Università degli Studi di Cagliari

DOTTORATO DI RICERCA

GEOINGEGNERIA E TECNOLOGIE AMBIENTALI

Ciclo XXIII

TITOLO TESI

USE OF ELECTROKINETIC AND REACTIVE BARRIERS TO TREAT HEAVY METALS-CONTAMINATED SOILS

Settore scientifico disciplinare di afferenza
ICAR/03 Ingegneria Sanitaria-Ambientale

Presentata da:	Daniela Spiga
Coordinatore Dottorato:	Prof. Ing. Luciano Curreli
Relatore:	Prof. Ing. Aldo Muntoni

Esame finale anno accademico 2009 - 2010

University of Cagliari
Doctoral School in Environmental and Land
Engineering and Sciences
PhD Course
Geoengineering and Environmental Technologies
XXIII Cycle

USE OF ELECTROKINETIC AND REACTIVE BARRIERS TO TREAT HEAVY METALS-CONTAMINATED SOILS

Advisor:
AP Eng. Aldo Muntoni
Dr Rod Lynch

PhD student:
Eng. Daniela Spiga

Academic Years 2007-2010

With Love and Affection
Dedicated To Nino,
My Unforgettable Father

Table of Contents

Chapter I

Chapter II

Chapter III

Chapter IV

Chapter V

Chapter VI

List of Figures and Tables

Chapter I

Chapter II

Chapter III

Chapter IV

Chapter V

Chapter VI

Table of Abbreviations

ACL	Acceptable Concentration Limit
AEC	Anion Exchange Capacity
Al	Aluminium
As	Arsenic
AMD	Acid Mine Drainage
BAT	Best Available Technology
BATNEEC	Best Available Technology Not Entailing Excessive Costs
C	Carbon or Concentration
Ca	Calcium
CARACAS	Concerted Action for Risk Assessment for Contaminated Sites in Europe
CCM	Caustic Calcined Magnesite
Cd	Cadmium
CEC	Cation Exchange Capacity
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CIPE	Interministerial Committee for Economic Planning
CLARINET	Contaminated Land Rehabilitation Network for Environmental Technologies
cm	centimetres
CNT-Co	carbon nanotube coated with cobalt
Co	Cobalt
Cr	Chromium
CSM	Conceptual Site Model
Cu	Copper
DC	Direct Current
DW	Distillated Water
EC	European Community or Electrical Conductivity
EDTA	Ethylenediamine tetraacetic acid
Eh	Redox potential
EIA	Environmental Impact Assessments
EK	Electrokinetic
EO	Electroosmotic
EPA	Environmental Protection Agency
EU	European Union
Fe	Iron
FIRS	Ferric Iron Remediation and Stabilisation
H	Hydrogen
Hg	Mercury
IARC	International Agency for Research on Cancer
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectroscopy
IPPC	Integrated Pollution Prevention and Control
K	Potassium
L/S	Liquid/Solid Ratio
Mg	Magnesium
MgO	Magnesium Oxide

Mn	Manganese
N	Nitrogen
Na	Sodium
Ni	Nickel
NICOLE	Network for Industrially Contaminated Land in Europe
NPV	Number of Pore Volumes
O	Oxygen
P	Phosphorous
Pb	Lead
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyl
ppm	parts per million
PRB	Permeable Reactive Barrier
PZC	Point of Zero Charge
P&T	Pump and Treat
RB	Reactive Barrier
RM	Red Mud
S	Sulphur
SEA	Strategic Environmental Assessments
SEP	Sequential Extraction Procedure
Si	Silicium
SIA	Strategic Impact Assessment
SNI	Site of National Interest
SSP	Special Strategic Plan
SSTL	Site Specific Target Level
TCC	Threshold Concentration of Contamination
TCLP	Toxicity Characteristics Leaching Procedure
TCR	Threshold Concentration of Risk
TRM	Transformed Red Mud
USCS	United Soil Classification System
USDA	United States Department of Agriculture
VOC	Volatile Organic Compound
wt	weight
Zn	Zinc
ZVI	Zero-Valent Iron

Preface

Industrial and mining activities throughout the world have contaminated the environment with heavy metals in excess of natural background concentrations. Indeed, especially in the past, the industrial waste residues have been often disposed off in surrounding land and water with a more or less environmentally acceptable management approach, often leading to serious environmental problem in industrialized countries as well as in developing ones, because of the wide distribution and the high toxicity manifested by this type of contaminants. Therefore, the past and current industrial activity has resulted in soil and groundwater contamination that now require remediation.

