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Electrokinetic decontamination of Hg polluted soil: state of the art

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The presence of heavy metals (mercury, in particular) in soils is one of the most critical forms of environmental pollution.

Once dispersed in the soil, heavy metals and their compounds may persist unchanged for a long time, as well as migrate to groundwater, thus spreading to other environmental matrixes.

The so-called *Electro-Kinetic Remediation Technology* (EKRT) is a relatively new approach for the treatment of matrixes contaminated by heavy metals and/or organic pollutants.

In its basic configuration [Acar *et al.*, *J. Hazard. Mater.*, **40**, 117 (1995)], the method requires to impose an electric current through the soil by polarization of suitable electrode arrays. The applied electric field will cause: (1) *electro-migration* of charged species (ions) towards the opposite polarity, and (2) *electro-osmotic flow* of the soil solution with mobilization of charged and uncharged species together with solvent itself.

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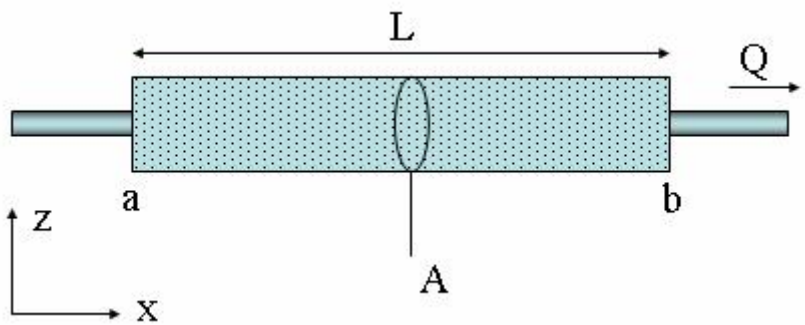
In hydraulics, the motion of a fluid in a porous medium is described by the *Darcy's law*. The ***hydraulic flow*** can be expressed as follows:

$$Q = \frac{kA}{\eta}\frac{(P_a - P_b)}{L}$$



where ***Q*** is the flow rate of the fluid, ***k*** is the hydraulic permeability of the medium, ***A*** is the section interested by the fluid, η is the viscosity, while P_a and P_b are the pressures measured at two different sections of the porous medium, located at a distance equal to *L*

By analogy…

$$q_A = k_e A E$$

where $\boldsymbol{k_e}$ is the coefficient of electro-osmotic permeability, ***E*** is the applied electric field and ***A*** is the section of the porous medium.

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The electro-osmotic flow rate, $\boldsymbol{v_{E.O.}}$, depends on the characteristics of the system:

$$v_{E.O.} = \frac{\varepsilon \zeta E}{\eta}$$

where ε and η are the permittivity and the viscosity of the liquid, respectively; ζ is the potential difference existing between the slipping plane and the liquid bulk, while ***E*** is the intensity of the applied electric field.

Making use of the above expression of $\boldsymbol{v_{E.O.}}$, the electro-osmotic flow rate can be expressed as follows:

$$q_A = \frac{\varepsilon \zeta E}{\eta} nA \qquad\qquad q_A = k_e AE$$

where *n* is the porosity of the medium.

By combining the two equations found for q_A, we obtain an expression for the $\boldsymbol{k_e}$ coefficient:

$$k_e = \frac{\varepsilon \zeta n}{\eta}$$

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According to the Helmholtz-Smoluchowski's theory, the coefficient of electro-osmotic permeability ($\boldsymbol{k_e}$) is independent of the size of the pores; this is obviously not true for the coefficient of hydraulic permeability, $\boldsymbol{k_h}$

$$k_e = 10^{-9} \div 10^{-8} m^2 V^{-1} s^{-1}$$

$$k_h = 10^{-13} \div 10^{-5} m\ s^{-1}$$

J.K. Mitchell (1993), *Fundamentals of Soil Behavior, 2nd Ed., Wiley,* New York

A.T. Yeung (1994), ñElectrokinetic flow processes in porous media and their applicationsò *Advances in Porous Media, Vol. 2, M.Y. Corapcioglu* ed., Elsevier, The Netherlands, 307-393.

An electrical gradient is more effective than an hydraulic gradient in moving a liquid in fine-grained soils and proportionally enhanced by the applied electric field; in addition, the liquid flow can be easily controlled, being confined within the area of application of the electric field.

The zeta potential of the soil determines the flow direction: typically $\zeta < 0$, and the flow is thus directed towards the cathodes.

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In general, the **displacement speed of an ionic specie** (pollutant) is given by:

$$v = \frac{\left(u_i^* + k_e\right)E}{R_d}$$

where u_i^* represents the *effective mobility* of the ionic specie *i* (if we consider the effects of tortuosity and porosity of the soil, this parameter lies between 10^{-5} and 10^{-4} $cm^2\ V^{-1}\ s^{-1}$, therefore comparable with the value of $\boldsymbol{k_e}$); R_d is a dimensionless factor of delay, which depends on the characteristics of the soil to be treated and on those of the pollutant to be removed.

