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CL:AIRE research bulletins describe specific, practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes the main outputs from the Resource Recovery and Remediation of Alkaline Wastes (R^{3}AW) project.

Resource Recovery and Remediation of Alkaline Wastes (R^{3}AW)

1. INTRODUCTION

Resource Recovery and Remediation of Alkaline Wastes (R^{3}AW) was a five-year research project (2014-2019), funded by the Natural Environment Research Council, Economic and Social Research Council and Department for Environment, Food and Rural Affairs. It was also approved as CL:AIRE Research Project 26.

The R^{3}AW project brought together an interdisciplinary academic team (from the universities of Hull, Leeds, Cardiff, Newcastle, Huddersfield and the Open University) and industrial partners to develop initiatives combining resource recovery from caustic industrial wastes with environmental remediation and waste stabilisation.

Over two billion tonnes of alkaline residues are produced each year from a range of globally-significant production and disposal processes (Gomes *et al.*, 2016). These include slags and residues from steel and alumina production as well as ashes from waste incineration. Such by-products are increasing in volume on a global basis and can pose environmental risks, such as water pollution from highly alkaline leachates containing toxic metals and metalloids (e.g. arsenic, chromium and vanadium), dust generation at disposal sites, and challenges for rehabilitating waste depositories into productive land given the extreme initial chemical conditions (Gomes *et al.*, 2016).

At the same time, alkaline residues can be enriched in a range of elements and minerals critical to future green technologies, for example vanadium, lithium and cobalt, which are increasingly used in mobile and static energy storage batteries (Gomes *et al.*, 2016). Recovery of elements like vanadium, which are environmental pollutants, could also make the residue safer for bulk reuse e.g. as aggregate. Furthermore, alkaline residues which are typically the product of high temperature processes, are enriched in silicate and oxide minerals that can take in atmospheric carbon dioxide (CO_2) when they are weathered (Mayes *et al.*, 2018). As such, there is a range of potential economic, environmental and social benefits that could be reaped from these major global waste streams.

Therefore, in the context of this research, resource recovery covered various facets (see Fig. 1), including:

- recovery of e-tech metals that are both crucial for modern environmental technologies and simultaneously environmental pollutants (e.g. vanadium);
- enhancing carbon sequestration in alkaline wastes;
- promoting the broader re-use of bulk by-products without environmental impacts; and
- improving remediation strategies at alkaline residue disposal sites.

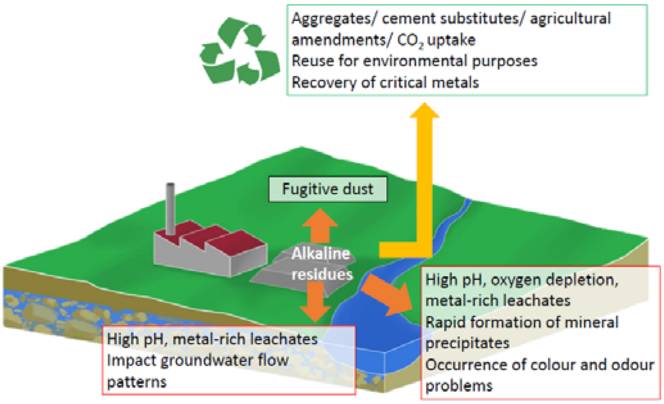

Figure 1: Alkaline residues - environmental risks and resource recovery opportunities. Green box highlights opportunities for valorisation of by-products; red boxes highlight potential environmental impacts under current management.

As well as the technical aspects of the project, the research has included the critical assessment of regulatory and governance frameworks that influence current alkaline residue management through stakeholder discussions and workshops.

This bulletin summarises the main aspects of the research and directs the reader to relevant journal publications for a more in-depth discussion, listed in the references section and also on the project website (https://alkalineremediation.wordpress.com).

2. VANADIUM – POLLUTANT OR RESOURCE?

Vanadium is present in high volume industrial alkaline wastes such as steel slag and bauxite processing residue (red mud) from alumina generation (Gomes *et al.*, 2016). Researchers within the R^{3}AW project have shown that vanadium can be leached from these residues in disposal areas and is most commonly in its most toxic (pentavalent) form downstream of slag and red mud disposal sites (Burke *et al.*, 2012; Hobson *et al.*, 2017). Given vanadium is often overlooked in regulatory monitoring (e.g. Mayes *et al.*, 2016), monitoring and understanding vanadium release processes is crucial

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to assessing environmental risks at disposal sites and the potential for vanadium recovery. Mineralogical analyses have identified key vanadium-bearing phases and shown that secondary mineral phases (carbonates and calcium silicate hydrate phases) that form under anaerobic conditions on the surface of the slag (rinds) can minimise vanadium mobility (Hobson *et al.*, 2017). Slag weathering should therefore take place under anaerobic conditions to encourage rind formation and minimise environmental risks for bulk after-use (e.g. in road construction applications).

