Article

Behaviour of Metals during Bioheap Leaching at the Talvivaara Mine, Finland

Hanna Tuovinen [1], Mila Pelkonen [1], Janne Lempinen [1], Esa Pohjolainen [2], David Read [3], Dina Solatie [4] and Jukka Lehto [1,*]

[1] Department of Chemistry—Radiochemistry, P.O. Box 55, University of Helsinki, 00014 Helsinki, Finland; hanna.tuovinen@stuk.fi (H.T.); mila.pelkonen@helsinki.fi (M.P.); janne.lempinen@helsinki.fi (J.L.)
[2] Geological Survey of Finland, FI-02151 Espoo, Finland; esa.pohjolainen@gtk.fi
[3] Department of Chemistry and National Physical Laboratory, University of Surrey, Guildford GU2 7XH, UK; d.read@surrey.ac.uk
[4] The Radiation and Nuclear Safety Authority, 00880 Helsinki, Finland; dina.solatie@kemijarvi.fi
[*] Correspondence: jukka.lehto@helsinki.fi

Abstract: The behaviour of base metals Ni, Zn, Cu, Co, Fe, and Mn, potentially toxic metals Pb, Cr, and Cd, and the radioactive elements, U and Th, in the Talvivaara mining process, Finland has been studied by tracing metal concentrations from the black schist ore, through ores subjected to bioheap leaching of varying duration, to pregnant leach solution (PLS), and solid process waste material deposited on site in gypsum waste ponds. It is apparent that Zn, Cu, Co, and Cd are leached from the ore in a similar manner and recovered efficiently in the PLS; however, Ni, though leached, was also found in the gypsum pond at relatively high concentrations. Relatively little Pb is released from the ore, but the small fraction that is mobilised accumulates in the gypsum pond. Of the radioactive constituents, Th is essentially immobile, whereas U is readily leached from the ore, again accumulating in gypsum pond waste. In addition, a laboratory-based sequential leach test was applied to assess the future leaching potential of metals from residual ore and process waste material under different environmental conditions.

Keywords: mining; bioheap leaching; waste; metals; environmental effects

1. Introduction

Heap leaching is an advantageous method to extract metals from low-grade ores and it has been utilized at large scales to extract gold, uranium, and copper [1]. A special type of heap leaching, bioheap leaching makes use of microbially-induced enhancement of the metals leaching from the ore. Bioheap leaching is particularly utilized in copper recovery from chalcopyrite ($CuFeS_2$) in which the microbes act as catalysts to oxidize sulphide to sulphate and, thus, produce copper sulphate in sulphuric acid [2]. Heap leaching is environmentally friendlier than pyrometallurgical processes with respect to considerably lower air emissions of carbon dioxide and, especially, sulphur dioxide. Heap leaching may, however, cause more severe environmental effects than conventional processing, especially with respect to contamination of surrounding water systems during ore processing and after closure of a mine [3]. The volumes of both the process waters and the solid waste materials left on site after mine closure are very high and can lead to severe environmental impacts if not properly managed. A special problem in the case of sulphide-bearing ores is acid mine drainage as sulphuric acid is generated in the oxidative dissolution of sulphide minerals [4]. Acidic environments can further dissolve potentially-toxic metals from surrounding materials and cause contamination of natural water systems. In recent years heap bioleaching has gained more interest, particularly for processing black shale ores which are difficult to process with conventional hydrometallurgical processes [5]. Due to

the exhaustion of high-grade ores, low-grade mineral resources, and also waste deposits from former mining activities, have been explored for their possible utilization as metals sources and bioheap leaching is a promising option for the extraction process [6].

The Talvivaara Ni-Zn-Cu-Co deposit, located in Sotkamo, Eastern Finland, comprises one of the largest known Ni resources in Europe [7]. Production from the Talvivaara ore deposit commenced in 2008 and it is still the only industrial-scale mine to utilize bioheap leaching for nickel production. The production process, described in more detail later, includes open pit mining, crushing, microbe-mediated heap leaching, metals recovery, and removal of metals having no current value.

In addition to the removed overburden, the mine produces three types of solid waste to be left on site after closure. First, the waste rock contains the bulk of the non-ore material, consisting mainly of quartz, feldspars, phlogopite, graphite, and pyrite, but also minor parts of the ore minerals, such as pyrrhotite [8]. This material is exposed to air and subject to leaching by circulating waters, but most of these minerals do not contain hazardous metals and are only sparingly soluble at the prevailing pH. However, waste rock also contains sulphide minerals, leading to the potential for acid mine drainage which, in turn, could increase the solubility and leachability of other minerals present.

Another, and more important, source of solid waste to be left on site is the leached ore. Its specific surface area is very large compared to the original rock, enhancing dissolution when in contact with water. Moreover, even though a large proportion of the sulphide ore is dissolved during the bioheap leaching process, enough remains to cause production of an acidic environment with ensuing leaching of a variety of metals, many of them toxic, into local waters.

The third category of solid waste comprises solid process waste generated after the recovery of valuable target metals, by removing major non-valuable elements, Fe and Mn, trace elements, and potentially toxic metals from the recovery process waters. This waste is generated in three process phases producing respectively, neutralization precipitate, Fe removal thickener underflow and final, neutralisation thickener underflow. This material, disposed of in large waste ponds, comprises gypsum, Fe hydroxides and calcium carbonate; the latter is highly soluble should conditions become acidic. Dissolution of minerals in the process waste tailings would release hazardous components co-precipitated with these minerals into local water courses. The latter occurred in 2013 when acidic process waters were directed to the pond causing the solid waste to partly dissolve and breaching the dam surrounding the pond.

In our previous paper we reported on the behaviour of radionuclides in the Talvivaara mining process [9]. The present paper focuses on the behaviour of associated metals, including base metals (Ni, Zn, Cu, Co) and potentially toxic metals (Cd, Cr, Pb), which were measured in the ore heaps, pregnant leach solution, and solid process waste to evaluate their fate through the various stages of the mining process. The main focus of the study is the long-term fate of those materials to be left as waste on site following the closure of the mine. Therefore, sequential extractions were also undertaken on ore materials and gypsum pond waste to obtain information on potential mobilisation of contaminants under different environmental conditions.