Also Sardinia (Italy) has to deal with significant problems related to heavy-metals contamination because of its millennial history of mining activities as a result of a large variety and wealth of mineral resources (gold, silver, zinc, copper and lead). The exploitation activity has usually developed without taking into account the consequences of contamination, leaving an inheritance of unsolved environmental problems. Current environmental conditions such as redox and pH or their eventual modification may cause the release of heavy metals: it is well known that under highly acidic conditions, metal ions including Cd, Cr, Cu, Mn, Ni, Pb and Zn, become more soluble and may be released from tailings. As result the mining areas are often characterized by groundwater contamination, accentuated by the presence of huge underground or superficial mine workings that increase rock degradation rate. In addition the extensions of these contaminated areas make difficult their remediation with sustainable costs and for this reason the intervention could be limited to prevent contaminant spread over the adjacent uncontaminated environment.

This book presents the results of three years of research for my PhD about reclamation matter, in which a specific technology has been applied for remediation of metals-contaminated soils. The research has been conducted in the laboratories of the Department of Geoengineering and Environmental Technologies (DIGITA) of the University of Cagliari, whilst a short period has been spent at the Department of Engineering of the University of Cambridge (UK).

I would like to thank Dr. Eng. Aldo Muntoni for the opportunity gave me, important experience of learning and of personal growth and for his invaluable support during my PhD, especially “moral support” in recent months giving me the strength and the courage to complete this experience, despite everything. I wish to thank Dr Rod Lynch for his precious help during my experience at University of Cambridge (UK). I would also like to thank Dr. Giorgia De Gioannis, colleague and friend, and Dr. J.J.P. Zijlstra for their contribution during the experimental activity. I am also grateful to Mrs. Orietta Masala of the IGAG – CNR (Environmental Geology and Geoengineering Institute of the National Research Council, Italy) of Cagliari for help with the chemical-physical analyses.

A special thanks go to all my colleagues for their encouragement and support during these three years of work and to my family for providing continuous moral support; undoubtedly the sweetest and most important thought goes to my father who always believed in everything I did and who will always be in my heart.

Introduction

In the present research the remediation of chromium/arsenic contaminated soils has been studied. The traditional approach consists of excavation and *ex situ* treatment (most typically solidification/stabilization) and/or disposal. However, the high cost of such practices has stimulated the development of *in situ* alternatives for remediation of contaminated soils that are less disruptive and, often, less costly than conventional treatment (Martin and Ruby, 2003). Indeed, especially when the contamination resides in fine-grained soils as clayey or silty soils, the in situ remediation with traditional technologies that use hydraulic gradients could not be applicable being hindered by low hydraulic conductivities of these soils and by their high sorption potential.

An *in situ* technology that has drawn attention by site governmental officials and technicians is electrokinetic (EK) remediation; it can separate the contaminants from low permeability soils by applying a low intensity direct current to the soil. Effective electromigration and electroosmotic flow provide the only option for in situ extraction of heavy metals using electric fields from clays and silts.

The in-situ electrokinetic remediation technique does not require handling material, thus reducing operating costs and risks; it may be easily installed, causing a low impact on the area, because consists of a system located underground with limited above ground installations. This is consistent with the indications of the Italian legislation on remediation of contaminated sites (Legislative Decree No. 152 April 3, 2006, Part IV, Title V), which states that the criteria for the selection and execution of actions have to be based on the BATNEEC principle (Best Available Technology Not Entailing Excessive Costs), that is to identify the best intervention techniques at affordable cost.

In the present research project the electrokinetic technique has been applied in two different conceptual ways: to remediate a contaminated soil, using the electrokinetic to move the contaminant towards the reactive area, and to create a barrier to prevent the spread of heavy metal pollution due to a hydraulic gradient.

In the first part of the study the combined use of electrokinetic and reactive barrier (RB) for the remediation of low permeability contaminated soils by chromium (Cr) and arsenic (As) was investigated. The combination of EK with RB is a possible way in order to enhance EK removal of Cr and As that are reported to be among the more difficult elements to remove by electrokinetics.

