Treatment and recovery of contaminated railway ballast

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Abstract: Experimental tests of metal extraction from stones sampled from artificially contaminated railway ballasts are presented and discussed. Metal extraction was performed by washing with aqueous solutions of disodium ethylenediaminetetraacetate (EDTA), at selected concentrations. The effectiveness of the remediation process was evaluated using leaching tests.

The results indicate that the washing technology represents a successful and affordable solution for the implementation of an on-site treatment aimed at a reuse process. Adopting a 0.05 M EDTA solution, extraction yields in the range between 40% and 70% were achieved, depending on contact time and pH of the washing solution.

Key words: Railway ballast, track maintenance, metal extraction, EDTA, leaching tests

1. Introduction
Railway ballast, consisting of a mixture of rocks of different size and nature, ensures geometry and stability of the railway track, by damping the vibrations caused by the vehicle traffic and allowing water drainage. Several minerals can be used, including either metamorphic rocks, such as serpentinite, amphibolites, and gneiss, or volcanic rocks such as basalt, porphyry, and trachyte [1]. Over time, mainly due to abrasion and wear, ballast loses its mechanical properties and cannot be reused within the rail industry, being sold on to other users to be recycled as an engineering fill material.

In the last decade, several cases of railway ballast contamination by organics and inorganic species have been reported [2]. Among the organic compounds, aliphatics, from loss of fuel or lubricants, and polycyclic aromatic hydrocarbons (such as creosote in timber sleepers) have been commonly identified as a major concern. As regards inorganic contamination, heavy metals (mainly Ni, Zn, Fe, Cd, V, Cr, Mn, Cu,) from lubricants, track corrosion and wear, and welding residues have been found in more recent studies [3,4]. In addition to anthropic pollution, a further release of hazardous compounds from ballast can be also attributed to the presence of naturally occurring species such as asbestos materials from ophiolite [5]. Polluted ballast gravel may easily transfer pollutants by rainfall, thus causing pollution of soil and groundwater.

Uncontaminated fine particles from attrition and splintering of the ballast can be easily removed by screening during the operation of a ballast cleaner, while in the presence of significant contaminant amounts special treatment and adequate disposal are required. Since the maintenance and renewal of ballast involve the use of huge amount of stones of different type and specific mechanical characteristics, all railway maintenance guidelines recommend recycling and reuse of ballast in accordance with waste management regulations.
Although several methods for ballast remediation have been tested [6], cleaning of the ballast generally involves washing with aqueous solutions of selected surfactant cleaning agents, each with different efficiencies and potential environmental impacts [7]. This technology currently represents the most promising method for sustainable ballast management.

Ex situ washing technology is widely used in the remediation of contaminated soil and sediments [8–10]: undesirable contaminants are removed by dissolving or suspending them in a washing solution. In the case of contamination by heavy metals, the washing solution is generally an aqueous solution of a chelating agent [11]. In many cases of remediation of both sediments and soils, the effectiveness of EDTA as a chelating agent in washing treatment has been demonstrated [12–15]. In comparison with other metal-sequestering agents, EDTA presents several advantages, including a low biodegradability in groundwater and soil and a high level of complexing capacity with respect to heavy metals [16].

However, the low selectivity of EDTA causes high consumption of this reagent due to the potential chelation of all the exchangeable cations present in soil, such as Ca$^{2+}$ and Fe$^{3+}$ [17]. A substantial excess of EDTA is thus generally adopted, increasing the cost of the whole remediation treatment, unless recovery of EDTA from the spent solution is realized [18, 19].

In the case of railway ballast remediation, washing technology should be preferred to other cleaning technologies, since it can ensure complete pollutant removal without altering the ballast’s mechanical and physical properties or inducing the dissolution of natural constituents. In addition, washing technology can be easily integrated in the actual ballast maintenance system that operates continuously along the railways, and that currently involves ballast replacement by rail mounted excavators, followed by disposal of landfills.

In this study, the effectiveness of EDTA as an extractant agent was tested on ballast contaminated by cadmium, copper, and zinc, using a laboratory-scale cleaning system. In particular the aim of the experiments was to optimize the operating parameters affecting the extraction process, such as the amount of chelating agent as well as the contact time.

2. Materials and methodology
2.1. Materials
Two series of experimental tests were performed. In the first series, leaching tests in distilled water and washing tests with aqueous solutions of EDTA were performed on stones typically used to make railway ballast in Italy, constituted with leucitic tephrites of volcanic nature (Type A). The tests were performed on unused stone and after artificial contamination. In the second series of tests, another commercially available ballast stone (metamorphic green rocks, Type B), generally used in northern Italy, was artificially contaminated and subjected to the same treatments. All the samples were initially crushed to achieve an average size of 3–5 cm.