2. Site Description

2.1. Physiography and Climate

The Talvivaara mine is located in Sotkamo, Eastern Finland (63°58′30″ N, 28°0′30″ E, WGS84). It is an open-cast mine, 22 km from Sotkamo and 28 km from Kajaani. The mine area extends over the watershed of two rivers, the Vuoksi and Oulujoki, and drainage from the mine affects both river systems. Surface waters near Talvivaara mainly comprise ponds and small streams where pH and buffering capacity are low and metal concentrations are naturally elevated. The climate is subarctic: the mean temperature is 1.0 °C and the mean annual precipitation 644 mm [10].

2.2. Characteristics of the Talvivaara Black Schist Ore

The Talvivaara Ni-Zn-Cu-Co deposit is hosted by metamorphosed black shales of the Kainuu schist belt. The total Talvivaara mineral resource is estimated to be 2053 Mt at 0.22 wt % Ni, 0.13 wt % Cu, 0.02 wt % Co, and 0.50 wt % Zn [11]. The main minerals in the Talvivaara ore are quartz, microcline, anorthite, phlogopite, muscovite, graphite, pyrite, and pyrrhotite. Ni is mostly incorporated in pyrrhotite ($Fe_{1-x}S$) and pentlandite (($Fe,Ni)_9S_8$), Zn in sphalerite (($Zn,Fe)S$), Cu in chalcopyrite ($CuFeS_2$), and Co in pentlandite and pyrite (FeS_2) [12]. A significant part of U at Talvivaara is incorporated in uraninite (UO_2), which is typically enclosed in poorly crystalline, undeformed, and globular carbonaceous nodules [13].

2.3. Mining Process at Talvivaara

Production from the Talvivaara ore deposit includes open pit mining, crushing, heap leaching, metals recovery and removal of metals having no current value (Figure 1). The leach solution percolates to the bottom of the leach pads and is either re-circulated through the heap or fed to metals recovery. The acidity of the leach solution (pH 2.0–2.5) is controlled by sulphuric acid, and leaching of metals is catalysed by bacteria (e.g., *Acidithiobacillus ferrooxidans*) endemic to the Talvivaara area [14]. After two years of primary leaching, the ore is reclaimed and re-stacked for secondary leaching to enhance metal release. The secondary leaching heaps also constitute the final disposal sites for the leached ore.
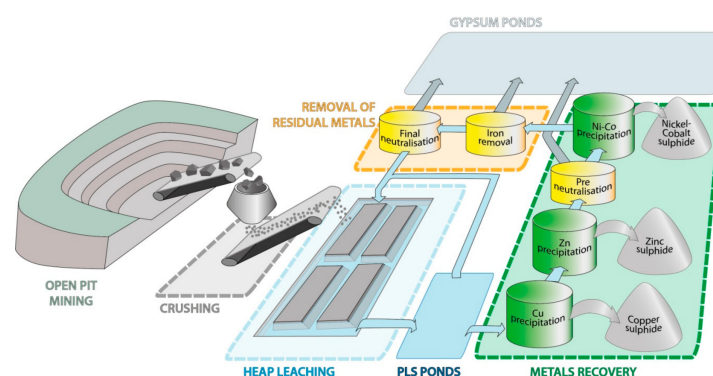

Figure 1. Talvivaara mining process.

During metals recovery, Cu, Zn, Ni, and Co are precipitated from the pregnant leach solution (PLS) and filtered to produce saleable metal products. After the target metals have been recovered, the solution is further purified to remove unwanted metals and returned to irrigate the heaps. During removal of residual metals, the pH of the PLS is raised to 9–10, using a lime slurry, leading to precipitation of residual metals (Mn, Mg, Fe) as hydroxides, together with gypsum and calcium carbonate. The resulting slurry is thickened and the thickener underflow is directed to gypsum waste ponds.

The Talvivaara ore deposit contains about 22,000 tons of U in 1305 Mt of measured and estimated resources grading at 0.0017% U. There are plans to recover U as a byproduct, using solvent extraction, but the licensing process for U production is still ongoing.

2.4. Mineralogy of the Leached Ore

The leached ore contains relict phases of the original minerals (e.g., quartz, feldspars, phlogopite), their alteration products (e.g., vermiculite after phlogopite) and secondary minerals formed as a result of heap leaching. Uraninite is completely dissolved after half a year's leaching and the proportion of sulphides decreases significantly [9]. Pyrite is more resistant in the heaps and residual grains are still found after two years' leaching. Other sulphides are less resistant, though pyrrhotite is still encountered in the leached ore after 18 months heap leaching. The main secondary minerals in

the heaps are jarosite, goethite, and gypsum. Jarosite and goethite are formed in the heaps after the first six months' and gypsum after one year's leaching. Phlogopite is replaced by vermiculite in the heaps typically after 18 months' leaching [9].

3. Materials and Methods

3.1. Sampling

Samples were collected from the primary heaps, secondary heaps, the PLS-ponds and the process waste pond in 2011, 2012, and 2013. Duplicate solid samples were taken from four different leaching heaps as well as from the unprocessed ore and process waste pond. The leaching time varies by approximately 0.5 years between the heaps. Four samples of the pregnant leach solution were taken from the PLS ponds linked to each of the above heaps.

3.2. Sample Pre-Treatment

Unprocessed ore, leached ore and process waste samples were dried at 40 °C for seven days. Ore and leached ore samples were ground to a fine powder using a Mixer Mill Type MM 200 (Retsch, Haan, Germany). Process waste samples were already of small grain size (<2 mm) and were not processed further. The samples were digested in concentrated nitric acid using a Mars microwave digestor (CEM, Matthews, NC, USA) for the determination of metals by inductively-coupled mass spectrometry (ICP-MS). Nitric acid was chosen based on sample digestion experiments performed previously [15]. The acids used were of suprapure grade (Merck) suitable for ICP-MS. After cooling, the digest was filtered through a 0.45 μm polypropylene filter and stored in Nalgene containers in the refrigerator pending analysis.

