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Fractionation of Metal(loid)s in Three European Mine Wastes by Sequential Extraction

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Abstract: Mine waste can constitute an environmental hazard, especially when poorly managed. Environmental assessment is essential for estimating potential threats and optimizing mine waste management. This study evaluated the potential environmental risk of sulfidic mine waste samples originating from the Neves Corvo Mine, Portugal, and the closed Freiberg mining district, Germany. Metal(loid)s in the waste samples were partitioned into seven operationally defined fractions using the Zeien and Brummer sequential extraction scheme. The results showed similar partitioning patterns for the elements in the waste rock and tailing samples from Neves Corvo Mine; most metal(loid)s showed lower mobility, as they were mainly residual-bound. On the contrary, the Freiberg tailing sample had considerably elevated (24–37%) mobile fractions of Zn, Co, Cd, and Mn. The majority of Fe (83–96%) in all samples was retained in the residual fractions, while Ca was highly mobile. Overall, Pb was the most mobile toxic element in the three samples. A large portion of Pb (32–57%) was predominantly found in the most mobilizable fractions of the studied waste samples. This study revealed that the three mine wastes have contamination potential for Pb and Zn, which can be easily released into the environment from these waste sources.

Keywords: sulfidic mine waste; metal(loid) fractionation; metal(loid) mobility; sequential extraction; environmental risk; contamination

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1. Introduction

The processing and extraction of mineral resources such as ores give rise to mine waste, one of the major waste streams in the EU. Compared to all other waste generated due to human activities, mining activities produce the highest volume of waste and have the most harmful effects on the environment [1]. Examples of mine waste include tailings, waste rock, and topsoil overburden. The rock that is excavated to access the ore is called waste rock and is often deposited as heaps or piles. Tailings consist of fine-grained waste generated during mineral processing (beneficiation) of mined ore and after the extraction of valuable minerals, usually containing elevated amounts of metals and residual processing chemicals. They are typically stored in tailings storage facilities (TSF) or ponds, which are usually surrounded by dams [2]. Mine waste poses a major risk to the environment due to the significant levels of metal(loid)s present in them and the likely tendency of sulfidic mine waste to form acid mine drainage [3]. Metal(loid)s released into the environment from mine waste can contaminate surface water, groundwater, soil, and plants, and may be incorporated into the food chain as well [4]. The assessment of environmental risks associated with mine waste could provide valuable information in order to better manage mine waste dumps and possibly reduce their impact on the environment and human health. The 2006/21/EC European Directives on the management of extractive waste stipulate that operators of extractive industries must carry out waste characterization covering different categories such as the geochemical characteristics and behaviour of waste. This provides information that will enable the management of mine waste under environmentally safe conditions in the long term [2].

The total concentration of an element is not very useful in specifying the mobility and toxicity of the element in the environment. On the other hand, an element's mobility and toxicity are related to its speciation and distribution in the solid phases of a given sample [5]. Sequential chemical extraction (SCE) is a valuable procedure used to estimate the mobility of elements under different conditions or environments. It helps determine the distribution of elements between geochemical fractions in environmental samples, thereby serving as a useful tool for assessing the environmental impact of an element. Though sometimes used to speculate the speciation of elements, available SCE methods cannot directly determine the exact speciation of an element [6]. The different extractants used in sequential extraction provide operationally defined information on the possible response of element fractions to conditions likely to occur in nature, such as changes in pH and redox potential [7]. Different sequential extraction methods have been developed over the years. The most widely used are Tessier's method [8], Kersten and Forstner's method [9], and the European BCR (Community Bureau of Reference) method [10,11]. Many of these methods have been developed based on the assumption that ions accompanying the environmental sample will be displaced from their adsorption sites by an excess of competing ions in the extracting agent [12]. Operationally defined fractionation of elements in various environmental samples has been conducted using sequential leaching methods. Examples are river sediments [13–15], soils [16–18], coal ash [4,19,20], green liquor dregs [21], black shale [22], phosphogypsum [23], sewage sludges [24–26], and mine wastes [27–31].

In addition to predicting the contamination potential of waste samples and optimizing their remediation, sequential extraction can be a good indicator of the industrial recovery potential of elements in a sample. It may be valuable to perform different sequential extraction methods on a given sample in order to determine the distribution of elements across operationally defined fractions. However, the different extracting agents, sequences, and conditions used per method make it difficult to compare different methods directly [32]. For example, Anju and Banerjee [33] observed systematic variations in the metal contents of residual fractions obtained when comparing the BCR and Tessier's sequential extraction schemes for the fractionation of Cd, Zn, and Pb in mine tailings. This further reiterates that the fractionation achieved by sequential extraction is only operationally defined by the reagents used, and is not selective of specific mineral phases. The major strengths of sequential leaching are the information it provides about the binding strength of elements and their potential for mobilization arising from changes in the environment over time [12]. The limitations of sequential extraction include unfavorable sequences of extraction solvents, low selectivity of solvents for target phases, possible alteration of phases during extraction, incomplete extraction, and analyte re-adsorption/redistribution during extraction [32,34,35].

