



LIFE+ PROJECT - SEKRET

LIFE12 ENV/IT/000442

"Sediment ElectroKinetic REmediation Technology for heavy metal pollution removal"

DELIVERABLE ACTION B5

“Policy oriented recommendations”



UNIVERSITÀ DI PISA



Port Authority Livorno

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LIST OF ABBREVIATIONS

CSC Contamination threshold concentration

EK Electrokinetic

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1 SUMMARY

Electrokinetic remediation is a technology proposed to remove several contaminants, especially heavy metals, from matrices such as soils and sediments with low hydraulic conductivity. Its most common implementation applies an electric field to the contaminated mass through electrode couples installed in wells with porous walls where specifically conditioned water is circulated. The electric field causes the electrolysis of such solutions, generating an acid front which migrates from anodes to cathodes inducing the desorption and solubilisation of contaminants, and an alkaline front which propagates backward hindering this process, and is hence tackled by dosing acids in the catholite. Electrolysis reactions, conditioning agents, and transport processes due to the electric field cause an increase in the electrolyte ionic strength and its management becomes necessary in order to:

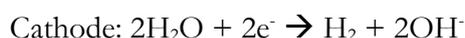
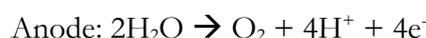
1. avoid species precipitation in the porous matrix, on the electrodes or on the casing walls,
2. avoid the possible inversion of diffusive transport process with the risk of recontamination of the treated matrix,
3. limit the increase in electrical conductivity because the removal efficiency can be reduced and can generate waste of electrical energy.

Scientific literature is mainly focused on the treatment of the contaminated matrix at laboratory scale and it rarely takes into account the field implementation of electrokinetic remediation and the problems related to the electrolyte management and treatment. Therefore, the present study aims at analysing these aspects, focusing on possible solutions, technical aspects and economical considerations.

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2 ELECTROKINETIC REMEDIATION

Electrokinetic drainage is based on the application of a low-intensity electric field to remove inorganic and organic contaminants from solid matrices such as soil and sediments (Reddy and Cameselle, 2009; Yeung, 2011). The process has been tested inserting in various way pairs of electrodes in the matrix to be treated, and adopting different possible methods of chemical conditioning and collection and removal of the contaminants. The most common technique, to which this work refers, applies the electric field through a matrix of equidistant electrodes placed inside vertical wells inserted into the material to be treated (Lageman, 1993). In the anodic and cathode wells two chemically conditioned electrolyte solutions are circulated to optimize the processes and control the operating parameters. The application of a potential difference between anodes and cathodes causes the electrolysis of the solutions, giving rise to the following reactions (Acar and Alshwabkeh, 1993):



H⁺ ions are produced at the anode and at the cathode ions OH⁻. Under the action of the electric field these ions migrate towards the opposite electrodes, generating a pH gradient in the matrix. The acidification propagated by the anode facilitates the desorption of metals and polar complexes which are brought into solution in the interstitial liquid. The basic front generated at the cathode, on the contrary, provokes their reprecipitation, limiting mobility. It is therefore opposed by dosing an acid in the catholyte. Alternatively, it is also possible to dose chelating substances in the electrolytes, while controlling the pH at the operating value. Once in solution, the contaminants are transported towards the electrodes, reaching the electrolytes circulating in the electrode wells, from which they can then be separated by suitable treatments of the liquid phase. The transport mechanisms of contaminants are essentially three (Probstein and Hicks, 1993):

- electromigration, or the transport, caused by the electric field, of ions and other complexes (with no charge) dissolved in the interstitial solution;
- electroosmosis, ie the transport of ions, complexes and dissolved substances (even without charge) due to the movement of the same interstitial solution, in turn generated by the presence of the double electric layer on the charged surfaces of the grains that make up the solid matrix;
- electrophoresis, that is the movement, inside the interstitial fluid, of colloidal particles with a surface charge, caused by the applied electric potential, considered lower than the other two processes in the usual operating conditions (Yu and Neretnieks, 1997).

The electrokinetic decontamination, compared to other remediation technologies, offers the following advantages (Reddy and Cameselle, 2009):

- applicability to porous low permeability matrices such as silts and clays;
- applicability to saturated or unsaturated soils and sediments (anyway in the presence of an interstitial fluid);
- ability to remove heavy metals, radionuclides, organic compounds;

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- flexibility in using ex situ or in situ;
- possibility of integration with other remediation techniques.

The main limitations are instead the following:

- the times may be long and the operating costs are high, above all due to the electricity required;
- the pollutants must be solubilized to be transported, and in the presence of strong bonds with the matrix to be treated, the process may be inefficient even by resorting to chemical conditioning;
- a process fluid is required, which must be supplied and requires appropriate additional treatment;
- some characteristics of the matrix to be treated, such as buffer capacity, can condition the feasibility;
- every single application requires a preliminary investigation based on laboratory tests not yet standardized to define the process.

The full-scale or pilot-scale application of soil Electrokinetic reclamation has achieved some development, showing excellent potential especially in the treatment of low permeability materials (Gent et al., 2004; B.-K. Kim et al., 2011 ; Lageman and Godschalk, 2007). Full scale marine sediment applications are much rarer, although several laboratory studies demonstrate their effectiveness (Chung and Kang, 1999; Colacicco et al., 2010; Iannelli et al., 2015; K.-J. Kim et al., 2011; Nystrom et al., 2005). Sea sediments have many negative factors, such as salinity, buffer capacity and high adsorbent properties, which hinder the acidification of the material and the transport of contaminants (Peng et al. ., 2009).