A point to be stressed is that the reactive barriers usually work as permeable ones in porous media where convective transport of contaminants is spontaneous, whilst in this research the evaluation of use of reactive barriers in porous media that are not characterised by high permeability has been investigated, providing external energy by the electrokinetic technique in order to make possible the flow of the contaminants through the reactive barrier.

As reactive medium to be used in the barrier a material produced, through a chemical-physical process, by an industrial residue known as red mud (RM) has been chosen. RM is a by-product of bauxite refinement for alumina production through the Bayer process in which $Al(OH)_3$ is precipitated from a sodium-aluminate solution. For each ton of alumina, 1–1.5 ton of residue is produced, consisting mainly of micron-sized aluminium-, silicium-, titanium- and iron-oxides that give the residue its typical brick-red colour and the name red mud. The mud contains a substantial amount of process water with significant sodium hydroxide and sodium carbonate concentration, responsible for its causticity (pH > 13), as well as neo-formed precipitates such as sodium-alumino-silicates (sodalite). Red mud and seawater/brine Transformed Red Mud (TRM), the latter used in this study, have been shown to effectively neutralize acid and immobilize various contaminants by means of precipitation or adsorption.

In the view of a EK-RB combined treatment of soils contaminated by arsenate and chromate, the TRM is a suitable material, as it will be better explained later on, having not only metal immobilizing but also acid neutralization capacity; moreover using low-cost reactive materials, such as this industrial residue, should contribute to improve economics of the proposed combined treatment and its environmental friendliness. Therefore one of the goals of the present research would involve a great environmental benefit, using and recovering a waste that, in turn, represents a significant environmental problem, particularly relevant in Sardinia because of the presence of a bauxite refinery that annually discharge tailings dams around one million tonnes of red mud.

Since immobilization by red mud of oxyanions such as arsenate and chromate has been proven to be most effective under acidic conditions during treatment, in this study the use of TRM mixed with soil as a reactive barrier fitted near the anode of a bench-scale electrokinetic system was investigated, in order to exploit the hydrogen ions production. Chromium and arsenic seem highly suitable to the proposed treatment due to their solubility under the high pH condition generated near to the cathode and the adsorption capacity of the TRM RB for these contaminants.

The goal and the novelty of the research consisted of evaluating the synergic interaction between the EK system and the RB and to compare the efficiency of such combined treatment with usual, unenhanced EK remediation process. Recently, several studies have been carried out on in-situ treatment of contaminated soils using EK coupled with a RB but the main reasons behind this technical approach were: i) EK makes possible using RB also in low permeability soils; ii) the RB adsorption capacity should avoid the contamination of the anolyte and need for its treatment. Therefore whilst in other studies the goal has been trapping into the barrier the contaminants mobilized and brought by electromigration and/or electroosmosis, in the present study also further positive effects were investigated: the TRM of the reactive barrier should help in mobilizing the anionic contaminants to be transported by EK, and, in the same time, the reactions occurring at the anode of the EK system should enhance the trapping capability of the TRM itself. Based on an extensive search, there are not studies where this kind of interaction between EK and RB was never proposed and studied. More in detail, the following advantages deriving from the joint application of EK and a TRM reactive barrier were expected:

- the acid neutralizing capacity of the TRM RB should suppress acidification of the contaminated soil (usually observed during EK treatment and which may hinder oxyanions EK removal) promoting the desorption of oxyanions under the influence of the alkalinity produced at the cathode and, in turn, enhancing their electromigration towards the anodic zone and the TRM RB;

- hydrogen ions generated at the anode during the EK process should provide the acidity required to increase the capacity of the nearby TRM RB to adsorb oxyanions.

Firstly bench-scale laboratory tests on spiked soil were performed as follows:

- illitic-kaolinitic soil spiked with chromate;
- illitic-kaolinitic soil spiked with arsenate;
- kaolinitic soil spiked with arsenate.

Secondly tests on a mine tailing soil and on an industrial site soil were performed to study a natural As contamination.

Unfortunately, it is necessary to highlight the serious difficulties in finding natural soils characterized by low permeability (suitable for the electrokinetic treatment) and contaminated with Cr and/or As. Generally tests were conducted without the use of conditioning agents to assess the effectiveness of TRM RB to mobilize and remove anionic contaminants. The use of conditioning agents in some runs without TRM RB has become necessary to obtain preliminary information on mobilization of contaminant and to joint its use to that of the reactive barrier for enhancing further the whole process. To this regard please note that the purpose of research was not the application of electrokinetic technology as traditionally used to remediate a contaminated soil, but to move the contaminants towards the TRM RB.

