Electrokinetic remediation of metal-polluted marine sediments: experimental investigation for plant design

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A B S T R A C T
This paper presents the results of an extensive set of laboratory experiments performed to design a demonstrative electrokinetic plant for extracting heavy metals from marine sediments dredged from the Livorno marine harbour. The investigated sediments displayed a high salinity, a high acid neutralization capacity, a low electrical resistivity (0.5 Ωm), a high alkalinity (pH≈8) and a large fraction of fine particles. The target metals were Cd, Cr, Cu, Ni, Pb and Zn at relatively weak and inhomogeneous concentrations with high non-mobile fractions. After an accurate characterization, several screening and full electrokinetic tests were performed using cells of different sizes, several conditioning agents (HNO3, HCl, H2SO4, citric acid, oxalic acid, ascorbic acid, EDTA), different applied current intensities and durations. The tests highlighted the need for long treatment times in order to obtain a significant pH reduction, with some appreciable metal removal being attained only after several weeks. The best results were obtained with strong acids used as the conditioning agents, with significant specific effects of each acid, including pronounced resistivity increase (from 0.5 up to 10 Ωm) and a high electroosmotic flow (EOF) with H2SO4, or a reversed EOF (electroendosmosis), and minor resistivity changes with HNO3. The use of the obtained data to design a demonstrative plant is also presented in the paper, with considerations on operating parameters such as energy and reagent consumption, characteristics of plant components and required safety measures.

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1. Introduction

Harbour sediments are often severely affected by heavy metal contamination, originating from different sources such as ship transport, harbour activities, industry, municipal sewage and other upstream sources. The presence of contaminants may turn sediment management, which is carried out in most commercial harbours for waterway maintenance, into a troublesome activity [1].

Traditional management strategies include more or less expensive alternatives such as open water placement and disposal in longshore confined disposal facilities or inland landfills. Beneficial uses such as beach nourishment or island creation are advisable, but they may be perceived as risky [2]. In fact, such practices often cause concerns due to potential contaminant exposure, slow dewatering and consolidation, high costs, and long-term liability [3]. In general, beneficial reuse of sediments represents a viable solution as long as contamination levels comply with regulatory standards. When such standards are not met, specific treatments are required. Such treatments must be relatively inexpensive to be sustainable, as the amounts of sediments to be processed are, in most cases, quite large. The type of remediation treatment to be applied depends on specific sediment characteristics, such as pollutant content and association/interaction with the solid particles as well as particle size distribution, mineralogical composition, alkalinity, buffering capacity and organic matter content [3–6]. Treatments that have been proved to be effective for soil decontamination require special precautions when being applied to sediments. Specifically, marine sediments are frequently characterized by low hydraulic conductivity, while most technologies are effective only for high

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permeability soils, and become costly or even fail when this condition is not met [7,8]. As a consequence, the treatment of metal-polluted sediments can be particularly challenging.

Among the several available treatment options, electrokinetic (EK) remediation is recognized as the most suitable technique for low permeability porous matrices. It can be applied, both in situ and ex situ, for several contaminants, also in combination [5,9–21]. The EK technology is based on the application of an electric field to contaminated porous media by means of two series of electrodes introduced in the media. The electric field induces the mobilization of metal ions through the media toward the electrodes, due to three main transport mechanisms [22–23]: (1) electromigration (movement of ionic species), (2) electroosmosis (movement of interstitial fluid), and (3) electrophoresis (movement of charged particles and colloids). Compared to most remediation techniques, EK is relatively easy to implement, but the complex physicochemical governing processes largely affect remediation efficiency [24] in relation to the nature of the polluted matrix and the type and level of contamination [25,26].

Metals can be present as soluble ions, or as oxides, hydroxides, carbonates, sulphates or other organic and inorganic complexes bound to sediment particles. Consequently, they can be directly mobilized from the sediment matrix as long as they are present in ionic forms bound to mobile polar complexes. Additionally, they can be transported by the circulating fluid using several possible enhancement strategies, which can reduce remediation time and overall costs [27]. Specifically, different liquids (purging solutions), have been effectively introduced into the electrode compartments with the aim of inducing favourable pH conditions and/or interacting with heavy metals [12,26–32]. In general, pH is the key parameter that affects heavy metal mobility in sediments [4] and its control can be achieved by adding acidic or alkaline solutions into the electrode compartments [5,33,34]. However, the achievement of the desired pH values in sediments can be strongly affected by their buffering capacity [35]. Further possible enhancing techniques involve the use of chemicals (such as chelating, complexing or oxidizing/reducing agents or surfactants) aimed at keeping contaminants in a mobile state. In particular, the use of chelating agents has been shown to be effective for improving metal solubility in high-buffering-capacity soils and sediments [36–39].

The EK technique has been extensively studied on a laboratory scale [3,15,25,40–46], but most investigations have been based on spiked soils/sediments and have focused on a limited range of metals [15,24–26,43,47,48]. However, the complexity of real matrices, the presence of multiple contaminants and the effect of ageing processes are commonly associated to lower remedial efficiencies than those observed for spiked, homogeneous matrices. In these situations, remediation can become longer and difficult to predict [49].

Reddy and Ala [3] investigated the feasibility of EK remediation of a fine-grained sediment polluted by a mixture of several polycyclic aromatic hydrocarbons and heavy metals. They performed four tests using flushing solutions of two surfactants, a cosolvent and a cyclodextrin. As for heavy metals, they concluded that none of the selected flushing agents effectively removed heavy metals, due to high organic content and the high buffering capacity of the sediment.

Kim et al. [5] investigated EK remediation under a constant voltage gradient of 1 V/cm for 15 days, using 0.1 M EDTA, citric acid, HNO3 and HCl as the catholyte, to remove Ni, Cu, Zn and Pb from dredged marine sediments containing more than 80% of sand. HCl and citric acid showed extraction efficiencies up to 70%. Rozas and Castellote [20] studied the EK removal of Cu, Zn, Cd, Cr, Pb and Ni from spiked dredged materials. Also in this case, the clay/silt fraction represented only 5% of the material mass. None of the enhancing solutions investigated (distilled water, citric acid, acetic acid, humic acids and EDTA), was found to be effective in removing all the target metals.

Hahladakis et al. [50] focused on the sequential application of a chelating agent followed by a non-ionic surfactant for enhancing the simultaneous removal of metals and PAHs from real contaminated sediments characterized by a sand fraction of more than 80%. The combined treatment with citric acid and non-ionic surfactant enhanced dramatically Zn and As removal, but did not affect the removal of Cu, Cr, Ni and Pb.