The Zeien and Brummer sequential extraction (ZBSE) method [34] involves the partitioning of elements into seven fractions operationally defined by the extractants. When theoretically compared to the BCR's three-step extraction method, it is believed that the ZBSE method breaks down the BCR's first extraction stage further into two fractions, namely, the mobile fraction (F1) and the easily-deliverable fraction (F2). F1 targets the exchangeable (weakly adsorbed) elements, as well as the easily-soluble organometallic complexes. F2 focuses on elements specifically adsorbed or surface-occluded, along with $CaCO_3$-bound forms of metals and organometallic complexes with low bond strength. The ZBSE method is thought to break down the BCR method's reducible fraction further into three fractions: the easily reducible fraction (F3), the moderately reducible fraction (F5), and the poorly reducible fraction (F6). Then, the ZBSE method includes the oxidizable fraction (F4), which is similar to the BCR method's oxidizable fraction. The last extraction step of the ZBSE method is the residual bound fraction (F7), which is the least mobile fraction. The mobility of elements in the fractions of the ZBSE scheme decrease in the following order: mobile > easily deliverable > easily reducible > oxidizable > moderately reducible > poorly reducible > residual bound [34].

This study is part of the European Training Network (ETN) for the remediation and reprocessing of sulfidic mining waste sites (SULTAN) project. The SULTAN project aims to alleviate environmental risks and economically recover valuable raw materials from selected active and closed European mine sites [36]. The present study focused on the Freiberg (Germany) and Neves Corvo (Portugal) mines, which are examples of a closed and an active mine, respectively.

This study aimed to determine the mobility or stability of metal(loid)s present in three European mine waste samples and to assess their contamination potential as regards their possible pollution of surrounding essential resources such as groundwater. This was carried out by partitioning the metal(loid)s (Cu, Pb, Zn, Co, As, Cd, Cr, Mn, Fe, Ca, and Al) into possible geochemical fractions using Zeien and Brummer's sequential extraction method [34] to determine the (1) mobile, (2) easily deliverable, (3) easily reducible, (4) oxidizable, (5) moderately reducible, (6) poorly reducible, and (7) residual-bound fractions of each element. The ZBSE method was chosen in this study because of its detailed fractionation pattern and its adequate applicability to the samples investigated. Previous experiments in our laboratory revealed that the Tessier method underestimated the metal mobility of similar mine waste samples in comparison to the ZBSE (unpublished data). In addition, Caraballo et al. reported underestimation of metal mobility for mine waste samples when using the BCR method [37]. The underestimation of metal mobility by these two methods (BCR and Tessier) is likely due to the elevated metal content of mine wastes. The two methods were originally developed for soils and sediments with low to moderate metal contents, and therefore need to be validated for samples with high metal contents such as mine wastes. Moreover, other extraction methods have been applied to mine waste samples; however, to the best of the authors' knowledge, there is no literature available for the estimation of geochemical fractions in mine waste using the Zeien and Brummer sequential extraction method.

2. Materials and Methods

2.1. The Mine Waste Samples

A tailing sample (FR_01) was obtained from the Davidschacht tailings dump (Figure 1) in the closed silver-rich Freiberg mining district of Germany. This mining district in Erzgebirge (meaning 'ore mountains') hosts three main types of polymetallic hydrothermal veins: quartz-bearing polymetallic sulfide, barite–fluorite–sulfide and carbonate-bearing polymetallic sulfide [38]. Mining activities in the Erzgebirge of the German Free State of Saxony began with the discovery of the first silver ores in 1168. Mining continued well into the 20th century, with both underground and open-pit mines operating up until the complete cessation of activities in 1969. The main product of the Freiberg mines was silver. However, base metals such as Pb and Zn were produced towards the end of the mining period, with Cu, Bi, As, Au, Cd, Tl, In, Ge, and pyrite as by-products [39,40]. Flotation tailings resulting from wet chemical ore processing were stored in the Davidschacht tailings dump from 1951 to 1964. The dump contains about 760,000 m^3 volume of flotation sludge covering an area of approximately 6.3 hectares [41]. The closure of mining activities in the Freiberg mining district and the discontinued use of the tailings dump led to the implementation of measures for recultivation and subsequent development of vegetation on the surface of the Davidschacht tailings for over forty years, with 88 plant species identified in a recent survey [42].

A fresh tailing sample (NC_02) and a fresh waste rock sample (NC_01) were obtained from the Cerro do Lobo tailings management facility (TMF) at Neves-Corvo mine, Portugal (Figure 2). Neves-Corvo is a currently-active underground high-grade Cu–(Sn)–Zn mine located in the Alentejo district of southern Portugal. The Neves Corvo volcanogenic massive sulfide (VMS) deposit is located at the western edge of the famous Iberian Pyrite Belt (IPB) [43,44]. Mining operations, currently conducted by SOMNICOR, Lundin mining's subsidiary in Portugal, started with surface drillings in 1977 and later progressed to underground exploitation of copper ore in 1988, tin ore in 1990 (depleted in 2005), and zinc ore in

2006 [45]. The mineralized zones consist of seven massive sulfide ore bodies (Neves, Corvo, Graça, Zambujal, Lombador, Monte Branco, and Semblana) [44] and the main products of the mine are copper, zinc, and lead concentrates [43]. Tailings and waste rock are the two major mine waste products from mining activities at Neves Corvo. In 2010, the mine shifted from sub-aqueous storage of tailings to sub-aerial deposition of thickened tailings in the TMF using waste rocks as containment berms. About 3.1 Mt of waste rock was stored in a temporary stockpile, while 7.3 Mt and 17 Mt of waste rock and tailings, respectively, were stored together at the Cerro do Lobo tailings management facility between 2010 and 2019 [46].

