Atmospheric CO_2 sequestration in iron and steel slag: Consett, Co. Durham, UK.

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Abstract

Carbonate formation in waste from the steel industry could constitute a non-trivial proportion of global requirements to remove carbon dioxide from the atmosphere at potentially low cost. To constrain this potential, we examined atmospheric carbon dioxide sequestration in a >20 million tonne legacy slag deposit in northern England, UK. Carbonates formed from the drainage water of the heap had stable carbon and oxygen isotope values between -12 and -25 ‰ and -5 and -18 ‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively, suggesting atmospheric carbon dioxide sequestration in high pH solutions. From the analyses of solution saturation states, we estimate that between

280 and 2,900 tCO_2 have precipitated from the drainage waters. However, by combining a thirty-seven-year dataset of the drainage water chemistry with geospatial analysis, we estimate that <1 % of the maximum carbon capture potential of the deposit may have been realised. This implies that uncontrolled deposition of slag is insufficient to maximise carbon sequestration, and there may be considerable quantities of unreacted legacy deposits available for atmospheric carbon sequestration.

Introduction

The steel industry produces around half a billion tonnes of an alkaline material (known as slag) globally each year[1]. Blast furnace slags commonly find uses as secondary aggregate[2], pozzolan[3] or agricultural lime[4]. However, due to the higher concentrations of oxides and hydroxides (which may cause expansion if used directly in aggregate), slag from steel production is typically 'weathered' for months to years prior to use[5]. While the proportion of slag being reused varies with regional demand, a sizable proportion of annual production is ultimately stockpiled in steelworks[6,7]. This, alongside historic deposits of iron and steel slag, creates environmental issues associated with highly alkaline leachates ($pH > 11$)[8,9]. The dissolution of these materials releases calcium and magnesium ions from oxide and silicate minerals and glass/amorphous material, which raises pH beyond that encountered in most natural settings (Equations 1 and 2, which show dissolution reactions for larnite and portlandite respectively).

$$Ca_2SiO_4 + 4H_2O \rightarrow 2Ca^{2+} + H_4SiO_4 + 4OH^- \qquad (1)$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (2)$$

These hydroxide-enriched leachates promote dissolution of atmospheric carbon dioxide (CO_2) into solution, which reacts to form carbonate and bicarbonate ions (Equation 3). Slag leachates are rich in dissolved calcium (Ca), which leads to supersaturation of calcium carbonate minerals (e.g., calcite) and rapid rates of precipitation of secondary carbonates (Equation 4[10,11]). Such leachates can pose enduring[12] and acute[13] environmental issues due to the physical smothering ('armouring') of receiving streams, alongside extreme pH, and potential metalloid enrichment and mobility[14–16]. However, carbonate precipitation buffers the waters back towards circum-neutral pH which limits metalloid solubility.

$$CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)} + H_2O_{\,(l)} \rightleftharpoons HCO^{-}_{3\,(aq)} + H^{+} \rightleftharpoons CO^{2-}_{3\,(aq)} + 2H^{+} \qquad (3)$$

$$Ca^{2+} + 2HCO^{-}_{3\,(aq)} \rightleftharpoons CaCO_{3\,(s)} + H_2O_{(l)} + CO_{2(aq)} \qquad (4)$$

The potential for steel slags to capture atmospheric CO_2 in the form of stable carbonates has been extensively studied, initially in reaction vessels at elevated temperatures (>200°C), enriched CO_2 gas-concentrations (>10 %), and/or pressures (~20 bar)[17–21], with a theoretical CO_2 sequestration capacity of 0.27 to 0.43 kg CO_2 per kg slag (see Supporting Information S1). This capacity can be improved through the application of 'enhanced weathering'[22,23], which is an alternative CO_2 sequestration pathway in which carbon is stored as dissolved bicarbonate in the ocean[24]. In this approach, almost twice as much CO_2 may be sequestered (Equation 5).

$$Ca_2SiO_4 + 4H_2O + 4CO_2 \rightarrow 2Ca^{2+} + H_4SiO_4 + 4HCO_3^{-} \qquad (5)$$

The removal of CO_2 from the atmosphere ('negative emissions' or 'greenhouse gas removal') is emerging as an important policy requirement for limiting global temperature change <2 °C [25,26]. Emissions reduction scenarios predicted to achieve this require between 180 - 900 Gt CO_2 to be removed from the atmosphere over the coming century[27], alongside limiting further emissions. Atmospheric carbon sequestration in the steel industry may provide a relatively cheap method of negative emissions, and, in the case of carbonate formation, a means for waste remediation[28]. The removal of atmospheric CO_2 into waste materials has previously been explored in chrysotile mine tailings (e.g.,[29]), in soils mixed with concrete from demolition[30,31]. To constrain the potential of CO_2 sequestration in waste from the steel industry, we quantify atmospheric carbon sequestration in a deposit of slag associated with an iron and steel works that closed nearly four decades ago.

Materials and Methods

Study Site

For over 100 years an iron and steel works located in Consett, Co. Durham, UK, produced cumulatively around 120 million tonnes of iron and steel. This led to the creation of >20 million of tonnes of slag, which were deposited in several large mounds adjacent to the works. Production ceased in 1980, and the heaps were landscaped, capped with thin clay topsoil, and have been passively managed (Figure 1). The deposits are underlain by alluvium and glacial till above Carboniferous Coal Measures, and the largest deposit was heaped over a partially culverted watercourse (the Howden Burn), which receives the bulk of the drainage water. A smaller heap is located to the south of the main workings (Figure 1), the drainage waters of which collect in a pond before discharging through a naturally developed wetland in the Hownsgill Valley and into a watercourse (the Dene Burn)[9] (see Supporting Information S2 for location and site detail)