Ammanni et al. [8] performed bench-scale EK tests to evaluate the effect of different operating parameters of a single-stage treatment aimed at removing heavy metals (Cd, Cr, Cu, Pb, Zn) and PAHs from dredged sediment. A mixture of a chelating agent (citric acid) and a synthetic surfactant (Tween 20) was used as the process fluid. At the highest tested citric acid dosage (1 M) the highest metal removal was achieved, but at a much lower dosage (0.1 M), combined with a voltage gradient applied in 5-day-on/2-day-off cycles, almost the same removal (approximately 50%, 35% and 30% for Zn, Cd and Pb, respectively) with a much lower consumption of chemicals was obtained.

These recent studies on real sediments with mixed aged contamination show that the identification of the best removal strategy is still controversial and requires further investigation. Additionally, the resolution of many practical issues is still a challenge for the EK remediation technology to be brought to the required reliability for field application [49].

In this framework, the suitability of EK remediation for removing heavy metals from silty-clayey marine dredged sediments is currently under investigation by the SEKRET Life + project (“Sediment Electrokinetic Remediation Technology for heavy metal pollution removal”), by way of a demonstrative 150 m3 treatment basin under construction in the commercial port of Livorno (Italy). In this port, almost 100,000 m3/year of sediments are regularly dredged, and an environmental seabed assessment performed in 2005 detected several local spots where sediments are polluted by significant concentrations of Cd, Cr, Cu, Ni, Pb and Zn [51]. As previously emphasized, each sediment/pollutant combination represents a specific case; thus no reclamation action can be designed without adequate preliminary tests aimed at selecting the most appropriate enhancing agent and evaluating its interactions with the contaminants and the solid matrix [52]. Within this context, a systematic investigation of the feasibility of EK remediation of a real contaminated sediment was conducted in the present study by exploring a wide variety of testing conditions and enhancing agents in a set of bench-scale experiments, in order to contribute to filling the existing gaps in the scientific literature, specifically for real matrices. Furthermore, the results from the bench-scale electrokinetic tests were used to derive considerations for the appropriate design of a full-scale electrokinetic remediation plant.

2. Experimental

2.1. Sediment sampling

The sediments were sampled from the harbour of Livorno (Italy). The sampling was performed manually, using a 250 cm2 van Veen-like bottom grab sampler, by picking up the sediment from the sea-bottom surface layer (0–50 cm) at a water depth of about 7 m. A total of 0.3 m3 of sediments were collected. The samples were stored in sealed buckets and were left to settle for 15 days, after which the supernatant was discarded. The whole collected material was then gathered in a tank and homogenized by mixing for 30 min with a mechanical stirrer. The homogenized material was then redistributed into 10 L buckets, that were delivered to to
the testing laboratories and stored at ambient temperature until analysis.

2.2. Physical-chemical characterization

Subsamples of homogenized wet sediment were generally oven-dried at 105 °C and sieved to remove the 2-mm oversize (mostly comprising shells). When required by the analytical procedures, oven-drying was performed at 60 °C so as to prevent any loss of volatile material.

Sediment characterization involved the analysis of grain size distribution, hydraulic conductivity, electrical resistivity, water content, pH, Acid Neutralization Capacity (ANC), Cation Exchange Capacity (CEC), total organic carbon (TOC), as well as metal fractionation. The particle size distribution was determined by sieve analysis and aerometry. The hydraulic conductivity was estimated by the oedometric test. The electrical resistivity was determined with the 4-electrode method in a cylindrical sample holder. Water content, pH and TOC were measured according to the standard methods prescribed by the Italian Ministry of Agriculture and Forests. ANC and CEC were determined according to the CEN/TS 14429:2005 and ISO 11260:1994 methods. Metal content was determined using either atomic absorption spectrometry (after sample digestion performed through lithium tetraborate melting at 1050 °C in platinum melting pots) or ICP-OES (after acid digestion in accordance with the US EPA 3050b 1996 and US EPA 7000b 2007 methods).

Metal speciation in the sediment was determined through a three-step sequential extraction according to the procedure recommended by the Standards, Measurements and Testing (former BCR) Programme of the European Commission. In this approach, heavy metals are divided into acid-soluble/exchangeable, reducible and oxidizable fractions, while the residue is considered as the mineral non-extractable form. The procedure is shown schematically in Table 1.

Morphological and chemical characterization of the material deposited over the cathode was performed by SEM and Energy dispersive X-ray spectrometry. Chloride concentration in solution was measured by potentiometric titration with AgNO₃.

All measurements and analyses were performed at least in three replicates.

2.3. Preliminary sediment washing tests

In order to evaluate the extent of metal mobilization in different chemical environments, a number of lab-scale batch washing tests was performed by contacting the washing solution with sediment on a rotating tumbler for 24 h. The following washing agents were tested: citric acid, oxalic acid, nitric acid, EDTA (known as an effective metal chelant) and ascorbic acid (used as a reducing agent with the purpose of releasing the metal fraction associated to the Fe and Mn (hydr) oxides). The concentrations of the washing solutions, as well as the liquid-to-solid (L/S) ratio, adopted in each test are reported in Table 2. After 24 h, the slurries were centrifuged at 4000 rpm; the supernatant was then filtered onto 0.45-μm membrane filters and acidified with 1:1HNO₃ for subsequent chemical analysis.

2.4. Electrokinetic tests

A set of 20 screening tests and 3 full tests was carried out in order to derive a thorough figure of the behaviour of contaminants under different EK treatment conditions.

The screening tests were performed in order to evaluate the effect of a large number of conditioning agents and dosages on the remediation yield, with the overall target of selecting the most effective process conditions for metal mobilization from sediment. They were conducted in parallel using small cells equipped with a voltmeter for recording the voltage drop along the sample. The duration of each screening test ranged from 7 to 60 days, where the longer treatment time was only tested for those operating conditions that gave the best performance already at lower durations.

The full tests were performed in a lower number of selected conditions, using a larger cell, with automated pH control and continuous multiple-point voltage monitoring. The duration ranged from 14 to 63 days. The aim was to accurately test a reduced number of options in order to obtain operational parameters and criteria to be adopted in the full-scale plant after a proper scale-up procedure.