Ballast contamination in both cases was carried out by mixing 1.3 kg of each ballast sample with an aqueous solution containing 357 mg of CdCl$_2$ monohydrate, 536 mg of CuCl$_2$ di-hydrated, and 417 mg of ZnCl$_2$.

Each contaminated sample was stored in a plastic container and allowed to dry at room temperature (22–24 °C) for 90 days before extraction.

All reagents were provided by Carlo Erba, Milan, Italy.

2.2. Leaching tests
Leaching tests were performed using distilled water, according to the procedure described by the Italian Environmental Regulation [20]. Both untreated samples (to estimate initial metals availability, also considering
the possible occurrence of heavy metals in stones’ mineral constituents) and previously washed samples (to investigate the effectiveness of the washing treatment) were subjected to leaching tests.

Preliminary tests on unused stones showed negligible metal extraction (data not shown).

The results were compared with the limit values reported in the Italian Environmental Regulation [21].

2.3. Washing tests

The washing solution was prepared by dissolving EDTA-Na$_2$ in distilled water. Two different EDTA concentrations were tested (0.01 and 0.05 M), based on previous studies [16]. The liquid/solid ratio adopted in all the tests was 10:1, to ensure complete immersion of the sample in the washing solution. Washing tests were performed in a rotating PVC tank at 10 rpm.

At selected time intervals, the contact solution was sampled and analyzed. Metal extraction yield was calculated based on the concentration of the contact solution.

All tests were performed in triplicate; the results were reported as mean values and the average standard deviation was calculated.

2.4. Analyses

pH was measured using a Crison 507 pH-meter and conductivity with an HD9213-R1 conductimeter. The total organic carbon of the solution (TOC) was determined using a Shimadzu 5000-A TOC Analyzer, after filtration through a 0.45 µm membrane filter [22].

Metal concentrations in the contact solution during washing tests and leaching tests were determined using an Agilent AA DUO 240 Fs atomic absorption spectrometer equipped with a graphite furnace.

3. Results and discussion

To assess the initial available metal amounts in the stones, leaching tests were first carried out.

In the leaching tests performed on samples from uncontaminated Type A and B stones, only a slight release of Cu and Zn was observed (data not shown); the extracted amount was always within the limits given by the Italian Environmental Regulation. Cd concentration in the leachate was always below the detection limits. In addition, no substantial difference in terms of metal leaching was observed before and after the washing with EDTA.

To better evaluate EDTA effectiveness in ballast remediation, the same tests were performed on artificially contaminated ballast samples. The results of the leaching tests on artificially contaminated samples are reported in the Table.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Type A samples</th>
<th>Type B samples</th>
</tr>
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<tbody>
<tr>
<td>Cd, mg/kg</td>
<td>550 ± 45</td>
<td>350 ± 30</td>
</tr>
<tr>
<td>Cu, mg/kg</td>
<td>550 ± 35</td>
<td>400 ± 25</td>
</tr>
<tr>
<td>Zn, mg/kg</td>
<td>310 ± 20</td>
<td>350 ± 40</td>
</tr>
</tbody>
</table>

Figures 1 and 2 show the metal extraction yields over time during the washing tests performed at the two EDTA concentrations investigated. The results show that the use of EDTA was indispensable to extract significant amounts of pollutants. In particular, in the treatment of Type A samples, only adopting the higher EDTA concentration (0.05 M), substantial metal extraction was observed within 3 h of treatment (55% for Cd,
63% for Zn, and about 70% for Cu). Conversely, for Type B samples, a lower increase in treatment efficiency was observed with increasing EDTA concentration in the extractant solution: the extraction yield for all the investigated metals was always lower than 40% after 3 h of treatment. This different behavior can be attributed to the alkaline character of Type A stones, causing an initial higher metal adsorption onto the stones’ surface (Dinelli and Tateo, 2001); as a result of the acidic extraction, metals were easily released from both stone samples.

![Graphs showing the effect of washing duration and extractant concentration on the metal extraction yield in Type A samples](image)

Figure 1. The effect of washing duration and extractant concentration on the metal extraction yield in Type A samples (the average standard deviation was 4.5%).