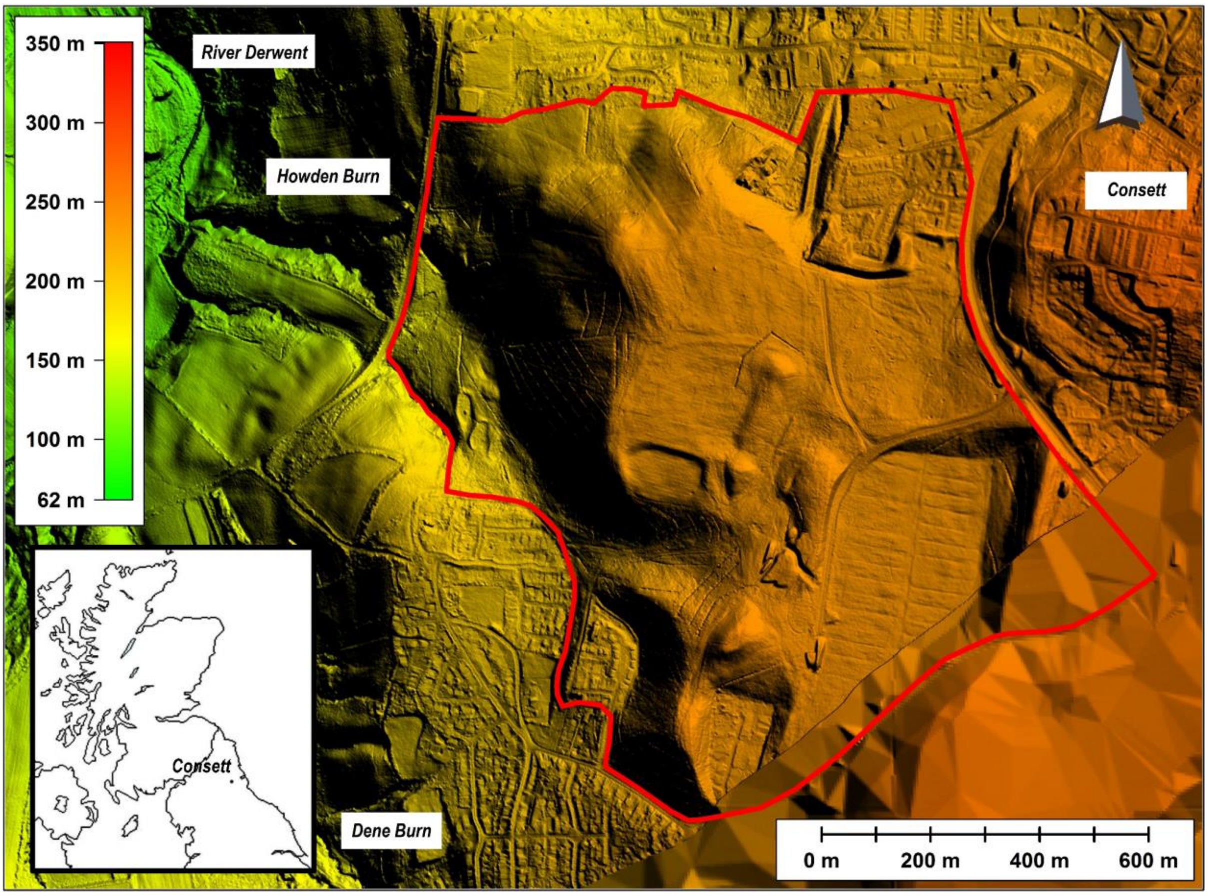

Figure 1: Location map showing the topography of the former Consett Steelworks, drainage systems (the colour scale represents elevation above sea level derived from 1 m and 5 m LIDAR Data[32] The red line denotes the boundary of the study site).

Volume Estimates

2 m and 5 m resolution LIDAR data[32] were compiled for the site, representing the modern ground surface. 41 spot heights were recorded from the historic 1890 Ordnance Survey map and used to create a low resolution 5.3 km^2 digital elevation model of the natural ground surface underlying the site. The comparison between these two digital elevation models was used to estimate the volume of the northern heap (using the terrain subtraction function in Global Mapper© v18 1.0, see Supporting Information S3).

Resistivity Tomography Survey

The depth of the slag deposit has been confirmed using Electrical Resistivity Tomography (ERT) surveys, which determined the depth of the contact between the slag and the underlying natural ground. A 72-channel IRIS Syscal resistivity system was used to acquire three profiles (A, B and C) across the slag deposits (shown in Figure 2). Profiles A and B transect the top of the slag deposit, to observe how slag thickness increases with distance away from the side of the valley; Profile B strikes towards the foundations of the now demolished steel work buildings (see Supporting Information). Profile C trends from the bottom of the slag deposit towards profile A. Profiles A and B were acquired with a 5 m electrode spacing, giving a maximum depth of investigation of ~50 m bgl. ERT Profile C was acquired with an electrode spacing of 2.5 m, giving a maximum depth of investigation of ~25 m bgl. The data were processed using Res2DInv software to derive modelled electrical cross-sections of the subsurface. The resulting resistivity models for Profiles A, B and C had an RMS error of 8, 17 and 9 %, respectively. Robust inversion was not used to allow for more geologically realistic results, hence the higher RMS values were condoned. The finalised models were calculated within 4 or fewer iterations. The elevation data were added to the models, using electrodes positions extracted from LIDAR data (Figure 1). Finally, these data were exported into Surfer 7, gridded and presented as a 2D cross-section of resistivity.

Chemical sampling and analysis

Long term water quality records from the site are compiled from monitoring by regulatory agencies (Environment Agency and their predecessor, the National Rivers Authority) who routinely sampled major physico-chemical parameters, major ions and minor elements from 1978 - 2000. However, sample collection was sporadic, ranging from monthly to annual sampling in frequency. From 2004 onwards, annual sampling (as a minimum) has been undertaken by the authors at the same locations in the Howden and Dene Burns. Bi-monthly samples were collected from the Hownsgill valley wetland between 2004 - 2006[9] and ad-hoc samples up to 2015. Field sampling consisted of major labile variables (pH, electrical conductivity, Eh, temperature using a Myron Ultrameter) and total alkalinity which was measured *in situ* using a Hach digital Titrator (0.8 moles/l H_2SO_4 with bromocresol green-methyl blue indicator). Samples were also taken in acid-washed HDPE bottles for field-filtered (0.45 μm) samples which were acidified with trace metal grade HNO_3, and analysed for major cation content using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer.