2.4.1. Screening tests

The screening EK tests were performed by means of a system composed of a Plexiglas cell, a DC generator able to maintain a constant current in the range 0–20 A, graphite electrodes, as well as a voltmeter coupled with a data logger (Fig. 1). The EK cell was built as a box with external sizes of 18 cm (L) × 7 cm (W) × 8 cm (H)

<table>
<thead>
<tr>
<th>Washing agent</th>
<th>Concentration (M)</th>
<th>Liquid-to-solid ratio (l/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>0.04</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>10</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.05</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.04</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>10</td>
</tr>
<tr>
<td>EDTA</td>
<td>0.2</td>
<td>10</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>0.17</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.68</td>
<td>20</td>
</tr>
</tbody>
</table>
and inner dimensions 15 cm (L) × 5 cm (W) × 8 cm (H). Each cell was divided into three compartments, the two external electrolyte chambers, where the graphite electrodes were placed, and the central chamber containing the sediment sample to be treated. The sediment sample was placed in the central chamber and compacted by applying a static pressure of 40 g/cm² for 24 h. After compaction, two graphite rod electrodes connected to the voltmeter and data logger were placed in the sediment; the two electrode chambers were then filled with the electrode solutions.

The experiments were performed at a constant DC density of 20 A/m², under the testing conditions reported in Table 3. At the end of each test, the electrode solutions were extracted and acidified with 1:1 HNO₃ for subsequent chemical analysis; in addition, the sediment sample was extracted and divided into three portions (close to the anodic compartment [S+], central section [Sc] and close to the cathodic compartment [S-]). Each slice was characterized for pH, then weighed, dried until constant weight and ball-milled in view of subsequent chemical characterization.

2.4.2. Full tests

The full electrokinetic experiments were carried out in an acrylic cell (Fig. 2), consisting of six principal parts: the sediment compartment, the electrode compartments, the water and acid reservoirs, the electrolyte solution overflow reservoirs, the power supply and the pH control system. The sediment compartment dimensions were 30 cm × 7 cm × 7 cm, with a volume of 1.47 dm³.

To separate the sediments from the electrode compartments, a nylon grid (mesh size 2 mm) and filter paper were used. The sediments were placed in the electrokinetic cell in layers and statically compacted by applying 40 g/cm² for 24 h, whereafter it was left in the cell for at least 3 days to achieve equilibrium before starting the tests.

The anode was a titanium mesh electrode with a Mixed Metal Oxide (MMO) coating provided by Industrie De Nora s.p.a., Italy, which was chosen for its very high chemical stability in environments with low pH values. The cathode was a stainless steel plate.

Six graphite rod electrodes (6 mm diameter) were placed along the surface of the sediments to monitor the voltage drop across the sediment. During the tests, the applied voltage, the current and the local voltage drops were recorded by a data logger. The local resistivity was computed from local voltage drops. At the end of each experiment, the material was divided into five locations (S1 . . . S5) and analyzed for pH and total metal content. Metal concentrations were also measured in the anode and cathode chambers.

During the experiments, the electroosmotic flow was calculated by measuring the volume change in the electrode reservoirs and operating a mass balance. The electroosmotic permeability $k_{eo}$ (m² V⁻¹ s⁻¹) was also estimated from the data during the experiment, through the following equation:

$$Q_{eo} = A k_{eo} \sqrt{(-\Phi)}$$

where $Q_{eo}$ is the electroosmotic flow rate (m³/day), $A$ (m²) is the cross-sectional area perpendicular to the direction of flow, $\sqrt{(-\Phi)}$ (V/m) is the local electric field, and $\Phi$ (V) the electric potential. Since the electric field is space-dependent, the average value was taken to calculate the electroosmotic permeability.

The catholyte was kept at constant pH conditions during the experiments by means of an automated control system. Two pH probes were placed inside the anode and cathode chambers and the measured values were used to automatically control a valve for acid injection into the cathode chamber. The pH probes were galvanically isolated from the external applied electric field by means of isolation amplifiers.

Finally, the cell was hermetically closed with a sealed cover, with a connection to a bubbling trap for chlorine gas detection and removal. At the anode, chlorine gas is produced due to the very low pH condition and high chloride content in the electrolytes. The trap was filled with 1 M NaOH and the solution was replaced every day. Three experiments were carried out, as shown in Table 4.

3. Results and discussion

3.1. Sediment characterization

The physicochemical properties of the sediment are presented in Table 5, whilst the results of the performed elemental composition analyses are summarized in Table 6.
Although the original sediment sample was homogenized before the analysis, Table 6 shows large differences in metal concentrations of the different batches, thus resulting in high standard deviation values. The inhomogeneity was constantly observed as being local, while no systematic shifts were observed between analyses performed in different laboratories or samples stored in the different tanks. Hence, the averages of all samples were considered as reference initial values for all electrokinetic tests, in comparison to the values obtained by massbalance calculation. This procedure allowed us to overcome the uncertainty deriving from the strong inhomogeneity of the raw material.

Table 4
Experimental conditions for full electrokinetic remediation tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Duration (days)</th>
<th>Applied current density (A/m²)</th>
<th>Anolyte</th>
<th>Catholyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP1</td>
<td>14</td>
<td>40–20</td>
<td>H₂O</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>EXP2</td>
<td>43</td>
<td>40–20</td>
<td>H₂O</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>EXP3</td>
<td>63</td>
<td>40</td>
<td>H₂O</td>
<td>HNO₃</td>
</tr>
</tbody>
</table>

* The applied current density was lowered from 40 to 20 A/m² after reaching the maximum allowed voltage of 125 V.

Table 5
Summary of detected physicochemical properties of dredged sediments.

<table>
<thead>
<tr>
<th>Properties of sediment</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution:</td>
<td></td>
</tr>
<tr>
<td>Coarse Sand (d = 500–2000 μm)</td>
<td>18.1%</td>
</tr>
<tr>
<td>Fine Sand (d = 63–500 μm)</td>
<td>35.2%</td>
</tr>
<tr>
<td>Clay + Silt (d &lt; 63 μm)</td>
<td>46.7%</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>7.85·10⁻¹⁰ ± 4.15·10⁻¹⁰ m/s</td>
</tr>
<tr>
<td>Moisture</td>
<td>34.7 ± 0.3%</td>
</tr>
<tr>
<td>pH</td>
<td>8.05 ± 0.2%</td>
</tr>
<tr>
<td>Electrical conductivity (EC)</td>
<td>15.54 ± 0.3 mS/cm</td>
</tr>
<tr>
<td>Acid neutralization capacity (ANC)</td>
<td>1.2 meq/g</td>
</tr>
<tr>
<td>ANC to pH 5.0</td>
<td>3.0 meq/g</td>
</tr>
<tr>
<td>Cation exchange capacity (CEC)</td>
<td>11.2 ± 0.9 meq/100 g</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>&lt; 0.5%</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>0.53 ± 0.05 Ω · m</td>
</tr>
</tbody>
</table>