3.3. Sequential Leaching

A sequential extraction was performed for unprocessed ore, leached ores from the primary and the secondary leaching heaps and process waste from the gypsum pond. In the leach tests there were two samples of unprocessed ores, twelve samples from the primary leaching heaps (leaching age approximately 0.5–2 years), five samples from the secondary leaching heap (leaching age approximately 2.5 years) and four samples from the process waste pond. Triplicate samples were taken from each solid for each extraction phase. Later results are given as mean values of the four solid types. The sequential extraction procedure selected was that of [16] with two modifications: NH_4Cl was used in the extractions rather than $MgCl_2$, as the dissolution of Mg was also studied. Additionally, two exchangeable fractions were used: one at pH 7.7, obtained with the addition of TRIS buffer (tris(hydroxymethyl)aminomethane) and another at pH 5.5. The fractions with the reagents used and measured pH values are presented in Table 1. For the extractions, 2.0 g solid samples were weighed into plastic centrifuge tubes and 30 mL of extraction solution was added. After each extraction step the solid was separated by centrifugation at 12,000 rpm for 15 min and the supernatant removed by pipetting for metal analysis with ICP-MS after filtering with 0.45 μm filter. The residual solid was then rinsed with 30 mL MilliQ-water, shaken, centrifuged, and the water removed by pipetting. The next extraction solutions were then added and the same procedure repeated with the leaching times and temperatures specified in Table 1.

Table 1. Sequential extraction procedure, modified from [16]. The pH values are initial pH values of the solutions.

	Fraction	Solution	pH	Leaching Conditions
I	*Exchangeable 1*	1 M NH_4Cl with tris-buffer	7.7	1 h, room temperature
II	*Exchangeable 2*	1 M NH_4Cl	5.5	1 h, room temperature
III	*Mild acid soluble*	1 M CH_3COONH_4 (in 25% CH_3COOH)	4.1	2 h, 50 °C
IV	*Reducible*	0.04 M $NH_2OH \cdot HCl$ (in 25% CH_3COOH)	2.1	6 h, 70 °C
V	*Oxidizable*	30% H_2O_2 and 0.05 M HNO_3	1.7	2 h, 70 °C
VI	*Strong acid soluble*	4 M HNO_3		4 h, 90 °C

3.4. Elemental Analysis by ICP-MS

In order to determine the elemental compositions of the ores, process waste and the liquid samples, the solutions were analysed by Agilent 7500 ce/cx ICP-MS (Agilent, Santa Clara, CS, USA) and the resulting spectra analysed using a Masshunter spectral analysis software. The elemental standard solutions were prepared by diluting single-element standard solutions (Merck). Standards and samples were diluted with 5% HNO_3. Water used in the preparation of dilute nitric acid was purified using a Milli-Q water purification system (Millipore, Billerica, MA, USA). For quality assurance, two reference waters were measured: Spectrapure Standards, Reference Material for Measurement of Elements in Surface Waters, SPS-SW2, batch 128 and Environment Canada, Certified Reference Materials, trace element fortified calibration standard, TM-27.3, lot 0510. Measured values are, in general, fairly close to the declared ones: on average the ratio of measured values to declared is 0.99 (range 0.77–1.18) for SPS-SW2 and 0.98 (0.70–1.33) for TM-27.2 (Table 2). Only in case of Ni the measured values differ markedly from declared, being only 70% and 77% of the declared values. Within the range of uncertainty eight measured values out of 21 are identical with declared ones.

Table 2. Certified and measured concentration values (ppb) of the studied metals in two reference waters SPS-SW2 and TM-27.3. Measured values are means of triplicates. n.d. = not determined.

Element	SPS-SW2		TM-27.2	
	Certified	Measured	Certified	Measured
Cr	10	8.64	1.74	1.43
Mn	50	46.9	2.25	2.18
Fe	100	95.7	10.9	9.88
Ni	50	38.3	2.42	1.70
Co	10	9.57	2.05	2.01
Cu	100	101	6.19	5.40
Zn	100	101	16.2	16.4
Cd	2.5	2.93	1.05	1.39
Pb	25	29.5	2.86	3.37
Th	2.5	2.55	n.d.	n.d.
U	2.5	2.55	2.03	2.17

4. Results and Discussion

4.1. Metals in the Heaps

Table 3 and Figure 2 present the metal concentrations in the Talvivaara heaps at various leaching times. There is a clear declining trend in the case of the major elements, Fe and Mn, together with U. With the exception of the initial values, the target metals Zn, Ni, and Cu, and the trace metal Cd, also show declining trends. Concentrations of Co, Pb, and Cr show little or no change over time.

When evaluating the results obtained one should bear in mind that the process circulates water through the heaps and only 10–20% of the PLSs are taken for metals recovery at each stage. When directed back to the heaps, the dissolved metals may undergo several reactions, such as adsorption onto mineral surfaces and precipitation. For example, in a pilot-scale trial at Talvivaara, dissolved Co was seen to re-precipitate in the heaps [10]. Interpretation is also hindered by the fact that sulphides of different elements do not dissolve in a congruent manner. In the above mentioned pilot-scale experiment Co, and especially Cu, leaching was seen to start only at a later stage when the majority of Ni and Zn had already been leached from the heaps. This was explained by galvanic effects as metal sulphides have different rest potentials. When in electrical contact with each other those sulphides having higher potential (Cu-bearing chalcopyrite and Co-bearing pyrite) act as cathodes, whereas those with lower potential (Ni-bearing pyrrhotite and pendlandite and Zn-bearing sphalerite) act as anodes and, thus, oxidize and dissolve more easily. The process is not straightforward, however, since both pyrrhotite and pendlandite also contain Co. Our results are in agreement with the postulated

galvanic effect in the case of Co but not in the case of Cu as the latter was seen to leach at a similar rate to Ni. Another difference from the results of the pilot-scale trial is that metal recoveries are much lower in our case. Reported pilot-scale recoveries were 80% for Ni and Zn, but results shown in Table 3 and Figure 2 suggest considerably lower recoveries. One possible reason for decreasing leach rates is the formation of secondary precipitates on ore mineral particles preventing further contact with leaching solutions. In addition, the permeability of the ore heaps decreases with time due to ore degradation and the formation of secondary minerals. Furthermore, formation of jarosite decreases the redox-potential by removing ferric Fe ions from the solution, thus decreasing oxidative dissolution of sulphide minerals [17].