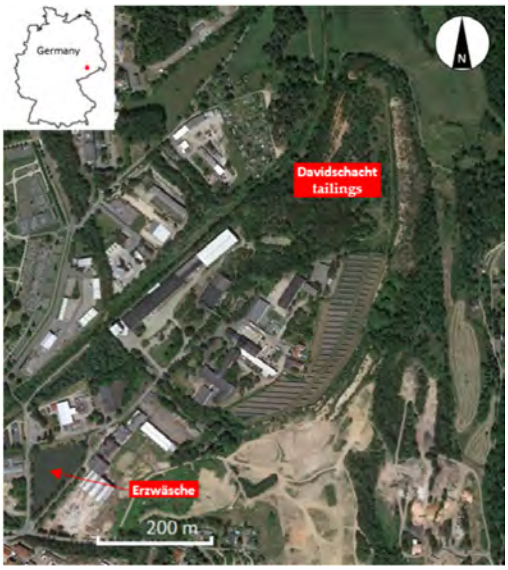


Figure 1. Map and satellite image of the Freiberg Davidschacht tailings dump, Germany (Coordinates: 50°55′14′′ N 13°22′23′′ E). The original satellite image was obtained from Google Earth.

Figure 2. Map and satellite image of the Neves Corvo mine, Portugal (Coordinates: 37°33′53′′ N 7°57′13′′ W). The original satellite image was obtained from Google Earth.

2.2. Sample Preparation and Characterization

The two tailing samples from the Freiberg and Neves Corvo mines were dried at 30 °C and ground with a mortar and pestle to obtain a particle size of less than 100 µm. The waste rock sample from the Neves Corvo mine was dried at 40 °C and crushed with a Retsch jaw crusher BB 200. The waste rock was further ground to less than 100 µm in a 100 mL

Tungsten carbide grinding set using the Retsch RS 200 vibratory disc mill. The samples were split into representative fractions ahead of the leaching experiments using a Fritsch rotary sample divider laborette 27. The metal(loid) compositions (Table 1) of the three samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (NexION 350x, 1300 Watts, Argon plasma gas, Perkin Elmer, Waltham, MA, USA) after acid digestion (65% HNO_3 + 30% HCl + ~48% HF, 1:3:1) in a microwave (Multiwave 3000, Anton Paar GmbH, Graz, Austria) at 240 °C and 800 W for 10 min. For acid digestion, HF was used in addition to aqua regia due to the ability of HF to break the strong Si–O bonds of silicate minerals [47].

Table 1. Total element concentrations of the three mine waste samples.

Metals (mg/kg)	FR_01	NC_01	NC_02
Cu	828.30	1840.00	3726.70
Pb	4420.00	826.30	3986.70
Zn	13,100.00	3560.00	10,666.70
Co	40.97	84.70	184.50
As	5590.00	766.70	4986.70
Cd	136.00	9.00	27.90
Cr	37.17	64.97	42.63
Mn	3393.30	724.30	735.00
Fe	165,666.70	122,333.30	283,000.00
Ca	11,776.82	5250.00	7106.70
Al	28,000.00	55,933.30	25,933.30

The respective mineral compositions of the three mine waste samples (Table 2) were determined by quantitative X-ray diffraction (QXRD) (PANalytical Empyrean, 35 kV and 35 mA, 5–80° scan range, Co anode material, PIXcel3D-Medipix3 1 × 1 Area detector, Malvern Panalytical Ltd., Malvern, United Kingdom). In preparation for the QXRD analysis, the samples were wet-milled in 10 mL ethanol using zirconium oxide grinding elements in a McCrone XRD-Mill (Retsch GmbH, Haan, Germany). After grinding, the samples were air-dried overnight in petri dishes. The dried samples were homogenized with steel balls (4 mm diameter) using a Retsch mixer mill MM 400. The samples were transferred into sample holders (24 mm diameter) using the backloading method and then measured. Mineral phase identification was carried out using Profex 4.1.0 software with Rietveld refinement by Döbelin and Kleeberg [48].

Table 2. Mineralogy of the three mine waste samples.

Mineral Groups (wt%)	FR_01	NC_01	NC_02
Quartz	42	45	23
Other silicates	17	39	18
Carbonates	5	3	2
Pyrite	22	12	53
Other sulfides	8	<1	<1
Oxides	<1	1	<1
Sulfates	5	<1	4
Other minerals	<1	<1	<1

2.3. Sequential Chemical Extraction

The Zeien and Brummer sequential extraction method (Table 3) [34] was applied to determine the fractionation of metal(loid)s in the three mine waste samples; 1 g of each waste sample was treated successively in seven extraction steps using seven solvents. The sequential extraction procedure comprised the following seven steps: (1) leaching of the mobile (exchangeable) fraction using 1 M ammonium nitrate (NH_4NO_3); (2) leaching of the easily deliverable fraction using 1 M ammonium acetate (CH_3COONH_4); (3) leaching of the easily reducible fraction using 0.1 M hydroxylammonium chloride (NH_2OH-HCl) with 1 M ammonium acetate (CH_3COONH_4); (4) leaching of the oxidizable fraction using 0.025 M ethylenediaminetetraacetic acid ammonium salt (NH_4-EDTA); (5) leaching of the moderately reducible fraction using 0.2 M ammonium oxalate ($(NH_4)_2C_2O_4$); (6) leaching of the poorly reducible fraction using 0.1 M ascorbic acid with 0.2 M ammonium oxalate; (7) extraction of the residual bound fraction after acid digestion with a mixture of hydrochloric acid, nitric acid, and hydrofluoric acid (65% HNO_3 + 30% HCl + ~48% HF, 1:3:1) in a microwave (Multiwave 3000, Anton Paar GmbH).