Long term patterns in saturation index for calcite were determined using the geochemical code PHREEQC[33] with the Lawrence Livermore National Laboratory database based on sample dates where synchronous pH, temperature, Ca and total alkalinity data were available. Trends in calcite saturation index ($SI_{calcite}$) for the Dene Burn and Howden Burn are assessed using Partial Mann-Kendall tests with flow as a co-variate (as per[12]). Flow at the time of sampling was either manually measured or determined from an adjacent permanent flow gauging station (River Derwent at Rowlands Gill, National River Flow Archive station: 23007) adjusting for catchment area (see Supplementary Information S2).

Synchronous sampling for water quality and flow along the courses of the Dene Burn and Howden Burn was undertaken from 2003 to 2015 on 14 and 8 occasions, respectively. The Hownsgill Valley wetland was sampled on 10 occasions from 2004 to 2006[9]. This enables determination of mass loss of Ca between successive downstream sample locations (the mass load being the product of flow and concentration) from which to assess carbonate precipitation rate, assuming all Ca load lost from the water column is as $CaCO_3$ (Equation 4). A source location and downstream location (in between which there were no major tributaries) along the course of each stream were sampled for major physico-chemical parameters as above. Flow was measured using a Valeport 801 velocity meter with a flat sensor suited to the shallow stream depths (typically <0.2m) via the velocity area method. The length of the channel reaches was determined through measurement in ArcGIS v.10 of 1:1000 Ordnance Survey base maps[34]. Average channel width was taken from manual spot measurements of channel width every 50 m of the study reaches. The area of the Hownsgill Valley wetland was determined by a manual field survey with differential GPS[9]. Synoptic sampling was undertaken over a range of flow conditions from which relationships between source chemistry (notably $SI_{calcite}$) can be related to the estimated mass of carbonates deposited on the downstream streambed (Equation 6).

$$P = 2.5\left(\frac{Q_d(C_s - C_d)}{A}\right) \qquad (6)$$

where P is the area adjusted calcium carbonate precipitation rate ($g/m^2/day^1$); Q_d equates to the mean daily flow-rate (m^3/day); C_s is the Ca source concentration (mg/l); C_d is the concentration of Ca at downstream sample location (mg/l); A is the stream area (m^2), based on length of reach (GIS-derived) and average width from spot measurements. The multiplier is the ratio between molar mass of Ca and $CaCO_3$.

A series of 14 surficial secondary carbonate samples were taken from the streambeds of the Howden and Dene Burns alongside samples from carbonate hardpans in the Hownsgill Valley wetland (See Supporting Information S5). The samples were crushed using an agate pestle and mortar and analysed for stable carbon and oxygen isotope ratios using Kiel IV Carbonate Device calibrated against a Vienna Pee Dee Belemnite standard. The standard error for the analysis is 0.001 ‰ and 0.003 ‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively. To this powder, ultra-pure acetone was added, and the resultant slurry was pipetted onto a clean glass slide. The slides were allowed to dry, and then analysed using a Philips PW1710 Automate Powder Diffractomer with a CuK radiation source operating at 35 kV and 40 mA. Samples were scanned from 2 to 70 º2θ at a step size of 0.02 º2θ with a counting time of 1 s per step. Diffraction patterns were analysed using PW1876 PC-Identify software (Version 1.0b) and compared with JCPDS cards of standard materials.

Results and Discussion

Volume Estimates and Resistivity Tomography

By creating and comparing elevation models of the current (from LIDAR data) and pre-slag (from spot heights of historic maps) terrain, it is possible to estimate the depth of the deposit and the total volume of the material (Figure 2). The analysis suggests depths of the largest deposit range up to 45 m, which is consistent with historic accounts of the site[35,36], and that the total volume of material is ~16 Mm^3, which is consistent with theoretical maximum historic production estimates (see Supporting Information S6). Given that the bulk density of slag is typically between 1 and 1.5 Mg/m^3 [37], and that the concentration of CaO and MgO is between 34 and 42 % and 8 and 12 % by mass, respectively[38], then the carbon dioxide sequestration potential for the largest heap is 6 - 11 million tonnes CO_2 (as mineral carbonate) or 10 – 19 million tonnes CO_2 (through enhanced weathering).