3.2. Metal fractionation

The results of the sequential extraction on four replicate samples are presented in Fig. 3. It can be observed that the exchangeable fraction was low for all observed metals, as it exceeded 10% only for Cd (33%) and Zn (19%). The fraction bound to Fe–Mn (hydr) oxides was significant for Pb (55%), Cu and Cd (about 40%). The fraction bound to organic matter was significant for Cu (46%) and Cd (33%). The residual fraction was particularly high for Cr (68%), Ni (51%) and Zn (47%). This fractionation, which prefigures a low rate of decontamination due to the generally low presence of the mobile fraction, is in accordance with that of similar harbour sediments with relatively mild heavy metal contamination levels mentioned in the literature [5].

3.3. Preliminary sediment washing tests

The results of the preliminary washing tests are depicted in Fig. 4. Sediment washing using acid solutions was able to mobilize the contaminants of interest under very low pH conditions, namely at pH = 0.79 in the case of HNO₃ (extraction yield of 81.71% for Zn and 61.05 for Cu), and at pH values lower than 2.67 units for citric acid (extraction yield from 58.61 to 66.71% for Zn and 30.25 to 52.59 for Cu). In the case of oxalic acid, maximum extraction yields of 46.6 and 32.2% were attained for Zn and Cu, respectively, at pH < 1.03, whilst ascorbic acid was not able to extract metals to a significant extent under the investigated operating conditions. The extraction yields for Zn obtained when using EDTA as the washing agent were found to be dependent on pH as well, and the highest performance (from 57 to 90%) was reached when the system pH was in the range 7.48 ± 8.01. Conversely, the extraction of Cu was found to be less influenced by the pH conditions of the system, and a clear trend of metal release as a function of pH was not evidenced, as it ranged from 40% at pH 10.24 to 64% at pH 7.97. The effect of pH cannot be unambiguously explained for all the investigated metals, as it is affected by a number of factors, including the aqueous metal concentrations, the related conditional stability constants of metal-EDTA complexes, the solubility of chelating agent, as well
Table 6
Summary of performed elemental composition analysis results.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>K</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Ni</th>
<th>Cr</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>g/kg</td>
<td>g/kg</td>
<td>g/kg</td>
<td>g/kg</td>
<td>g/kg</td>
<td>g/kg</td>
<td>g/kg</td>
<td>g/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
</tr>
<tr>
<td>Lab1</td>
<td>230.16</td>
<td>37.16</td>
<td>23.12</td>
<td>13.80</td>
<td>21.52</td>
<td>0.28</td>
<td>22.60</td>
<td>61.26</td>
<td>31.20</td>
<td>411.28</td>
<td>301.30</td>
<td>5.17</td>
<td>72.43</td>
<td>114.61</td>
</tr>
<tr>
<td></td>
<td>±11.94</td>
<td>±2.14</td>
<td>±0.84</td>
<td>±2.44</td>
<td>±1.20</td>
<td>±0.02</td>
<td>±0.66</td>
<td>±5.16</td>
<td>±6.49</td>
<td>±102.62</td>
<td>±64.81</td>
<td>±1.73</td>
<td>±18.97</td>
<td>±56.81</td>
</tr>
<tr>
<td>Lab2</td>
<td>18.14</td>
<td>7.67</td>
<td>5.45</td>
<td>20.76</td>
<td>0.38</td>
<td>10.06</td>
<td>77.70</td>
<td>33.11</td>
<td>63.90</td>
<td>401.69</td>
<td>0.95</td>
<td>51.09</td>
<td>67.40</td>
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</tr>
<tr>
<td></td>
<td>±2.37</td>
<td>±0.34</td>
<td>±2.27</td>
<td>±0.91</td>
<td>±0.02</td>
<td>±0.34</td>
<td>±6.78</td>
<td>±8.38</td>
<td>±70.15</td>
<td>±111.86</td>
<td>±0.28</td>
<td>±3.81</td>
<td>±4.12</td>
<td></td>
</tr>
<tr>
<td>Lab3</td>
<td>63.91</td>
<td>890.26</td>
<td>522.43</td>
<td>1.20</td>
<td>50.47</td>
<td>61.94</td>
<td>19.39</td>
<td>289.20</td>
<td>158.38</td>
<td>0.15</td>
<td>12.37</td>
<td>10.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>±19.39</td>
<td>±480.6</td>
<td>±378.38</td>
<td>±0.15</td>
<td>±12.37</td>
<td>±10.13</td>
<td>(4)</td>
<td>(4)</td>
<td>(4)</td>
<td>(4)</td>
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<td>(4)</td>
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<td>±0.06</td>
<td>±6.10</td>
<td>±10.33</td>
<td>±16.12</td>
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<td>80</td>
<td>120</td>
<td>100</td>
<td>360</td>
</tr>
</tbody>
</table>

Italy regulatory standards for heavy metals:
- DLgs. 152/06 col. A: 70 mg/kg for Hg.
- DLgs. 152/06 col. B: 30 mg/kg for Hg.
- ICRAM guideline (baseline ref. content): 100 mg/kg for Hg.
- ICRAM guideline (threshold contamin. level): 200 mg/kg for Hg.

as the chemical and physical interactions between sediment particles and each metal (sorption/desorption and ion exchange), as observed by some studies [53,54]. The extraction yield observed for Cr was lower than 5% for all the investigated washing agents over the whole pH range. In the case of citric and oxalic acid, Ni removal (data not shown) appeared to be approximately equal to 100%. However, it should be underlined that Ni concentration is very close to the instrumental detection limit. Due to the low initial content of Ni and Cr, the results are not shown in the graph. In general terms, the results from the preliminary washing tests demonstrated the low mobility of the metals of interest.

3.4. Electrokinetic tests

3.4.1. Screening tests

The results of the screening tests are reported in Fig. 5 as the C/C0 ratio along the sediment sample, where C and C0 represent, respectively, the final and initial metal concentrations in each of the three sediment regions. The extent of metal mobilization was evaluated as well (see Table 7), as the ratio between the overall amount of metal mobilized from the sample and the corresponding initial mass in the sediment. The amount of metal mobilized was calculated as the sum of the metal exceeding the initial content of each section and the amount of metal detected in the two electrolytes.

