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## The use of a four-stage sequential leaching procedure and the corresponding one-phase extractions for risk assessment of potential harmful substances in waste rock utilized in railway ballast

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The purpose of environmental legislation in the EU is prevention, minimization, and utilization of waste, respectively. When utilization is not possible, the purpose becomes the safe landfill disposal of waste, or disposal by other ecologically beneficial methods. In addition, material efficiency is an essential topic nowadays to promote the sustainable use of natural resources, waste materials, and industrial by-products, in agreement with the principle of sustainable development and LCA. To promote these goals, a four-stage sequential leaching procedure and determination of total concentrations was used in this research to determine the distribution of Cu, Pb, Zn, and V samples taken from waste rock material, originating from a Finnish zinc mine, and used as railway ballast in Northern Finland. The leaching procedure consists of the following five sequential fractions: (i) an acidic water-soluble fraction (H<sub>2</sub>O, pH = 4), (ii) an exchangeable fraction (CH<sub>3</sub>COOH), (iii) an easily reduced fraction (NH<sub>2</sub>OH-HCl), and (iv) oxidizable fraction (H<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>COONH<sub>4</sub>). The results show that conditions and the size of ballast have a significant effect on the solubility of all heavy metals, and therefore on their mobility, bioavailability, and environmental risk. In addition, the total concentration of every element is much larger than its solubility in each four fractions (i)–(iv) or the sum of these concentrations – this sum can be called by the potential bioavailability – because the highest concentration is in the residual fraction. The leachability results determined here for waste rocks utilized as railway ballast show in good agreement with all earlier investigations determined for other waste or industrial by-products. Sequential leaching studies provide valuable information about the effect of conditions on the leachability/solubility, mobility, and bioavailability for risk assessment of harmful heavy metals. This information is necessary if we want to know the real environmental risk of metals in different conditions, possible in natural conditions now and in the future, i.e. not only in terms of the conditions pertaining to permission applications.

**Keywords:** railway ballast; waste rock; bioavailability; risk assessment; leaching; heavy metals

### Introduction

Leaching is a procedure that is applied for the purpose of extracting elements from various environmental samples such as soils, sediments, airborne particles, sludge, fly and bottom ashes, green liquor, and waste rock, and has become a common term in the environmental analytical field.[1–4] Leaching does not mean total decomposition, and therefore, the leachable recoveries of chemical species are generally lower than their total concentrations. Recoveries can only reach the total values if an element is completely soluble in the leaching solvent. Leaching studies are carried out in the assessment of worst case environmental scenarios, in which the components of the sample become soluble and mobile.[5]

From an environmental point of view, it is not the total concentration in waste, sludge, railway ballast, and other residues which are of most importance, but rather how easily the metals can be mobilized in the environment. Bioavailability is a measure of the

“environmental mobility and bioavailability” of elements. The loosely bound fractions, e.g. water-soluble fraction and the fraction leachable with ammonium acetate or acetic acid, are much more environmentally mobile than those associated with silicate structure, i.e. leachable with a mixture of strong mineral acids. Thus, the loosely bound fractions are most likely to be release into aqueous solutions and therefore are potentially bioavailable.[1]

The mining industry is at the present time a rapidly increasing production sector in northern and eastern parts of Finland. Many new mines have been opened recently and others are in the planning phase. Mining legislation has been recently revised and the compilation of an ID – directive [6] required to implement environmental law revision is in progress. Finnish mining legislation has been revised to comply with the corresponding EU legislation. The goal of this new legislation is to support the national and EU strategy concerning waste materials.

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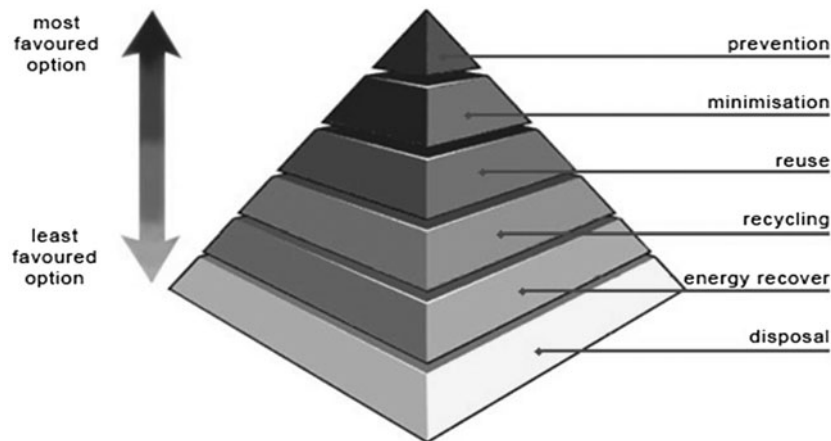


Figure 1. The waste hierarchy pyramid.[19]

The purpose of environmental legislation in the European Union is prevention, minimization, and utilization of waste, respectively. When utilization is not possible, the purpose becomes safe landfill disposal of waste, or disposal by other ecologically beneficial methods. In addition, material efficiency [7,8] is an essential topic in promoting sustainable use of natural resources, waste materials, and industrial byproducts in agreement with the principle of sustainable development and LCA (life cycle assessment). The different options available for dealing with waste can be described clearly by a “waste hierarchy” as shown in Figure 1. Comprising of six levels, the first goal of the waste hierarchy is the prevention of waste. If this is not possible, the next step down the pyramid is the minimization of waste followed by reuse, recycling, energy recovery, and finally, if none of the initial five steps is feasible, waste can be disposed by ecologically beneficial methods.

