Re-Mining of Mine Water Sludges in Germany: An Opportunity?

Bastian Reker[1], Sebastian Westermann[1]

[1]*Technische Hochschule Georg Agricola, Research Center of Post-Mining, Herner Straße 45, 44787 Bochum, Germany, Bastian.Reker@thga.de*

Abstract

Many natural resources are critical for the economy and the technologies of our daily lives. The utilization of deposits or resources that were until recently considered waste materials may contribute to a secure and sustainable supply of these resources. Against this background, the RAG-Stiftung has funded the IAW3³ project at THGA Bochum to conduct an initial screening and evaluation of whether mine water and its sludges from the former hard coal mining areas in the Ruhr region, the Saarland, and Ibbenbüren (NRW) offer an opportunity to extract metals classified as critical.

Keywords: Critical elements, natural resources, hard coal mining, Ruhr area, Saar area, Ibbenbueren

Introduction

Rising prices due to the depletion of natural resources, continuously increasing demand, and strong dependence on third-party countries led the European Commission in 2011 to publish a list of critical elements, most of which are metals. This list is updated every two years and, as of 2023, comprises 34 elements (EC 2023), predominantly (transition) metals, including Rare Earth Elements (REE). Other parts of the world are also aware of the strong dependence on critical metals from third-party countries, which has led to several investigations – e.g., in the USA (Cravotta III 2007, Ziemkiewicz *et al*. 2016, Stewart *et al*. 2017), Portugal (Prudêncio *et al*. 2015), and South Africa (Dube *et al*. 2020) – to determine whether mine water sludges in old tailing ponds provide sufficient enrichment factors for some of these metals, particularly REEs. This concept was adopted for the former hard coal mining regions in Germany (Ruhr and Saar areas, Ibbenbüren), where the last two active collieries were closed at the end of 2018. In 2022, the project "IAW33" was launched at the Research Center of Post-Mining at THGA Bochum, funded by the RAG-Stiftung for three years. This project systematically screens and evaluates, for the first time, whether critical metals show similar enrichment tendencies in mine water sludges and deposits in old tailing ponds in the former hard coal mining regions of Ruhr, Saarland (ongoing investigation), and Ibbenbüren (NRW).

Methods

For the collection and sampling of mine water sludges, two types of precipitation reactors were constructed to facilitate the oxygenation of mine waters and the precipitation of dissolved iron species within a defined volume. The first reactor was designed for low-mineralized mine waters (i.e., iron concentrations < 5 mg/L, no dissolved NaCl). It consists of two commercial 600 L IBC containers connected to each other and equipped with a solar-powered pump for aeration. This design enables operation in remote areas without access to a stationary power supply. A key advantage of this setup is its relatively large volume of 1,000 L, which allows for larger-scale experiments. This reactor was used for the mine waters from the former mining sites "Friedlicher Nachbar" and "Robert Müser" in Bochum, as well as "Heinrich" in Essen (all located in the Ruhr area). The second type of reactor was designed to prevent iron ochre deposition in the pumps of the first reactor when handling highly mineralized mine waters (i.e., Fe concentrations > 5 mg/L, presence of dissolved NaCl). These reactors consist of a single 600 L IBC container, where aeration is facilitated by an external oxygen compressor (HighBlow® HP-80) with six outlets installed inside the container (Fig. 1). This reactor type has been used for the mine waters from the former mining sites "Walsum" in Duisburg (Ruhr area), "Duhamel" in Saarland (still in operation), and Ibbenbüren (NRW). Additionally, several sludge samples were collected and analyzed from two tailing ponds at the "Friedlicher Nachbar" site and in Ibbenbüren.

The collected sludge samples were dried overnight at 100 °C and analyzed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) at the German Mining Museum in Bochum (Deutsches Bergbau-Museum, DBM). For analysis, the dried and pulverized sludge was dissolved in aqua regia and examined for 55 elements, including alkaline and alkaline earth metals, transition metals (including REEs), metals, and semimetals. To enhance readability and interpretation, the results (originally in weight percent) were converted to grams of the respective metal per ton of dried sludge. It is important to note that the total metal concentration only accounts for the analyzed elements and does not include certain semimetals (e.g., B, Si, As) or some alkaline and alkaline earth metals (e.g., Na, K, Ca). Moreover, selected samples were analyzed using X-ray Diffraction (XRD) to identify impurities and by-products. Experiments for the actual extraction of metals from the sludge were conducted in cooperation with the Max Planck Institute for Sustainable Materials in Düsseldorf, using an innovative technology approach (Jovičević-Klug *et al*. 2024). In this process, the dried and pulverized sludge is pressed into a 10 g pellet and heated in an arc furnace (Edmund Bühler GmbH, type Arc-Melting AM200) under a reducing atmosphere (90% Ar, 10% H_2) at approximately 3.6 kW (18 V, 200 A).