The results of test 1 (unenhanced EK) evidenced an only slight mobilization of Zn, Cu and Ni from the sediment region close to the cathode. The observed behaviour was related to the fact that the pH along the specimen (which ranged from 8.6 to 9.2) was kept almost unchanged with respect to the original sediment due to its high buffering capacity. This specific characteristic of the material increases the complexity of the remediation treatment required if compared to other types of fine-grained soils investigated in previous research.

Fig. 3. Heavy metal fractionation.

Fig. 4. Results of preliminary washing tests.

To this regard, some authors [15,24,26] working on low buffering soils were capable of reducing pH to acidic conditions for a large portion of the specimen even for low treatment durations. Nevertheless, the low remediation yield obtained in the unenhanced EK test confirms the results of the above mentioned and other studies (see e.g. [20,31]), pointing out the need for appropriate treatment conditions (addition of extracting agents, increase in treatment duration) to improve metal mobilization.

Fig. 5. Results of the screening tests (left y-axis: c/c₀; right y-axis: pH).
Furthermore, it should be mentioned that spiked soils or sediments generally display fairly higher metal remediation yields (see e.g. [15,20,24,26,31]) compared to real contaminated materials ([5,39,50]).

When assisted EK was applied, the remediation results were found to vary with the specific treatment condition adopted. When HCl was used in the catholyte (tests 2–7), the metal distribution profiles along the specimen were found to be affected by both the acid dosage and the test duration adopted. The final pH of the sediment was similar in all runs (ranging from 4.9 to 6.5), except for run T6 (duration = 60 d; HCl dosage = H), where some appreciable acidification of the solid matrix could be accomplished. Metal migration occurred in general towards both the electrode compartments, likely due to the formation of Cl-metal complexes of either charge, as already reported in previous literature studies [5]. Adding the acidic agent to both the electrode compartments (test T7; duration = 21 d; HCl dosage = H) was found to produce a pH reduction in the S+ section, with some associated relevant metal removal in the same section and migration towards the anolyte, again probably as a consequence of the formation of anionic Cl-metal complexes. In overall terms, however, there was no appreciable improvement in metal removal when HCl was used as both the anolyte and the catholyte. On the other hand, it was found that prolonging the treatment time to 60 days produced a more appreciable accumulation of metals in the cathodic compartment, likely due to the preferential formation of cationic aqueous complexes as favoured by the more acidic conditions established in the system (final pHs of 2.7, 2.5 and 4.5 in sections S+, Sc and S−, respectively). This effect was also accompanied by a notably increased degree of metal mobilization, which ranged from 22% for Cr to 63–67% for Cu, Ni and Zn (see Table 7).

These results clearly indicate that treatment duration is a key parameter which determines the extent of pH decrease and the related metal mobilization under the electric field.

Acetic acid produced a different behaviour of the system in terms of both pH and metal mobilization compared to HCl. Again, at low treatment durations, sediment pH was not appreciably affected and some slight metal migration towards the cathode was observed, as also reported by other investigators [26]; compared to HCl, the direction of metal migration appeared to be reversed, suggesting that the prevalent charge of the formed metal complexes was different in the two cases depending on the nature of the electrolytes added to the system. The 21-d tests with CH3COOH, at both acid dosages, displayed lower pH values in section S+, which may tentatively be related to a different utilization of the electrons generated by the anode: it is hypothesized that when HCl was used as the catholyte, the Cl− ions migrating to the anodic compartment and there preferentially oxidized to Cl2 due to the favorable oxidation potential subtracted part of the electrons from H+ production caused by H2O oxidation. Compared to HCl, the relatively low metal mobilization yield attained in the 21-d runs with CH3COOH (see Table 7) may be affected by the fact that in such tests the chemical characterization of the anolyte could not be performed due to some analytical problems encountered, therefore no conclusive comparative remarks may be derived in this regard.

The use of acids in both electrode compartments (tests 12–15), which was also investigated in previous experiments on both spiked and real soils (see e.g. [20,56]), did not produce any relevant effect on both sediment pH and metal migration, likely due to the low process durations adopted. Among the enhancing agents investigated, the use of EDTA (tests 16–18) was found to be the most effective in terms of metal mobilization and removal from sediment. Nevertheless, treatment time was still found to play a relevant role in affecting the remediation yield: as a matter of fact, the 7-d run (test 16) displayed relatively low metal removal yields with only some slight Ni and Zn mobilization along the specimen, the 21-d run (test 17) showed a slight trend of metal migration towards the anode along with an accumulation into the central section, although metals still largely accumulated within the sample, while the 60-day run (test 18) exhibited a strong removal of contaminants from the whole test cell. The results obtained for test 18 are considered to be notably valuable on account of the high mobilization yields attained, particularly for Ni (65%) and Zn (61%), even more when taking into account that a relevant portion of the target metals was associated to non-labile sediment fractions (see the sequential extraction results in Section 3.2). The observed effectiveness of EDTA confirms the results of previous studies [20,38,39,57] where a number of chelating agents were used for

Table 7
Total metal mobilization (%).

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<th>Ni</th>
<th>Zn</th>
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<td>14.32</td>
<td>15.68</td>
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</table>

Fig. 6. Resistivity changes along time in different cell sections during full tests: H2SO4 14 d (left); H2SO4 43 d (center); HNO3 63 d (right).
electrokinetic metal removal from soils and sediments under a variety of process conditions.

Combining ascorbic acid with HCl (tests 19 and 20) in order to promote the reduction of Fe and Mn (hydr) oxides and favour the release of metals, did not enhance metal mobilization if compared to tests 2–5, where only HCl was applied.

3.4.2. Full tests

Three full tests were performed, using sulphuric acid (tests 1 and 2) and nitric acid (test 3), with overall durations of 14, 43 and 63 days respectively. As for the screening tests, the treatment runs were performed at constant current rather than constant voltage. The reason for this choice (which is different from many earlier studies on sediments [3,5,8]) was that of reproducing the operative conditions of the full-scale plant to be scaled-up, where a maximum allowable specific current of \( \approx 5 \text{ A/m}^2 \), due to cost-effective design and safety reasons, will lead to keep that value during the whole decontamination process in order to maximize the voltage, hence reducing the decontamination time.