The new waste law in Finland was approved on 17 June 2011 with its changes taking effect on 1 May 2012. The main goal of the revised waste law was to modernize legislation so that it complied with the emphasis of environment politics and the demands of EU legislation. With this revision, prevention of waste formation and regulations that promote waste recycling was evaluated.[9]

Government Degree (VNa 214/2007) [10] established the basic criteria of fees and charges related to the development, analysis, and verification of documentation for registration in the land cadaster. Assessment of soil contamination and remediation needs should be based on an assessment of the hazard or harm to health or the environment represented by harmful substances in the soil.[4,10] The guideline values for harmful substances in soil, prescribed in the appendix to this Decree, must be used as a tool in assessing soil contamination and remediation needs. Unless otherwise determined in the assessment referred to the Government Degree (VNa 214/2007) [10], soil is regarded as contaminate:

- (1) in an area used as an industrial, storage, or transport area or other corresponding area if the concentration of one substance or several substances exceeds the prescribed upper guideline value;
- (2) in an area other than that referred to in paragraph 1 if the concentration of one substance exceeds the prescribed lower guideline value. The threshold and guideline values for the concentrations of some common harmful substances in soil, expressed as total concentration per dry matter, are presented in Table 1.

Table 1. Guideline values of VNa 214/2007.

Element	Threshold value <sup>a,b</sup>	Lower guideline value <sup>a,b</sup>	Higher guideline value <sup>a,b</sup>
As	5	50	100
Cd	1	10	20
Co	20	100	250
Cr	100	200	300
Cu	100	150	200
Ni	50	100	150
Pb	60	200	750
Sb	2	10	50
V	100	150	250
Zn	200	250	400

<sup>a</sup>VNa 214/2007.

<sup>b</sup>[mg/kg] dry weight. Boldface highlights are concentrations which are higher than their higher guideline values in VNa 214/2007.

### The aim of this work

Only scarce information is available from the use of sequential leaching as the study of utilization of the mine gangue [4,11]. Thus, the first aim of this study was to obtain more information about the suitability of a sequential leaching procedure for the utilization of the mine gangue. It is this lack of scientific knowledge which is necessary if we are to know the real environmental risk of metals in rocks in different conditions, possible sometimes in the future in natural conditions, not only in terms of the conditions pertaining to permission applications.

The second aim of this study was to compare results of a four-step sequential leaching procedure and its corresponding one-phase extractions separately by determining the distribution of zinc, copper, lead, and vanadium in combination samples taken from waste rock materials, originating from the Lampinsaari mine, and used as railway ballast in Northern Finland. Knowing that the size of studied material in all standard methods must be less than 2 mm, we also wanted to find out what particle size of the ballast effects on the bioavailability/solubility of hazardous heavy metals.

It is generally known that in the case of sulfur in nature, we must take into account slow sulfide oxidation to sulfate  $\text{SO}_4^{2-}$ , or acid production potential (AP). So, we have determined in co-operation with Geological Survey of Finland (GTK), the large Finnish Geological Institute, the values of acid production potential (AP), neutralization potential (NP), as well as the values of neutralization potential ratio ( $\text{NPR} = \text{NP}/\text{AP}$ ) for some waste rock samples originating from the Lampinsaari zinc mine. The values of NPR varied obviously but show that the effect of their neutralization potential ratio NPR on the environment in their use as railway ballast is not significant. Investigated waste rocks go mainly to the classification of inert waste category. In addition, we would mention that this kind of procedure has not been yet required for permission in Finland when waste rock has been utilized as railway ballast outside of mining area.

## Experimental

### Sampling

The waste rock material investigated here was originally obtained from the zinc mine in Vihanti situated in northern Finland and has been utilized as railway ballast since the 1960s. The main ore minerals in the Vihanti mine were sphalerite ( $\text{ZnS}$ ), chalcopyrite ( $\text{CuFe}_2$ ), pyrrhotite ( $\text{FeS}$ ), and pyrite ( $\text{FeS}_2$ ). The same minerals also occur in Vihanti mine's gangue, but values of heavy metals can repeatedly change. Combination samples were collected from single railway ballast samples in June 2009 in Vihanti. The waste rock materials were washed and crushed into two suitable fractions (<2 mm and 8–16 mm) in Oulun Geolaboratorio Oy before any chemical analyses could be made.