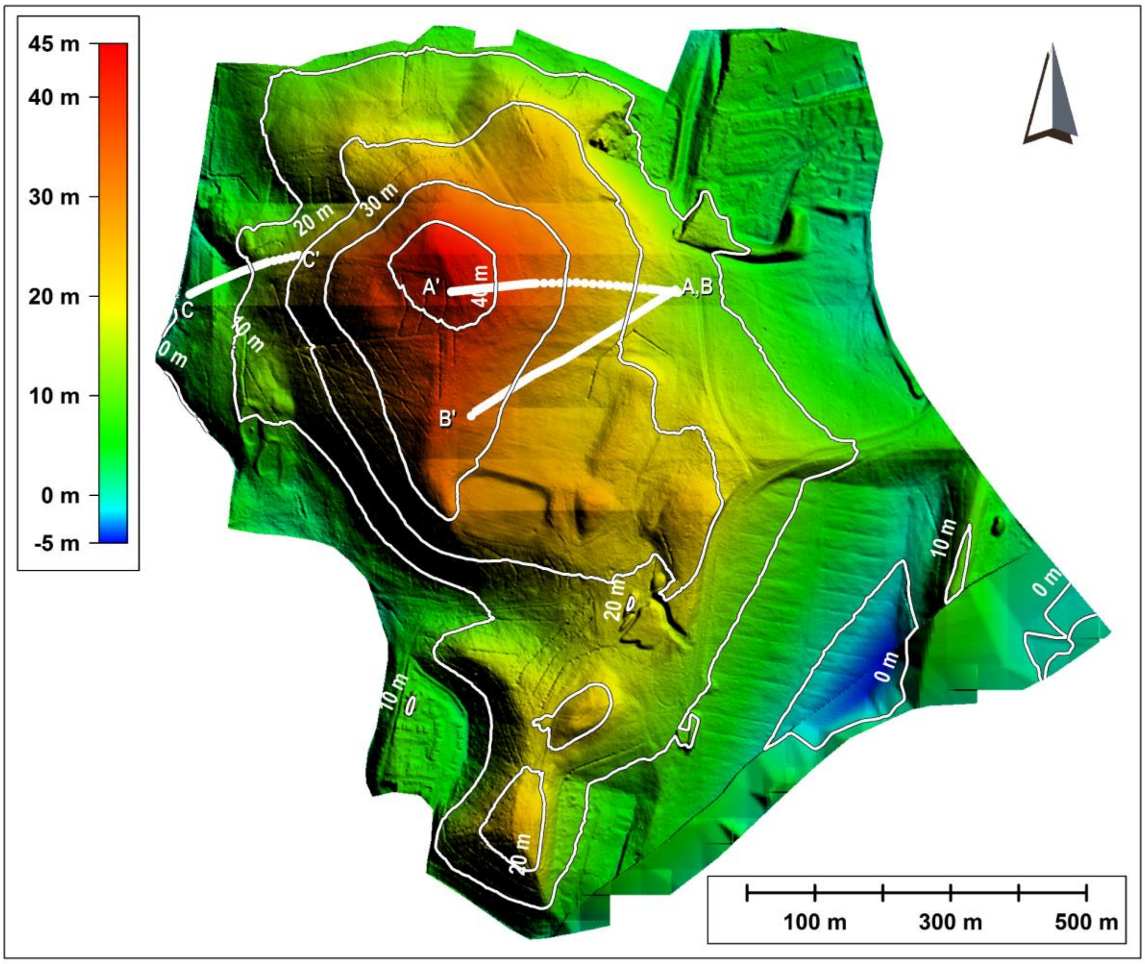

Figure 2: An estimate of the depth of the slag deposit based on the comparison of pre- and post-deposit digital elevation models. The bold white lines (A/A', B/B' and C/C') represent the locations of the resistivity survey (see Figure 3).

The results of the ERT geophysical surveys are shown in Figure 3. The interpretation for each technique is obtained by comparison with known values of common materials[39]. Each ERT profile shows a more resistive material overlying a more conductive material. In this scenario, the slag deposits are more resistive than the underlying natural geology which is composed of alluvium, clays and mudstones. This may be due to a well-drained slag overlying saturated natural ground, or that the conductive metals contained in the slag are fixed within a silicate matrix, creating a more resistive material than the natural ground. Profile A shows an undulating boundary (Feature, F1) between more resistive and more conductive material which begins at ground level, 50 m along the profile and deepens to the west. The authors interpret this as the boundary between the slag and natural ground. Profile A also shows a shallow less resistive feature which may be related to groundwater flow. Profile B shows a highly heterogeneous image of resistivity; the very low resistivity feature (F2) is likely to be a plume of highly conductive ground water caused by solutes within the slag. Profile C shows a clear boundary between a more conductive underlying geology and a more resistive overburden. Feature (F3) is likely to represent the boundary between the slag deposit and the underlying geology. The boundary on the west side of the profile (F4) is caused by made ground due to a nearby road and is not related to the slag deposit.