In the tests performed on Type A samples, quick initial extraction occurred, followed by a progressive decrease in the metal mobilization rate, until a plateau was almost reached after 3 h of treatment. A progressive increase in the extraction rate was observed in the tests with Type B stones, suggesting that further slow extraction could be obtained with increasing contact time.

As regards the behavior of the three investigated metals, a similar trend and extraction efficiency were found in the two samples. Metal concentrations measured in the solution after 3 h of mixing were in accordance with the different metal-EDTA stability constants (Cu > Zn > Cd) for the Type A samples, while, for Type B sample a slightly higher Zn extraction was calculated. This behavior can be attributed to the natural presence of zinc in Type B stones, thus yielding, under the strong acidic conditions induced by EDTA, a higher Zn released from the matrix [23].

As a result of the metal mobilization from the solid to the liquid phase, treatment of the extracted solution should be considered to complete the overall remediation process.
Figure 2. The effect of washing duration and extractant concentration on the metal extraction yield in Type B samples (the average standard deviation was 5.2%).

To evaluate the effectiveness of washing treatment, leaching tests were repeated on samples previously subjected to the washing tests.

Figure 3 shows the results of the leaching tests performed on the contaminated Type A samples, after washing treatment, compared with the leaching tests performed on the same sample, but untreated (i.e. not subjected to washing).

The results show that the washing treatment caused a strong reduction in the leachable amount of all the considered metal in the samples. As expected, an increase in the EDTA concentration of the washing solution resulted in a lower residue amount of metal adsorbed onto the ballast.

By comparing the amount of any considered metal extracted during the leaching tests, it can be assessed that, before the washing treatment, the amount of metal adsorbed onto the solid was higher with respect to the limits permitted by the Italian Environmental Regulation. Moreover, after the washing treatment, even in the more severe conditions (0.05 M EDTA), the total amount of metals released during the leaching tests was higher than those limits. However, the results show that EDTA can be successfully used to extract metals from the ballast constituents, but, at the operating conditions tested, did not ensure the complete cleaning of the ballast.

The same consideration can be made for the samples from Type B stones, even considering their different mineralogical nature; the results of leaching tests performed on this sample are reported in Figure 4.

It must be considered that leaching tests, according to the Italian Regulation [21], were performed at the same pH of the distilled water solution (about 6.5), while in this work the extractions were carried out at the pH corresponding to the EDTA solutions (about 4.9 and 4.2 for 0.01 and 0.05 M, respectively); it is well known that
Figure 3. Results of leaching tests performed on Type A samples (the average standard deviation was 4.5%).

Figure 4. Results of leaching tests performed on Type B samples (the average standard deviation was 3.7%).
metal release is strongly influenced by pH and natural leaching by atmospheric precipitation occurs under slight to more acidic conditions [24], and this should be taken into account in evaluating the actual contamination of an operating ballast.

The results for both Type A and B samples show that at the end of the washing treatment, even using the 0.05 M EDTA solution, a substantial amount of metals remained adsorbed on the ballast; a higher extraction yield was observed for Cu from Type A samples (about 70%) and for Zn from Type B samples (about 41%).

Finally, TOC analyses of the leaching solution show that only a slight amount of EDTA remained adsorbed on the stone after the washing treatment; in particular after the 0.05 M EDTA treatment 53 mg L\(^{-1}\) and 15 mg L\(^{-1}\) TOC were measured for Type A and Type B samples, respectively, and 29 and 8 mg L\(^{-1}\) for the extractions performed at 0.01 M for Type A and Type B, respectively. In the view of a future optimization of the washing conditions, this should be taken into account and a final washing with water is required before reuse or disposal of the stones, as generally required after chelant-assisted washing of contaminated soil and sediments [19,25].

4. Conclusions

In this paper experiments of metal extraction from railway ballasts are presented. The extractions were performed on both naturally and artificially contaminated samples, by washing with aqueous solutions of EDTA. The results show that washing technology can be successfully used for ballast cleaning, as a simple and nondestructive technique ensuring metal extraction without altering the stones’ mechanical and physical characteristics in the view of the reuse of ballast material. The extraction effectiveness with respect Cd, Cu, and Zn was found to be strongly dependent upon contact time and EDTA concentration in the washing solution. In addition, to complete the overall remediation process, due to the high extraction yield during washing treatment, the contact solution at the end of the tests required treatment to remove the mobilized metals.

References

[23] Dinelli E, Tateo F. Sheet silicates as effective carriers of heavy metals in the ophiolitic mine area of Vigonzano (northern Italy). Miner Mag 2001; 121–132.