If, for example, complexing agents are used to solubilize the heavy metals, the factor R_d should be appropriately modified.

The above equation highlights the main methods for displacing an ionic specie (pollutant) in a soil: ***electro-migration*** and ***electro-osmosis***.
In particular, *when solubilizing agents have to be used, the contribution associated to electro-osmosis may decrease* (this is due to the relatively high ionic strength)

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The application of the EKRT, when aimed at the removal of pollutants present in metallic form (like mercury) or as poorly conductive minerals (like some sulfides), requires their preliminary dissolution, which can be facilitated by adding appropriate chemicals.

Evidences exist that the presence of an electric field is decisive, possibly because the pollutant-containing particles are able to act as polarizable species (and thus as improper electrodes), as a result of the presence of impurities.

Most described remediation approaches require the introduction into the soil, through the electrode wells, of a leaching system capable of reacting with the metal-containing compounds (*e.g.* [Verdonckt, Maes, *EP 1,090,695* (2001); Foust, *US 5,226,545* (1993)]). However, we verified that an aqueous solution containing iodide (as a complexing agent) plays an effective action against metal contaminants even in the absence of oxidizing species [Bagatin, De Battisti, Rosestolato, Ferro, *EP 2,727,663 A1* (2014)], and a similar behavior applies in case of semiconductor particles such as natural sphalerite (a zinc sulfide doped with iron): as a matter of fact, the leaching of contaminating metals (ion species) from a portion of soils subjected to an electric field has been found to be more important than in the case of a sample simply "washed" with the electrolyte [Ferro, De Battisti, Bagatin, *Research Report*].

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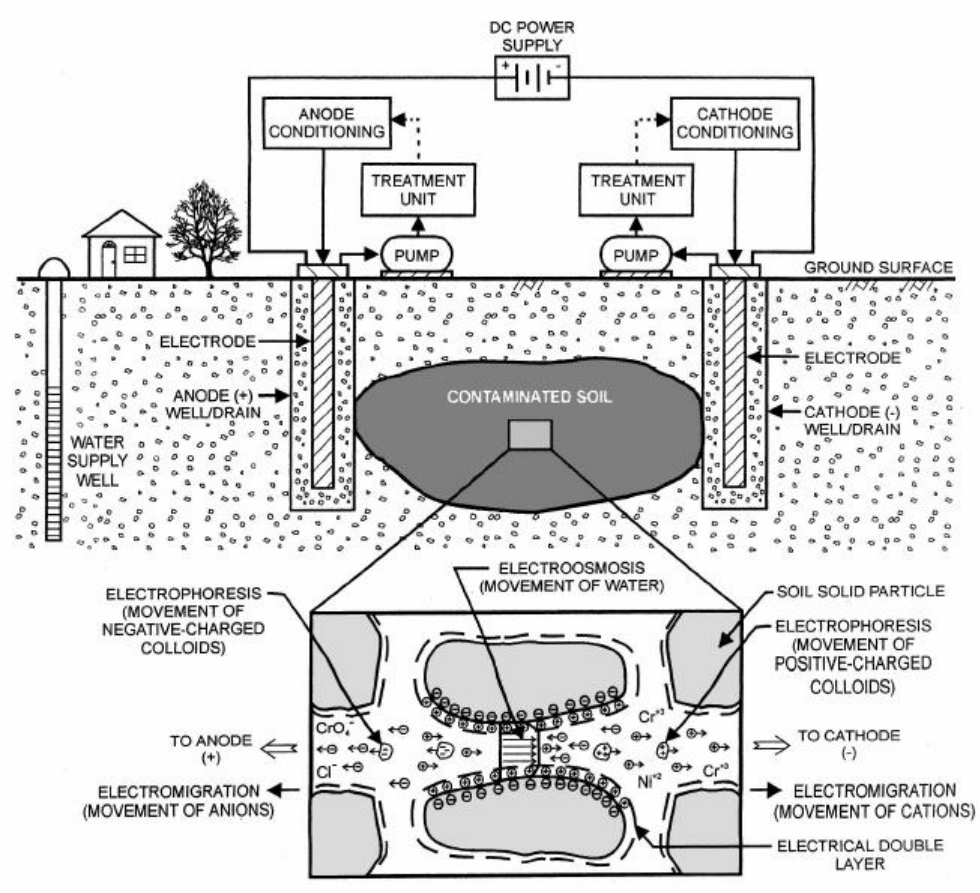

In summary, the energy supplied through the application of an electric field allows the movement of ions and charged particles towards the oppositely charged electrodes

- electrokinetic migration
- chemical reactions
- water electrolysis
- variation of soil properties
- production of radical species