The full scale application to marine sediments is the objective of the LIFE + SEKRET ("Sediment ElectroKinetic REmediation Technology for heavy metal pollution removal") project, which aims to demonstrate its feasibility by the treatment of sediments contaminated by heavy metals dredged by the seabed in a pilot plant of the port of Livorno. In this port, about 100,000 m³ / year of sediments are dredged on average, partly contaminated by hydrocarbons and by Cd, Cr, Cu, Ni, Pb and Zn just above the contamination threshold concentration (CSC) of Tab.1 Col.B All .5 of the Legislative Decree No. 152/06. The design hypothesis object of demonstration is the electrokinetic treatment in appropriately equipped filler tanks. The pilot plant consists of a tank designed to treat 150 m³ of specially dredged sediment for a period of approximately 18 months. The project also includes a preliminary laboratory phase aimed at defining the operational parameters of the demonstration plant, and some final activities aimed at the ex-post evaluation of the treatment through Life cycle assessment, the definition of application guidelines based on the experience acquired and dissemination of the results obtained.

The present work describes the characteristics and operational experiences deriving from the first months of operation of the demonstration plant, with particular reference to the electrolyte treatment section, which is an important phase of the process rarely treated by the technical-scientific literature, despite the relevant impact on full scale application of the process.

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2.1 Demonstration system

Based on the results of tests conducted in the laboratory for the determination of design and operational parameters (Iannelli et al., 2015; Masi and Iannelli, 2015), the demonstration plant was equipped with the following units (Figure 1):

1. a covered treatment tank equipped with wells (slotted pipes) connected to the hydraulic circuits for recirculation of the electrolytes;
2. energization of the cathode and anode electrodes;
3. pH conditioning of electrolytes;
4. treatment of the electrolytes for the control of salinity and the removal of the transferred metals.
5. abatement of the chlorine gas emissions of the anolyte circuit.

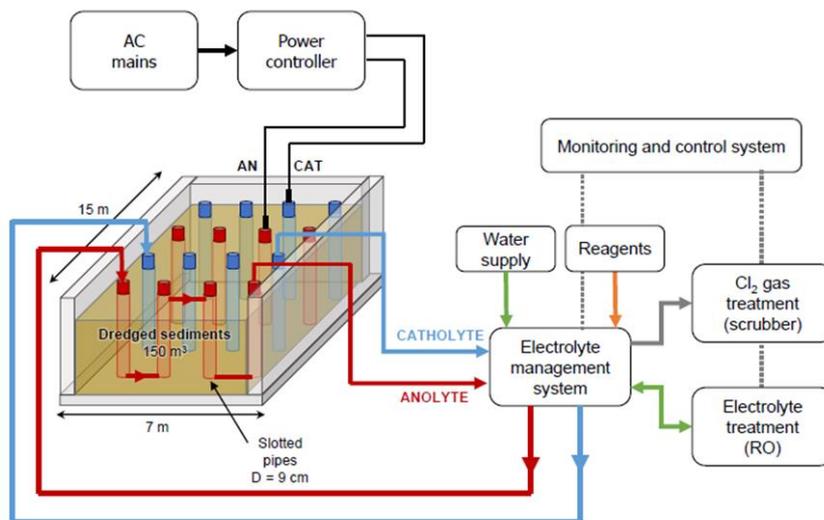


Figure 1 Schematic of the SEKRET demonstration plant

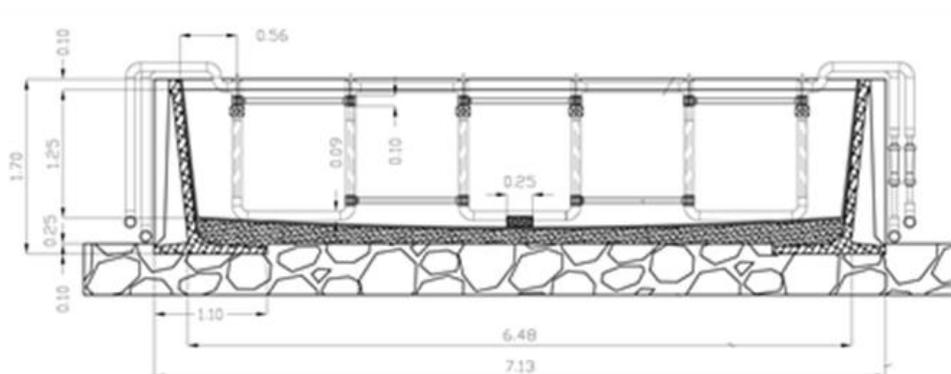


Figure 2 Cross section of the treatment basin

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Figure 3 Treatment tank during filling and operation

2.1.1 Treatment tank

The treatment tank was built in elevation with self-standing reinforced concrete prefabricated panels with a height of 1.70 m. The impression in an external plant, measured at the foot of the basin, is 15.18 x 7.13 x 1.70 m; The thickness of the sediment is about 1.25 m (Figure 2). The tub is internally waterproofed with rubberized Panama fabric protected by geotextile. The tank is equipped with 42 anodes and 42 cathodes inserted in as many micro-perforated tubes arranged vertically in the sediment on 14 alternate lines (7 anodic and 7 cathodic) of 6 electrodes each, arranged on a square mesh of 1 m side. In such tubes the catholyte and the anolyte are circulated by means of two independent pH conditioning circuits. The reinforcements of the prefabricated elements are electrically connected to the cathode to guarantee cathodic protection.

2.1.2 Energization and electrodes

The main characteristics of the energizing section are shown in Table 1, which also shows the operating parameters as a function of the resistivity of the sediment. The plant is made by connecting to the 380V three-phase power grid with a maximum output of 50 kW. The voltage and current control is carried out on each single pair of electrodes by means of solid state power regulators which allow to vary the voltage applied to keep the current constant as the resistive load varies. The devices are managed via a PC, via the Modbus interface on the RS-485 bus. The software installed on the PC communicates with the power regulators and sets the output voltage so as to maintain the current density value of 5 A / m², with the maximum limit of 30V imposed for safety reasons.

