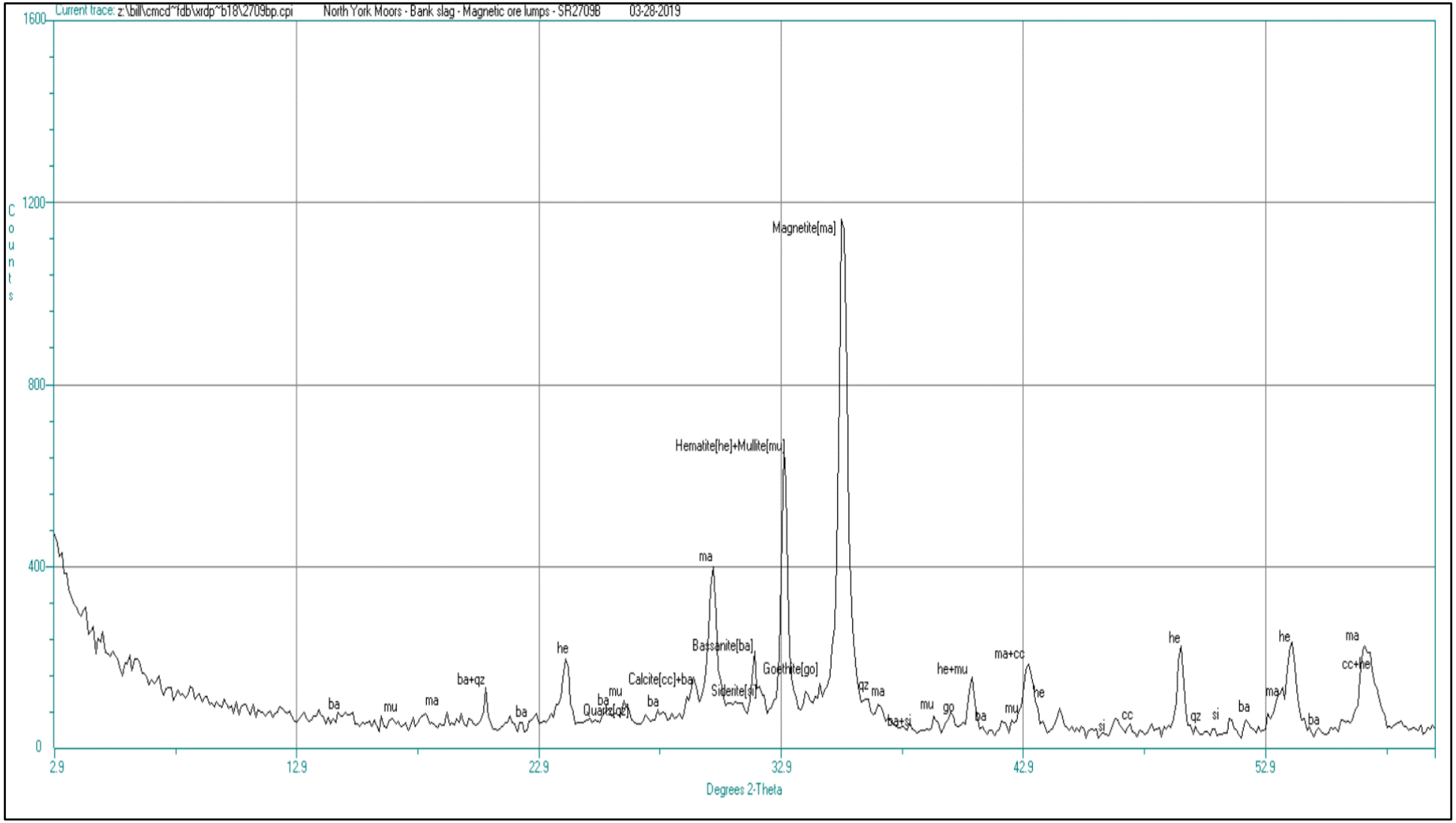

Figure No. 3: SR2709-S1B Sample of slag – crushed magnetic fragments.