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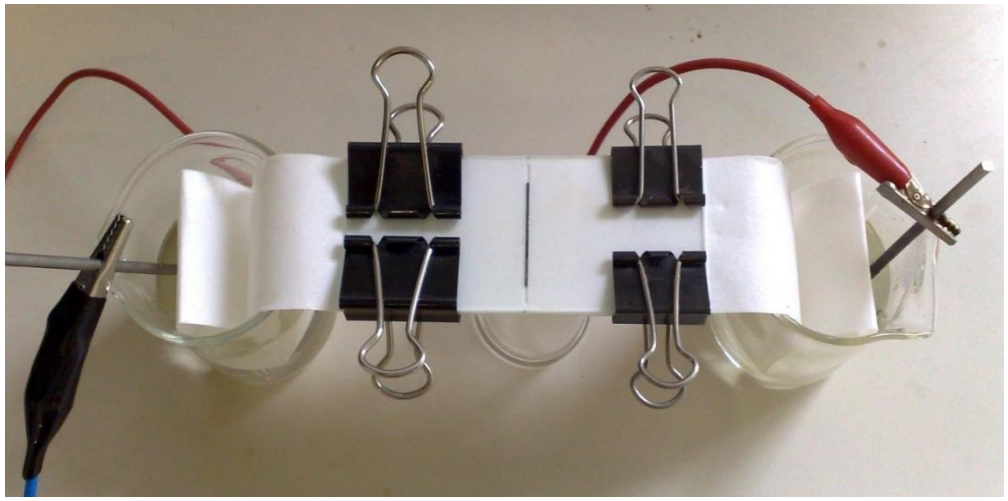
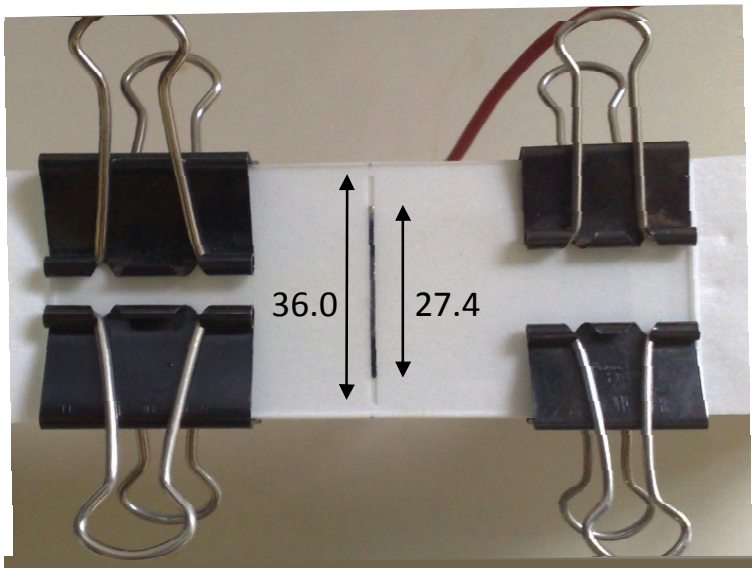
Test "micro" aimed at verifying the reactivity of metallic Hg, when immersed in an electric field

Å“droplet” of $Hg^{(0)}$
Åelectrolytic solution (KI 0.1M)
Åpotentiostatic polarization (15.3V ⇒ about 75 V/m)





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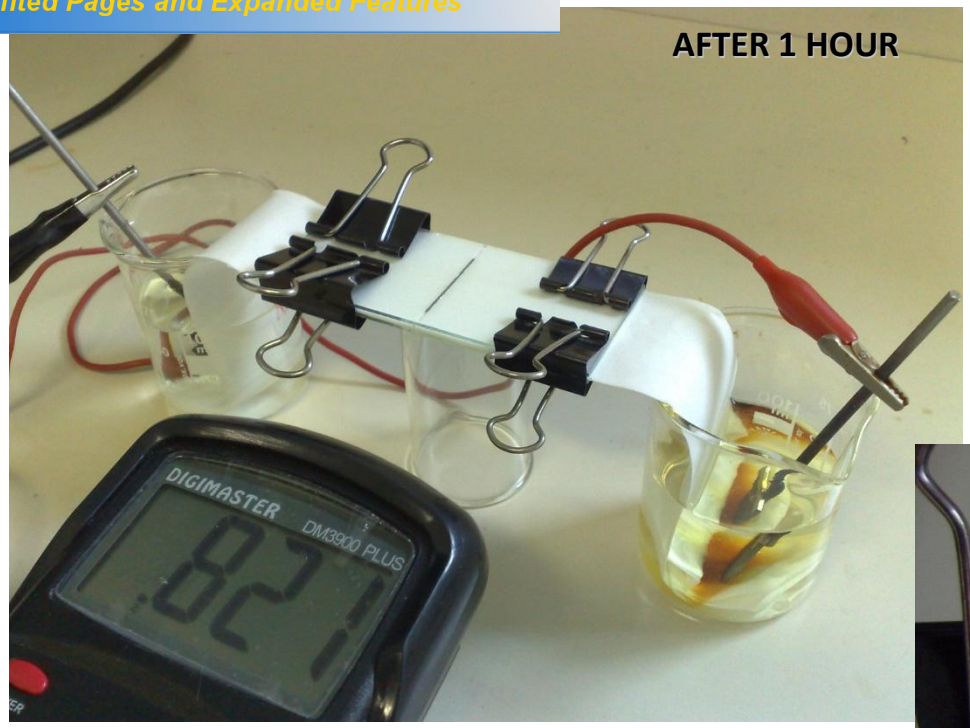