Table 1 Characteristics of the energy system

<i>Scenario</i>	<i>Resistivity min</i>	<i>Resistivity max</i>
<i>Resistivity of sediment (Ω m)</i>	0,5	5
<i>Number of anodes</i>	42	42
<i>Current density (A / m²)</i>	5	5
<i>Current for electrode (A)</i>	12,5	12,5
<i>Total current (A)</i>	526,5	526,5
<i>Specific power (W / m³)</i>	12,5	125
<i>Total power * (kW)</i>	1,9	18,75
<i>Maximum voltage * (V)</i>	2,7	26,5

* The reported total power and maximum voltage values do not take into account the additional potential drops occurring at the electrode-electrolyte interface and those due to the well walls.

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The anodes are constructed with a rectangular sheet in a melamine titanium mesh of 1200 x 60 mm dimension, longitudinally bent to 90 ° in an "L" profile. At one of the two ends a titanium bar (D = 6.5 mm) is welded for electrical connections. The cathodes, which do not present the problem of galvanic corrosion, are made up of stainless steel half-pipes with a diameter of 22 mm and a thickness of 2 mm, obtained by longitudinal laser cutting of commercial pipes. Also in this case a stainless steel bar for the electrical connection was welded at one end.

2.1.3 Conditioning of electrolytes

The cathode and anodic wells are connected to two independent recirculation circuits, each of which is equipped with a disconnected free-floating tank and a pair of recirculation pumps. Each circuit is equipped with two groups of continuous pH measurement probes, redox potential, temperature and conductivity placed in and out of the tank. The pH of the catholyte is automatically adjusted by metering nitric acid to neutralize the OH⁻-produced ions and maintain its value in the 2.5 - 3.5 range by PID control at adjustable set-points. To avoid excessive acidity, the pH of the anolyte is similarly adjusted by measuring sodium hydroxide at the adjustable set-point of about 1.5. As an alternative strategy, the pH of the anolyte can be controlled by exchanging an adjustable amount of electrolytes between the two circuits upon removal of the salt content.

The consumption of reagents has been estimated as a function of the applied current of 5 A / m², which corresponds to a production of 472 mol H⁺ / g and 472 mol OH⁻ / g. The results are 31.1 L / g of HNO₃ at 68% and 36.4 L / g of NaOH at 37%. The consumption of nitric acid is estimated to be about 17 m³ for the entire duration of the 18-month treatment. A significant reduction can be achieved by adopting the electrolyte exchange strategy.

The overall flow rate required for the circulation of electrolytes on the 14 6-well lines was calculated using the following criteria:

1. The pH exiting each individual line must not exceed 3, so as to allow sediment acidification;
2. The pH difference in the wells must be minimized.

Criterion 2 is due to the series operation of the six wells present in each of the 14 lines. In fact, in flowing from one well to another, the electrolytes are progressively enriched with H⁺ ions in the anolyte and OH⁻ in the catholyte, generating a significant pH gradient in the circuit.

The curves in Figure 4 show, as a function of the recirculation flow rate and the applied current density, the pH values to be introduced in the anodic and cathodic circuits to obtain pH = 3 at the output. Based on these, the maximum flow rate of the recirculation pumps in 10 L / s has been dimensioned.

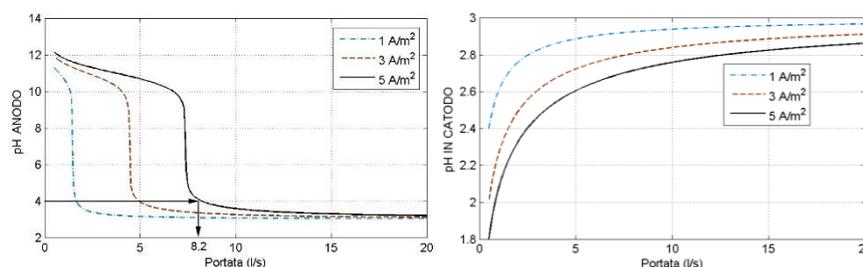
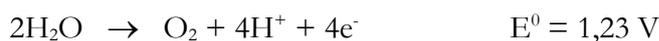


Figure 4 pH of the anolyte (on the left) and of the catholyte (on the right) entering a line according to the total recirculation flow rate

2.1.4 Treatment of gaseous effluent

In the presence of chlorides in the electrolytes, which occurs in marine sediments due to the presence of saline water as an interstitial liquid or even when hydrochloric acid is used as a conditioning agent, the following two competing reactions take place at the anode (Paz-García et al., 2013):



where E^0 (V) is the potential reduction standard. Therefore, a chlorine production occurs when the potential of the chloride oxidation reaction exceeds or equals that of the water electrolysis reaction. The generation of Cl_2 increases significantly as the pH decreases and the chlorides increase. Under the same conditions, with the same applied current, the production of H^+ ions is reduced, and therefore the acidification efficiency of the matrix necessary to desorb the contaminants.

To control the emissions of Cl_2 , an air intake system was implemented from the electrolytic tanks, equipped with a final abatement tower with plastic filling bodies and a wet treatment cycle with sodium hydroxide. To avoid the risk of accidental releases of chlorine from the electrode wells, the entire treatment tank has been fitted with a sealed cover, connected to the suction system sized to guarantee 10 spare parts / hour. However, during the first few months of operation, significant chlorine emissions were detected from the anolyte tank, but not from the treatment tank.