### Sequential extraction procedure and element determination

The effects of external conditions on the leachability/solubility of heavy metals in combination samples for sample material less than 2 mm and 8–16 mm, respectively, were studied using a four-stage sequential leaching extraction procedure.

The leaching procedure used here (Figure 2) consists of the following four sequential fractions: (1) water-soluble fraction ( $\text{H}_2\text{O}$ ), (2) exchangeable fraction ( $\text{CH}_3\text{COOH}$ ), (3) easily reduced fraction ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), and (4) oxidizable fraction ( $\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$ ). To determine the total heavy metal concentration in samples of less than 2 mm,  $c_{\text{tot}}$  (M), the dried material was decomposed with a mixture of  $\text{HNO}_3$  and  $\text{HCl}$  in a CEM Mars 5 microprocessor-controlled microwave oven with CEM HP 500 Teflon vessels using the US EPA method 3051A. In the sequential leaching procedure, the element concentrations in the extracts and the total element concentrations in the samples were determined with a Thermo Electron IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer. In the second part of this investigation, single one-phase leachings, the same as in sequential leaching procedures, were carried out separately for waste rock material samples of less than 2 mm (the size used in the standard method, US EPA 3051A [12]). The leaching procedure has been previously described in much detail in our previous publications.[2,4,13–15]

In the second part of this study, single one-phase leachings were performed for the combination sample, whereas every leaching stage in the four-stage sequential leaching procedure was carried out separately for the waste rock material sample. Separate leaching stages were performed as described above. Thus, the values of leachability of heavy metals can be compared to corresponding values taken from the four-stage sequential leaching procedure (Figure 2).

In order to minimize possible chemical changes in the samples, the extraction was carried out using wet samples instead of dried samples. After each extraction step, the extract was separated from the solid residue by filtration through a 0.45- $\mu\text{m}$  membrane filter (47 mm diameter). In order to avoid losses between the extraction stages, the filters and adhering waste rock material particles from the previous extraction stage were also included in the next stage. In the sequential leaching procedure, element concentrations in the extracts were determined with a Thermo Electron IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer at Suomen Ympäristöpalvelu Oy, a FINAS accredited test laboratory (T231).

For quality control purposes, all analyses from real samples and method blanks were carried out as duplicate determinations. As an internal check on the validity of the test results, the total amounts of the extracted elements in the previously described five-stage sequential

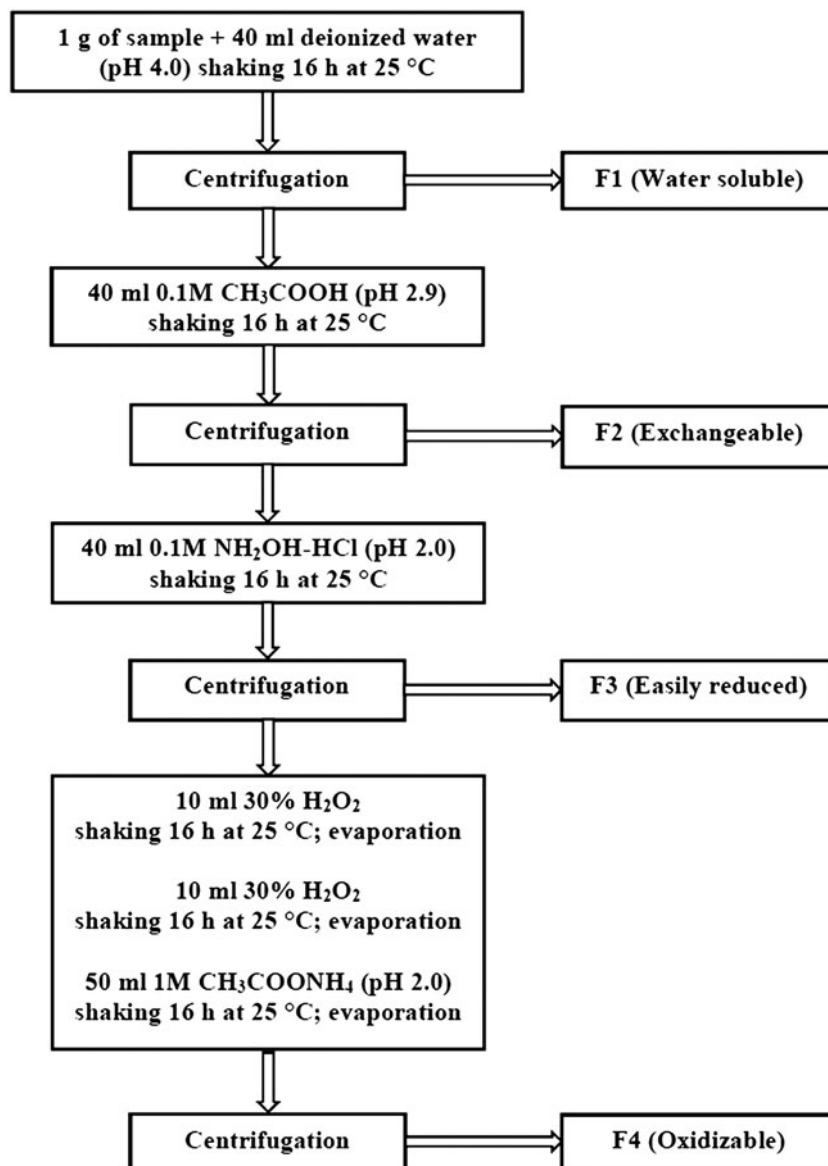


Figure 2. Four-stage sequential leaching procedure used in this study.