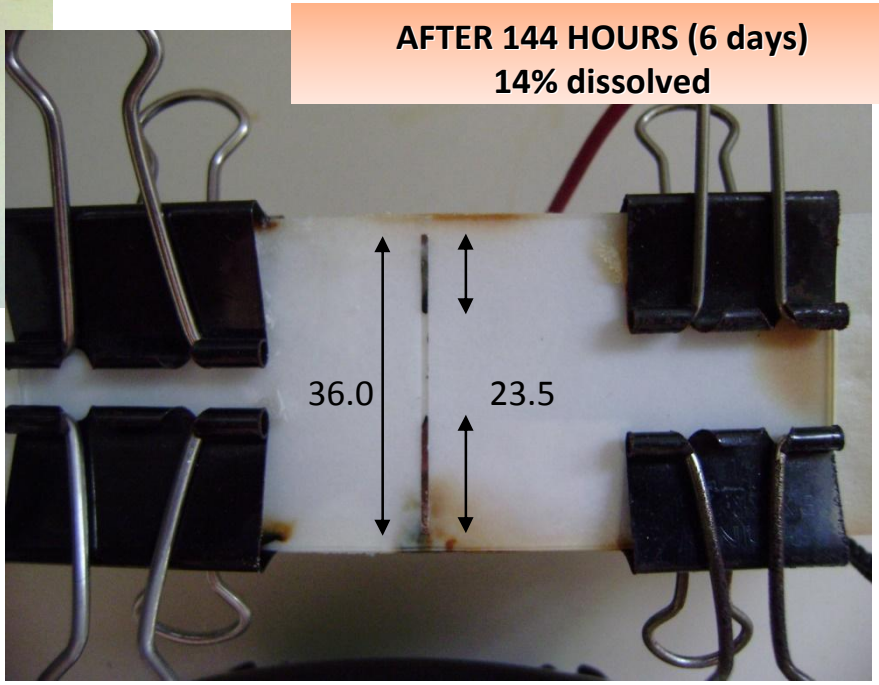

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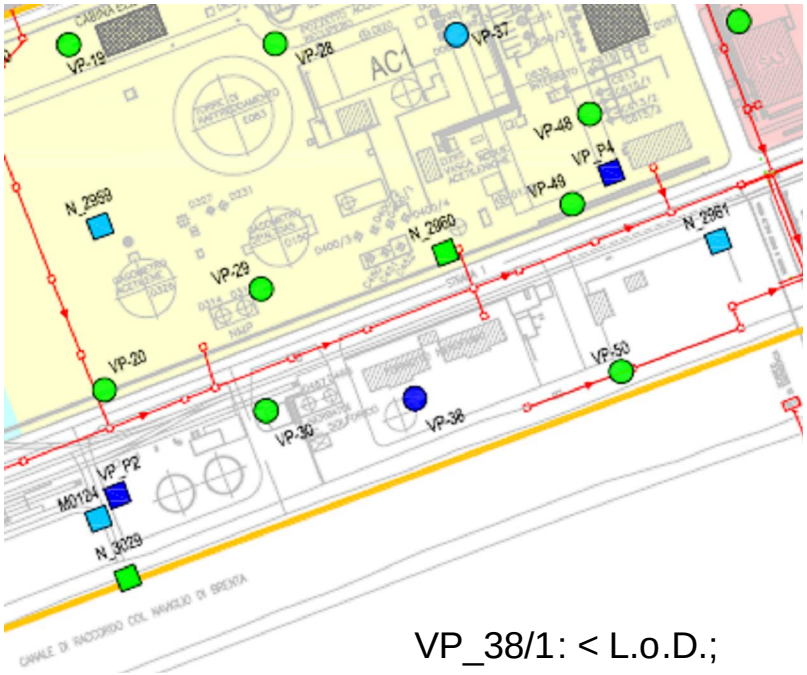
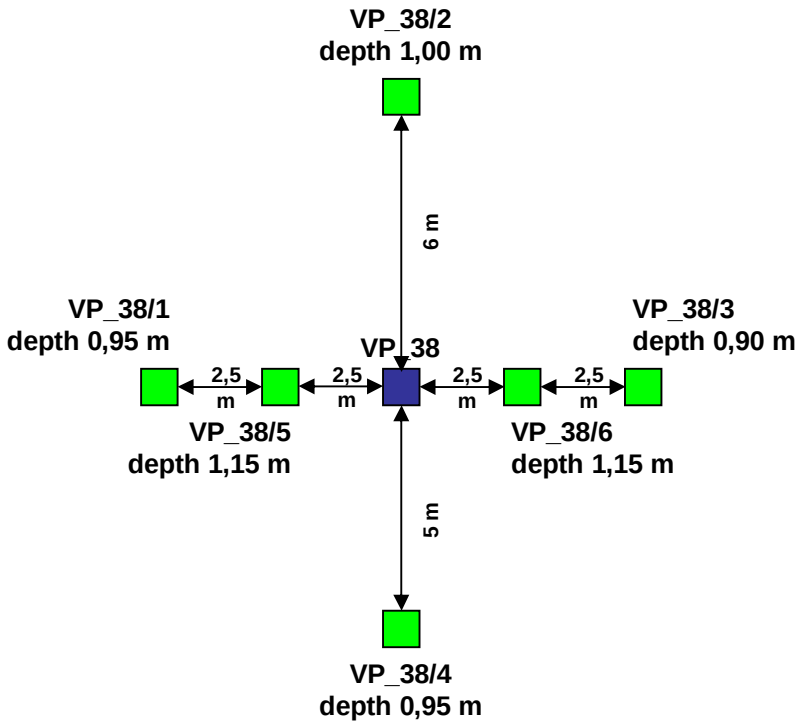