The electrolytes treatment section has been sized in the conservative hypothesis that the applied current promotes only the chlorine electrolysis reaction (which corresponds to an estimated production of 17 kg / d of Cl_2).

2.2 Economic considerations and comparison with other remediation techniques

The estimated costs for the application of electrokinetic treatment have been formulated in the working hypothesis that the treatment is carried out by suitably fitting a reclaimed tank in any case destined to receive the contaminated sediments coming from dredging. Under this assumption, the estimated costs for the pilot plant can be translated to full scale without introducing corrections. On the other hand, as regards the investment costs for the construction of the works, it has been hypothesized that the treatment is carried out by means of special equipment in a reclaimed tank.

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The equipment consists of a network of filtering wells for housing the electrodes connected to hydraulic circuits for recirculation and treatment of electrolytes. This network is expected to be constructed in the catchment tank before the sediment is transferred, and at the end of the treatment it is left untreated. It has been estimated that, considering a current density of 5 A m^{-2} , a resistivity of $0.5 \text{ } \Omega\text{m}$ and a treatment duration of 550 days, the total electric energy to reach the required decontamination level is 165 kWh m^{-3} . The total cost of treatment was estimated at $\text{€ } 62 / \text{m}^3$. The detailed items of estimated costs are shown in our previous work (Masi and Iannelli, 2015).

To compare the electrokinetic technique with other remediation technologies for the removal of heavy metals from marine sediments with silt-clay matrix, the most significant alternatives are represented by sediment washing, thermal desorption, phytoremediation, capping and solidification / stabilization. In the case of sediment washing, experiments carried out on a pilot scale have generally shown considerable difficulties in the treatment of materials with a silt-clay structure (Mulligan et al., 2001; Peng et al., 2009). With regard to thermal desorption, the field of application is very limited because at temperatures below $800 \text{ } ^\circ\text{C}$ only mercury, cadmium and arsenic can be volatilized. The energy expenditure and treatment costs are also extremely high (Mulligan et al., 2009) and well above those we estimated for electrokinetic treatment. As for the phytoremediation, experiences previously conducted on the same matrix (Puccini et al., 2013) have shown very interesting costs (about $1/3$ of those estimated here), but treatment times in the order of several years. This makes this technique applicable only when contamination levels are very limited and the reclaimed tanks can be planted and kept green for long periods of time, as there are no imminent projects for the construction of new port docks. Finally, capping and solidification, stabilization methods are widely applied but being techniques of securing and not reclamation, the comparison is not appropriate.

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3 TREATMENT OF ELECTROLYTES

In addition to controlling the pH, electrolytes must be treated for:

- remove any particulate material that could cause obstructions to the circuit;
- remove heavy metals transferred from the matrix;
- check the salinity increase due to the transfer of macroelements from the treated matrix and to the dosage of the pH conditioning agents.

The increase in salinity of the electrolytes decreases the efficiency of the process as it reduces, with the same current supplied, the electric potential gradient applicable to the matrix. The maximum applicable current, in turn, is limited by the increase in temperature due to the Joule effect, which can lead to overheating of the electrolytes. In other words, very conductive electrolytes are rich in charge carriers antagonistic to H^+ ions which acidify the matrix and transport metal ions by electromigration, hindering reclamation.

Salinity is strongly influenced by the type of reagent used to condition the pH of electrolytes. Nitric acid generates very soluble nitrates which progressively increase salinity to very high values. Sulfuric acid produces sulphate ions which, even in an acidic environment, precipitate rapidly in the matrix, on the cathode and on the porous walls of the cathode wells. On the one hand, this precipitation reduces the ions in solution, increasing the resistivity of the electrolyte and the treated matrix, and on the other it creates obstruction risks on the porous walls and in the circuit. Hydrochloric acid introduces Cl^- ions, aggravating the problem of the generation of gaseous chlorine.

The first months of operation of the pilot plant with dosage of HNO_3 to the catholyte and $NaOH$ to the anolyte have shown the ability to keep all the compounds extracted in soluble form, protecting the plant from obstructions but progressively increasing the conductivity of the electrolytes. Occasionally the generation of a colloidal precipitate rich in trivalent iron has occurred which has caused reddish-brown turbidity to the catholyte. The dosage of soda to contain the acidity of the anolyte significantly increased the consumption of reagents and hindered the removal of chlorides by blocking their conversion to gaseous Cl_2 . If this effect reduced dangerous gaseous emissions, it also reduced energy efficiency by hindering matrix acidification and electromigration transport, as previously described. The recirculation of a catholyte aliquot in the anolyte circuit, balanced by the recirculation of the same anolyte flow rate in the opposite circuit, appeared to be the most promising option for controlling excessive acidification at the anode without increasing the conductivity of the electrolytes. It is however necessary to treat the electrolytes to limit their conductivity and remove the heavy metals transferred from the matrix.

The characteristics of the electrolyte are extremely heterogeneous and the chemical composition varies over time. Figure 5 shows an example of the conductivity of the two electrolytes in the plant. As shown in the figure, both the anolyte (above) and the catholyte (below) are progressively enriched with ions, determining a continuous increase in conductivity. In the two graphs 4 discontinuities are observed that correspond to the instants in which a water replenishment occurred in the circuits. The electrolyte was reintegrated with the addition of treated water to compensate for the losses occurring inside the tank by evaporation of the electrolyte itself.