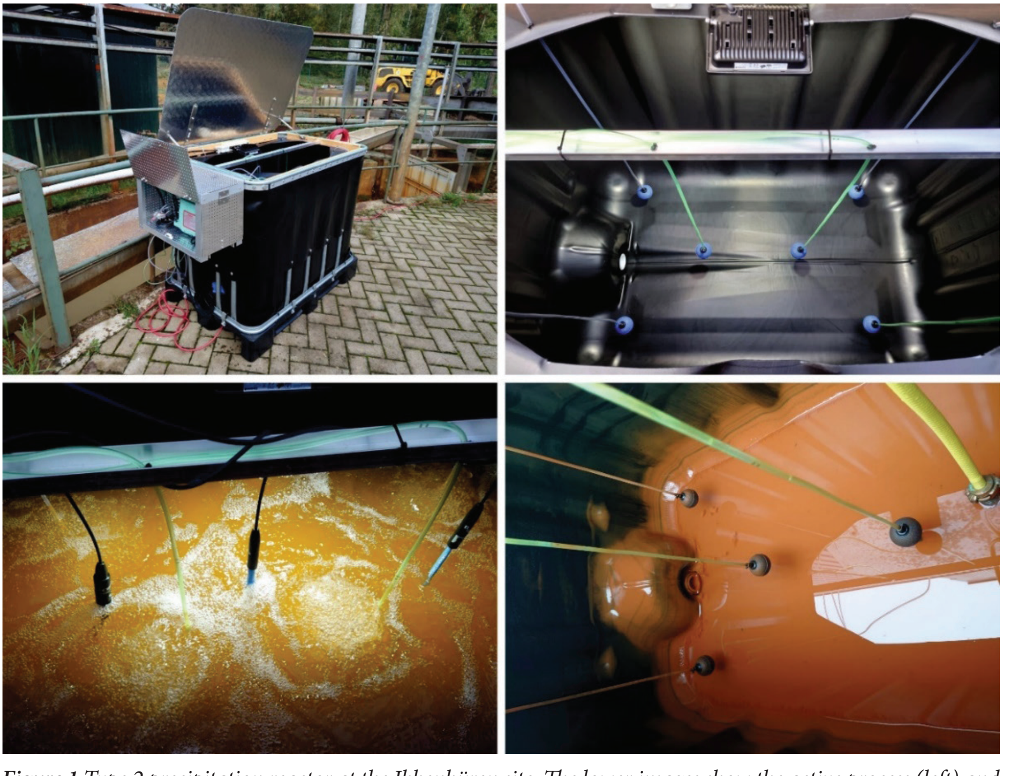

Figure 1 *Type 2 precipitation reactor at the Ibbenbüren site. The lower images show the active process (left) and the sampling procedure (right).*

The resulting products will be analyzed by ICP-MS at the DBM, following the same procedure as for the original sludge samples

Results Ruhr area

In the Ruhr region, four mine water pumping stations were evaluated: "Friedlicher Nachbar" (FN) (including its tailing pond, FN-TP) and "Robert Müser" (RM) within the city of Bochum, "Heinrich" (HR) in Essen, and "Walsum" (WS) in Duisburg (located in the western part of the Ruhr area). As expected, each site exhibits distinct characteristics, leading to varying results. While the sludges from FN, RM, and HR show relatively low total metal concentrations ranging between 2% and 5%, FN-TP and WS demonstrate significantly higher concentrations of 68% and nearly 74%, respectively (Table 1).

The high total metal concentrations observed in FN-TP and WS are primarily due to the iron and manganese fractions, which account for 99.0% and 98.6%, respectively. In contrast, the other samples (FN, RM, and HR) exhibit high levels of impurities, including lime, gypsum, and anhydrite, which significantly reduce their total metal concentrations. This is further supported by the relatively high proportions of alkaline and alkaline earth metals in these samples compared to FN-TP and WS. Additionally, all samples from the Ruhr area lack valuable and critical transition metals, rare earth elements (REEs), and semi-metals (e.g., cobalt, nickel, titanium).

