# Recovering metals from waste through co-precipitation from hyperalkaline leachates.

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**Project Highlights:**

- Investigation of metals leaching at high pH from legacy industry waste site.
- Characterisation of water and tufa using state-of-the-art micro-analytical techniques.
- Precipitation of calcareous tufa and its ability to trap metals and $CO_2$ in its structure.

**Overview:**

Metals leaching from industrial waste sites can lead to contamination of soil and water affecting human and environmental health (Riley et al., 2020). One solution is to utilise tufa formation to capture metals whilst simultaneously sequestering $CO_2$. Tufa is a secondary calcium carbonate ($CaCO_3$) deposit that forms as a precipitate (e.g., calcite) from groundwater. Formation of natural tufa occurs where groundwater becomes supersaturated with respect to calcite through a process of $CO_2$ outgassing. At a number of legacy waste sites deposits of tufa are found associated with (hyper)alkaline leachate (Fig.1) (Bastianini et al., 2019). With water above ~pH 9, the precipitation mechanism differs at these sites as atmospheric $CO_2$ reacts with dissolved $Ca(OH)_2$, leading to $CaCO_{3(s)}$. Previous investigation of the outflow and the precipitated material at one NE England site has shown that these 'anthropogenic' tufa depositions contain metals within their structure (Fig.1 D&E)(Cumberland et al., 2022). Other studies show the rapid precipitation associated with hyperalkaline systems can lead to amorphous precursors (Lacinska et al., 2024). Depending on how these precursors evolve, different metal trapping mechanisms are possible. Simultaneous measurement of stream water chemistry above and below these depositions show a reduction in soluble metals downstream together with reduced stream pH (Holdsworth et al., 2022). Additionally, microorganisms living on the tufa's surface may contribute to tufa growth, structure and how metals are deposited.

Engineered calcite precipitation designed to trap metals was successfully demonstrated in a recent doctoral thesis, co-supervised by Cumberland (Kalabová, 2024). The study showed that a significant reduction of selected soluble metal salts could be achieved e.g., (Zn(94-96%), Cu(43-60%), Ni(25-70%)) under batch and column experiments. This work also identified several Scottish field sites where metal and calcium co-precipitate.

In this PhD project, you will investigate the biogeochemical processes that drive calcite and metal co-precipitation in the field with complimentary experiments. By characterizing hyperalkaline leachate and examining factors like particle size and metal species, your research will strengthen our understanding of how to optimize tufa for metal capture. The outcomes are expected to enhance efficiency of engineered tufa as a sustainable metal-capturing tool, providing benefits for industry, landowners and regulators.

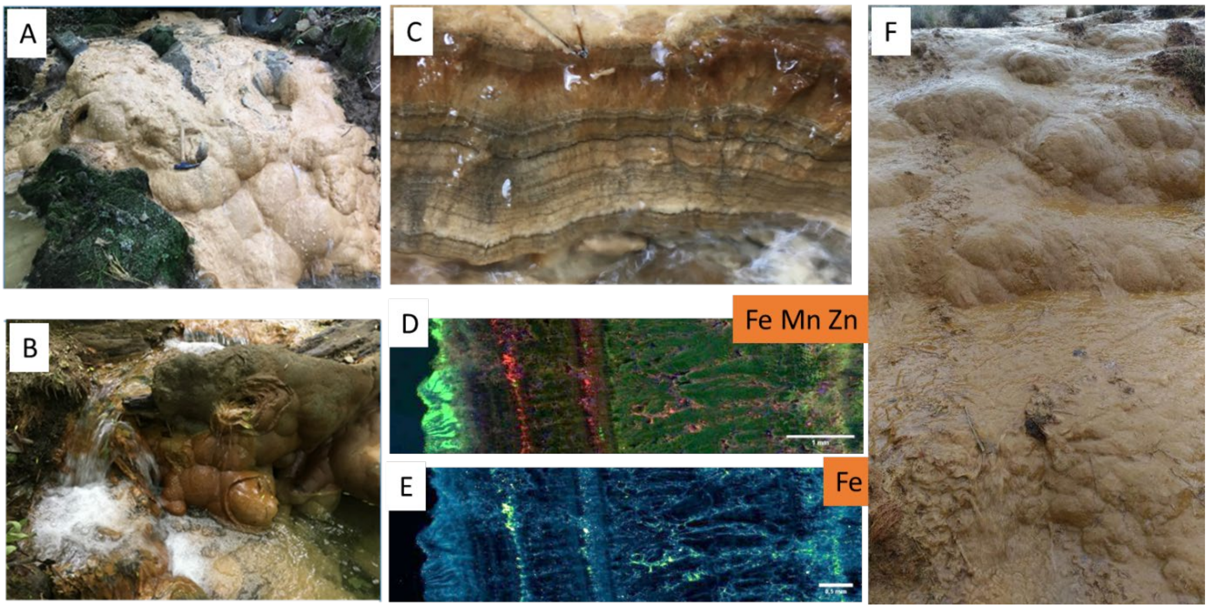


*Figure 1: (A-C) Anthropogenic tufa at the Howden Burn, Consett, UK. (D & E) False colour synchrotron X-ray images of metal distribution between calcite growths within Howden Burn Tufa: (F) Iron-rich tufa forming on site at Neilston, Glasgow, Scotland.*