Table 3. Metal concentrations (ppm) in the unprocessed Talvivaara ore and in the leaching heaps. Leaching times are approximate values.

Leaching Time (Year)		Ni	Zn	Cu	Co	Fe	
Unprocessed ore	mean	1030	2800	740	67	86,000	
Leached ore 0.5 years	mean	2200	5800	2210	181	72,000	
	range	1500–2900	2800–8700	650–4100	84–280	40,000–11,000	
Leached ore 1 year	mean	1600	4900	1700	140	67,000	
	range	600–2900	2300–8700	790–3700	30–310	49,000–100,000	
Leached ore 1.5 years	mean	2500	4400	2400	250	67,000	
	range	1300–3100	1900–6400	1400–4200	13–410	39,000–110,000	
Leached ore 2 years	mean	1000	2200	1200	180	68,600	
	range	630-1700	830–5100	460–3170	78–400	35,200–110,000	
Secondary heaps 2.5 years	mean	1000	2400	490	220	68,000	
	range	370–2400	700–4900	44–1900	63–350	48,000–93,000	
Leaching Time (Year)		**Mn**	**Pb**	**Cr**	**Cd**	**U**	**Th**
Unprocessed ore	mean	12,800	54	368	18	39	9
Leached ore 0.5 years	mean	5700	110	149	25	21	6
	range	3300–10,000	32–250	97–284	17–44	12–25	3–12
Leached ore 1 year	mean	4700	130	178	23	15	7
	range	3100–7700	41–260	126–314	11–50	6–27	3–13
Leached ore 1.5 years	mean	3700	120	169	20	15	5
	range	2600–5500	35–270	84–223	11–24	11–20	3–8
Leached ore 2 years	mean	2970	137	187	7	9	5
	range	2130–3990	40–256	87–280	2–15	7–13	2–10
Secondary heaps 2.5 years	mean	3039	137	167	8	10	7
	range	1810–4670	77–260	117–204	2–18	4–13	3–10

Table 4 presents the mutual correlations of metal concentrations in the heaps. Only correlations with a value of at least 0.88 have statistical significance. There are only a few significant positive mutual correlations, those of Cr/Fe, Cr/Mn, Fe/Mn, U/Fe, U/Mn, Cu/Ni, and Cd/Zn. The pairs Co/Th, Cr/U, Cu/Zn, Mn/Th, and Ni/Zn also have high positive correlation coefficients above 0.8, but the low number of measured values precludes assigning statistical significance. Interestingly, Co has a high negative correlation with Cr, Fe, Mn, and Th and Pb with Cr, Fe, Mn, and U.

Table 4. Pearson correlation coefficients for metals in the Talvivaara leaching heaps. Values having statistical significance (two-tailed $p < 0.05$) are in bold.

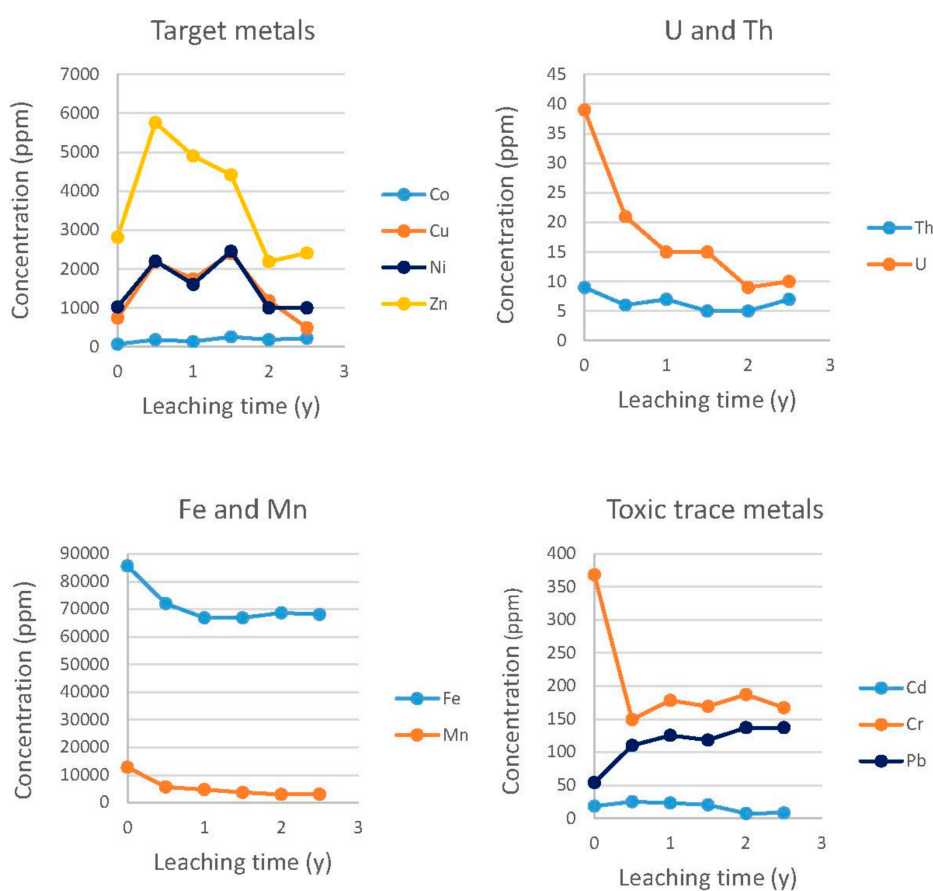|	Ni	Zn	Cu	Co	Fe	Mn	Pb	Cr	Cd	U
Zn	0.84									
Cu	***0.95***	0.84								
Co	0.47	0.10	0.39							
Fe	−0.34	−0.22	−0.41	−0.80						
Mn	−0.21	−0.05	−0.27	−0.85	***0.97***					
Pb	0.07	−0.01	0.15	0.75	***−0.95***	***−0.98***				
Cr	−0.47	−0.40	−0.50	−0.81	***0.93***	***0.92***	***−0.89***			
Cd	0.73	***0.92***	0.71	−0.22	0.13	0.32	−0.38	−0.01		
U	−0.07	0.07	−0.15	−0.16	***0.94***	***0.99***	***−0.99***	0.86	0.43	
Th	−0.49	−0.19	−0.59	−0.81	0.77	0.81	−0.73	0.78	0.13	0.76

Figure 2. Concentration (ppm) of metals in the unprocessed Talvivaara ore and in the leaching heaps as a function of leaching time.