Table 3. The sequential extraction procedure.

	Fraction	Extraction Agent/Solvents	Reaction Times and Conditions
F1.	Mobile	1 M NH_4NO_3	24 h
F2.	Easily deliverable	1 M CH_3COONH_4 (pH 6.0)	24 h
F3.	Easily reducible	0.1 M NH_2OH-HCL + 1 M CH_3COONH_4 (pH 6.0)	30 min
F4.	Oxidizable	0.025 M NH_4-EDTA (pH 4.6)	90 min
F5.	Moderately reducible	0.2 M NH_4-Oxalate (pH 3.25)	4 h (in the dark)
F6.	Poorly reducible	0.1 M Ascorbic acid + 0.2M NH_4-Oxalate	30 min (96 °C)
F7.	Residual fraction	65% HNO_3 + 30% HCl + ~48% HF, 1:3:1	10 min (240 °C, 800 W, microwave)

The seven extraction agents or solvents and their individual reaction times and conditions are presented in Table 3. The extractions were conducted with triplicate samples using 25 mL of each solvent in 50 mL Greiner reaction tubes. A REAX 20 overhead shaker (Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) rotating at 15 rpm at room temperature (unless otherwise stated), was used to mix the reactants during the extraction process. At the end of each extraction step, the leachates were separated from residues by centrifugation at 5000 rpm for 20 min. The leachates were filtered with 0.2 µm filters and analyzed by ICP-MS (NexION 350×, Perkin Elmer, Waltham, MA, USA). The residues were washed with 25 mL of deionized water before the addition of the successive solvent. All chemicals and reagents used in the study were of analytical grade; information about the chemicals is presented in Supplementary Table S1. The quality of the analytical results was checked by calculating the percentage recovery of the sequential extraction procedure following Equation (1):

$$\text{Recovery } (\%) = \frac{\text{Step 1} + \text{Step 2} + \text{Step 3} + \text{Step 4} + \text{Step 5} + \text{Step 6} + \text{Step 7 } \left(\frac{\text{mg}}{\text{kg}}\right)}{\text{Total metal concentration } \left(\frac{\text{mg}}{\text{kg}}\right)} \times 100 \qquad (1)$$

3. Results and Discussion

The concentrations (mg/kg) of Cu, Pb, Zn, Co, As, Cd, Cr, Mn, Fe, Ca, and Al in the three mine wastes obtained from each extraction step are presented in Table 4. The relative concentrations (%) of these elements leached at each extraction step are illustrated in Figure 3. The recovery (percentage) of sequential extraction was determined by comparing the amount of a given element obtained by sequential extraction to the total concentration of the element in the sample. The recovery of elements by sequential extraction was between 90–130%, which is similar to that reported by other authors [49]. The variability in the recovery can be explained by the highly heterogeneous nature of the studied samples. Discussion of the results below focuses mainly on the mobility and association of metal(loid)s with possible geochemical fractions rather than the specific mineralogy of the waste samples. In this study, the mobile and easily deliverable fractions were considered to be highly mobile because these forms can be easily released into the environment. Environmental risk, as discussed below, pertains to the contamination potential of an element as regards its release from the waste samples into the environment.

Table 4. Fractionation of metal(loid)s (concentration in mg/kg) in operationally defined fractions using Zeien and Brummer's sequential extraction scheme for one waste sample originating from the Freiberg mine and two from the Neves Corvo mine.