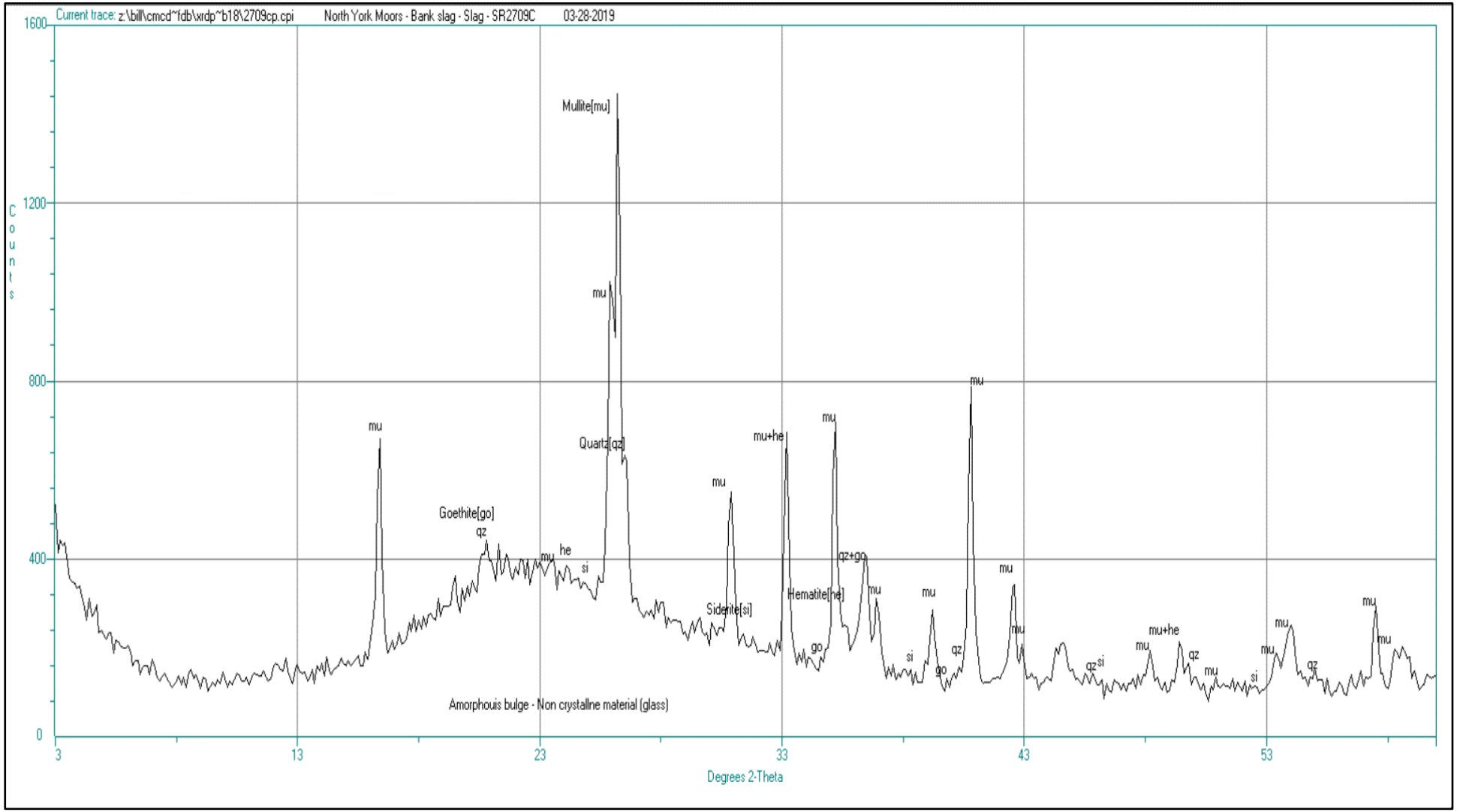

Figure No. 4: SR2709-S1C Representative sample of the vitreous slag particles.