procedure  $C_{\text{sum}}(\text{M})$  were compared with total concentrations  $C_{\text{tot}}(\text{M})$  obtained by the US EPA 3050 method. Mean recovery (%) ( $n = 3$ ) for each element was calculated using the following ratio:  $[C_{\text{sum}}(\text{M})/C_{\text{tot}}(\text{M}) \times 100]$ . The validity on the test method has been investigated in more detail in our earlier studies.[3,13,16]

#### Up-flow percolation test

The release of constituents from waste rock material was studied using a column with a leachant percolating through it. The upflow percolation test (under specified conditions), CEN/TS 14405:2004,[17] was carried out at Suomen Ympäristöpalvelu Oy. This investigation was performed only for the sample with the smallest particle size (<2 mm) using a 31 cm-height column. The column was filled with crushed railway ballast under strict instructions. After filling the column with waste rock to

be investigated, the column was saturated with water using a pump. The flow rate of the water was such that the linear velocity was  $15 \pm 2$  cm/day through the empty column. The leachant was then percolated through the column at a specified flow rate up to a fixed L/S (liquid to solid) ratio. The eluent was collected in seven separate fractions so that the last one collected had an L/S ratio of 10. Finally, the collected samples were analyzed with a Thermo Electron IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer. For the analysis of each fraction, 5 ml of extract was taken and added to 500  $\mu\text{l}$  69–70%  $\text{HNO}_3$  (Table 3).

#### Results and discussion

Table 2 presents the results of the leachable concentrations in stages 1–4 of a four-stage sequential leaching procedure for two samples with a particle size less than 2 mm and

Table 2. Leachable concentrations in stages 1–4 for a four-stage sequential leaching procedure for two samples (particle size <2 mm and 8–16 mm), and the total concentrations  $c_{\text{tot}}$  (M) determined by the EPA Method 3051A and the degree of potential bioavailability PBP (Equation (1)) for the sample with the smallest particle size (<2 mm).

Metal	Results of analysis (mg/kg dry weight)								Total concentration <sup>a</sup> <2 mm	PBP (%) <sup>b</sup> <2 mm
	Stage 1 <sup>a</sup>		Stage 2 <sup>a</sup>		Stage 3 <sup>a</sup>		Stage 4 <sup>a</sup>			
	<2 mm	8–16 mm	<2 mm	8–16 mm	<2 mm	8–16 mm	<2 mm	8–16 mm		
Al	5.4	<1	210	34.9	1060	220	1790	230	12500	24.5
As	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.75	<0.75	5	51
Ba	1.5	1.7	14.7	6.9	17.0	2.9	15.5	4.7	170	28.7
Be	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.25	<0.25	<1	85
Cd	<0.08	<0.08	0.22	<0.08	0.094	<0.08	1.53	<0.1	3.8	50.6
Co	<0.12	<0.12	0.80	<0.12	0.68	<0.12	5.40	1.7	29	24.1
Cr	<0.4	<0.4	0.92	<0.4	0.86	<0.4	0.70	<0.5	11	26.2
Cu	<0.4	<0.4	6.5	0.72	10.0	1.95	290	30.5	500	61.4
Fe	<0.6	<0.6	380	58.8	1250	210	10300	1920	58000	20.6
Mn	0.27	0.32	46.2	7.3	15.0	4.1	14.6	6.9	200	38
Mo	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.45	<0.25	3	35
Ni	<0.2	<0.2	3.6	<0.2	3.1	0.39	27.8	6.1	53	65.5
Pb	0.69	<0.6	910	10.6	300	10.4	73	5.0	1330	96.5
Sb	<0.6	<0.6	<0.6	<0.6	0.78	<0.6	1.3	<0.75	6	54.7
Se	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	1.1	<1	<4	87.5
Sn	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.75	<0.75	<2	DN <sup>c</sup>
V	<0.4	<0.4	<0.4	<0.4	3.3	0.52	1.6	<0.5	<u>180</u>	3.2
Zn	<0.4	<0.4	59.8	1.8	24.1	2.0	310	9.2	590	66.8

<sup>a</sup>[mg kg<sup>-1</sup>] dry weight. Bold highlights are total concentrations which are higher than in 214/2007.