As can be seen, moreover, the increase in conductivity does not occur equally in both electrolytes, but each has its own peculiar trend. The conductivity of the anolyte grows mainly due to the

production of H + ions at the anode and to the enrichment due to the transport of NO₃⁻ and CL⁻ attracted ions towards the anode. The trend of growth of the conductivity is in fact almost linear because both the production of hydrogenions and the transport are approximately constant since the applied electric current is in turn constant. On the other hand, the main cause of the conductivity increase at the catholyte is the nitric acid dosage. As can be seen in Figure 5 (below) the dosages, very close (every about 10 minutes) produce conductivity deviations with respect to the average trend, due to the probe's response to the sudden change in conductivity due to the introduction of concentrated acid (more conductive than electrolyte). In the case of the catholyte, the increase in conductivity is lower, due to the lower mobility of the nitrate ions (NO₃⁻) which, although produced in the same quantity of H + ions, develop a lower conductivity than the latter.

In-line treatment of electrolytes appears difficult to do, especially due to the need to condition their pH. In the pilot plant an off-line treatment was implemented consisting in periodically transferring the electrolytes into a process tank, replacing them with a similar volume of liquid already treated in order not to interrupt the electrokinetic process. Because of the frequent presence of suspended colloidal particles in the electrolyte, constituted as already said mainly by iron, NaOH is measured in the tank to correct the pH from a value of 1-3 to about 4-5 in order to promote precipitation. Once precipitated, the iron is removed either by sedimentation, by purging the bottom of the treatment tank, or by filtration with a sand filter. Subsequently a reducing agent (sodium metabisulphite) is dosed to eliminate any presence of active chlorine. After removal of the precipitate, the treated liquid is subjected to reverse osmosis to regenerate the electrolyte, reducing its conductivity. For the disposal of the concentrate a system of solar evaporation tanks has been implemented.

Table 2 shows the chemical composition of the electrolyte that was collected in the early stages of plant operation.

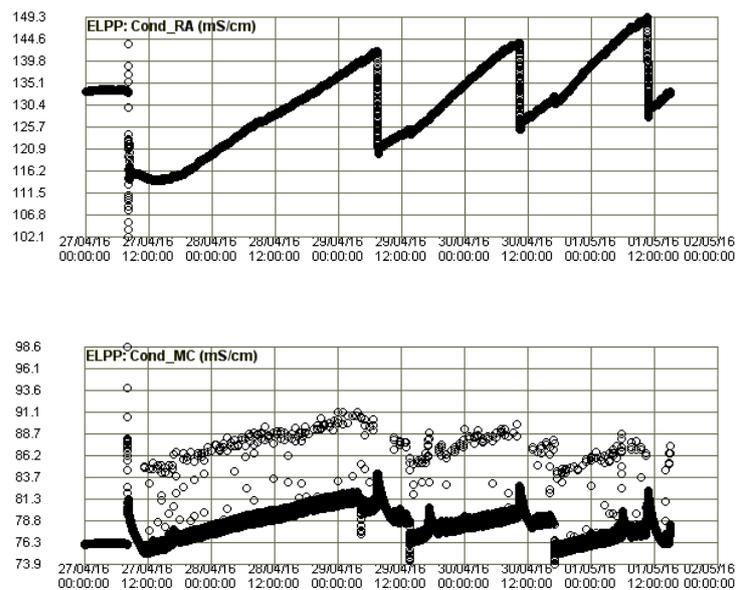


Figure 5 Example of the conductivity of the anolyte (above) and of the catholyte (below)

Table 2 Characteristics of the electrolyte. The analyses were performed on 4 replicate samples

<i>Parameter</i>	<i>Mean</i>	<i>St. dev.</i>	<i>Unit</i>
<i>Conductivity</i>	47,8	0,8	mS/cm
<i>pH</i>	1,58	0,51	-
<i>Aluminum</i>	12,1	4,1	mg/L
<i>Calcium</i>	1495	93	mg/L
<i>Cadmium</i>	0,017	0,003	mg/L
<i>Total chrome</i>	0,4	0,25	mg/L
<i>Iron</i>	18,3	1,7	mg/L
<i>Magnesium</i>	562,5	47,9	mg/L
<i>Manganese</i>	3,38	0,05	mg/L
<i>Nickel</i>	0,24	0,01	mg/L
<i>Lead</i>	0,3	0,05	mg/L
<i>Potassium</i>	328	33	mg/L
<i>Copper</i>	0,18	0,04	mg/L
<i>Silicon</i>	12,6	1,7	mg/L
<i>Sodium</i>	7512	386	mg/L
<i>Zinc</i>	1,38	0,19	mg/L
<i>Sulfur</i>	497,8	36,1	mg/L
<i>Ammonium</i>	211,3	21,3	mg/L
<i>Sulfates</i>	952	149	mg/L
<i>Nitrates</i>	4621	809	mg/L
<i>Nitrite</i>	< 0,5	-	mg/L
<i>chloride</i>	4835	202	mg/L
<i>bicarbonates</i>	< 10	-	mg/L

Being the single treatment tank for the two electrolytes, the analysed liquid was extracted from the aforementioned tank and represents a mixture between anolyte and catholyte. The analyses were performed with ICP-OES (US EPA 7000b: 2007 method). Note the rather high values of sodium, chlorides and nitrates, which are the main ions responsible for high electrical conductivity. The value of the iron refers to that in solution to the pH of the sample; in reality, the iron content is at least one order of magnitude higher if we also analyse the iron contained in the colloidal dispersion present also at very acid pH, which was filtered before the ICP analysis.

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3.1 Reverse osmosis treatment

Given the peculiar nature of the liquid to be treated, the design of the reverse osmosis plant concerned in particular the analysis of the most critical aspects of the electrolyte, namely the extremely acidic pH, the high salinity and the presence of particulate in Suspension.

As far as particulate matter is concerned, made up as already mentioned by colloidal particles composed mainly of iron, it is planned to eliminate it completely through a series of pretreatments, in order to prevent membrane fouling.