Results Ibbenbueren

The analysis results of sludge samples from the former Ibbenbüren mining area, collected from both the precipitation reactor and the tailing ponds, indicate potential for secondary raw material production. The total metal concentration in the tailing pond (Table 1) reaches nearly 50%, with significant portions of transition metals (including approximately 15,273 g/t Mn, 383 g/t Ti, 323 g/t Co, and 472 g/t Ni), (semi-)metals (12,044 g/t Al), and rare earth elements (about 100 g/t). Conversely, the sample from the precipitation reactor also exhibits a high total metal concentration of about 63% (Table 1); however, it lacks critical and valuable metals. This can be attributed to a pH drop during the experiment from 6.7 to 3.1, caused by the hydrolysis of dissolved iron (initial concentration: 150–200 mg/L in the mine water), which led to the release of protons. As a result, most other metals remained in solution. To address this, a second experiment was conducted using a staggered precipitation approach to account for the varying solubilities of different metal species at different pH levels (Wolkersdorfer 2021). After each pH adjustment (using lime milk at pH 3, pH 5, pH 7, pH 9, and pH 11), the water was transferred to a second reactor, and the corresponding sludge was sampled and analyzed (Table 2):

- The pH 3 sequence produced results similar to those observed for IB in Table 1, as expected.

__Table 1__ The table below presents the summarized analysis results for the mining sites: "Friedlicher Nachbar Tailing Pond" (FN-TP), "Friedlicher Nachbar" (FN), "Robert Müser" (RM), "Heinrich" (HR), and "Walsum" (WS) (all located in the Ruhr area), as well as "Ibbenbüren Tailing Pond" (IB-TP) and "Ibbenbüren" (IB). All data are given in grams of metal per ton of dried sludge (g/t). The total metal concentration (expressed as a percentage) is calculated as the sum of the individual metal concentrations divided by 10,000.

g/t	FN-TP	FN	RM	HR	WS	IB-TP	IB
Alkaline (earth) metals	5,276	10,363	18,766	14,000	5,159	11,821	493
Transition metals (excl. Fe)	30,962	1,803	1,979	2,648	4,710	17,726	210
(Semi-)metals	387	121	101	195	4,349	12,075	1,485
Rare Earth Elements	8	1	1	1	1	100	5
Iron	644,600	21,300	2,106	31,182	722,000	441,574	627,926
Sum	681,234	33,588	22,953	48,025	736,218	483,296	630,120

Table 2 Summarized analysis results for the staggered precipitation experiment at Ibbenbueren. All data in grams of metal per ton of dried sludge (g/t). The total metal concentration in percent equals the sum divided by the factor 10,000.

g/t	IB pH3	IB pH5	IB pH7	IB pH9	IB pH11
Alkaline (earth) metals	1,084	1,495	9,047	16,626	20,068
Transition metals (excl. Fe)	316	719	23,882	31,964	2,665
(Semi-)metals	2,203	5,980	43,822	9,740	8,102
Rare Earth Elements	9	28	840	53	34
Iron	609,153	799,028	277,284	7,935	5,313
Sum	612,764	807,250	354,875	66,265	36,148

- At pH 5, the highest total metal concentration of nearly 81% was recorded, mainly due to the high iron content. Additionally, metals, semi-metals, and REEs showed slight enrichment (Table 2, Fig. 2).
- At pH 7, the total metal concentration dropped significantly, as most of the iron had already precipitated at lower pH levels. However, the concentration of transition metals increased by a factor of 33 (including titanium and cobalt, Fig. 2). Moreover, the levels of (semi-)metals (mostly aluminum) and rare earth elements peaked (Table 2, Fig. 2), making this near-neutral pH – or slightly above – the optimal condition for potential metal recovery from mine water.
- As the pH increased further, the concentration of transition metals rose again, primarily due to the highest manganese precipitation at this stage. Additionally, the increasing levels of alkaline and alkaline earth metals were largely a result of reactions between dissolved magnesium and the added lime milk used for pH adjustment.