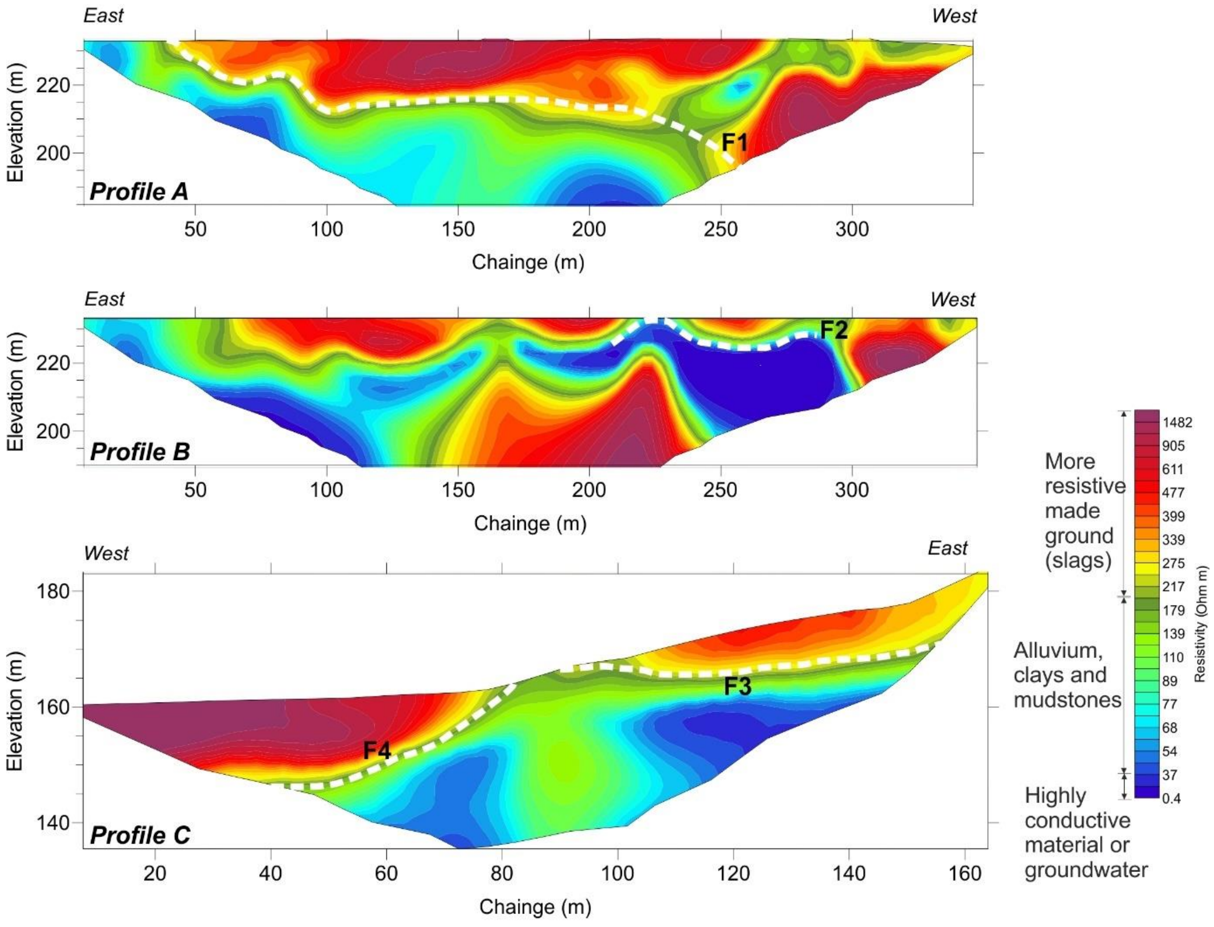

Figure 3: Results from the Electrical Resistivity Tomography. Location of the lines are presented in Figure 2. Transition between high and low resistivity potentially denote changes in ground conditions (e.g., between slag and the natural ground in F1 and F3)

Stream water geochemistry

Three drainage streams at the site are characterised by hyperalkaline pH (typically in the range 10 to 12.5 at source), dominated by Ca-OH-SO_4 waters (see Supporting Information S7), where the sulphur potentially originates from the coke or coal used in the blast furnace. All drainage streams are consistently supersaturated with a range of carbonate phases (Supporting Information S7), with calcite dominant in the extensive downstream secondary deposits (Supporting Information Figure S11). As such, long term changes in aqueous chemistry focus on saturation indices for calcite hereafter (Figure 4). Flow in each of the systems is relatively steady, receiving a mixture of groundwater from within the slag or spring water from the underlying Coal Measures[11] generally rich in Ca, which are occasionally diluted by solute-poor surface runoff (Supporting Information S7)[11-12].

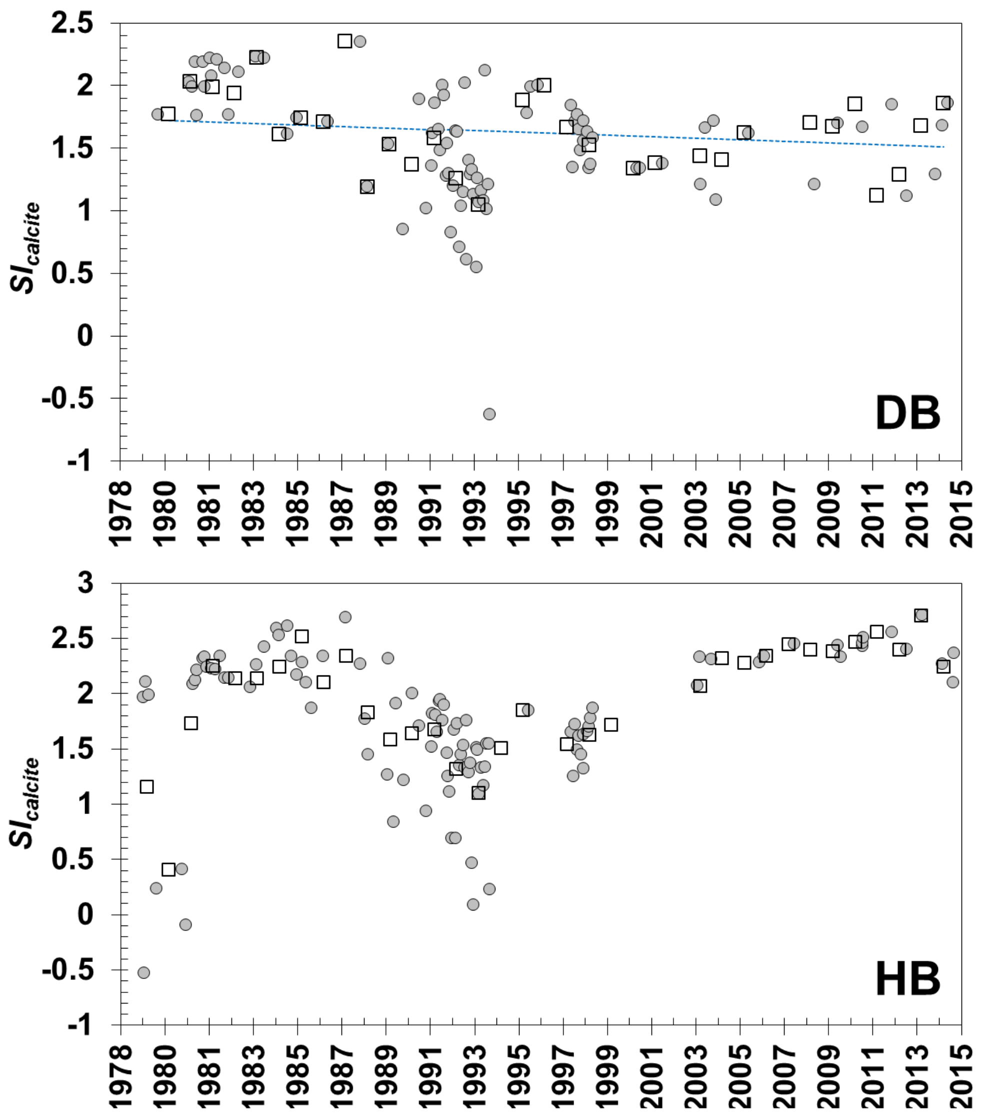

Figure 4: Long-term calcite saturation index ($SI_{calcite}$) values for the Dene Burn (DB) and Howden Burn (HB). Closed grey circles show individual measurements; open squares show averages for each hydrological year (1st October - 30th September). Blue trend line in upper plot (Dene Burn) based on the Sen's slope statistic shows the significant decline in $SI_{calcite}$ from Partial Mann Kendall Tests (see text). No significant trend was apparent in the Howden Burn (lower plot).