<sup>b</sup> $PBP_M = \frac{\sum_{i=1}^4 c_i(M)}{c_{\text{tot}}(M)} \times 100\%$  higher guideline values in (VNa 214/2007). The underlined total concentration is higher than its lower guideline value in VNa.

<sup>c</sup>Not determined.

between 8 and 16 mm. In addition, the total concentrations ( $c_{\text{tot}}$ ) determined by the EPA Method 3051A and the values of potential bioavailability ( $PBP_M$ ) for the sample with a smaller particle size (<2 mm) are also presented in the same table. Since the conditions in stages (1)–(4) represent realistic possible risk conditions at least in the future, potential bioavailability percentages  $PBP_M$  (%) can be calculated from the sum of the concentrations of M in (1)–(4), and the total concentration  $c_{\text{tot}}$  (M), using Equation (1), where  $c_i$  (M) is the concentration of metal M in stage  $i$ . The value of  $c_{\text{tot}}$  (M) can be calculated either from the sum of concentrations in all stages or directly by some standard determination method. The values of residual percentage (%) and concentration  $c_{\text{residual}}$  (M) can be calculated with Equations (2) and (3).

$$PBP_M = \frac{\sum_{i=1}^4 c_i(M)}{c_{\text{tot}}(M)} \times 100\% \quad (1)$$

$$\text{Residual (\%)} = 100\% - PBP_M \quad (2)$$

$$c_{\text{residual}} (M) = (100 - PBP_M) \times c_{\text{tot}} \quad (3)$$

Potential bioavailability ( $PBP_M$ ) of railway ballast has been studied in much detail in our earlier studies.[4]

It can be seen from Table 2 that  $[Cu_{\text{tot}}]$ ,  $[Zn_{\text{tot}}]$ ,  $[Pb_{\text{tot}}]$ , and  $[V_{\text{tot}}]$  values are much higher than their values in each of the first four “bioavailable” fractions (1–4); the highest concentrations of all metals occurred on the residual

fraction, called “the inert phase” (cf. Equations (1)–(3)). The total concentration of  $[Zn_{\text{tot}}]$ ,  $[Cu_{\text{tot}}]$ , and  $[Pb_{\text{tot}}]$  (500 mg/kg, 590 mg/kg, and 1330 mg/kg) is higher than their guideline values 400 mg/kg, 200 mg/kg, and 750 mg/kg, respectively, in the Finnish Pima decree ([10]; Table 1) but their real solubility (e.g. PBP values) is relatively poor. This will be discussed later. It is noteworthy to suggest that the results of sequential leaching can be utilized in the future according to the current EU strategy of waste policy and the principle of material efficiency for the recycling of industrial waste materials, such as the waste rock studied here (Figure 1).

### Potential bioavailability percent (PBP)

Values of the degree of potential bioavailability of heavy metals PBP (%) in the studied railway ballast, with Equation (1), are presented in Table 2. The PBP values show that the degree of potential bioavailability changes strongly with the heavy metal. This is in agreement with our earlier observations of heavy metals [4] and can be calculated also for ash and other waste materials.[2,3,15] PBP value for lead compound is near 100% (96.5%) which shows that lead is potentially bioavailable in natural conditions, but in contrast, vanadium with a  $PBP_V$  value of 3.2% is very poor bioavailable in potential environmental conditions. PBP values for copper and zinc, 61.4 and 66.8%, respectively, show that they are partly bioavailable in any potential environmental conditions.

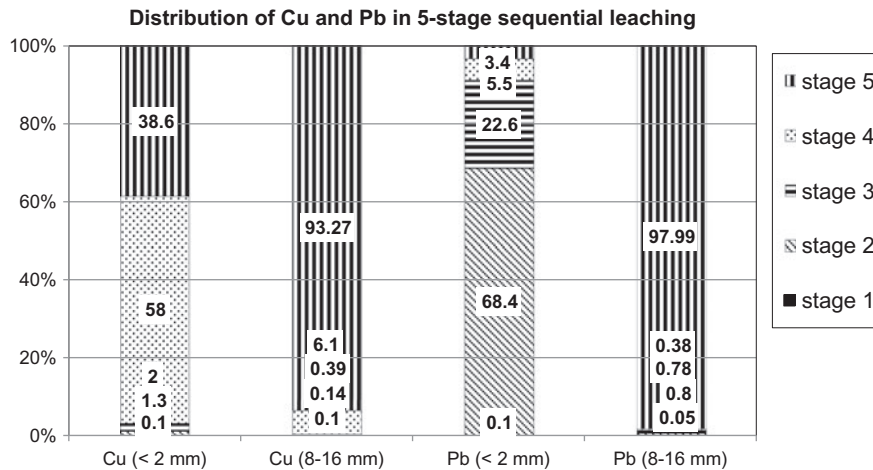


Figure 3. Distribution of Cu and Pb leachable concentrations in stages 1–5 where the values in stages 1–4 are determined from a four-stage sequential leaching procedure (particle size <2 mm and 8–16 mm), whilst the values obtained in stage 5 are calculated from  $M_{\text{tot}}$  using Equations (1)–(3).