Taking these results into account, the large tailing ponds in close proximity to the mine water treatment plant in Ibbenbüren present an opportunity for the future extraction of critical and valuable raw materials. With a total area of 236,000 m² (Fig. 3), these ponds contain a big volume of sludge, which has been deposited since the early 1980s. The sludge depth is between 2 m and 4 m, resulting in an overall deposit volume ranging

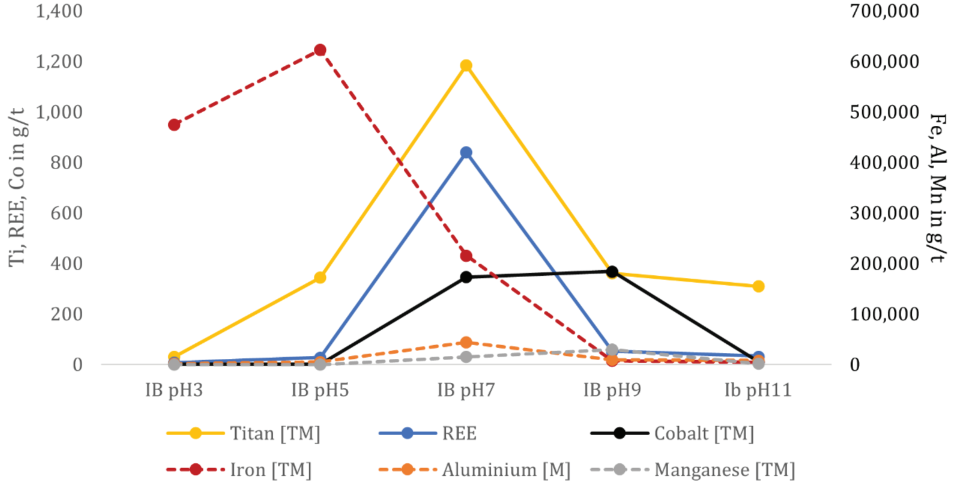

Figure 2 Concentration trends for selected (transition-)metals in the staggered precipitation process in Ibbenbueren. All data in grams of metal per ton of dried sludge (g/t). The dotted lines refer to the right y-axis (Fe, Al, Mn), the solid lines to the left y-axis (Ti, REE, Co). [TM] = Transition metal; [M] = Metal.

from 472,000 m^3 to 944,000 m^3. Based on this volume range, the analysis results, and taking into account the density and solid-to-water ratio of the sampled sludge (67.5% water, 32.5% solids), the expected recoverable amounts of pure metals can be estimated as follows: 88,000–176,000 t of Fe, 2,400–4,800 t of Al, 3,000–6,000 t of Mn, 90–180 t of Ni, 75–150 t of Ti, 65–130 t of Co and 20–40 t of Rare Earth Elements.

Considering that the tailing pond samples were collected only from the surface (for safety reasons) and that the western hard coal field of Ibbenbüren was flooded in the early 1980s, a clear first flush effect (Younger 1997) has been detectable for the past 40 years (Reker *et al.* 2022). As a result, the calculated tonnages likely represent a lower-end estimation

Metal extraction

In cooperation with the Max Planck Institute for Sustainable Materials in Düsseldorf, experiments were conducted using a novel CO_2-neutral approach for metal extraction from these sludges (Jovičević-Klug *et al.* 2024). As a result, two 10 g sludge pellets yielded a 4.7 g "nugget" of pure iron with a purity of over 98% (with minor impurities of Co and Ni), along with 4.3 g of slag (Fig. 4). Further experiments and analysis of the slag are currently ongoing.

Conclusion

This research project represents the first systematic screening and evaluation of mine water sludges in the former hard coal mining areas of the Ruhr, Saarland, and Ibbenbüren. The results indicate potential for the extraction of critical and valuable raw materials such as manganese, cobalt, nickel, titanium, and rare earth elements – particularly from old tailing ponds like those in Ibbenbüren. A new, sustainable, and climate-neutral extraction method utilizing electrical energy without emitting greenhouse gases was successfully tested. However, further work is required, particularly in upscaling the extraction process to optimize energy consumption (e.g., reducing thermal losses) and facilitate the treatment of larger material volumes. Overall, the re-mining of tailing ponds

Figure 3 *Tailing Ponds at the mine water treatment plant in Hoerstel (Ibbenbueren). The mine water treatment plant in Hörstel processes mine water from the "Dickenberger Stollen," which has been dewatering the western field of the hard coal deposit since the early 1980s. The samples presented in this study were collected from the western side of the pond, near the center, which covers an area of 53,288 m².*

not only provides a valuable opportunity to enhance the independence of critical raw materials from third-party countries in a climate-neutral way, but it also helps reduce land consumption for the deposition of new mine water sludges – which will continue to accumulate in the future – while simultaneously lowering the costs of mine water treatment.