**Methodology:**

- It is envisaged that the study will be field-based complimented with laboratory experiments. Initially, fieldwork will involve characterising solid and water samples collected from well-known natural and anthropogenic tufa such as at Consett. Seeking and investigating new tufa sites will be essential in broadening our understanding of processes of metal capturing tufa.
- Characterisation of water samples will involve using field monitoring equipment and lab-based ICP-MS. Characterisation of solid material will use state-of-the-art-analytical equipment available at the University of Leicester, BGS (XRF, TEM, SEM/SEM-FIB, XRD, X-CT) and national facilities such as the Diamond Light Source-synchrotron, Oxford, to investigate particle size, metal type and distribution. Additional techniques for particle sizing and separation using filtration, particle size analysers and electron microscopy will be implemented.
- Batch experiments including with metals at alkaline pH will be conducted following the field characterisation. Equilibria modelling using PhreeqC or Geochemist's workbench (GWB) would enhance field and experimental data.

**Possible Timeline**

**Year 1:** In year one the student will engage with background literature searches setting project objectives and preliminary field work. Analytical training at Leicester and BGS will occur using the student's own samples collected in the field. Characterisation techniques and learning of specialised computer software. Starting trial laboratory experiments precipitating tufa.

**Year 2:** During the second year it is expected that field sites are identified, and fieldwork routines established. Experimental objectives will have been determined and complementary laboratory experiments on precipitating tufa with metals will be in full flow. Data characterisation and interpretation. Possible opportunities for conference participation.

**Year 3:** Characterisation and data interpretation will likely dominate with additional fine tuning of laboratory experiments and field visits for additional limited data collection. Manuscript drafts for publication and thesis chapter drafts underway. Thesis writing and submission.

**Training and skills:**

TARGET researchers will participate in a minimum of 40 days training over the 3.5 years of study composed of:

- an annual one-week workshop dedicated to their year group, and tailored to that cohort's needs in terms of skills development – *for the first three years of their study*;
- an annual all-TARGET workshop with cross-year interactions, advanced training and opportunities to specialise in particular areas – *all years of study*;
- a number of one-day workshops;
- additional online events and in-person workshops attached to relevant conferences.

Training specific to this proposal:

- BGS will provide training to the researcher in the use of SEMs and microanalytical attachments, as well as in approaches to petrographic analysis. There will also be training in sample preparation. Training is anticipated to be 'front-loaded' with the bulk of the training in years 1-2. Total of 8 days, 4, 3 and 1 day(s) over years 1,2 and 3 respectively.
- Leicester will supply training through the doctoral college, which is ongoing through the program.
- Specific skills in TEM, X-CT, FIB-SEM (Leicester's HERCULES facility), field sampling, analysis of water sediments and hard material. Computer-based skills in analytical and characterisation software.

**Partners and collaboration (including CASE):**

The successful student will be located at the University of Leicester, and ideally work between Leicester and BGS, Keyworth, according to research and analytical needs. BGS Keyworth, is a short train/bus ride from Leicester Station via Nottingham. Regular contact between the student and supervisors, Dr. Cumberland (UoL) and Dr. Rushton (BGS) will take place as formal and informal supervisory meetings, with formal meeting held **fortnightly, then monthly** as the project progresses either in person or via video link.

**Further reading:**

Bastianini, L., Rogerson, M., Mercedes-Martín, R., Prior, T. J., Cesar, E. A., and Mayes, W. M., 2019, What Causes Carbonates to Form "Shrubby" Morphologies? An Anthropocene Limestone Case Study: Frontiers in Earth Science, v. 7, no. 236.

Cumberland, S., Tierney, K., Renshaw, J., Geraki, K., and MacDonald, J., Analysis of metal entrapment within anthropogenic tufa using synchrotron micro-XRF, *in* Proceedings EGU General Assembly 2022, Vienna, Austria, 23–27 May 2022 2022, Volume EGU22-4044, Copernicus Meetings.

Holdsworth, C., MacDonald, J., and John, C., 2022, Non-Linear Clumped Isotopes from DIC Endmember Mixing and Kinetic Isotope Fractionation in High pH Anthropogenic Tufa: Minerals, v. 12, no. 12, p. 1611.

Kalabová, M., 2024, Water to Rock? Tufa formation for capture of contaminants in industrial waste leachate [PhD: University of Strathclyde, 381 p.

Lacinska, A. M., Bateman, K., Chenery, S., Kemp, S. J., Liddy, T., Rushton, J. C., Saha, D., and Schroeder, S. L. M., 2024, Immobilisation of chromium in magnesium carbonate minerals: Mineralogical Magazine, v. 88, no. 2, p. 162-169.

Riley, A. L., MacDonald, J. M., Burke, I. T., Renforth, P., Jarvis, A. P., Hudson-Edwards, K. A., McKie, J., and Mayes, W. M., 2020, Legacy iron and steel wastes in the UK: Extent, resource potential, and management futures: Journal of Geochemical Exploration, v. 219.

**Further details:**

Please visit https://target.le.ac.uk/ for additional details on how to apply.

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for additional information.