	Elements (mg/kg)	**F1 Mobile**	**F2 Easily Deliverable**	**F3 Easily Reducible**	**F4 Oxidizable**	**F5 Moderately Reducible**	**F6 Poorly Reducible**	**F6 Residual Bound**	**Recovery (%)**
FR_01 (Freiberg tailing)	Cu	56.8 ± 5.6	25.1 ± 2.4	<0.1	21.4 ± 1.9	18.3 ± 2.4	<0.1	751.3 ± 1	105
	Pb	1910.8 ± 260.1	906.7 ± 38.8	280.8 ± 6.3	724.2 ± 43	251.6 ± 7.8	92.6 ± 19.5	736.3 ± 1	111
	Zn	3716.7 ± 212.6	98.5 ± 1.6	22.0 ± 1	179.3 ± 11.4	760.0 ± 60.1	48.9 ± 3.7	11066.7 ± 153	121
	Co	18.0 ± 0.4	0.5 ± 0.03	0.1 ± 0.005	0.2 ± 0.005	0.5 ± 0.05	0.2 ± 0.02	30.7 ± 0	122
	As	7.1 ± 0.7	28.2 ± 3.7	12.2 ± 0.7	351.7 ± 11.3	2493.3 ± 77.5	111.8 ± 16.2	3436.7 ± 15	115
	Cd	54.3 ± 5.2	1.1 ± 0.08	0.4 ± 0.02	1.3 ± 0.05	0.7 ± 0.14	0.1 ± 0.004	118.3 ± 1	130
	Cr	0.1 ± 0.008	0.1 ± 0.02	0.2 ± 0.008	0.3 ± 0.02	6.7 ± 0.4	1.8 ± 0.1	38.5 ± 1	129
	Mn	990.8 ± 18.8	63.3 ± 0.4	3.9 ± 0.1	60.4 ± 0.5	351.7 ± 9.5	522.5 ± 58.5	1215.5 ± 6	95
	Fe	36.9 ± 3.4	28.3 ± 8.8	315.0 ± 9.0	4466.7 ± 38.2	17,033.3 ± 398.7	5975.0 ± 894.8	137,744.8 ± 1000	100
	Ca	8941.7 ± 152.8	520.8 ± 6.3	6.0 ± 0.5	353.3 ± 9.5	15.0 ± 2	20.2 ± 2.4	2656.7 ± 15	106
	Al	77.3 ± 10.6	17.1 ± 2.3	5.3 ± 1.3	65.2 ± 7.2	551.3 ± 48.2	248.2 ± 22.5	36,433.3 ± 404	134
NC_01 (Neves Corvo waste rock)	Cu	16.1 ± 0.3	47.5 ± 1.5	<0.1	29.8 ± 1.2	34.3 ± 1.2	<0.1	1790.0 ± 10	104
	Pb	6.3 ± 0.3	235.8 ± 5.4	47.4 ± 0.4	143.7 ± 2.7	160.8 ± 1.9	10.6 ± 0.5	149.3 ± 1	91
	Zn	83.7 ± 0.6	167.8 ± 3	21.7 ± 0.6	71.4 ± 1.1	114.4 ± 1	39.8 ± 2.9	3046.7 ± 35	100
	Co	9.7 ± 0.1	6.7 ± 0.1	0.8 ± 0.02	4.4 ± 0.1	4.1 ± 0.04	0.5 ± 0.04	59.4 ± 1	101
	As	<2.5	5.1 ± 0.2	< 2.5	14.4 ± 0.2	129.7 ± 1.7	27.3 ± 3	634.0 ± 5	106
	Cd	0.7 ± 0.006	0.4 ± 0.001	0.05 ± 0.001	0.1 ± 0.0001	0.1 ± 0.0004	0.02 ± 0.005	8.1 ± 0	105
	Cr	0.1 ± 0.003	0.1 ± 0.005	0.2 ± 0.002	0.2 ± 0.01	2.7 ± 0.06	1.6 ± 0.08	69.4 ± 1	114
	Mn	95.8 ± 1	21.1 ± 1.3	3.8 ± 0.09	10.3 ± 0.3	107.9 ± 1	101.8 ± 6.1	396.3 ± 1	102
	Fe	<2.5	17.1 ± 0.7	113.2 ± 3.7	941.7 ± 42.6	9966.7 ± 152.6	5258.3 ± 203.6	121,333.3 ± 2309	113
	Ca	2022.8 ± 11.5	258.8 ± 0.3	70.2 ± 2.3	347.3 ± 2.5	20.6 ± 0.4	25.0 ± 0.1	2543.3 ± 42	101
	Al	<0.25	37.7 ± 0.4	12.4 ± 0.4	204.1 ± 3.3	1043.4 ± 3.9	743.1 ± 13.5	56,900.0 ± 693	105

Table 4. *Cont.*

NC_02 (Neves Corvo tailing)	Cu	172.2 ± 3.5	98.8 ± 1.4	<0.1	111.3 ± 1.2	69.6 ± 2.2	<0.1	3543 ± 3	107
	Pb	1541.7 ± 25.2	565.8 ± 13.8	186.7 ± 4.5	550.8 ± 10.1	190.7 ± 3.6	15.1 ± 3.4	781 ± 10	96
	Zn	676.7 ± 16.1	115.6 ± 1.9	19.9 ± 1.3	92.7 ± 2.5	208.8 ± 2.1	96.3 ± 2.9	9440 ± 30	100
	Co	8.6 ± 0.1	2.7 ± 0	0.3 ± 0.03	0.7 ± 0.03	1.4 ± 0.02	1.5 ± 0.07	190 ± 3	111
	As	1.3 ± 0.1	38.1 ± 0.5	64.3 ± 0.4	310.8 ± 1.4	650.8 ± 2.9	1.7 ± 0.1	4093 ± 25	103
	Cd	2.3 ± 0.02	0.3 ± 0.001	0.1 ± 0.002	0.1 ± 0.001	0.2 ± 0.002	0.03 ± 0.008	26.8 ± 0	106
	Cr	0.1 ± 0.02	0.1 ± 0.007	0.2 ± 0.01	0.2 ± 0.02	9.6 ± 0.4	1.4 ± 0.04	37 ± 0	115
	Mn	70.6 ± 2.4	24.3 ± 1.4	5.2 ± 0.2	26.3 ± 1.4	95.1 ± 3.8	101.8 ± 0.7	430 ± 3	103
	Fe	28.6 ± 0.9	98.3 ± 0.1	556.7 ± 12.6	1808.3 ± 30.6	7658.3 ± 212.6	4133.3 ± 14.4	310,666.7 ± 1155	115
	Ca	2850.0 ± 50	411.0 ± 5.5	107.7 ± 0.5	432.8 ± 8.8	19.3 ± 0.2	19.1 ± 1	3066.7 ± 29	97
	Al	5.0 ± 0.1	3.2 ± 0.1	1.9 ± 0.1	54.8 ± 1.1	310.6 ± 7.9	425.8 ± 17.1	25,633.3 ± 58	102