However, vanadium is also increasingly vital for green technologies and was added to the European Union Critical Raw Material list in 2017. Vanadium has traditionally been used in high-strength steel alloys but emerging uses in redox flow batteries – for large scale renewable energy storage – are leading to rapid increases in global demand (Watt *et al.*, 2018). As such, opportunities for recovering vanadium from by-products could play an important role in both meeting this increased demand and managing potentially impactful environmental releases.

Ion exchange resins have been used to successfully recover vanadium and other oxyanions from alkaline steel slag and bauxite processing residue leachates. Removal and recovery are very effective (>95% and >65% respectively) and the research demonstrated for the first time the possibility of vanadium recovery from highly alkaline waters (Gomes *et al.*, 2016b, 2017b). While this shows promise in terms of environmental protection, the data suggest it is unlikely such a recovery mechanism would be viable for vanadium recovery on economic grounds alone currently.

However, materials like steel slag would be safer for bulk after-uses (e.g. as aggregate) after this vanadium is leached. Where opportunities for resource recovery can offset environmental remediation costs, there may be compelling combined economic and environmental cases for intervention.

3. BAUXITE RESIDUE REHABILITATION

During alumina production from bauxite ore, 1 to 2 tonnes of residue are produced for every tonne of product. Despite bauxite residue containing potentially valuable metals it currently has no commercially viable bulk reuses and is commonly stored in large purpose-built bauxite residue disposal areas (Mayes *et al.*, 2016).

Waters interacting with untreated bauxite residue can have pH values up to 13, have elevated concentrations of sodium, and contain potentially harmful elements such as aluminium, arsenic and vanadium (Mayes *et al.*, 2016). Establishment of protective vegetation cover at bauxite residue disposal areas is therefore often resource intensive and involves importing large volumes of topsoil. Adding smaller volumes of organic matter, such as spent compost, and gypsum directly to the residue has been proposed as a much cheaper method to achieve revegetation (Courtney and Harrington, 2012). However, doubts remained about the long-term efficacy of this approach.

Data from organic matter amended bauxite residue plots deposited 20 years ago showed that the surface treatments lower alkalinity and salinity, and thus produce a substrate more suitable for seedlings (Bray *et al.*, 2018). The reduction of pH leads to much lower aluminium, vanadium and arsenic mobility in the treated residue, with beneficial effects extending passively 20-30 cm below the original amendment (Fig. 2).

Figure 2: Rehabilitated red mud landfill.

The research has shown that the positive rehabilitation effects are still maintained after two decades due to the establishment of an active and resilient biological community. This treatment was estimated to provide cost savings of over £2M to site closure plans at just one bauxite residue disposal area, with additional environment benefits in terms of reduced transport emissions and alternative uses for organic wastes (Bray *et al.*, 2018).

4. SEQUESTRATING ATMOSPHERIC CO_2 IN SLAG

During the process of steel-making, iron ore is mixed with limestone or dolomite and heated to extremely high temperatures. The end results are steel and slag, a waste mixture of calcium and magnesium silicates and oxides. Around 500 million tonnes of slag are produced globally each year.

As the slag minerals weather, when in contact with rainwater, the resulting alkaline solutions react with atmospheric CO_2 and form calcium carbonate – one of the most stable forms of carbon (Fig. 3). This reaction offsets some of the greenhouse gas emissions associated with steel production.

Figure 3: Calcium carbonate deposits downstream of the former Consett Steelworks – the end product of slag leaching and atmospheric CO_2 uptake (water pH >11.0).

The R^3AW project investigated the carbon balance of some of the largest slag heaps in the UK at the former Consett Steelworks. Researchers measured the volume of the slag mounds by geophysical mapping and compared this with four decades of water chemistry data to calculate how much calcium carbonate has precipitated. The results showed that less than 1% of the potential atmospheric carbon uptake has been realised in the mounds, nearly four decades after the steelworks closed (Mayes *et al.*, 2018).

This implies that uncontrolled deposition of slag in mounds or waste depositories does not efficiently promote carbon sequestration – a major potential value of these industrial by-products. Ongoing research in a related project is investigating how we can engineer both new and historical slag deposits to encourage atmospheric carbon uptake (Pulin *et al.*, 2019).

5. IMPROVED MANAGEMENT OF ALKALINE WATERS

Highly alkaline waters from residues like steel slag require effective management so that discharge waters meet environmental targets (usually pH<9). For short-lived discharges (e.g. during groundworks) this can be readily addressed with mobile CO_2 dosing units (e.g. Hall, 2008) or traditionally via acid dosing. However, in some disposal settings, high pH can persist for decades (Riley and Mayes, 2015) which is not conducive to ongoing reagent or energy input. In such situations, passive approaches similar to those adopted for mine waters (e.g. CL:AIRE, 2005; CL:AIRE, 2006) may be more suitable. During this project, extensive laboratory flume experiments (Figure 4) on the management of highly alkaline waters demonstrated the physical structures and biological communities that can promote lowering of pH in alkaline waters towards regulatory limits (Gomes *et al.*, 2016b). These principles were then scaled up using field trials at an active steel slag repository. This field pilot test at Scunthorpe demonstrated the effectiveness of reedbeds in buffering waters (Figure 5; Gomes *et al.*, 2018a). Crucially there is no evidence that exposing aquatic plants to extremely alkaline pH increases risk of uptake of potentially ecotoxic elements such as chromium and vanadium in field conditions (Gomes *et al.*, 2018b). Such approaches to managing highly alkaline waters may be particularly suited to deploy during site decommissioning and longer term restoration of post-industrial settings.