4.2. Metals in Pregnant Leach Solution Ponds (PLS)

After leaching the heaps, the resulting solution is diverted to ponds that correspond to each heap. A 10–20% side flow is taken for metals recovery and the remainder of the solution is diluted with fresh water in order to keep the volume of solution constant. Approximately 80–90% of the solution from the PLS ponds is recycled back to heap irrigation to increase the metal grade.

Table 5 presents trace element concentrations in the PLS samples. The ponds correspond to heaps subjected to leaching times of between 0.5 and 2.0 years. Since a fraction of the solution is taken out of the ponds at frequent intervals, no quantitative evaluation can be made with respect to leaching time.

However, a general feature with respect to the valuable target metals is that Ni and Zn concentrations in the two oldest ponds are about half of those in the two youngest and, in the case of Cu and Co, about one quarter, indicating that most of these are leached during the first year.

Dividing the metal concentrations in the heaps by those in the PLS and normalizing the values obtained to that giving the lowest value (U), gives the following pattern in descending order: Pb (12,500) > Cr (84) > Th (23) > Fe (8.3) > Co (7.9) > Cd (2.2) > Zn (1.8) > Ni (1.5) > Mn (1.1) > U (1.0). This represents the relative resistance of each metal to leaching; i.e., Pb is leached least and U most readily. For Pb the value is a minimum, since it is based on only one value, while the other three were below the detection limit (see Table 5). With respect to the immobility of the target metals, they follow the sequence, Co > Ni > Zn. This is in accordance with the results of the pilot-scale trial [10] and the galvanic properties discussed earlier. Ni and Zn are leached more readily, and Co less so. Unfortunately Cu could not be measured reliably from PLS.

Table 5. Trace element concentrations (ppm) in pregnant leach solutions (PLS) at the Talvivaara mine, Finland. Leaching time is an approximate. Concentrations are mean values of four samples and the uncertainty is their standard deviation.

Leaching Time	Ni	Zn	Cu	Co	Fe	Mn	Pb	Cr	Cd	U	Th
0.5 year	2150 ± 300	5030 ± 280	n.d.	44 ± 1	14,900 ± 330	6070 ± 170	LOD	4 ± 0.5	18 ± 1	24 ± 1	0.5 ± 0.01
1.0 year	2100 ± 300	4480 ± 250	n.d.	85 ± 1	8790 ± 330	5100 ± 140	0.03 ± 0.01	7 ± 1	18 ± 1	21 ± 1	1.0 ± 0.01
1.5 year	980 ± 140	2800 ± 140	n.d.	9 ± 0.3	12,300 ± 1860	7130 ± 130	LOD	0.3 ± 0.01	4 ± 0.1	16 ± 0.2	0.1 ± 0.01
2.0 year	860 ± 120	1920 ± 120	n.d.	22 ± 1	7070 ± 820	3810 ± 60	LOD	2 ± 0.2	6 ± 0.2	14 ± 0.1	0.2 ± 0.01

n.d. = not determined; LOD = below the detection limit.

Samples of the PLS were clear when taken from the ponds. On storage, a white flaky precipitate was seen to precipitate at the bottom of the vials when in contact with open air. XRD measurements revealed that this precipitate consists of gypsum and natrojarosite (approximately 50%:50%). These precipitates also contain fairly high concentrations of the target metals: 23 ppm Co, 110 ppm Cu, 1400 ppm Ni, and 2300 ppm Zn, on average, as measured by ICP-MS from dissolved solids. The concentration of U was low at 11 ppm. We may assume that the same process takes place on site and that there may be metal-bearing precipitates at the bottom of the ponds.

4.3. Metals in Waste Ponds

Non-valuable and residual metals are removed from the process liquids in three steps; one between ZnS and (Ni/Co)S precipitations and two after the latter. These processes use lime (CaO/Ca(OH)$_2$) and limestone (CaCO$_3$) to raise the pH for the precipitation/co-precipitation of the metals. Liquid is directed back to the leaching process whereas solids are pumped into a waste pond. This solid is composed of two major components, gypsum CaSO$_4$·2H$_2$O and calcium carbonate (CaCO$_3$) [9]. Amorphous ferric hydroxide is also present due its high amounts in ore materials. It cannot be seen by XRD but is indicated by the reddish brown colouration. The three processing steps result in heterogeneous solids, as shown in Table 5, where mean concentrations of metals in four replicate solid waste samples are given. The concentrations of metals vary over a large range from one sample to another, reflected in the high standard deviations of the mean, on average 130%. The solids mainly comprise Fe and Mn, but concentrations of Ni, Zn, and U are also fairly high. However, concentrations of the toxic trace metals, Cd, Cr, and Pb, are low. The second last row in Table 6 presents the ratios of the metal concentrations in the solid waste material to those in the unprocessed ore. The ratios obtained are in the order U > Ni > Mn > Fe > Co > Th > Pb > Zn = Cd > Cr > Cu, reflecting the tendency of metals to progressively accumulate from the ore to the waste. The corresponding series for accumulation from PLS to waste is Pb > Cr > Th > Fe > Co > Cd > Zn > Ni > Mn > U. These data are discussed later.

Table 6. Trace element concentrations (ppm) in process waste pond solids. Concentrations are the mean values of four samples.