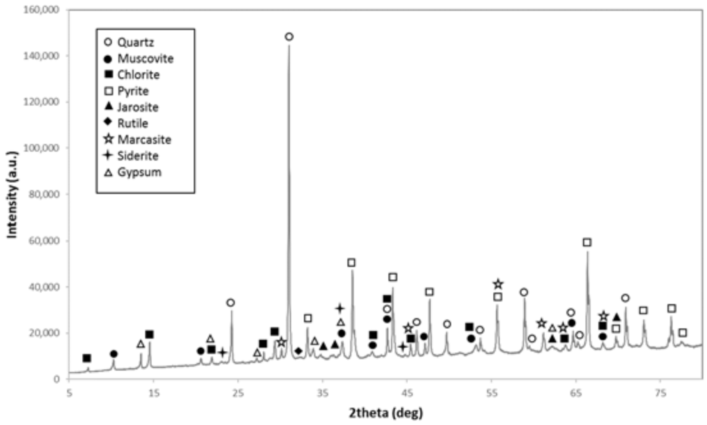
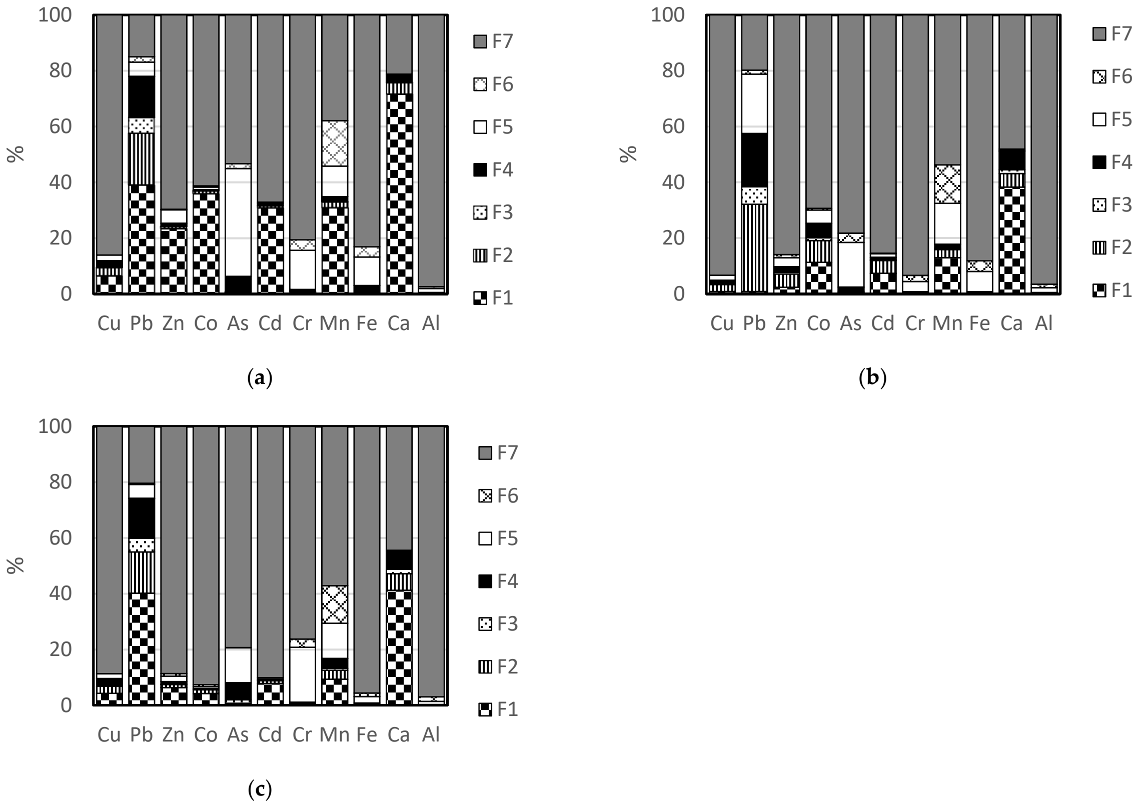


Figure 3. XRD scan of the Freiberg tailing sample (FR_01).

3.1. Total Composition and Distribution of Elements in the Freiberg Tailing

The mineral composition of the tailing obtained from the Freiberg region of Germany (FR_01) is presented in Table 2. FR_01 is composed mainly of silicate (59 wt%), sulfide (30 wt%), carbonate (5 wt%), and sulfate (5 wt%) minerals. The sulfide minerals were pyrite (22 wt%) and marcasite (8 wt%), while the sulfate mineral was mainly gypsum. The XRD scan of the FR_01 sample is presented in Figure 3. The chemical composition of FR_01 (Table 1) shows elevated concentrations of metal(loid)s, especially Cu, Pb, Zn, As, Mn, and Fe, ranging between 828–165,667 mg/kg. The respective concentrations of these elements as distributed across the operationally defined fractions are presented in Table 4, while the concentrations relative to the sum of all fractions are illustrated in Figure 4a.



(**a**) (**b**)

(**c**)

Figure 4. Fractionation of metal(loid)s in: (**a**) Freiberg tailing (FR_01); (**b**) Neves Corvo waste rock (NC_01); (**c**) Neves Corvo tailing (NC_02). F1—mobile fraction, F2—easily deliverable fraction, F3—easily reducible fraction, F4—oxidizable fraction, F5—moderately reducible fraction, F6—poorly reducible fraction, F7—residual bound.