The pretreatments consist of:

1. correction of pH with sodium hydroxide (NaOH) to bring the pH to a value of ≤ 5 . It has been estimated that about 2.5 L of concentrated hydroxide (10 M) per cubic meter of solution to be treated has to be used. Once the pH is conditioned, the formation of flakes occurs which can settle on the bottom of the treatment tank;
2. addition of sodium metabisulphite (Na₂S₂O₅) using 3 g of Na₂S₂O₅ for each gram of Cl₂ present in the liquid to be treated. In this way the residual free chlorine, which is harmful to the membrane, can be reduced to chloride;
3. removal of precipitates through purge of the treatment tank and subsequent filtration of the liquid with a sand filter and two cartridge filters of 20 μ m and 5 μ m;
4. possible correction of the pH with HNO₃, to bring the pH back to about 2-3 and to clear any possible reprecipitation of salts before treatment with osmosis.

The sizing of the reverse osmosis system was carried out in two steps. Firstly, the feasibility of the treatment was tested in the laboratory with a pilot plant. Subsequently, the design and verification of the system installed in the field were carried out with the help of the ROSA 9.1 software (Dow Water & Process Solutions). The experimental data obtained in the laboratory were used to validate the simulations performed with the software.

The chemical composition of the electrolyte used in laboratory tests and as input data for software simulations is shown in Table 2.

The membrane used in laboratory tests is the model AG1812C produced by GE Osmonics - Desal (USA), characterized by a permeate operating flow in the 6-14 l / h range and a concentrate flow rate of 80-140 l / h. The membrane has a filtration area of 0.32 m² and works at a maximum pressure of 40 bar.

Laboratory tests were conducted maintaining the constant concentration and pressure of the concentrate at 20 bar and 87 l / h respectively, varying only the salinity of the electrolyte. To simulate the experimental data, the same experimental conditions were set in the ROSA software. In the selection of the membrane in the software the same model used in the laboratory was not available (AG1812C), therefore a membrane with similar characteristics was chosen (RO4040FF) taking care to scale the quantities such as flows, flows and pressures.

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The simulations were carried out by varying the chemical composition of the electrolyte while maintaining the proportions between the elements unchanged.

The results of the tests and simulations are shown in Figure 6. The figure on the left shows recovery (%) and flow rate of the permeate (L / h) as a function of electrolyte conductivity (mS / cm). The graph on the right instead represents the rejection of salts (%) as a function of conductivity. Under the operating conditions adopted, the very low pH (about 2) ensures that no anti-scale is required. Nevertheless, the type of membrane does not seem to be suitable for the treatment of the liquid under examination either because of the very low recovery, or because of the insufficient rejection of salts. The software, however, is able to predict with sufficient accuracy the recovery and maximum rejection of the salts.

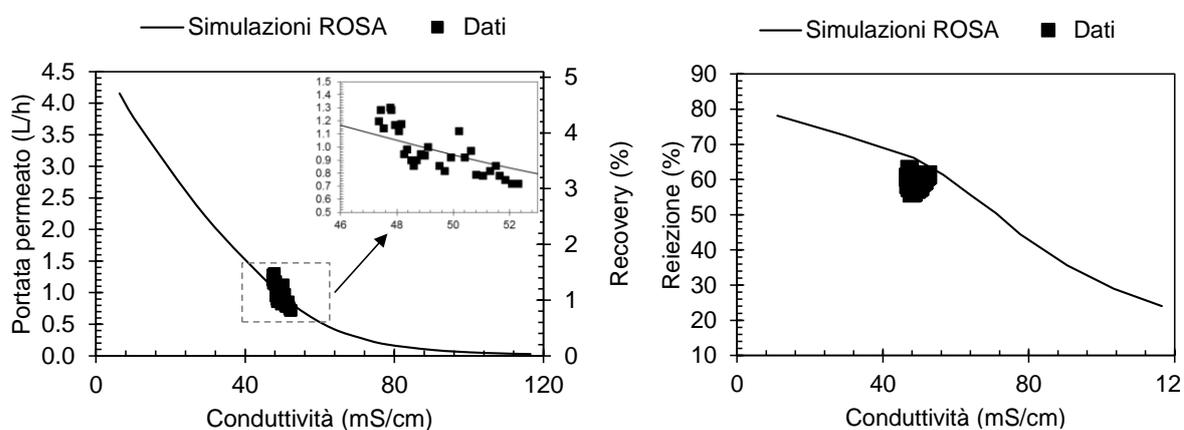


Figure 6 Reverse osmosis test in the laboratory. Flow and recovery as a function of electrolyte conductivity (left) and rejection of salts according to conductivity (right).

Regarding the type of membrane to be adopted in the field, a DOW membrane model SW30-2540 was selected, characterized by a maximum operating pressure of 69 bar, pH range between 2 and 11, maximum supply of 33.6 m³ / d.

We chose to install on the plant a commercial solution produced by Osmosea snc (Osmosea EVO model), equipped with the membrane SW30-2540 and able to work up to a pressure of 60 bar and a concentrate capacity of 10, 8 m³ / d. The verification of the operation of the plant was carried out through simulations with ROSA. The results of the simulations are shown in Figure 7. Also in this case simulations were carried out by varying the concentrations maintaining the same proportions among the chemical species. The simulations were carried out by adopting the configuration shown in the specifications provided by the manufacturer, ie flow rate of 10.8 m³ / g and pressure of 58 bar.