	Ni	Zn	Cu	Co	Fe	Mn	Pb	Cr	Cd	U	Th
Mean concentration	420	160	5.0	10.0	30,500	4840	5.1	14	1.0	58	1.3
STDEV	340	140	2.5	6.0	24,700	13,900	5.2	31	0.7	93	2.7
Accumulation from ore to waste [1]	0.41	0.06	0.01	0.15	0.36	0.38	0.09	0.04	0.06	1.5	0.14
Accumulation from PLS to waste [2]	0.28	0.05		0.25	2.8	0.88	2000	4.1	0.10	3.1	2.9

[1] Ratio of the mean metal concentration in the solid pond waste to its concentration in the unprocessed ore; [2] Ratio of the mean metal concentration in the solid pond waste to its concentration in the pregnant leach solutions.

4.4. Release of Metals from the Ore in Laboratory Sequential Leach Tests

As discussed in the introduction, there will be three types of solid waste left on site when the mining process is complete: waste rock, secondary leaching heaps and process waste. The potential for re-mobilisation of metals from these materials was studied using a sequential leaching protocol in the laboratory. In this section we give the results for both unprocessed and leached ore; process waste is discussed in the next section.

Sequential leaching of target metals (Ni, Zn, Cu, Co) from the unprocessed ore shows that they behave in a more or less identical manner (Figure 3). In the first four fractions, exchangeable at 7.7 and 5.5, mild acid soluble and reducible fractions, the percentage of metals leached is between 5% and 10%. The values are unexpectedly high for the exchangeable fractions. In the fifth, oxidizable fraction, removal is around 50% for all of the above metals due to partial oxidation of sulphides to sulphates and dissolution. In 4 M HNO_3 (strong acid soluble fraction), which is also an oxidizing medium, all metal sulphides are oxidised and dissolved. Cd behaves similarly to the target metals except that, in the oxidizable and strong acid soluble fractions, the released percentage was considerably lower. Cr was the least soluble of all the metals investigated. U, Th, and Fe concentrations were also low in the exchangeable fractions.

The sequential leaching process was also applied to the primary stage and secondary stage leached ores in order to investigate how the bioleaching process affects the leachability of metals from Talvivaara ores. The leaching of metals from these two materials, when compared to their behaviour in the unprocessed ore, varies from one metal to another with no obvious systematic trend; however, the following tentative observations can be drawn. During leaching of the primary stage ore, the metal concentrations were, on average, 104% higher than in the unprocessed ore. This increase is due to leaching of the two exchangeable fractions, whereas in the oxidizable and strong acid soluble fractions, the concentrations decreased by 10–20% compared to unprocessed ore. The increase in the exchangeable fractions is evidently not caused by the increase of the exchangeable metals, but by the increased quantity of water soluble metal salts in the heaps due to water circulating from the PLS ponds back onto the heaps. In sequential leaching of the ore from the secondary leaching heap, metal concentrations decreased by 19% on average when compared to the values observed from leaching of the unprocessed ore. In this case, the metal concentrations were higher in the first exchangeable fraction (pH 7.7) than in the unprocessed ore but to a much lower extent than in the case of the primary leaching heap. One should also bear in mind that leached ore samples from a secondary leaching heap used in this study were not from heaps corresponding to the end of the bioheap leaching process but to heaps where leaching was still ongoing. Thus, it is likely that the leachability of metals will decrease still further up to the end point of the leaching process.
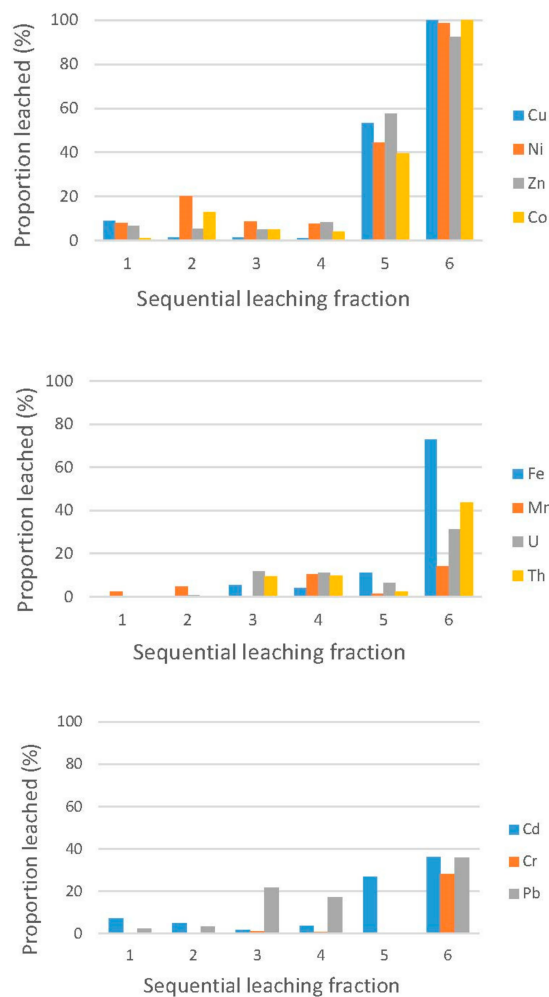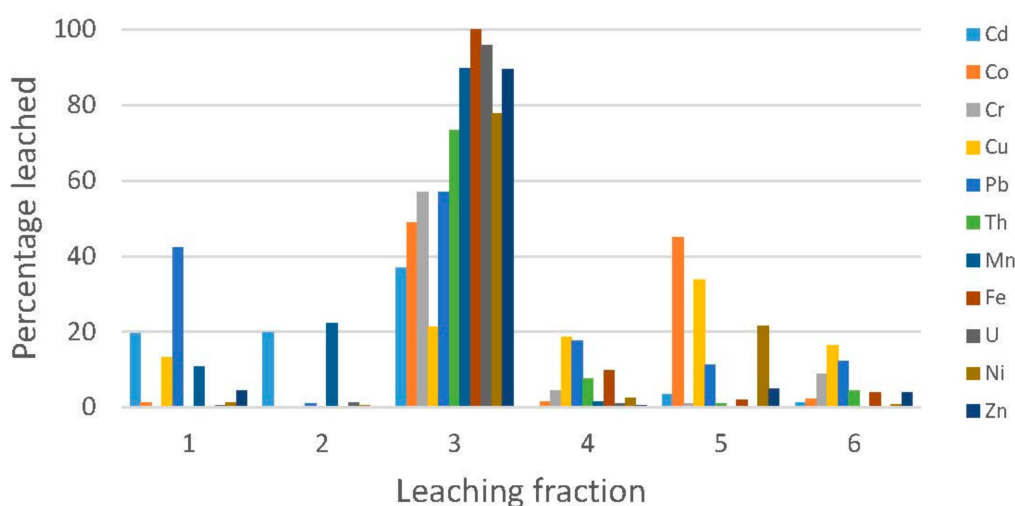
Figure 3. Release of metals from unprocessed Talvivaara ore in laboratory sequential leach tests. Leaching solutions: (1): exchangeable at pH 7.7, (2): exchangeable at pH 5.5, (3): mild acid soluble, (4): reducible, (5): oxidizable, and (6): strong acid soluble.