#### *Leachability of heavy metals in a sequential procedure*

The distribution of zinc, copper, lead, and vanadium metals in a five-stage sequential leaching procedure for two samples (particle size <2 mm and 8–16 mm) are shown in Figures 3–4. The values of stage 5 are calculated from the results of the four-stage procedure by Equations (2)–(3). The conditions of this phase – three strong acids and strong, long-lasting shaking – are never possible in nature. From an environmental point of view, this residual fraction is therefore environmentally the least harmful. From these results, it can be seen that external conditions, which vary strongly in this study, have a large effect on the leachability of all elements, and therefore, it is easy to conclude – this is important for practical purposes – that the conditions also have a strong effect on the solubility of heavy metals in nature. In addition, the diagrams in Figures 3–4 clearly change for each individual heavy metal which means the effect of external conditions on the

leachability/bioavailability/mobility is very different for different species. This conclusion is in good accordance with earlier results determined for the same heavy metals of different waste or industrial byproduct materials.[2–4,13–16]

It is important to observe that in the sequential leaching procedure, metals are extractable in all fractions, but the highest concentrations of all metals occur in the residual fraction, stage 5. We can also see from Figures 3–4 that the size of the ballast sample/block has a strong effect on the extractability/bioavailability of all heavy metals studied. When the particle size is 8–16 mm, the proportion of each heavy metal is much larger in the residual fraction (fraction 5) than its corresponding value when the particle size is less than 2 mm, or the particle size in all common standards. From a practical point of view, this conclusion is very important because at least the size of waste rocks utilized in railway ballast is much larger than the particle size required by standards.

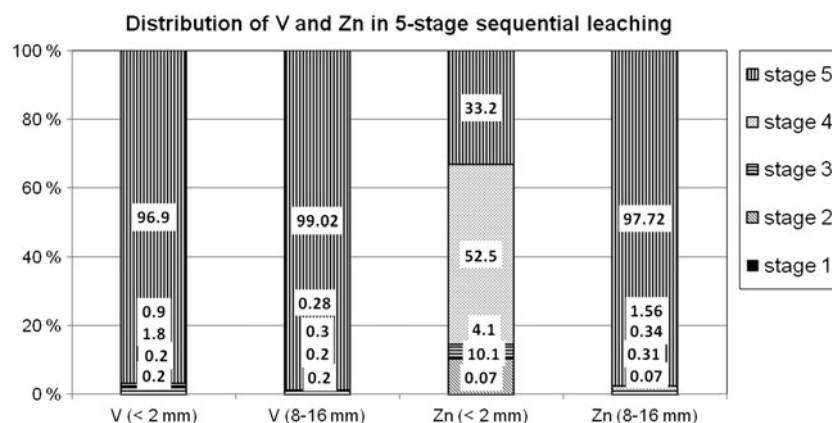


Figure 4. Distribution of V and Zn leachable concentrations in stages 1–5 where the values in stages 1–4 are determined from a four-stage sequential leaching procedure (particle size <2 mm and 8–16 mm), whilst the values obtained in stage 5 are calculated from  $M_{\text{tot}}$  using Equations (1)–(3).

### Distribution of heavy metals in stages 2–4; four-stage leaching procedure and single extractions

Figures 5–8 present the results for heavy metals Zn, Cu, Pb, and V using (i) a single extraction fraction of sequential leaching procedure (centre of each diagram), (ii) the corresponding amount in this extraction stage (on the left side of each diagram), and (iii) the sum concentrations  $\Sigma c_i$  (M) ( $i = 2$  for step 2,  $i = 3$  for step 3 and

$i = 4$  for step 4; on the right side of each diagram), all presented in proportions (%) of  $c_{\text{tot}}$  (M). Values of the studied heavy metals in steps 2, 3, and 4 expressed in three ways are all quite similar in each leaching step, being different for each heavy metal. These surprising results can be explained by the fact that the conditions in the sequential procedure are becoming more difficult step by step. As far as, we know this kind of combination of

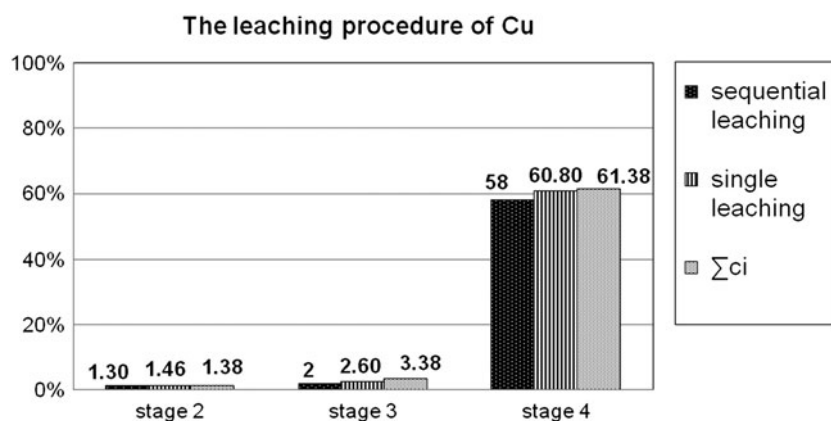


Figure 5. Distribution of Cu in stages 2–4 in the 4-stage sequential leaching procedure.  $\Sigma c_i$  (Cu) describes the sum value where  $i = 2$  for step 2, 3 for step 3 and 4 for step 4, respectively. The proportions (%) are calculated by dividing the concentration values by  $c_{\text{tot}}$  (Cu) and then multiplied by 100.