Acknowledgement

The authors express their gratitude to the RAG-Stiftung for funding this research project over a period of three years and to RAG AG for their valuable collaboration and support. Furthermore, we sincerely thank Dr. Michael Bode from the Deutsches Bergbau-Museum (DBM) for conducting the ICP-MS analyses and the Max Planck Institute for Sustainable Materials for carrying out the metal extraction experiments.

References

Cravotta III CA (2007): Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations. Appl Geochem 23 (2008), p 166–202, doi:10.1016/j.apgeochem.2007.10.011

EC (European Commission) (2023): Critical raw materials. Online: https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en (11.03.2025)

Dube G, Vadapalli VRK, Malatji M, Mothupi T (2020): Recovery of Rare Earth Elements (REE) from Acid Mine Drainage (AMD) passive treatment systems – A review. Presentation on the SAIMM Conference (online) on 12.11.2020

Jovičević-Klug M, Souza Filho IR, Springer H, Adam C, Raabe D (2024): Green steel from red mud through climate-neutral hydrogen plasma reduction. Nature 625, p 703–717

Prudêncio MI, Valente T, Marques R, Sequeira Braga MA, Pamplona J (2015): Geochemistry of rare earth elements in a passive treatment system built for acid mine drainage remediation. Chemosphere 138 (2015), p 691–700

Reker B, Westermann S, Melchers C (2022): Grubenwässer als Ressource kritischer Rohstoffe in Deutschland. GeoResources 4/2022, p. 43–47

Stewart BW, Capo RC, Hedin BC, Hedin RS (2017): Rare earth element resources in coal mine drainage and treatment precipitates in the Appalachian Basin, USA. Int J Coal Geol 169 (2017), p 28–39, http://dx.doi.org/10.1016/j.coal.2016.11.002

Wolkersdorfer C (2021): Grubenwasserreinigung – Beschreibung und Bewertung von Verfahren. Heidelberg (Springer), https://doi.org/10.1007/978-3-662-61721-2

Younger PL (1997) The longevity of minewater pollution – a basis for decision-making. Sci Total Environ 194–195:457–466. https://doi.org/10.1016/S0048-9697(96)05383-1

Ziemkiewicz P, He T, Noble A, Liu X (2016): Recovery of Rare Earth Elements (REEs) from Coal Mine Drainage. Online: https://wvmdtaskforce.com/wp-content/uploads/2016/04/2016-etd30-pfz-a.pdf (11.03.2025)

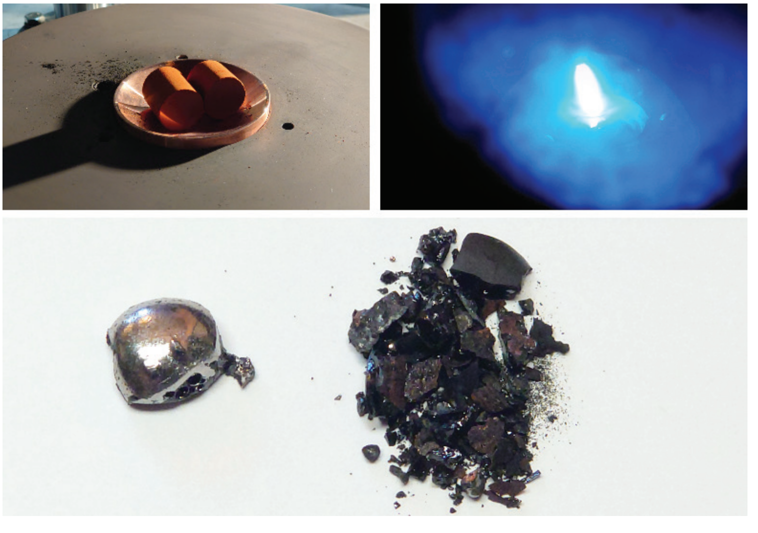

***Figure 4** Two pellets of sludge in the copper crucible of the arc furnace before the experiment conducted at the Max Planck Institute for Sustainable Materials (upper left); plasma-arc during the experiment (upper right) and the final products: pure iron nugget and slag (lower picture).*