VP_38/1: < L.o.D.;
VP_38/2: 37,6 mg/kg;
VP_38/3: 11,1 mg/kg;
VP_38/4: 44,4 mg/kg;
VP_38/5: < L.o.D.;
VP_38/6: 6,40 mg/kg.

Analysis of mercury (VP_38)

Depth m	Lithology	M.U.	Data referring to fraction < 2mm	D.M. 471/99
0.2 - 0.45	landfill	mg/kg	6,8	5
0.45 - 1	landfill	mg/kg	270	5
1 - 1.5	landfill	mg/kg	11	5



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In March 2010, about 400 dm^3 of soil were withdrawn from a polluted industrial site and provided to UniFE for further laboratory investigations.

The pre-treatment analyses were carried out in parallel by two different laboratories: speciation of the pollutant was performed following the procedure suggested by Boszke *et al.* "Mercury mobility and bioavailability in soil from contaminated area", *Environmental Geology* (2008) 55: 1075-1087.

total Hg : 25 mg/kg vs. 22.36 mg/kg;

the sum of metallic Hg and extractable Hg (organic, water-soluble, associated with humic matter) amounted to 57.4% of total Hg (average between the outputs of the two labs).

Moreover, the Hg associated to sulfides amounted to 33.2% of total Hg (average between the outputs of the two labs).

The % of non-removable Mercury was thus close to 1/3 of the Hg (total) present in the soil analyzed by the two labs.

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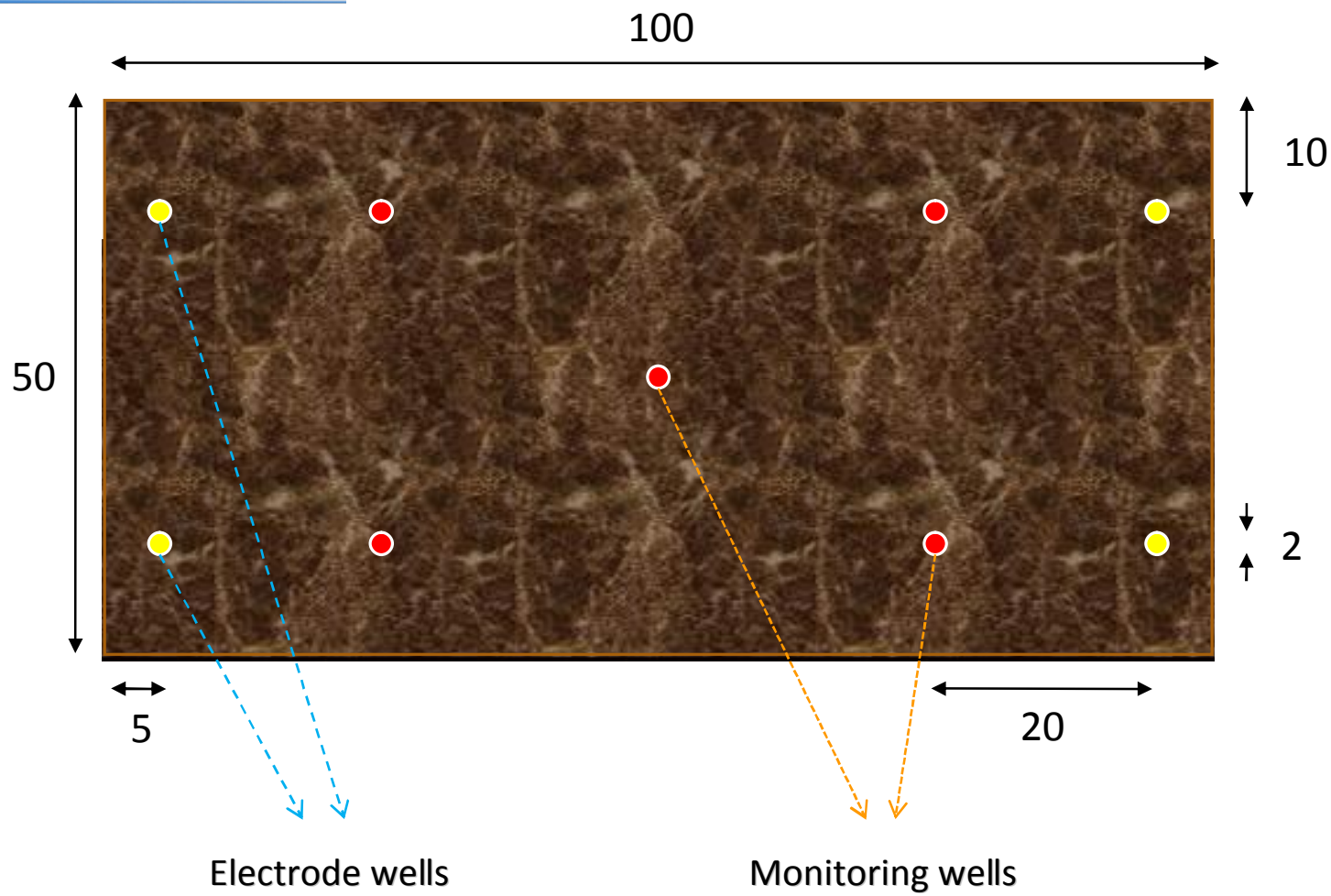