In conclusion, we may state that bioheap leaching becomes less efficient with time as the more soluble fractions are progressively removed from the ore. Nevertheless, the inventory of valuable metals remaining, as well as those of toxic Cd and Pb, is still significant from an environmental perspective. Even the oxidizable fraction is relevant here due to the likelihood of low pH values prevailing in the secondary heaps after the reclamation process and the potential for oxidation of residual pyrite generating acid mine drainage:

$$4FeS_2 + 15O_2 + 2H_2O \leftrightarrow 4Fe^{3+} + 8SO_4^{2-} + 4H^+ \tag{1}$$
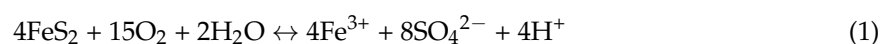
Thus, we may expect further leaching of metals from the processed ore after closure of the mine, if not properly sealed. Major points to be considered during sealing are prevention of water and oxygen intrusion into the heaps by means of impermeable barriers. According to current plans, the waste will be protected with a composite 1.5–2.0 m barrier comprising a plastic membrane, sand, and clay designed to prevent water ingress from above and below [18].

4.5. Release of Metals from Process Waste in Laboratory Sequential Leach Tests

The process waste stored in gypsum pond comprises mainly calcite, gypsum, and iron hydroxides [9,14]. The most effective leachant for metals from the process waste was acetic acid at pH

4.1 in which, on average, 68% of the metal content was dissolved (Figure 4). Most of the metals studied are known to form sparingly-soluble carbonates or co-precipitate with $CaCO_3$. Thus, dissolution of $CaCO_3$ releases these metals from the waste into solution. Mn and Cd were also found in both of the exchangeable fractions. Fairly large proportions of the Co and Cu were found in the oxidizable fraction, which may reflect the presence of residual sulphides of these metals in the process waste. Fraction 4 (Reducible), assumed to dissolve iron hydroxides, does not contain a large share of the metals, or at least not as great a share as the previous leaching step.

Figure 4. Release of metals from Talvivaara mine process waste in laboratory sequential leach tests. Leaching solutions: (1): exchangeable at pH 7.7, (2): exchangeable at pH 5.5, (3): mild acid soluble, (4): reducible, (5): oxidizable, and (6): strong acid soluble.

When evaluating prospective releases of metals from the materials to be left on site, i.e., secondary ore and process waste, it is apparent that concentrations are generally much lower in the latter (Table 7). The exceptions are the concentration of Mn, which is similar in the two materials, and the concentration of U, which is six times higher in the process waste. Conversely, the concentrations of Fe and Ni in the process waste are around half of those in secondary leaching ore, whereas the concentrations of other metals are 1–13% of those in the secondary leaching ore. On this basis, the secondary leaching ore might be considered the waste of greater environmental concern. However, when considering metal releases from sequential leaching, the picture is very different. The most environmentally-relevant steps are I–III, comprising exchangeable and mild acid soluble fractions. Here, the high mobilisation potential from process waste becomes evident from the values on the third row of Table 7; all metals are clearly more soluble from process waste than from secondary leaching ore, particularly in the case of U, Mn, Fe, and Cr. Further, the values for the secondary leached ore shown in Table 7 represent only two and a half years of heap leaching. By the end of the leaching process, metal concentrations are expected to be considerably lower.

Table 7. Ratios of metal concentrations in process waste to those in the leached ore from a secondary leaching heap.

Ratio	Ni	Zn	Cu	Co	Fe	Mn	Pb	Cr	Cd	U	Th
I	0.42	0.07	0.01	0.05	0.45	1.6	0.04	0.08	0.13	5.8	0.19
II	1.6	1.5	0.05	0.61	9.6	61	1.5	10	0.63	110	3.5

(I). ratio of concentration in process waste to that in the secondary leaching ore; (II) same ratio for concentrations in sequential leaching steps I–III (exchangeable and mild acid soluble fractions).

5. Conclusions

Very large quantities of solid material will be disposed of at the Talvivaara mine in Eastern Finland during the operation of the mine and at closure. The main mining waste types at the Talvivaara mine site are waste rock, leached ore, and process waste. In each case, the surface area exposed to circulating waters is very much higher than in the original rock, thus enhancing dissolution of minerals and the leaching of metals. Of these materials, the process wastes have the highest surface area and largely consist of calcium carbonate, which is soluble in mild acid; dissolution of calcium carbonate would release associated metals. The waste rock and leached ore contain residual sulphides, constituting a source of acid mine drainage which, in turn, would considerably enhance dissolution and leaching processes. Key factors in the final disposal plans are prevention of water and oxygen intrusion into the waste; this can be achieved by construction of impermeable barriers around the waste and diverting drainage water away from the waste deposits. These factors have been taken into account in current decommissioning and reclamation plans; nevertheless, geological processes will continue to affect the site over the very long term and the prevailing environmental conditions may well change.