Fractionation results showed that a considerably large portion of Pb (57%), Ca (75%), Mn (31%), and Zn (24%) from FR_01 were released in the first and second extraction steps, that is, the mobile (F1) and easily deliverable (F2) fractions. This was similar to the fractionation of Pb and Zn in other tailing samples studied previously [33]. The two highly mobile fractions (F1 and F2) are the most soluble forms of an element and represent a major environmental concern. Elements with high mobility are more likely to cause environmental problems [35]; for example, Pb, Ca, Mn, and Zn could be easily released from FR_01 into the environment in cases of acidic rainfall [21], which would in turn threaten the quality of the surrounding surface and groundwater. The mobile fraction includes exchangeable elements that are weakly adsorbed to the material's surface by relatively weak electrostatic interactions. The mobile fraction can be easily released by changes in the ionic composition of water, such as ion exchange processes [50,51]. The easily deliverable or acid-soluble fraction includes carbonate-bound metals and is usually targeted for extraction with a mild acid [52] or salt of a weak acid in this study. Elements in this fraction are weakly bound to the solid phase and are susceptible to changes in environmental conditions such as changes in pH [53]. Such changes lead to the dissolution of carbonates and subsequent release of carbonate-bound metals [50,54,55]. Metals complexed with organic acids such as acetic acid could be dissolved in this extraction stage (F2) as well [56].

The dissolution of carbonate minerals is usually accompanied by the release of divalent cations such as Ca^{2+} [57]. The release of Ca in the highly mobile fractions may be associated with the dissolution of the carbonate minerals present in the Freiberg tailing, as well as gypsum, which is a sulfate mineral. The presence of soluble carbonate minerals in this tailing indicates that these minerals may buffer the acidity likely to be generated by the oxidation of sulfide minerals [58]. Soluble Pb-bearing minerals such as cerussite were not detected in any of the studied mine waste samples. Considering that this is a sulfidic tailing, it is reasonable to assume that most of the Pb released in the mobile, easily deliverable, and oxidizable fractions (accounting for 72% of the total Pb content) was associated with sulfidic minerals such as galena, which has been previously reported to be present in tailings from the same site [41]. Galena has particularly low resistance to oxidation and is observed to dissolve more easily than certain other sulfidic minerals such as pyrite [57].

Large portions of Co (37%) and Cd (32%) were highly mobile, and could significantly impact the environment despite their considerably lower total concentrations (41 and 136 mg/kg, respectively) in the sample. The Cd and Co extracted in these fractions could be as a result of their associations with sulfide minerals present in the tailing, as no cobalt- or cadmium-bearing minerals were detected by QXRD. The most abundant fractions (83–97%) of Fe, Cu, and Al were found in the most resistant geochemical fraction (the residual fraction), which could be associated with minerals that are highly resistant to oxidation. Examples of such minerals are crystalline Fe oxides (e.g., magnetite), and in the case of the Freiberg tailing, primary sulfides (e.g., pyrites) and silicates [35]. This is not surprising, as the major sources of Al in the tailing were chlorite and muscovite (silicates), while Fe and Cu were associated with pyrite and chalcopyrite (sulfides). These elements do not seem to pose a major environmental risk, as they were less mobile. Arsenic was less mobile as well, as fractionation was dominated by the residual (53%) and reducible (41%) fractions. The As extracted in the residual fraction could be as a result of the dissolution of sulfide minerals such as arsenopyrite, while the reducible As fraction could be associated with oxide minerals such as rutile. Overall, the Freiberg tailing has contamination potential for Pb, Mn, Co, Cd, and Zn due to the significant large concentrations of the highly mobile fractions.

3.2. Total Composition and Distribution of Elements in the Neves Corvo Waste Rock

Table 2 shows that the fresh waste rock (NC_01) from the Neves-Corvo mine is composed mainly of silicate minerals (84 wt%) and pyrite (12 wt%), as well as small amounts of carbonate (3 wt%) and oxide (1 wt%) minerals. The XRD scan of the NC_01 sample is presented in Supplementary Figure S1. The chemical composition of the waste rock (Table 1) indicates high concentrations of metal(loid)s (Cu, Pb, Zn, Mn, As, Al), between 724–122,333 mg/kg. The partitioning of elements in operationally defined fractions in the waste rock is presented in Table 4 and illustrated in Figure 4b. The results show that Pb was the most soluble toxic element in the waste rock; 32% of the total Pb content was highly mobile.

The oxidizable and reducible fractions were equally important for Pb in the waste rock sample, as they accounted for 19% and 28% of the total Pb content, respectively. These fractions are less mobile and are relatively stable under normal conditions [42]. The oxidizable fraction includes elements bound to organic matter or humic substances such as coatings on minerals, detritus, and living organisms via bioaccumulation or complexation processes [59]. This fraction is not considered mobile due to the stability and high molecular weight of organic substances, which only release small quantities of elements slowly over time. Nevertheless, decomposition or oxidation conditions such as microbial activity and weathering can lead to the release of associated elements from these fractions [54]. It is expected that a considerable amount of metals bound to sulfide minerals will be released along with the oxidizing fraction in this fourth extraction stage (F4) [51]; however, the more stable/resistant sulfide minerals will only be released in the last extraction stage. The reason for this is that the oxidizing conditions induced by the extractant can oxidize sulfide minerals present in the material, resulting in the dissolution of metals associated with these sulfides. Considering the low organic content of the waste rock, it is reasonable to assume that most of the Pb released in the oxidizable fraction (19%) at the fourth extraction stage (F4) originated mainly from the sulfide minerals present in the waste rock.