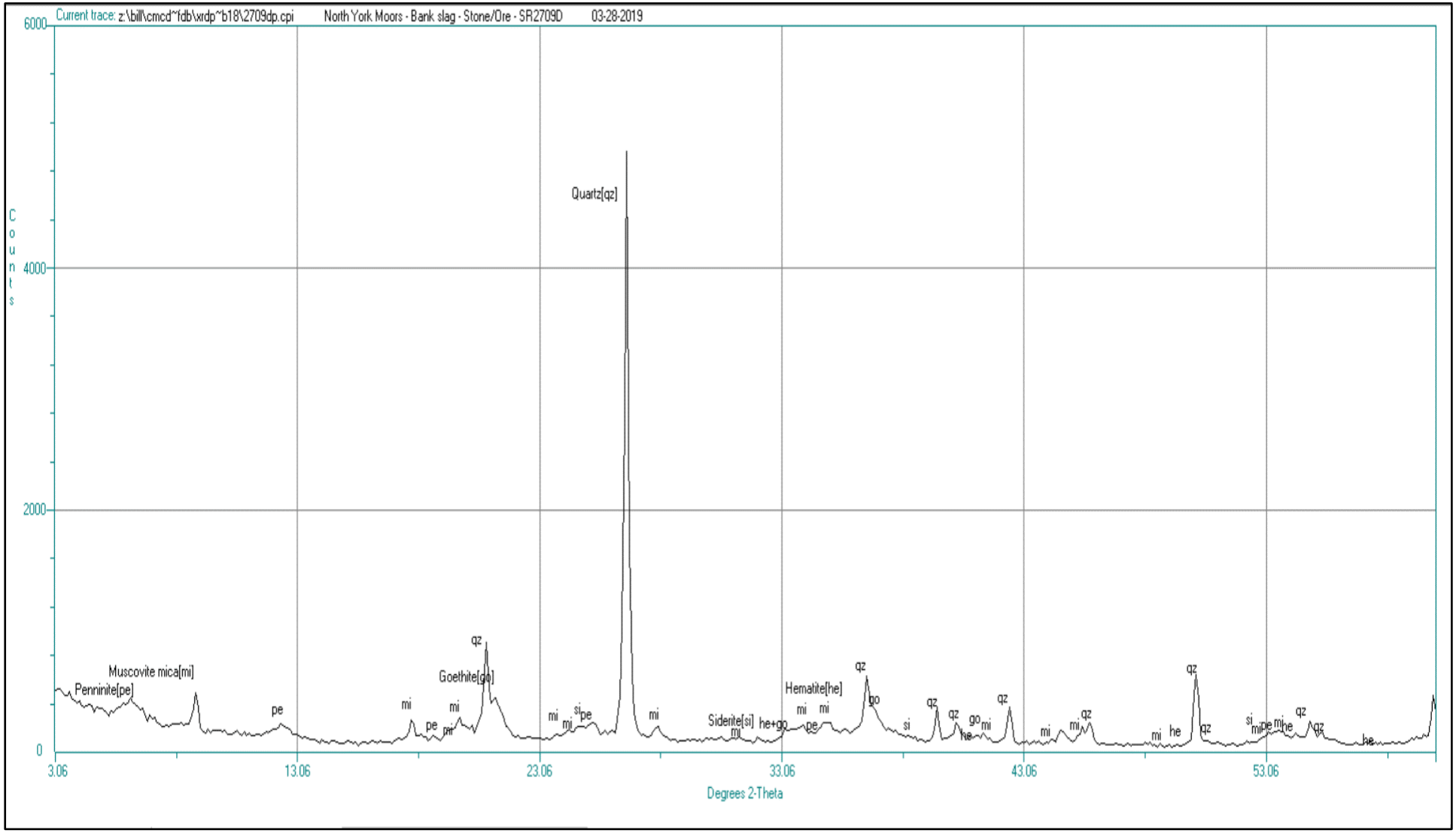

Figure No. 5: SR2709-S1D Sample of a stone fragment.