3.4.2.1. Resistivity considerations. The use of sulphuric acid caused a significant electrical resistivity increase in the sediment during the treatment. As shown in Fig. 6, in the first test the resistivity increased from an initial value of \( \approx 0.5 \text{ ohm} \) to \( \approx 10 \text{ ohm} \) after two weeks of treatment. In the second, longer, sulphuric acid test, a maximum value of \( \approx 6 \text{ ohm} \) was reached again in about two weeks, and this value stayed almost at the same level in the sections near the cathode (where pH stayed constantly alkaline), while it decreased again in the sections near the anode, where pH lowered to 6–7.

The pronounced resistivity increase observed with sulphuric acid is most probably due to massive sulphate precipitation, which reduced the porosity and increased the tortuosity. Specifically, it may be related to two major phenomena:

1) The main charge carriers are H\(^+\), Na\(^+\), Cl\(^-\) and SO\(_4^{2-}\). OH\(^-\) is not taken into account since it is neutralised at the cathode compartment. H\(^+\) production is constant and its migration rate can be considered constant in the short term (few days) since the acidification of sediment is very slow due to its high buffer capacity. However, since the high initial chloride content of the sediment is gradually transported to the anode where it is released as chlorine gas, in the short time SO\(_4^{2-}\) takes over the main charge carrier role from Cl\(^-\). The mobility of SO\(_4^{2-}\) is of the same order of magnitude when compared to Cl\(^-\):

\[
\text{U}_{\text{Cl}^-} = 7.91 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}, \quad \text{U}_{\text{SO}_4^{2-}} = 8.27 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1},
\]

ionic mobilities from Leinz et al. [58]) but sulphates react with the species present in the sediment and in the pore solution and tend to form precipitates (e.g. calcium sulphate) thus reducing their rate of migration leading to an increase of ohmic resistance of the system.

2) The precipitation of sulphates may cause a modification of the porous structure of the sediment, thus reducing the pore spaces and increasing the tortuosity. As a consequence, the overall electromigration rate is reduced and a further increase in the resistivity is induced.

Since the migrational ionic flux is proportional to voltage drop, the increase of sediment resistivity could, in this respect, have a positive effect in the full-scale treatment, as it makes it possible to increase the voltage drop, and consequently the migrational ionic flux, without exceeding the maximum allowed current limit.

It is interesting to note that H\(_2\)SO\(_4\) tests showed a trend pattern clearly split in three periods. During the first period, of approximately five days, the resistivity kept its initial value almost constant. During the second period, of approximately nine days, the resistivity raised sharply, mostly in the central section. In a third period, starting after two weeks, the resistivity inverted its trend and started to lower especially near the anode. Our interpretation is that the high presence of Na\(^+\) and Cl\(^-\) ions initially hindered the transport of H\(^+\) and OH\(^-\) ions, thus limiting any pH changes in the sediment and favouring the precipitation of calcium sulphates especially in the central section, where both the electrolyte pH conditioning at the anode (due to electrolytic H\(^+\) generation) and at the cathode (due to H\(_2\)SO\(_4\) dosage) were minimal. As a confirmation, the pH values measured at the end of test 1 (Fig. 8) were almost constantly around 7.5 for all sections but for the one immediately close to the anode, which decreased to

![Fig. 7. Crystallization at the cathodic chamber after 43 days during the H\(_2\)SO\(_4\) test.](image-url)
about 6.5. The subsequent depletion of Na’ and Cl’ ions triggered the migration of H+ ions, which favoured calcium sulphate resolubilization. Finally, calcium sulphates were, in turn, transported towards the cathode mainly by the significant EOF, thus causing their crystallization in the cathodic chamber, despite the pH control set-point of 3.

In the second sulphuric acid test, the concentration of sulphates was kept controlled to a fixed value (20 g/l) by adding a constant flow of deionised water at the cathode chamber. The sulphate dilution resulted in a lower increase of resistivity with time, thus validating the hypothesis of the pore blocking mechanism, which was less prominent in this case. However, the formation of gypsum in the cathodic chamber could not be avoided.

The precipitation of calcium sulphate was assessed using a Visual MINTEQ speciation model of Ca in aqueous solution in the conditions detected during the experiments: CO₂ saturation, 25°C temperature, SO₄²⁻ = 20 g/l, Na’ = 18 g/l and Cl’ = 12 g/l. Speciation of Ca was calculated as a function of pH and total dissolved Ca²⁺ concentration. The simulations showed that gypsum (CaSO₄·2H₂O) precipitates even at pH < 1 when Ca²⁺ concentration is higher than 500 mg/l. As long as pH decreases starting from anode, calcite dissolves and a calcium front migrates from anode to cathode. The high Ca content in the solid matrix causes a rapid increase of dissolved Ca over the threshold level.

Unfortunately, since the use of sulphuric acid caused massive crystallization of sulphates at the cathodic chamber (Fig. 7), although not causing specific problems during the laboratory tests, it presents high risks of clogging of the catholyte management circuit, and hence is not advisable to be adopted for the full-scale plant.

### 3.4.2.2. pH variations

The pH profiles (Fig. 8) exhibited the same behaviour in all the tests, with an increase from the anode to the cathode as a result of H⁺ transport towards the cathode. However, due to the high acid buffering capacity of the sediments, the acid front did not significantly propagate towards the cathode. Heavy metal removal is mostly affected by pH distribution in the sediment and metals generally assume soluble form only at low pH. After 14 days of treatment with sulphuric acid, the minimum pH was about 6.4 near the anode and higher than 7 in the rest of the media. After 43 days of treatment, pH had only decreased a little bit and only a slight shift of the pH curve to lower values was observed.

As already discussed, this could be due to the buffering effect of calcium sulphate precipitation in the sediment as a consequence of sulphuric acid dosage. Conversely, nitric acid could lower the pH of the sediment to about 3.6 near the anode and less than 7 in the other sections, except for the last one.

### 3.4.2.3. Electroosmotic flow

In sulphuric acid tests, electroosmotic flow (EOF) increased significantly as a consequence of the considerable voltage gradient rise due to the increase of sediment resistivity (Fig. 9, left). The coefficient of electroosmotic permeability was approximately constant with time (Fig. 9, right), thus allowing us to hypothesize that zeta potential variations were small, also due to the limited variations in sediment pH.

Conversely, during nitric acid test, the EOF direction reversed towards the anode after about 10 days of treatment and stayed moderately negative for the rest of the test (Fig. 9, left). The EOF reversal was attributed to both the higher pH reduction that occurred in this test, and the different nature of pore solution due to the presence of NO₃⁻ ions. The combined effect of these factors increased the zeta potential of sediment particles: indeed, for pH values lower than pH₋ＰＺＣ (with pH₋ＰＺＣ indicating pH at the “point of zero charge”, where the net charge of a solid particle is zero), the particles had a net positive charge (positive zeta potential). The progressing sediment acidification raised further the positive surface charge, thus causing a reduction of the electroosmotic permeability coefficient (Fig. 9, right).