There has been a slight change in bulk drainage chemistry in 37 years of monitoring. There was a significant decline in saturation index in waters draining to the Dene Burn

(Figure 2A; PMK: -856; P = 0.002) irrespective of flow condition which showed no significant long-term trend (PMK: 220; P = 0.421). This may be indicative of gradual exhaustion of alkalinity generating minerals (e.g., Ca-silicates, free lime, or portlandite) in the slag deposits with weathering (see Supporting Information S7)[12]. No significant trend in $SI_{calcite}$ or flow in the Howden Burn is apparent (Figure 2B; $SI_{calcite}$: PMK: 9.3: P = 0.80; Flow: PMK: 22; P = 0.95), although a clear decline then subsequent recovery in $SI_{calcite}$ is apparent between the mid-1980s and the early part of the 21st Century, respectively. This has previously been attributed to changes in flowpaths and significant groundworks in this sub-catchment as part of broader restoration works[12]. The Howden Burn drains a much greater proportion of the slag deposits at the site (>3/4 total area and much greater depths) than the Dene Burn and as such which may explain why there has been no sign of decline in alkalinity generation yet in the Howden Burn. Regardless of temporal changes, the $SI_{calcite}$ in all systems is typically in a range where spontaneous calcium carbonate precipitation would be anticipated (>+0.3) and generally above >+1.5 where homogenous precipitation is expected[40] (see supporting information Table S2).

Evidence of carbonate precipitation

Observations of calcium carbonate precipitation are common in the drainage waters emanating from slag deposits[8] and provide a means for translating the long-term saturation index data into carbon mass balances for the drainage streams. The mass loss of Ca between source and a downstream sample location is divided by reach area (Equation 9). The synoptic sampling of the receiving streams at Consett reveals a strong and significant positive relationship (Spearman r_s: 0.82; p <0.001; ANOVA regression: F: 52.1, p <0.001) between empirical estimates of $CaCO_3$ precipitation rate and $SI_{calcite}$ at the source of the discharge (Figure 5). The higher $CaCO_3$ precipitation rates are apparent in the Howden Burn with a range of 8 - 259 g/m^2/day, where waters are typically further from equilibrium (see higher $SI_{calcite}$ values in Table S2) as compared to the Dene Burn (range 7 - 116 g/m^2/day: Table 1) which have lower $SI_{calcite}$ values.

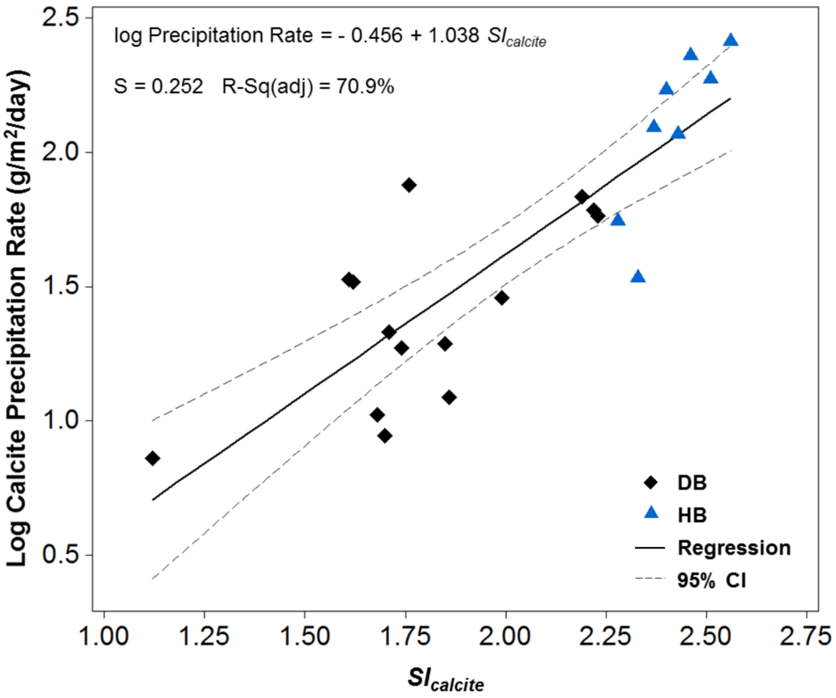

Figure 5: Relationship between $SI_{calcite}$ and empirically observed calcium carbonate precipitation rate (shown as $\log_{10}$ values) across the Dene Burn (DB) and Howden Burn (HB) streams.

Table 1: Estimated calcium carbonate precipitation rates for the three drainage systems at the site of the former Consett Steelworks derived from loadings-based assessments. Flux data show median and range in parentheses.

	Dene Burn	**Howden Burn**	**Hownsgill Valley**
Area between sample locations (m^2)	2310	525	2863
n	14	8	10
Ca^{2+} load loss (kg/d)	28.4 (6.7 - 107.6)	30.9 (1.7 - 54.4)	6.2 (1.2 - 10.9)
$CaCO_3$ precipitation rate (g/m^2/day)	31 (7 - 116)	147 (8 - 259)	5 (1 - 10)

Precipitation rates across the wetlands that receive leachate in the Hownsgill Valley have been previously published, based on intensive monitoring of aqueous geochemistry[9,30] and are in the range of 1 to 10 g/m^2/day (Table 1). These lower rates are readily ascribed to the topographical differences between the Hownsgill Valley wetland, which is low gradient and thus limited by the rate of diffusion of atmospheric CO_2 (in addition to microbially-generated CO_2 in the water column and substrate[9]), compared to the cascading Howden and Dene Burns. In the faster-flowing systems, the dissolution rates of CO_2 into solution are likely to be far greater given the turbulent flow of the shallow waters over secondary carbonate barrage cascades (see Supporting Information S4[41]).