All quotes are expressed in centimeters

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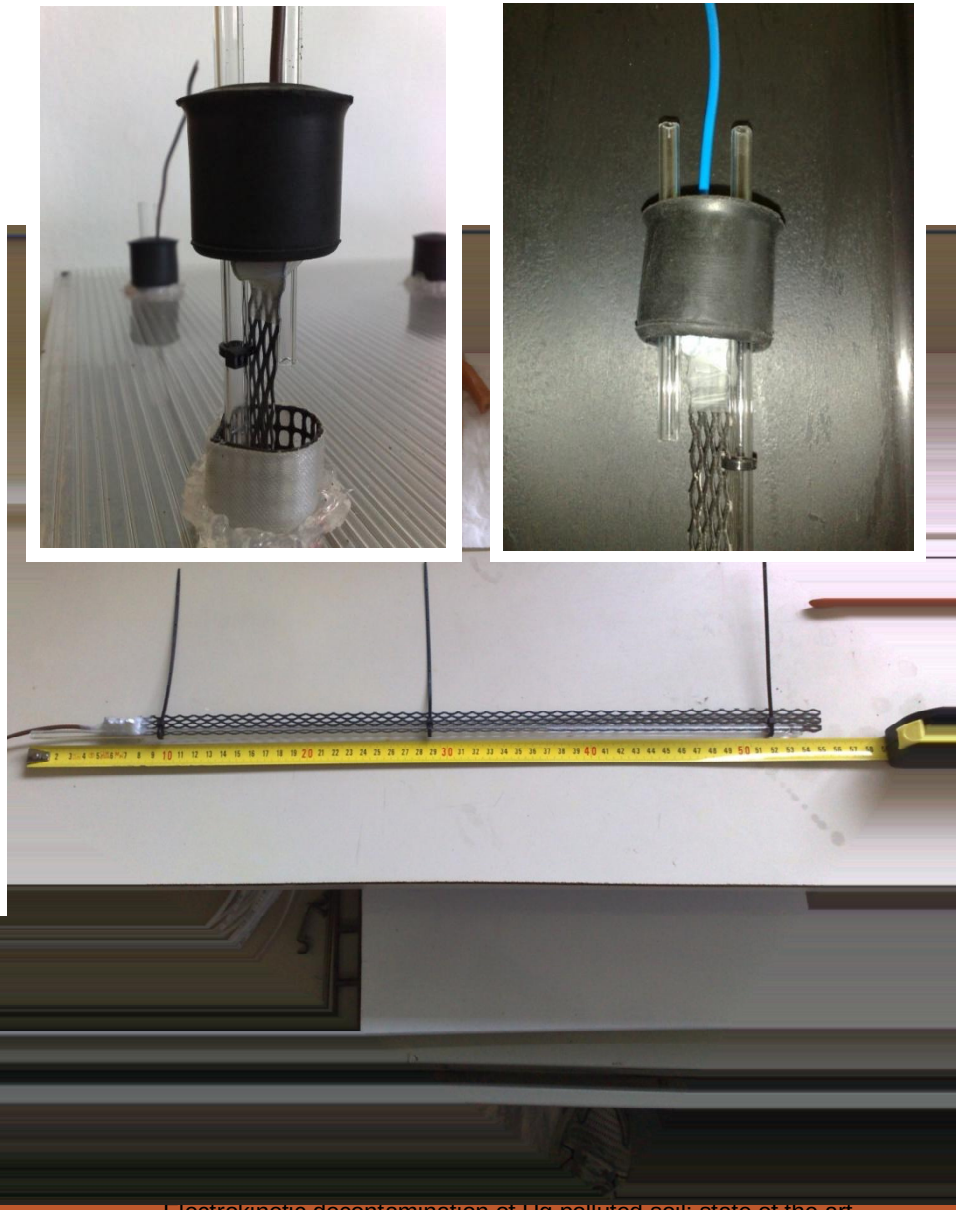