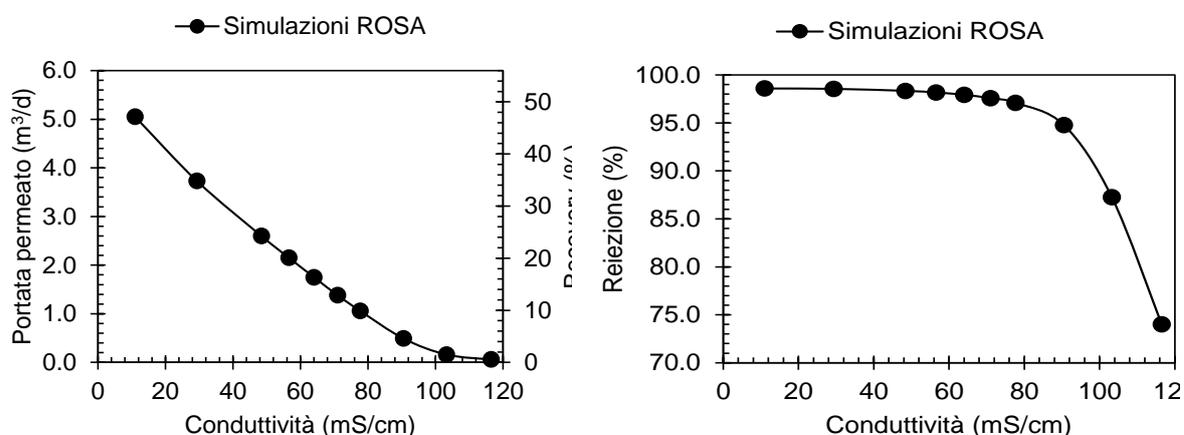


Figure 7 Verify the reverse osmosis system in the field. Flow and recovery as a function of electrolyte conductivity (left) and rejection of salts according to conductivity (right).

The membrane seems to possess ideal characteristics as regards the rejection of the salts, allowing the treatment of the electrolyte within the range of conductivity of interest (50-90 mS / cm). The permeate flow rate, in this conductivity range, is between 0.3 and 2.5 m³ / g. Considering the variations in electrolyte conductivity recorded in the operating conditions adopted (current density and nitric acid dosage), it has been estimated that to contain the increase in conductivity one should replace about 1 m³ / week of anolyte and 0.5 m³ / week of catolith. This estimate was made on the basis of experimental observations because it is very complex to estimate the actual amount of ions carried by the electric field.

It can therefore be concluded that the reverse osmosis plant is effectively sized to meet the demand in terms of treated water.

3.2 Concentrate disposal system

The concentrate produced after reverse osmosis treatment is a liquid with a high salt concentration (electrical conductivity > 80 mS / cm) which must therefore be disposed of.

A simple evaporative system consisting of plastic trays for rapid evaporation of the liquid has been set up for disposal. The trays were placed inside the treatment tank, placed directly above the sediments and can contain up to about 23 L of liquid each, up to a total of 1.5 m³ (65 trays). Evaporation is facilitated by the rather high temperatures that develop inside the tank cover, especially in the summer months. In addition, the trays are made of black plastic that heats up as a result of solar irradiation and further accelerates evaporation.

An estimate was made of the maximum volumes that the system is able to dispose of by calculating the amount of energy necessary for evaporation of the liquid in the solar irradiation conditions present on the site. Table 3 shows the characteristics of the solar evaporation disposal system and the parameters used for the calculation of evaporation volumes. The results of the calculation are shown in Table 4.

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Table 3 Characteristics of trays for the disposal of the electrolyte with solar evaporation

<i>Num. File</i>	13
<i>N. elem. by row</i>	5
<i>Width. Element</i>	0.6 m
<i>Length. Element</i>	1 m
<i>Total number of items</i>	65
<i>Sup. Evap. Total</i>	39 m ²
<i>yield</i>	60 %
<i>Lat. Heat Evap.</i>	2272 kJ/kg

Table 4 Monthly volumes of electrolyte disposal capacity with solar evaporation system

	<i>Detected monthly solar radiation (kJ/m²g)</i>			<i>mean</i>	<i>Mass evap.</i>	<i>Capacity</i>
	2013	2014	2015	kJ/m²g	kg/m²g	evap. m³/mese
<i>January</i>		4049		4049	1.07	1.3
<i>February</i>	5529			5529	1.46	1.6
<i>March</i>	6748		5399	6074	1.60	1.9
<i>April</i>	4184	15341	18131	12552	3.31	3.9
<i>May</i>	20245	20920	20245	20470	5.41	6.5
<i>Down</i>	25104	23709	25104	24639	6.51	7.6
<i>July</i>	25644	21595	25644	24294	6.42	7.8
<i>August</i>	22945	20245	20920	21370	5.64	6.8
<i>Sept.</i>	15341	15341	16039	15574	4.11	4.8
<i>October</i>	8098	10123	8098	8773	2.32	2.8
<i>November</i>	5579		5579	5579	1.47	1.7
<i>December</i>	4724		3374	4049	1.07	1.3
					Total (m3)	48.1

At the end of evaporation, the volumes of liquid are completely disposed of and the only residual waste consists of solid salts.

3.3 Removal of metals with ion-exchange resins

Alongside the reverse osmosis treatment, whose objective is mainly to reduce salinity, the implementation of an ion-exchange resin treatment for the removal of the metals present in the electrolyte coming from the sediments has been considered.

To this end, a laboratory-scale ion-exchange resin column was set up to test the process efficiency directly on the pilot plant electrolytes. Following a selection of the type of resin to be used, depending on the characteristics of the electrolyte, it was decided to use the chelating resin AMBERLITE IRC748 produced by Rohm & Haas (Dow Chemical Company).