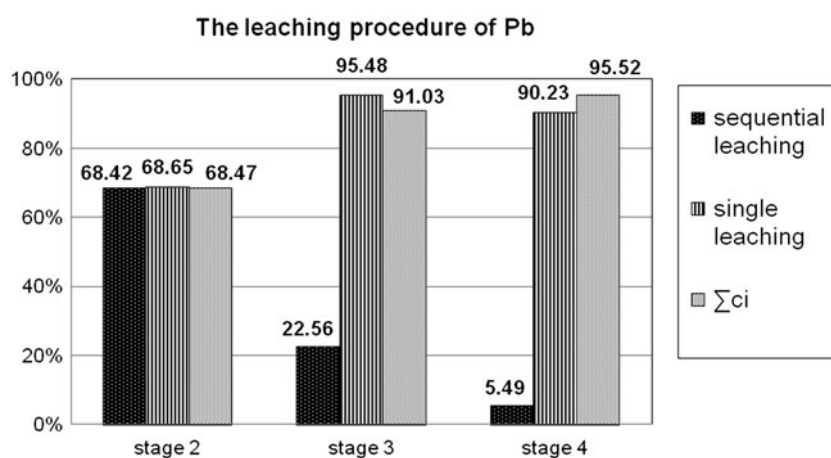


Figure 6. Distribution of Pb in stages 2–4 in the 4-stage sequential leaching procedure.  $\Sigma c_i$  (Pb) describes the sum value where  $i = 2$  for step 2, 3 for step 3 and 4 for step 4, respectively. The proportions (%) are calculated by dividing the concentration values by  $c_{\text{tot}}$  (Pb) and then multiplied by 100.

Table 3. Up-flow percolation test under specified conditions.

Sample <2 mm Metal	Results [mg/kg] of analysis according to cumulative L/S ratio [L/kg dry matter]							Limit values <sup>b</sup>
	L/S 0.1 <sup>a</sup>	L/S 0.2 <sup>a</sup>	L/S 0.5 <sup>a</sup>	L/S 1.0 <sup>a</sup>	L/S 2 <sup>a</sup>	L/S 5 <sup>a</sup>	L/S 10 <sup>a</sup>	
Cu	<0.001	<0.002	<0.005	<0.01	<0.02	<0.05	<0.1	2
Pb	<0.0015	<0.003	<0.0075	<0.015	<0.030	<0.075	<0.15	0.5
V	<0.001	<0.002	<0.005	<0.01	<0.02	<0.05	<0.1	–
Zn	0.010	0.019	0.030	0.037	0.047	0.075	0.13	4

<sup>a</sup>L/S is expressed in [L/kg] dry matter.

<sup>b</sup>Limit values according to VNa 202/2006.



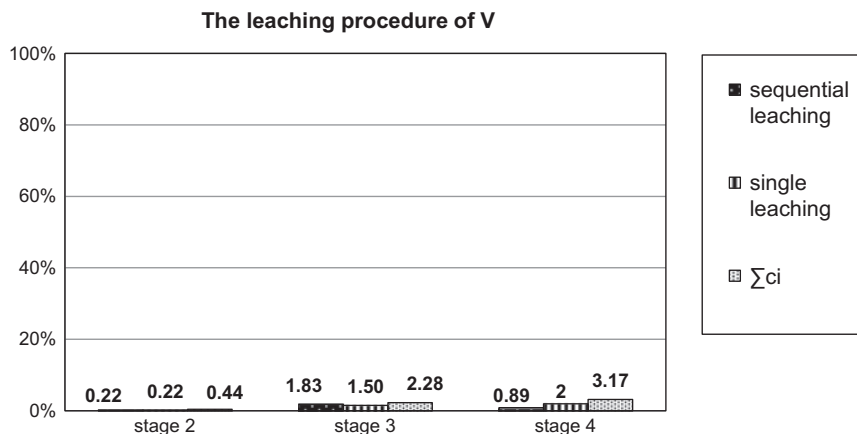


Figure 7. Distribution of V in stages 2–4 in the 4-stage sequential leaching procedure.  $\sum c_i$  (V) describes the sum value where  $i = 2$  for step 2, 3 for step 3 and 4 for step 4, respectively. The proportions (%) are calculated by dividing the concentration values by  $c_{tot}$  (V) and then multiplied by 100.