6. BUILDING A CIRCULAR ECONOMY IN THE EUROPEAN CONTEXT

R^3AW researchers considered how the project outcomes could be applied in practice and noted the complexity created by evolving layers of regulation. While the EU circular economy strategy only dates from 2015, the strategy is building on policies that have been evolving since the 1975 Waste Framework Directive. These policies cover a wide range of activities related to the production process, management of residues, incentivising the use of secondary materials and disincentivising disposal.

The potential for regulations to have counter-productive effects has been recognised by the EU. Over the past decade, there have been efforts to reduce barriers to recovery that have inadvertently been instituted by earlier efforts to ensure that residues were disposed of without harm to the environment. The 2008 and 2018 Waste Framework Directives therefore discuss how to define terms such as end of waste and by-products. However, the definitions are not straightforward. They include safeguards against the generation of inadvertent environmental impacts and also require an actual, not just potential, market for the recovered material. The status of a given substance is therefore strongly context dependent.

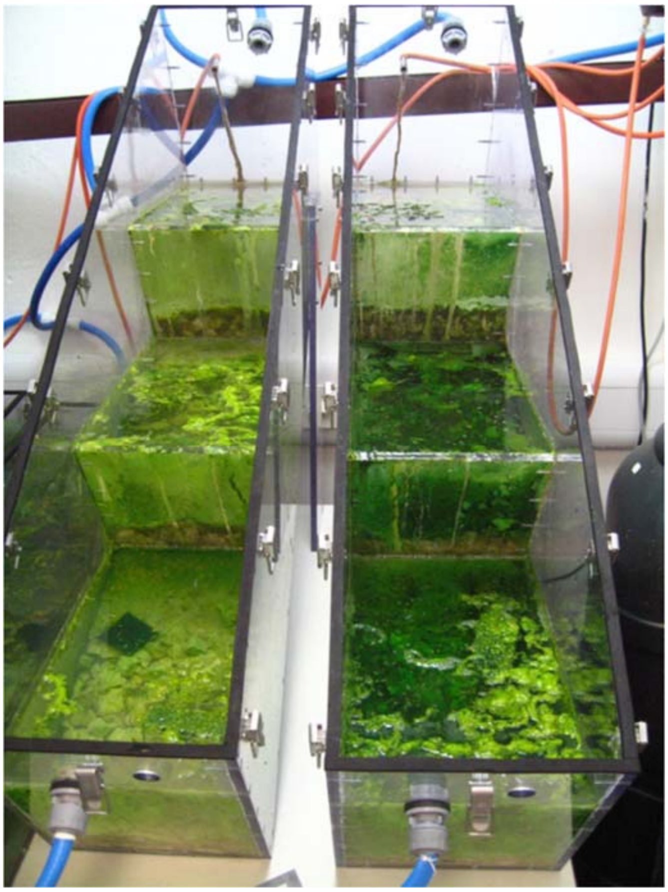

Figure 4: Laboratory flume experiments using cascade structures and biofilm (sourced from local steelwork sites) to buffer the pH 12 steel slag influent.

Figure 5: Pilot reedbed dominated by Common Reed (*Phragmites australis*) treating alkaline (up to pH 12) leachate at Scunthorpe

In addition to the policy-based work, the project team conducted over 20 in-depth interviews with key producers in the steel slag production, management and after-use chain, and ran a workshop at the former Redcar Steelworks on opportunities for resource recovery with participation from industry, regulators, academia and local communities. This work highlighted key challenges that need to be overcome for new resource recovery technologies for steel by-products, particularly due to inflexibility in regulation driven primarily by environmental protection, as well as complex liability issues with long-standing downstream user agreements and changing ownership of sites.

Recommendations based on the R^{3}AW research are already informing operational environmental management of leachates and rehabilitation strategies at bauxite residue disposal areas with project partners.

7. WIDER RRfW RESEARCH

The R^{3}AW project is part of the wider Resource Recovery from Waste (RRfW) theme funded by NERC, ESRC and DEFRA. RRfW is a collaborative research programme engaging academia, industry, government and the general public to develop knowledge and tools to reduce pressure on natural resources and create value from wastes. It was set up to deliver the environmental science needed to support a radical change in the waste management landscape. With six projects at leading UK universities, the programme is building tools to model the multiple dimensions of value whilst also developing enabling biogeochemical technologies for new supply chains. Further details of projects can be found at www.rrfw.org.uk.

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