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The reason for this choice is that the characteristics shown on the technical sheet, in particular the selectivity scale towards the different metals, have indicated it as the most suitable for the specific case: it is in fact a cationic macroreticular resin that uses as a group functional exchange of the iminodiacetic acid that provides chelating capacities with much greater selectivity for heavy metals than alkaline ones.

The absolute values of selectivity provided in the technical data sheet are however those obtained from the manufacturer by testing the resins with standard solutions that contain in solution only the metallic ionic species to which the value refers. In real operating conditions, the actual selectivity also varies according to the simultaneous presence of different metallic ionic species, of the different concentrations in which these are present and to a lesser extent by other conditions.

For AMBERLITE IRC748 resin the following order of selectivity can be indicated:

$Fe^{3+} > Hg^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} >> Na^{+}$

To test the resin on the specific electrolytic solution for which it is intended to be used, a laboratory setup was set up consisting of a 28mm diameter glass column inside which the resin was loaded. At the top and bottom, the resin is contained in position inside the column by two permeable filters equipped with o-rings for the hydraulic seal and hydraulic connections at the inlet and outlet to connect the column to the hydraulic circuit. During the operating phases, the column is fed with a down-flow flow by means of a peristaltic pump which doses the electrolytic solutions to be treated. At the exit from the column the flow crosses a pH meter arranged in line and finally reaches the hydraulic terminal of the circuit, in correspondence with which the outgoing flows are discharged or collected to be then analysed. The column was loaded with about 185 grams of resin. At the beginning of the experiment, the resin is completely hydrated with deionized water. At the end of the test it was then proceeded to perform a complete regeneration cycle with 9% concentrated HCl acid after a washing with deionized water. The analysis of the concentrations of the metals present in the collected samples was carried out through an ICP-OES.

In the tests, through the peristaltic pump, 380 or 400 ml of electrolyte solution were sent in a column at a flow rate of 10.5 ml / min which is equivalent to 3.15 BV / h. The washing was carried out with 350 ml of HCl.

Two preliminary tests were carried out to verify the behavior of the resin with standard solutions and finally a test was carried out directly on the electrolyte solution sampled at the pilot plant. For the preliminary tests, two standard solutions were used, containing respectively 0.1 mg / L and 2 mg / L of copper.

The electrolytes, before being tested in the column, were preliminarily treated as expected from the pretreatments designed for reverse osmosis treatment, ie the pH of the electrolyte was brought to pH = 4 with sodium hydroxide and the precipitated iron was removed by filtration.

All tests were performed in two replicates each. At the end of each test a mass balance was calculated to check the validity of the analytical procedures. The test results are shown in Table 4.

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Table 4 - Cu abatement test with Amberlite IRC748 ion exchange resin

<i>TEST</i>	<i>Concentration Cu input ($\mu\text{g} / \text{L}$)</i>	<i>Volume solution (mL)</i>	<i>Concentration Cu output ($\mu\text{g} / \text{L}$)</i>	<i>Cu reduction (%)</i>
<i>Standard solution A</i>	100	380	$2,6 \pm 0,4$	$97,4 \pm 0,4$
<i>Standard solution B</i>	2000	380	$3,2 \pm 0,5$	$99,8 \pm 0,03$
<i>Electrolyte</i>	178	400	$3,9 \pm 0,9$	$97,8 \pm 0,5$

The efficiency against copper killing can be considered satisfactory (97.8%). The test result demonstrates the feasibility of applying ionic exchange resins for the eventual recovery of heavy metals present in the electrolyte. However, in the present case the treatment has not been implemented, given the extremely low concentrations of metals in the electrolytes due to the low contamination of the sediment. However, the treatment with resins remains a very promising option in all cases where the content of heavy metals in the solid matrix to be treated is significantly high.

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4 CONCLUSION

The management and treatment of electrolytes deriving from treatment of contaminated matrixes with electrokinetic technique is an aspect rarely analysed in literature but of fundamental importance both from the point of view of process efficiency and from the point of view of waste management and disposal costs. liquids.

In the present work, we analysed the characteristics and operational experiences deriving from the first months of operation of the demonstration plant implemented in the "SEKRET" life project for electrokinetic treatment that was carried out to decontaminate 150 m³ of sediment dredged from the port from Livorno.

Because of the electrolysis reactions, the dosage of conditioning agents and the transport phenomena due to the electric field, the electrolytes are enriched with the removed contaminants and other macroelements, making it necessary to manage them:

- i) remove any particulate material that could cause obstructions to the circuit,
- ii) remove the heavy metals transferred from the matrix,
- iii) control the salinity increase due to the transfer of macroelements from the treated matrix and to the dosage of the pH conditioning agents.

In the pilot plant an off-line treatment was implemented that involves the periodic transfer of the electrolytes into a process tank, replacing them with a similar volume of liquid already treated in order not to interrupt the electrokinetic process.

The main process is the reverse osmosis treatment to regenerate the electrolyte by breaking down its conductivity. The design of the reverse osmosis plant was carried out taking into consideration the most critical aspects of the electrolyte, namely the extremely acidic pH, the high salinity and the presence of chlorine and suspended solids.

The feasibility of a treatment with ion-exchange resins for the removal and / or recovery of metals transferred from the sediment to the electrolyte during reclamation was also analysed. Although it is a very promising option, in the present case it was not implemented because the recovery of heavy metals was considered of little convenience, due to the low concentrations of metals found both in the liquid and in the solid matrix (sediments).

The reverse osmosis treatment is therefore configured as an optimal management option in the case under examination and allows both to limit the volumes of liquid to be disposed of and to produce water with low salt content in place of the exhausted electrolyte, increasing the effectiveness of the electrokinetic process. The disposal of the concentrate was effectively and simply carried out by means of solar evaporation tanks.

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