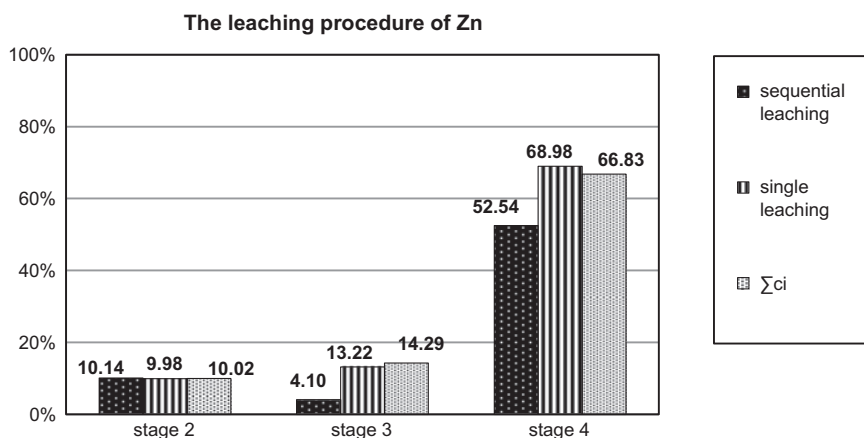


Figure 8. Distribution of Zn in stages 2–4 in the 4-stage sequential leaching procedure.  $\sum c_i$  (Zn) describes the sum value where  $i = 2$  for step 2, 3 for step 3 and 4 for step 4, respectively. The proportions (%) are calculated by dividing the concentration values by  $c_{tot}$  (Zn) and then multiplied by 100.

results from single extractions with the data from the corresponding sequential leaching procedure has not been reported previously in literature.

#### *Up-flow percolation test*

The results of the upflow percolation test are presented in Table 3. According to test, the leachable recoveries of species are all very low. In addition, the solubilities of all elements studied are below the limits given for the permanent waste landfills solubilities.[18] Unfortunately, conditions in nature are never the same as in laboratories and the continuing upflow test does not represent real conditions in nature. This is because the test provides information on dissolution in only one selected condition. However, our results based on this study are below the limit values (VNa 202/2006) and the results are in accordance with the corresponding values in acidic water-soluble fraction, shown in Table 2.

#### **Conclusions**

The policy of recycling and the eco-efficient utilization of railway ballast require better control of the undesired release of contaminants into the environment. The single chemical determination methods (the total contents) used in the EU and in Finland provide only poor information for risk assessment on solubility, mobility, and the bioavailability of harmful heavy metals. Therefore, it is important to estimate the leaching potential of toxic metals when assessing the possible environmental impacts associated with railway ballast reuse.

In summary, we can note:

- (1)  $[Cu_{tot}]$ ,  $[Zn_{tot}]$ ,  $[V_{tot}]$ , and  $[Pb_{tot}]$  values are much larger than their values in each of the first four “bioavailable” fractions (1)–(4); the highest concentrations of all metals occurred on the residual fraction, called “the inert phase”.

- (2) The total concentration of  $Zn_{tot}$ ,  $Cu_{tot}$ , and  $Pb_{tot}$  is higher than its guideline values in the Finnish Pima decree, but their possible solubilities in natural conditions are poor.
- (3) The size of a ballast sample/block has a large effect on the solubility of all heavy metals, and therefore, on the mobility, bioavailability, and environmental risk of harmful heavy metals.
- (4) The conditions have a large effect on the leachability/solubility of all heavy metals, differing between the various metals tested and therefore, the total concentration of heavy metal is a poor measure of the real environmental risk.
- (5) The obtained values of Zn, Cu, V, and Zn in steps 2, 3, and 4 using a corresponding single leaching determination are quite similar to their concentrations in these steps in the sequential procedure, as well as to their sum concentrations  $\Sigma c_i$  (M) ( $i = 2$  for step 2,  $i = 3$  for step 3 and  $i = 4$  for step 4).
- (6) The solubilities of all elements studied in the upflow percolation test are below their limits given for the permanent waste landfills solubilities in Finland.
- (7) It can be supposed that the results of sequential leaching can be utilized in the near-future according to current EU strategy of waste policy and the principle of material efficiency for the recycling of industrial waste materials, such as waste rock studied here.

The leachability results presented here for waste rocks utilized as railway ballast show in good agreement with all previous investigations that sequential leaching studies provide valuable information about the effect of conditions on the leachability/solubility, mobility, and bioavailability for risk assessment of harmful heavy metals. This information is necessary if we want to know the real environmental risk of metals in different natural conditions, now and also in the future. Currently, it is usual that the licensing authority considers only total element concentrations when admitting permit decisions in Finland. So, we believe that our studies provide a new perspective on the risk assessment of the contaminated soil and legislative reform work in Finland and in the EU.

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No potential conflict of interest was reported by the author.

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