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The remediation test, which involved **0.2 m³ of contaminated soil**, was carried out for a **period of two months and a half**.

The soil was impregnated with a 0.1 M KI solution and, during the first month, the cell voltage was maintained between 20 and 40 V, which allowed the passage of a current between 0.1 and 0.2 A.
A dewatering stage (*i.e.*, the removal of the soil solution that can be withdrawn through the different wells) was performed after two weeks, and then at the end of the month; after the removal of the soil solution (which was enriched with the contaminant), an equal volume of fresh electrolyte solution was added, in order to restore the saturation condition for the soil.

Because of the various additions of KI, the resistivity of the soil progressively decreased, and it was possible to increase the current at 0.3 A with a voltage not exceeding 30 V.
During the last two weeks, the current was further increased to 1 A.

At the end of the test, the soil was washed with three subsequent tap water aliquots (with no electrolyte), in order to remove the greater part of dissolved contaminant; once added, each aliquot was left in contact with the soil for one hour.

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Test started on April 6, 2010, and terminated on June 25, 2010

Treatment period	*dewatering*	Removed volume (liters)	Concentration of Hg (ppm)	Amount of removed Hg (mg)	Applied current and voltage
06/04 – 26/04	26/04	5.5	~0.5	2.75	0.1÷0.2A 21÷39V
28/04 – 05/05	05/05	~6	0.73	4.38	0.2A 26.6V
05/05 – 17/05	17/05	6	3.13	18.78	0.2÷0.3A 21÷32V
17/05 – 31/05	31/05	~6	3.2	19.2	0.2÷0.3A 16÷24V
31/05 – 14/06	14/06	6	5.9	35.4	0.3A 20.3V
14/06 – 25/06	**21/06**	0.01	**10.8**	0.108	**1A 49÷60V**
	25/06	6	7.78	46.68	1A 49÷60V
(washing stage)	28/06	5	7.47	37.35	---
		5	5.94	29.7	
		5	2.90	14.5	

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Since the water samples extracted during the washing stage showed gradually decreasing color, due to the presence of the $HgI_4^{=}$ complex (and/or I_3^- species), the operation was repeated 3 times.

Analytical results clearly showed that significant amounts of mercury were removed from the soil during the washing stage; besides, the value of the third aliquot appeared still significant, confirming the fact that *not all the mobilized and complexed mercury can be easily extracted from the soil*.

It is therefore likely that a part of the total mercury still found in the soil was present as a soluble form; nonetheless, the concentration of the mercury in the earthy matrix dropped from the initial 22 mg/kg of dry matter to 9 mg/kg (-60%).

Soil analysis: *pre*- and *post*-treatment comparison

	pre-treatment	*post*-treatment	variation
total Hg	22.4 mg/kg DM	8.9 mg/kg DM	-60%

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The mercury extracted through the dewatering operations (about 200 mg) does not justify the significant decrease observed by analyzing the soil samples, before and after the EK treatment (about 4.4 g).

Actually, the pollutant can be displaced from the soil, without remaining in the processing water:

- electrodeposition at cathodes, and/or
- adsorption on the geotextile used to wrap the electrode and monitoring wells.

After the treatment, the mercury still present in the soil is partly associated to sulfides (45% of the total) and partly present in metallic form (55% of the total). Anyway, the mercury sulfide fraction represents a non-mobile form and, as such, it does not represent a pollutant of concern.

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- As a result of the application of an electric field (in laboratory), not only the "intrinsically mobile" forms of Hg can be affected, but also the metallic form
- The target of an EK remediation is thus the **"available fraction" of Hg** (mobile and *mobilizable* forms)
- The residual concentration, which is largely *not able to spread in the environment*, should be managed in terms of **risk analysis**
- The solution containing the HgI_4^{2-} complex can be withdrawn from the soil; remediation processes for the removal of Hg may allow to reuse the water
- A *scale-up* is currently in progress, with the aim to reproduce, and possibly to confirm, the interesting results obtained in lab; moreover, further data acquisition will allow to estimate the efficacy and the costs of the remediation.