Carbonate deposit analysis

Stable carbon and oxygen isotope ratios have been widely used to assess provenance of carbonate minerals (e.g.[42]). Carbonates formed from highly alkaline solutions derived from the dissolution of steel slags, lime waste, cement wastes, or alkaline mine tailings[30,43,29] have very characteristic negative $\delta^{13}C$ isotopic signatures[30,44,45]. These have been ascribed to a stable carbon isotopic enrichment factor ($\varepsilon_{CaCO3\text{-}CO2}$ = -19 ‰) in carbonate and dissolved aqueous CO_2 from the reaction between aqueous CO_2 and hydroxide ions ('hydroxylation')[46]. The isotopic value of oxygen in carbonate minerals formed from high pH solutions is a mixture of the isotopic value of hydroxide ions, and atmospheric CO_2[46–48]. This fractionation gives rise to the highly negative $\delta^{18}O$ isotope values (-24 and -19 ‰) characteristic of hyperalkaline sites (eg., cements[30,49,50] and hyperalkaline groundwater[51]). The use of isotopic values unambiguously demonstrates incorporation of atmospheric CO_2 into solid carbonate minerals.

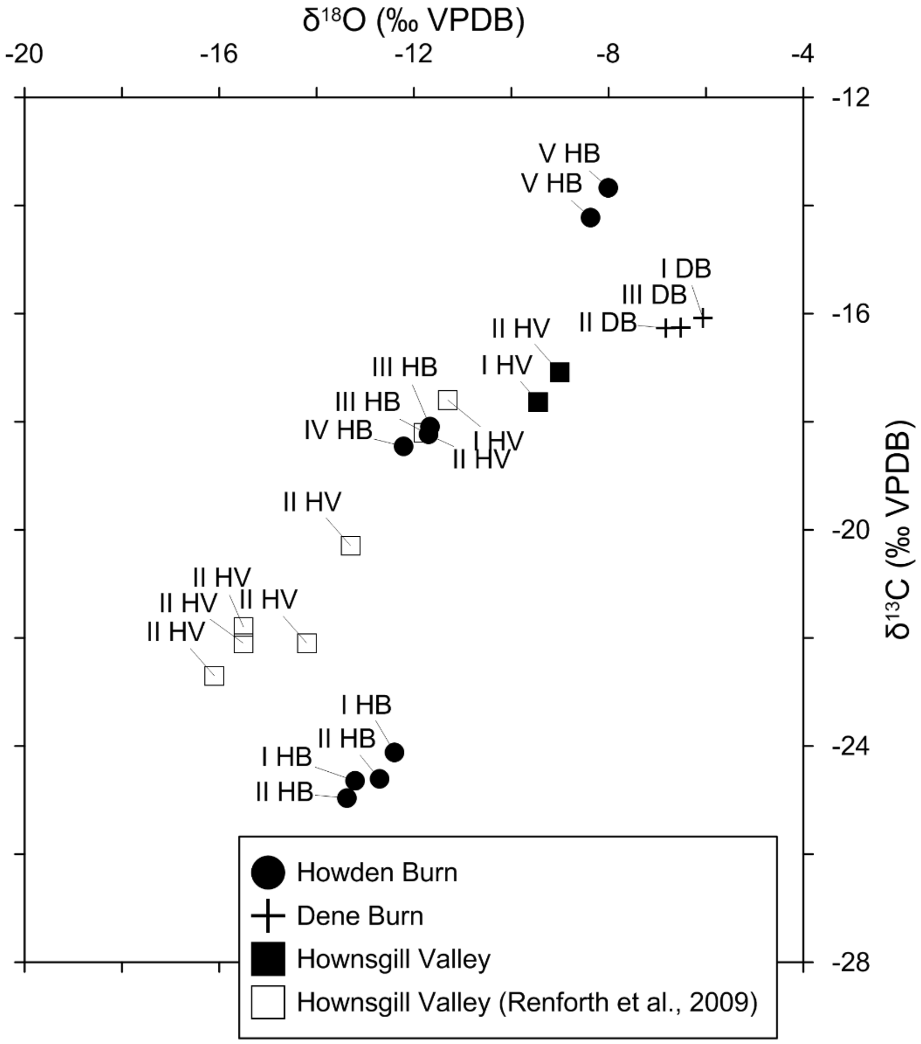

Figure 6: $\delta^{18}O$ and $\delta^{13}C$ values of carbonates formed in the drainage waters of the slag heaps at Consett, Co. Durham.

The stable carbon and oxygen isotope ratios for the deposits in the three drainage streams at Consett are presented in Figure 6. The more negative $\delta^{13}C$ and $\delta^{18}O$ values were recorded in samples from the Howden Burn and Hownsgill Valley, where dilution of the leachate by uncontaminated ground or surface waters was minimal[11]. The Dene Burn, which receives drainage rising from a spring line in the Coal Measures (rich in bicarbonate[52]), has the least negative $\delta^{13}C$ and $\delta^{18}O$ values. A common approach to assessing the relative portion of atmospheric CO_2 in the secondary mineral deposits produced from highly alkaline solutions is via the use of a linear mixing model that assumes carbon in a mineral sample is sourced from two endmember reservoirs (e.g., [53]). If atmospheric CO_2 is the only source of carbon in hydroxylation isotopic fractionation, the proximity of the isotope values in the samples to end members can be used to determine the quantity of sequestered atmospheric CO_2 in the secondary deposits. Hydroxylation will produce an end member with an isotopic ratio of -25.3 ‰ for $\delta\ ^{13}C$, see [31]). Therefore, based on the proximity of the data in Figure 6 to a 'lithogenic' ($\delta\ ^{13}C$ = 0 ‰) and the 'hydroxylation' end members, it is estimated that between 54 and 99 % of the carbon in the carbonate is derived from the atmosphere and the remaining carbonate is derived from lithogenic sources.