### 3.4.2.4. Heavy metal removal

The distribution of heavy metal concentrations at the end of the three full tests is shown in Fig. 10. The initial heavy metal concentration is reported as a horizontal line. The initial value is uncertain, due to the high inhomogeneity of the sediment. For this reason, an estimation of initial values was calculated from a mass balance of final concentrations in sediment and electrolytes. The graphs show that longer tests achieved better removal of all considered metals and the concentration distribution along the cell was similar, with the lowest values reached near the anode. For Cr and Pb the maximum value was reached in the middle of the cell, and a lower value near the cathode. It is also evident that the low concentration near the anode was reached in relatively short time, while the concentration lowering near the cathode was much slower, hence denoting a clear performance improvement in the longest tests. This is likely the result of a combined effect of pH change, migrational ionic flux and electroosmotic transport.

Since in nitric acid test the electroosmotic flow developed towards the anode, a certain transport of negative and neutral compounds towards the anode occurred continuously. This resulted in higher metal concentration observed in the anolyte solution at the beginning of treatment. This can be explained by the initial presence of chloride in the sediment, which contributed to form negatively charged metal complexes. This trend was confirmed by a comparison of the mass of heavy metals detected in the two electrolytes during H₂SO₄ and HNO₃ tests. At the beginning of all tests, irrespective of the adopted conditioning agent, the detected mass of all target metals was higher in the anolyte than in the catholyte, where it was almost negligible.

To assess the nature of possible metal complexes and their precipitation conditions, Visual MINTEQ was used to perform speciation as a function of solution pH. Cu, Ni, Pb and Zn were analysed under the assumption that all metals were present in the sediment in soluble form with CO₂ saturation and 25°C temperature. Four scenarios were simulated: a) in presence of 3.5% dissolved NaCl and SO₄²⁻ = 20 g/l; b) same NaCl concentration and 20 g/l NO₃⁻; c) low NaCl concentration (Na’ = 8.5 mg/l; Cl’ = 10 mg/l) and SO₄²⁻ = 20 g/l; d) low concentration NaCl and 20 g/l NO₃⁻.

Model calculations showed that all metals were present in soluble form for pH < 7, except Cu and Pb. At pH from 5 to 7, Cu could precipitate as Cu₂(OH)₂Cl in presence of high Cl⁻ concentration, or as Cu₆(SO₄)₂(OH)₈ when sulphuric acid was used as conditioning agent. Conversely, when nitric acid was used, Cu precipitated as CuO at the same pH.

Pb complexes with sulphates could form PbSO₄ precipitate even at low pH. On the contrary, when nitrates were present, Pb was soluble for pH < 5 and could form solid Pb(CO₃)₂(OH)₃ or PbCl(OH) at pH > 5. This could explain the poor Pb mobilization when
sulphuric acid was added, and the higher removal rate observed near the anode in nitric acid experiment, where pH lower than 5 was achieved. In sulphuric acid experiment Pb moved toward the cathode but it accumulated in the middle section. In nitric acid test, Pb was removed from the first two sections where pH was lower. Pb was found in both electrolytes as it possibly migrated toward the anode as a negative complex with chlorine (PbCl₃⁻) and by electroosmosis, while it migrated toward the cathode as Pb²⁺ and PbNO₃⁺ forms.

In the sulphuric acid test, Zn removal was achieved mostly because Zn²⁺ moved toward the cathode by electromigration and soluble Zn(SO₄) was transported in the same direction by electroosmosis. An increased removal was observed in the longer sulphuric acid experiments near the anode because at pH < 7 Zn formed negatively charged complexes (Zn(SO₄)₂⁻) which migrated toward the anode. In nitric acid test zinc moved towards the cathode as Zn²⁺, and as complexed forms ZnCl⁺ and ZnNO₃⁺. A high concentration of Zn was found in the anolyte in nitric acid test, which can be attributed to electroosmotic transport toward the anode.

Ni formed positively charged complexes with nitric acid ([NiNO₃]⁺), but migration occurred towards the anode, thus suggesting a predominance of reversed electroosmotic flow over electromigration. In sulphuric acid test, Ni migrated toward the cathode by electroosmosis as it forms mainly soluble NiSO₄ with neutral charge at low pH transported by electroosmosis and lower

![Image](image_url)

**Fig. 9.** Electroosmotic flow (left) and electroosmotic permeability (right) in the three full tests.

**Fig. 10.** Observed metal removal at the end of full tests.
amount of Ni\(^{2+}\) transported by electromigration. Ni was also found in the anolyte probably due to diffusion.

### 3.5. Comparison with earlier sediment electrokinetic removal studies

A proper comparison of heavy metal removals achieved by screening and full tests with results of earlier studies requires to take into consideration some important parameters, among which the most important are:

- properties of matrix: particle size distribution, hydraulic permeability, pH, ANC, organic matter content, electrical resistivity;
- properties of pollution: type, combination, concentration, speciation;
- operative parameters: distance between electrodes, applied current and voltage, treatment duration, adopted purging solutions, type of installation and control.

In all our experiments, the final pH of sediment and the duration of the process were the key parameters that determined removal yield for the investigated metals. Since the acidic front slowly propagated from the anode to the cathode at a nearly constant speed, a comparison of the removal yields achieved by the screening and full tests must consider the different inter-electrode distance (5 cm for screening tests, 30 cm for full tests). In this perspective, the removal obtained using HNO\(_3\) in the full test at the section close to the anode, when compared to the middle section of all the screening tests, was the highest for all metals except Cr, which was better removed by HCl and H\(_2\)SO\(_4\). HNO\(_3\) was also the agent that achieved the best pH reduction (3.5 near the anode, 6–6.5 in central sections), thus showing that, for the sediment under concern, pH reduction was the key parameter for the removal of all metals except Cr. Kim et al. [5] also reached the highest pH reduction effect with HNO\(_3\) but, differently from our results, they obtained better removal with HCl despite the higher pH achieved. The results of this study show that, despite the high initial pH (8.05) and ANC, the best removal strategy was the use of strong acids, and specifically HNO\(_3\), possibly in relation to the low organic contents.