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Supporting material

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ach and speciation: applied methods

Method by Boszke *et al.* (ÎMercury mobility and bioavailability in soil from contaminated areaô, Environ. Geol. (2008) 55:1075-1087).

- total Mercury;
- organo-mercury species;
- water-soluble species;
- acid-soluble species;
- mercury associated with humic matter;
- insoluble mercury, which comprises:
  - ĭ metallic mercury;
  - ĭ mercury associated with sulfides.

EPA 3200 Method

- extractable-Hg fraction;
- non-extractable Hg fraction (which comprises metallic Hg and Hg associated with sulfides) subsequently separated in:
  - ĭ semi-mobile Hg (including metallic Hg);
  - ĭ non-mobile Hg (including the Hg associated with sulfides).

Analytical methods: AMA254
ICP-MS
atomic absorption

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ach and speciation: applied methods

Initial Soil (from *industrial site*)
Soil after electrokinetic remediation

Each laboratory carried out the speciation procedure by operating on two distinct aliquots of soil. Analyses on extracts and on relating residuals have been repeated three times, in order to determine the standard deviation of the measurement.

The work has highlighted the extreme heterogeneity of the soil under investigation, as well as the problem of sampling comparable amounts of the different residuals, as evidenced by the high standard deviations obtained.

The **method by Boszke *et al.*** has been validated as the **protocol for Hg speciation** on soils, and it represents, at present, a reproducible and reliable approach.

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...ion and speciation: results on initial

	Laboratorio 1		Laboratorio 2	
	Hg [mg/kg]	RSD %	Hg [mg/kg]	RSD %
Terreno VP38 secco	25.00	17	22.36	13
Hg organico	0.038	15	-	-
Hg solubile in H2O	0.279	2	0.192	1.2
Hg solubile in acido	0.414	10	0.134	2.2
Hg frazione Acidi Umici	1.214	39	0.123	0.6
Somma frazioni estratte	1.945	25	0.449	1.3
Hg residuo	22.14	12	19.83	9
Hg metallico	15.27	17	9.808	0.1
Hg associato a solfuri	6.87	12	8.703	0.8

	Laboratorio 1		Laboratorio 2	
		RSD %		RDS %
Hg residuo/Totale	0.886	29	0.887	22
Somma frazioni estratte/Totale	0.078	42	0.020	14
Hg metallico/Totale	0.611	34	0.439	13
Hg solfuro/Totale	0.275	29	0.389	14
Hg non assegnato/Totale	0.037		0.093	

*Both laboratories have applied the **method by Boszke et al.***

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Considerations

- The ratio between residual (sulfides + metallic) Hg and total Hg is always very high, close to 89% (as evidenced by the two determinations);
- As a result, the sum of extractable fractions is small: 7.8 ï 2%.
- The main component of the residual is constituted by metallic Hg, for which values between 44 and 61% have been estimated; considering the relative uncertainty and the different procedures adopted for its determination, the obtained results are encouraging.
- The Hg associated with sulfides is between 27.5 and 39%.

Objective of the remediation

- The **extractable/removable Hg** (sum of metallic Hg and of the various soluble fractions) represents the actual objective of the remediation, and it amounts to **57.4% of total Hg** (average of the outcomes produced by Eni Donegani and TPS Labs), with a 38% RSD;
- The mercury associated with sulfides is the 33.2% of total Hg (average of the outcomes produced by Eni Donegani and TPS Labs), with a 29% RSD.

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	Laboratorio 1		Laboratorio 2	
	Hg [mg/kg]	RSD %	Hg [mg/kg]	RSD %
Hg totale	7.20	3	8.56	5
Hg estraibile(*)	*trascurabile*			
Hg residuo			7.34	3
Hg semi-mobile(*) /Hg metallico	~ 50%		4.11	2
Hg non mobile(*) /Hg associato a solfuri			3.23	1

	Laboratorio 1		Laboratorio 2	
		RSD %		RDS %
Hg metallico/Totale	~ 50%		0.480	7
Hg solfuro/Totale			0.377	6

(*) EPA 3200 Method

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...ch and speciation: results after ...
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Concluding considerations

A significant abatement of the total Hg is obtained: its content decreases from about 22 mg/kg (initial value) to about 8 mg/kg d.m., after the electrokinetic remediation (the observed decrease is slightly higher than 60% of the total Hg).

The Hg that remains in the soil, after the treatment, is present in both forms, metallic and associated with sulfides; interestingly, the remaining sulfide fraction is lower than the initial one.

The latter outcome can be explained on the basis of:

- the heterogeneity of the soil under investigation;
- the limited duration of the electrochemical test;
- the possibility that also the sulfide fraction is transformed into extractable species.

The EPA 3200 method represents and interesting alternative to the Boszke-based speciation of Hg.