THE USE OF SEQUENTIAL LEACHING PROCEDURE AND CORRESPONDING ONE-PHASE EXTRACTIONS FOR RISK ASSESSMENT OF HEAVY METALS IN WASTE ROCK UTILIZED IN RAILWAY BALLAST

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Juhani Kaakinen
Toivo Kuokkanen
Official background (25 years)
I am working in Centre for Economic Development, Transport and the Environment in Finland (13)
Environmental protection (land, air, water, contaminated sizes)
I am PhD student in University of Oulu
ELY Centres and offices

- **Lapland**: Rovaniemi, Kemi
- **Kainuu**: Kajaani
- **North Ostrobothnia**: Oulu, Ylivieska
- **Ostrobothnia**: Vaasa, Kokkola
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- **Uusimaa**: Helsinki

Juhani Kaakinen, Chief of Environmental Protection Unit
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Background

- The waste rock material investigated in this study was originally obtained from the zinc mine in the village of Vihanti and utilized as railway ballast since the 1960s. All the railway ballast samples were taken in 2009.
- This presentation will provide some more details related to the text presented in the abstract.
Four-stage sequential leaching procedure used in this study

1 g of sample + 40 ml deionized water (pH 4.0) shaking 16 h at 25 °C

Centrifugation → F1 (Water soluble)

40 ml 0.1M CH₃COOH (pH 2.9) shaking 16 h at 25 °C

Centrifugation → F2 (Exchangeable)

40 ml 0.1M NH₂OH·HCl (pH 2.0) shaking 16 h at 25 °C

Centrifugation → F3 (Easily reduced)

10 ml 30% H₂O₂ shaking 16 h at 25 °C; evaporation
10 ml 30% H₂O₂ shaking 16 h at 25 °C; evaporation
50 ml 1M CH₃COONH₄ (pH 2.0) shaking 16 h at 25 °C; evaporation

Centrifugation → F4 (Oxidizable)
The idea of sequential leaching procedure

- Sequential leaching consists of sequential extraction steps – going all the time forwards stronger conditions - and gives information about the effects of external conditions on the solubilition, bioavailability and environmental risk of different species like heavy metals.

- Sequential leaching is not one exact method, it is the way to carry out the extraction.
Since the conditions in stages (1) - (4) represent realistic possible risk conditions in the future, the potential bioavailability percent $\text{PBP}_M$ can be calculated from the sum of the concentrations of M in stages (1) - (4) and the total concentration $c_{\text{tot}}(M)$ by using equation (1) in Fig 1., where $c_i(M)$ is the concentration of metal M in stage i.
Potential bioavailability (2/3)

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

- Residual [\%] = 100 \% - PBP_M \quad (2)
Potential bioavailability (3/3)

- The percent of residual fraction, calculated by equation (2), describes the fraction of element which doesn’t dissolve in steps (1) – (4) and therefore it is not bioavailable in any potential conditions, never in the nature.

- Potential bioavailability is described in more details in our publication: J. Kaakinen, T. Kuokkanen, H. Jokinen, K. Kujala and I. Välimäki: The Use of five-stage sequential leaching procedure for risk assessment of heavy metals in waste rock utilized in railway ballast. - *Soil and Sediment Contamination, 21, 2012, 322-334.*
Distribution of Cu and Zn in sequential leaching procedure
Distribution of Cu and Zn in stages 2-4 in sequential leaching procedure. \( \sum c_i \) describes value that is the calculated sum of the previous leaching stages.
Results

The results, Figures 2-3, show with earlier studies (Kuokkanen et al., 2006; Kaakinen et al., 2012; Nurmesniemi et al., 2008) that:

1. $[\text{Cu}_{\text{tot}}]$ and $[\text{Zn}_{\text{tot}}]$ 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 size of 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.
Results

3. The conditions have a large effect on the leachability/solubility of all heavy metals, being however different for different metals and therefore the total concentration of heavy metal is poor measure of real environmental risk.

4. The total concentration of zinc \([\text{Zn}_{\text{tot}}]\) and copper \([\text{Cu}_{\text{tot}}]\) (500 mg/kg and 590 mg/kg) are higher than their guideline values 400 mg/kg and 200 mg/kg, respectively, in the Finnish Pima decree but their real solubility is poor.

5. The values of both Zn and Cu in steps 2, 3 and 4 using corresponding single leaching determination are quite similar that the concentrations in these steps in sequential procedure or compared with the sum concentration \(\Sigma c_i (M)\) (\(i = 2\) for step 2, \(i = 3\) for step 3 and \(i = 4\) for step 4).
Conclusions

- The leachability results determined here for waste rocks utilized as railway ballast show good agreement with all earlier investigations that sequential leaching studies give valuable information about the effect of conditions on the leachability/solubility, mobility and bioavailability for environmental 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.
Thank you!

Juhani Kaakinen, Chief of Environmental Protection Unit

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