In this study we observed the three following series for the transfer of metals in the Talvivaara process:

- mobilisation from ore to PLS decrease in the order U > Mn > Zn > Ni > Cd > Co > Fe > Th > Cu > Cr > Pb;
- accumulation from ore to waste decrease in the order U > Ni > Mn > Fe > Co > Th > Pb > Zn = Cd > Cr > Cu;
- accumulation from PLS to waste decrease in the order Pb > Cr > U > Th > Fe > Mn > Co > Ni > Cd > Zn

Based on these series we may draw conclusions on the behaviour of metals in the Talvivaara mining process relative to each other:

- U is easily leached from the ore and not retained in the metals recovery process, accumulating in the waste pond;
- Pb is not easily released from the ore and the very small fraction that is mobilised passes efficiently through the metals recovery process into the waste;
- Co is not easily released from the ore but is efficiently retained in the metals recovery process;
- Zn and Cd mobilise from the ore and are retained reasonable well in the metals recovery process. The same is true for Ni to an extent although a larger fraction is found in the waste pond; and
- Co behaves in an intermediate manner in all phases of the process compared to other metals

Author Contributions: Hanna Tuovinen carried out all experimental work except sequential leaching tests that were done by Mila Pelkonen. Janne Lempinen was a research assistant to some of the experiments done by Hanna Tuovinen. Jukka Lehto and David Read were supervisors whereas Esa Pohjolainen and Dina Solatie worked as experts.

Conflicts of Interest: There are no conflicts of interest in this study.

References

1. Ghorbani, Y.; Petersen, J.; Franzidis, J-P. Heap leaching technology—Current state, innovations, and future directions: A review. *Miner. Process. Extr. Metall. Rev* **2016**, *37*, 73–119.
2. Panda, S.; Akcil, A.; Pradhan, N.; Deveci, H. Current scenario of chalcopyrite bioleaching: A review on the recent advances to its heap-leach technology. *Bioresour. Technol.* **2015**, *196*, 694–706. [CrossRef] [PubMed]

3.　Reichardt, C. Heap leaching and the water environment—Does low cost recovery come at high environmental risk. In Proceedings of the 10th International Mine Water Association Congress, Karlsbad, Czech Republic, 2–5 June 2008.

4.　Akcil, A.; Koldas, S. Acid mine drainage (AMD): Causes, treatment and case studies. *J. Clean. Environ.* **2006**, *14*, 1139–1145. [CrossRef]

5.　D'Hugues, P.D.; Spolare, P. Bioshale Consortium, Biohydrometallurgy applied to exploitation of black shale resources: Overview of Bioshale FP6 European project. *Trans. Nonferr. Met. Soc. China* **2008**, *18*, 1485–1490. [CrossRef]

6.　Kutschke, S.; Guezennec, A.G.; Hedrich, S.; Schippers, A.; Borg, G.; Kamrath, A.; Gouin, J.; Giebner, F.; Schopf, S.; Schlömann, M.; et al. Bioleaching of Kupferschliefer blackshale—A review including perspectives of the Ecometals project. *Miner. Eng.* **2015**, *75*, 116–125. [CrossRef]

7.　Loukola-Ruskeeniemi, K.; Lahtinen, H. Multiphase evolution in the black shale-hosted Ni-Cu-Zn-Co deposit at Talvivaara, Finland. *Ore Geol. Rev.* **2013**, *52*, 85–99. [CrossRef]

8.　Talvivaara Sotkamo, Oy. *Talvivaaran Kaivoksen Kaivannaisjätteen Jätehuolto-Suunnitelma*; Lapin Vesitutkimus Oy: Rovaniemi, Finland, 2012. (In Finnish)

9.　Tuovinen, H.; Pohjolainen, E.; Lempinen, J.; Vesterbacka, D.; Read, D.; Solatie, D.; Lehto, J. Behaviour of Radionuclides during microbially-induced mining of Ni at Talvivaara, Eastern Finland. *J. Environ. Radioact.* **2016**, *151*, 105–113. [CrossRef] [PubMed]

10.　Riekkola-Vanhanen, M. Talvivaara mining company—From a project to a mine. *Miner. Eng.* **2013**, *48*, 2–9. [CrossRef]

11.　Riekkola-Vanhanen, M. Talvivaara Sotkamo mine—Bioleaching of a polymetallic Ni ore in subarctic climate. *Nova Biotechnol.* **2010**, *10-1*, 7–14.

12.　Kontinen, A.; Hanski, E. The Talvivaara black shale-hosted Ni-Zn-Cu-Co deposit in eastern Finland. In *Mineral Deposits of Finland*; Maier, W.D., O'Brien, H., Lahtinen, R., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 557–607.

13.　Lecomte, A.; Cathelineau, M.; Deloule, E.; Brouand, M.; Peiffert, C.; Loukola-Ruskeeniemi, K.; Pohjolainen, E.; Lahtinen, H. Uraniferous bitumen nodules in the Talvivaara Ni-Zn-Cu-Co deposit (Finland): Influence of metamorphism on U mineralization in black shales. *Miner. Depos.* **2014**, *49*, 513–533. [CrossRef]

14.　Pitkäjärvi, J. Bioheap leaching of black schist-hosted Ni-Co-Co-Zn ore in subarctic conditions at Talvivaara, Finland. In *Seventh International Mining Geology Conference: 17–19 August 2009, Perth Western Australia*; Australasian Institute of Mining and Metallurgy: Carlton, Australia, 2009; pp. 239–244.

15.　Tuovinen, H.; Vesterbacka, D.; Pohjolainen, E.; Read, D.; Solatie, D.; Lehto, J. A comparison of analytical methods for determining U and Th in ores and mill tailings. *J. Geochem. Explor.* **2015**, *148*, 174–180. [CrossRef]

16.　Outola, I.; Inn, K.; Ford, R.; Markham, S.; Outola, P. Optimizing standard sequential extraction protocol with lake and ocean sediments. *J. Nucl. Radioanal. Chem.* **2009**, *282*, 321–327. [CrossRef]

17.　Ahonen, L.; Tuovinen, O.H. Solid-phase alteration and Fe transformation in column bioleaching of a complex sulfide ore, in Environmental Geochemistry of Sulphide Oxidation. *ACS Symp. Ser.* **1994**, *50*, 79–89.

18.　*Talvivaaran kaivos, Alustava Sulkemissuunnitelma*; Pöyry Report; Pöyry Environment Oy: Oulu, Finland, 2009; (In Finnish)