### 4. Plant design criteria and considerations

The performed analyses and electrokinetic tests allowed us to obtain some important indications for the design of the plant that will be built for full-scale feasibility demonstration of electrokinetic remediation of sediment dredged from Livorno’s harbour seabed. The most significant considerations are reported in the following sections.

#### 4.1. Selection of conditioning agent

The screening tests compared several possible conditioning agents, including strong and weak acids, a chelating agent, a weak acid promoting pH decrease under reducing conditions and water as the electrolytes. All the agents displayed better results than the unenhanced process. Strong acids performed better than weak acids, and EDTA yielded some significant metal removal, although HCl and HNO\(_3\) also showed good results. The use of HCl resulted in the best mobilization yield for Ni, Cu and Zn (higher than 60% in the screening tests), while HNO\(_3\) performed well for all metals, including Pb and Cr (20% removal in full tests). The use of H\(_2\)SO\(_4\) guaranteed the best mobilization yield for Cr, but on the other hand, it appeared to raise a number of side issues related to the massive precipitation of sulphates. On the basis of the acid consumption observed in the corresponding full test, the estimated HNO\(_3\) consumption for treating 150 m\(^3\) of sediment is about 22 m\(^3\) of a 68% HNO\(_3\) solution. A significant reduction of this amount can be obtained by circulating the acidic anolyte to the catholyte circuit. The sequential or combined use of HCl and HNO\(_3\) can be explored as a possible strategy to pursue the best results for both acids.

#### 4.2. Plant assembly and components

Graphite, stainless steel and MMO coated titanium mesh were tested for the electrodes. All of the three materials worked well for the cathode, while only coated titanium exhibited perfect performance for the anode. Graphite underwent some surface decay only in the longest tests. Its brittleness is a further limitation to its use in full-scale plants. The use of stainless steel for the cathode can significantly lower the cost of a full-scale plant, but special care must be posed when strong acids are used as catholyte conditioners, as even short voltage breakdowns can cause cathode corrosion due to the acidity of the conditioning agent. Real-time pH control is required for plant operation, but continuous pH detection is tricky, as pH probe readings are disturbed by the applied electric field. The adoption of isolation amplifiers as galvanic isolators could solve the problem in our full test assembly. The electrolyte composition observed during our tests showed that apart from pH conditioning, the electrolyte management circuit of the full-scale installation should include specific treatments for salinity control and metal removal, in both dissolved and particulate form. The initial salinity of sediment leads to significant chloride gas generation at the anode, thus making a gas control scrubber strongly required in the full-scale plant. The problem is exacerbated if HCl is used as the conditioning agent.

#### 4.3. Main design parameters

The distance between anode and cathode is a crucial parameter. The better removal obtained in screening tests (with 5 cm sediment–chamber length and 20 A/m\(^2\)) than in full tests (30 cm and 40 A/m\(^2\)) allowed us to set 1 m as the maximum allowable inter-electrode distance for the full-scale experiment, with a planned duration of 18 months and an applied current density of 5 A/m\(^2\).

The electrical resistivity of the matrix under treatment is an important parameter for process design and operation. Electro-reclamation of metal pollution can be simplified in two subsequent stages: metal solubilization and transport. pH conditioning (also induced by electrode reactions as a consequence of electric field application), ligand dosage and desorption methods are possible strategies to promote metal mobilization. After mobilization, metals are available as ions, complexes or particles that are transported towards the electrodes by electromigration, electromigration, electro-osmosis or, to a lesser extent, electromigration. In all of the three mechanisms, migration is proportional to voltage drop by a mobility constant. A higher resistivity enables application of a higher voltage with the same electrical current, thus improving the migrational speed and reducing the overall transport duration. Like most marine sediments, those examined in this work showed very low initial resistivity (0.5 \(\Omega\)m). During our tests, the initial value changed as a function of the selected conditioning agents (it was kept almost unchanged with HNO\(_3\), while it rose with H\(_2\)SO\(_4\) and HCl). As the electrokinetic movement of ions in porous media is a matter of desorption and adsorption processes along the way from anode to cathode, the possible positive effect of resistivity increase is not immediately visible in lab or bench-scale experiments, while it is likely to be amplified in full-scale application, when the inter-electrode distance is extended up to 1 m. Since the observed resistivity variation was not constant along the treated mass, in full-scale application with several electrodes, the voltage applied...
to each electrode couple must be controlled separately in order to keep the applied current as close as possible to the maximum allowed value. In this way treatment duration will be minimized.

4.4. Energy considerations
Considering a specific current of 5 A/m², a resistivity of 0.5 Ωm and a treatment duration of 550 days, the total electric energy request to reach the required decontamination is estimated as 24,750 kWh, which is 165 kWh/m³.

5. Conclusions
On the basis of the set of experiments performed, the following most significant findings are emphasized:

- The high alkalinity (pH 8.05) and acid neutralization capacity of the investigated sediment made it particularly resilient to electrokinetic metal removal.
- pH conditioning through anolyte agents was the main factor affecting the remediation effectiveness for almost all investigated metals. EDTA was also found to promote metal removal. However, given the good performance of some strong acids and the environmental risks associated to full-scale use of EDTA, the application of strong acids (HCl, HNO₃) appeared to be a more advisable enhancing strategy.
- Long treatment times were required to obtain significant removal efficiencies: under laboratory test conditions, a good performance was reached only after 60 days, although the electric current densities adopted were 4-8 times higher than those applicable at the full scale.
- Sulphuric acid produced a relevant increase in electrical resistivity and electroosmotic flow, but it also generated significant precipitation of sulphates both within the solid material and in the catholyte, thus making it hardly suitable for full-scale application.
- Among the acid solutions investigated, HCl turned out to be the most effective agent in screening tests, as it removed >60% of Cu, Ni and Zn and 22.3% of Cr in 60 days (screening tests). In view of a system scale-up, however, the high HCl dosages required imply the generation of large amounts of chlorine gas at the anode, requiring a specific gas treatment unit.
- Nitric acid, which was used in a 63-day full test, could effectively reduce sediment pH, but it neither increased the electrical resistivity nor promoted a significant electroosmotic flow. Metal removal was comparable to HCl for Cu and Ni, and it was better for Cr and Pb.
- The best removal of Cr was reached with sulphuric acid, but this acid appeared to raise a number of side issues related to the massive precipitation of sulphates.
- Since the various enhancing agents were found to display different selectivities towards the target metals, further investigation may be conducted on exploring the use of sequential or combined use of extracting solutions.

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