Fe, Cu, Zn, As, Cd, Cr, and Al displayed similar partitioning patterns across the different fractions. The majority ($\geq$85%) of their total content was concentrated in the residual fraction, while only about 12% or less was highly mobile. Metal fractions that are residual bound do not pose immediate threats to the environment. This is due to their high binding strength to the solid phase of naturally occurring or primary stable minerals such as silicates. It would take longer to release Fe, Cu, Zn, As, Cd, Cr, and Al from NC_01 into the environment, and only strong conditions such as weathering are likely to cause this effect [54]. The high concentrations of these elements associated with the residual fractions could represent the high silicate content (84 wt%) of the waste rock. Co and Mn do not seem to pose a major risk to the environment. Less than 20% of the total concentrations of Co and Mn were highly mobile, while over half of their total contents were residual-bound; 43% of total Ca was highly mobile, suggesting the possible dissolution of carbonate minerals which could have acid buffering potentials. Of all elements analyzed, the Neves Corvo waste rock mainly has potential for Pb contamination, based on the large portion of the total Pb content in the highly mobile fractions. However, Zn could pose a threat to the environment as well considering its elevated concentration (251.5 mg/kg) in the highly mobile fractions.

3.3. Total Composition and Distribution of Elements in the Neves Corvo Tailing

The flotation tailing from the Neves Corvo mine (NC_02) contains the highest concentration of sulfide minerals, especially pyrite. The tailing comprises 53 wt% of pyrite, 41 wt% of silicate, 4 wt% of sulfate (gypsum), and 2 wt% of carbonate minerals (Table 2). The XRD scan of the NC_02 sample is presented in Supplementary Figure S2. As in the Freiberg tailing, the Neves Corvo tailing contains relatively high concentrations of metal(loid)s, between 3727–283,000 mg/kg of Cu, Pb, Zn, As and Fe (Table 1). The distribution of these metal(loid)s across possible geochemical fractions is presented in Table 4 and illustrated in Figure 4c. Similar to the other two mine waste samples, Pb was the most soluble toxic element in the tailing (Figure 4c). More than half (55%) of the total Pb content was highly mobile. Smaller concentrations were distributed among the oxidizable and reducible fractions, while 20% was residual-bound.

As in the waste rock, the residual fraction was the dominant phase for Fe, Cu, Zn, As, Cd, Cr, Co, and Al, accounting for over 70% of their total concentrations. This may be associated with the high sulfide and silicate mineral content of the tailing. Less than 10% of these metal(loid)s were highly mobile, indicating lower contamination potential, except for Zn. Although only about 7% of the total Zn content was highly mobile, this fraction poses a risk to the environment due to the high concentration (over 700 mg/kg) this portion represents. The mobile and oxidizable fractions were of minor importance for Mn, accounting for only 12% and 3% of total Mn in the tailing, respectively. Mn was preferentially concentrated in the reducible (28%) and residual (57%) fractions, which may be associated with Fe oxide and silicate minerals. Generally, the fractionation results show that the Cu, Zn, Co, Cr, Cd, Al, As, and Mn contents of NC_02 do not pose a significant risk to the environment. They will most likely not be released under normal conditions because they are tightly held within the crystalline matrix of naturally occurring minerals [51]. However, Pb and Zn are potential threats to the environment surrounding the tailings pond, as large amounts of Pb and Zn in the tailing are highly mobile and can contaminate the environment.

4. Conclusions

Mineralogical and geochemical compositions are useful indicators of the potential environmental impact of sulfidic mine wastes. This study assessed the contamination potential of three European sulfidic mine waste samples as case studies by investigating the possible geochemical fractions of the elements. Zeien and Brummer's sequential extraction method was used to partition elements of the samples into seven operationally defined fractions. The results provide information about the mobility and stability of metal(loid)s from their host minerals, giving insight into the solubility and reactivity of the minerals in the samples. All mine waste samples contained elevated metal(loid) levels, although most of these metal(loid)s were not mobile. Pb was implicated as the most mobile toxic element in all samples, and a high concentration of Zn was highly mobile in all samples as well. The high mobile concentrations of Pb and Zn in the mine wastes raise concerns about the safety of the environment where these waste dumps are located. The Freiberg tailing was observed to possess contamination potential for Co, Cd, and Mn due to large highly mobile fractions of these elements; other metal(loid)s were less mobile.

The residual fraction was the most abundant Fe fraction in the three mine wastes, accounting for 83–96% of total Fe content. The limited oxidation of pyrite in the studied mine wastes as observed in the extraction scheme may indicate a low tendency for acid mine drainage. This is because acid mine drainage is generated by the oxidation of pyrite and other sulfide minerals, resulting in the release of associated metal(loid)s and sulfate into the environment. In addition, the high mobility of Ca in all studied samples suggests that the associated carbonate minerals present in these mine wastes were highly soluble and may have acid-buffering effect against acid mine drainage. However, it should be stated that sequential extraction cannot correctly predict acid mine drainage or other potential risks associated with mine waste. Various other factors and complex reactions which were not covered in this method may play significant roles in the fate of sulfidic mine waste.

Sequential extraction results provide information on the mobility of elements, which in this study was a valuable tool to assess the contamination potentials of three mine wastes. However, future works should integrate the sequential extraction method with mineralogical studies via techniques such as electron microscopy. In addition, the quality control of subsequent experiments should include the use of reference materials with certified extractable contents.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/separations9030067/s1: Figure S1: XRD scan of the Neves Corvo waste rock (NC_01); Figure S2: XRD scan of the Neves Corvo tailing (NC_02); Table S1: Chemicals used in the study.

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