Carbon budget and storage potential

The drainage water chemistry and flow suggests that approximately 314 tonnes of calcium have been leached from the heaps over the past 37 years, which is approximately >0.004 % of the potentially available calcium based on the volume and typical composition of slag[16]. Even if the same concentration of calcium was present in the drainage waters since rapid expansion of the heaps in the early 1900s (~8.5 t/yr), and that the flow through the site was similar to present levels, then approximately 850 tonnes of calcium would have been leached over 100 years. Estimates of carbonate precipitation from stream waters suggest between 281 and 2,890 tonnes of CO_2 have been sequestered since the work's closure in 1980 (Table 2). For comparison, this equates to approximately 255 – 2,627 tonnes of calcium; the upper value is consistent with calcium leach values. Given the heaps may contain 3.9 – 7.2 million tonnes of calcium, only a very small proportion has been leached, and that the carbon sequestration potential of the material has not been exploited.

Table 2: Total carbon flux estimates based on long term $SI_{calcite}$ data, empirical loading measurements and isotopic characterisation of secondary deposits. Total estimated low and high range (in parentheses) based on aggregated margin of error of relationship between $SI_{calcite}$ and precipitation rate (Figure 4) and standard deviation of isotopic characterisation. *Hownsgill Valley calculations based on minimum and maximum recorded average precipitation rates in intensive sampling; long term total extrapolates from this single year

Site	**Average $CaCO_3$ formation in drainage waters t/y**	**$\%CO_2$ from atmosphere**	**Average atmospheric CO_2 uptake t/y**	**Total CO_2 t (1978 - 2015)**
Dene Burn	17.6 (5.4 - 57.1)	64	3.5 - 36.5	130 - 1,351
Howden Burn	13.0 (4.0 - 42.1)	80	3.2 - 33.7	118 - 1,247
Hownsgill Valley	5.7 (1.1 - 9.9)*	79	0.9 - 7.8	33 - 292
TOTAL	-	-	-	281 - 2,890

The poor conversion of the carbon capture potential may be attributed to limited ingress of atmospheric CO_2 into the heap. For instance, if the groundwater inside the heap was in equilibrium with $Ca(OH)_2$, atmospheric CO_2, and $CaCO_3$ (and thus precipitating carbonate minerals) waters would have a pH of 10.2 and 0.1 mmol l^{-1} of Ca (see Supporting Information S7 for geochemical modelling). However, the concentration of Ca (~1-5 mmol l^{-1}) and pH (~11.5) in the drainage waters is more consistent with the equilibrium concentration ([Ca] = ~20 mmol l^{-1}, pH = 12.5) of portlandite ($Ca(OH)_2$) or larnite (Ca_2SiO_4) which are common minerals in slag [54]. The lower than expected pH and calcium concentration could be caused by dilution of leachate with meteoric or ground water, and/or a kinetic limitation of weathering (e.g., surface armouring of slag with carbonate or C-S-H phases limiting weathering rates [15,17]).

Implications

The steel industry is responsible for more than 5 % of the total greenhouse gas emissions worldwide[55], with more than 2 tonnes CO_2 released per tonne of steel manufactured[19], which equates to over 6 tonnes of CO_2 released for every tonne of slag. Slag has the potential to capture ~0.4 tCO_2 per tonne as a mineral carbonate or up to 0.7 tCO_2 per tonne through enhanced weathering. The full carbon cycle of iron and steel slag production and weathering is currently far from a negative emissions technology, and would merely offset emissions from the production site. However, the iron and steel industry will be under increasing pressure to reduce emissions, which may fall to 0.3 tCO_2 per tonne of steel (0.5 tCO_2 per tonne of slag) primarily by mixing low carbon fuels into the blast furnace, exploiting a low carbon power sector, and capture and geological storage of CO_2 emissions[56]. If these emissions reductions were achieved, then the additional carbon sequestration through slag weathering may be sufficient to create an overall carbon negative steel industry. Furthermore, there may be considerable atmospheric removal potential of legacy slag deposits which are plentiful in many current steel producing areas and post-industrial settings. If the requirements of COP21[57] are to be implemented, there is likely to be a requirement for ‘negative emissions’ technologies to keep atmospheric CO_2 within targets[25,58]. Half a billion tonnes of slag are produced annually[1], which may increase to over a billion tonnes in the current century. Considering these production values, it is estimated that the industry may be able to remove half a billion tonnes of CO_2 out of the atmosphere per year.

Proactive management of slag to account for, and accelerate, carbon uptake (e.g., through comminution of slag where carbon budgets are favourable) while addressing any potential environmental concern of hyperalkaline discharges on recipient watercourses could provide mutual benefits. Leachate management to minimise subsequent impacts on the aquatic environment is likely to be best addressed via (a) aeration of waters (e.g., CO_2 sparging, cascading of thin films of leachate over barrages where hydraulic head is suitable[10,41]), (b) settlement lagoons, to allow accumulation and ready recovery of precipitated calcium carbonates (e.g.,[59]), and (c) residual buffering of alkaline leachates with wetlands[60–61]. In addition to wetland habitat creation as part of broader post-industrial restoration, there may be opportunities, through careful treatment of the leachate, to recover and reuse the high purity precipitated calcite (potentially used as a filler and coating in paper manufacture[18,62]) and typically benign in terms of trace element content[61].

Acknowledgements

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Supporting information

Experimentation conditions for previous carbonation experiments, local map of the study site, slag deposit volume estimates, photographs of carbonate deposits in drainage waters, previous production estimates, supplementary geochemical data and modelling.

References

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