This part of the research was conducted in the laboratories of the Department of Geoengineering and Environmental Technologies (DIGITA) of the University of Cagliari.

In the second part of this work, an *in situ* electrokinetic fence was compared with the performance of different permeable reactive barriers (PRB) made of TRM, sodium-treated zeolite, magnesium oxide and biochar. The electrokinetic fence was supposed capable to prevent, contain or retard contaminants migration by configuring cathodes and anodes in a manner that causes contaminants to flow toward the centre of a contaminated area of soil. Copper was the contaminant used.

Several tests were performed in two dimensions (2D). In the electrokinetic barrier runs, a DC electric field was applied to counteract pollutant spread due to an imposed hydraulic head. In PRB runs, different permeable reactive barriers were used so as to seek the best reactive material. The aim of the research was to compare the efficiency of each barrier system on the containment of the copper in order to withstand the spread of contaminant through the soil due to diffusion or hydraulic gradient.

This research was conducted in the laboratories of the Department of Engineering of the University of Cambridge (UK).

Regarding to the general structure of the present manuscript, firstly the outlines of more recent Italian legislation is examined and characteristics of soils and contaminants are illustrated. Secondly a concise theory of the applied technologies to remediate metals-contaminated soils is described and a brief review of research investigations available in the literature about the application of similar technologies for the treatment of arsenic and chromium is provided. Finally, the results from all the performed bench-scale laboratory tests are shown and discussed.

Chapter I

Environmental Legislation on Reclamation

I.1 *The international scene*

The production of waste and the release, continuous or accidental, of hazardous substances into the soil and groundwater and surface water are the main causes of the interaction between production activities and the surrounding environment. These events may directly or indirectly cause an environmental contamination and contaminated sites, clearly posing risks to human health, need to be cleaned-up (Mariani et al., 2008). Contaminated sites remediation represents not only a tool to protect both territory and human health, but also to support socio-economic development of entire areas by favouring the conversion of totally unproductive land into improved environmental, urban and economic areas.

The United States of America were the first, in December 1980, to adopt specific legislation regarding environmental damage and remediation of contaminated sites with the CERCLA (Comprehensive Environmental Response, Compensation and Liability Act). To avoid that the community paid the cost of contaminated sites remediation, this measure (amended in 1986) has established prohibitions for industrial sites and has imposed on companies operating in the chemical and oil industry a specific tax to create a fund called *Super Fund*; it was planned for the rehabilitation of heavily contaminated sites for which can not be found guilty and to finance scientific research in the field of reclamation, so that gave great impulsion to the development of new technologies for remediation of contaminated environmental media.

The authority to prosecute subjects responsible for the contamination is attributed to EPA (Environmental Protection Agency), with the task of providing for site restoration if the responsible person was not available or in case of conditions of urgency, after recovering the costs by identifying responsible people.

This legislation, aimed primarily at land reclamation and ecological recovery of severely contaminated areas, has been joined in 1995 by EPA's “Brownfields Initiative”, whose goal is to work with federal agencies, state and local authorities, non- government organizations, citizens and the private sector to prevent, assess, clean and then reuse the so-called brownfields (sites little or mildly contaminated or perceived as contaminated sites, often consist of old abandoned industries) in a sustainable manner.

The European Union has not adopted a specific directive on the remediation of contaminated sites that uniform procedures and standards and harmonize the many regulations already in place in member countries, although recognizing the importance of protecting soil and groundwater. However, some initiatives has been in this direction, including for example the Community Action CLARINET (Contaminated Land Rehabilitation Network for Environmental Technologies) which started in July 1998. It was attended by sixteen member countries coordinated by the Austrian Environment Agency (Umweltbundesamt), with the aim of building a common technical base between the EU countries, focusing in particular on the analysis of key factors of decision-making field remediation (risk analysis, decision support tools and technologies for rehabilitation), the establishment of a network for exchanging information on methods, technologies and policies adopted in different contexts, on stimulating international cooperation. Other projects that have given impetus to research and collaboration about the remediation of soils have been NICOLE (Network for Industrially Contaminated Land in Europe), an industry-led concerted action programme, and CARACAS (Concerted Action for Risk Assessment for Contaminated Sites in Europe).

With the Decision of the European Parliament and the Council n.1600/2002/CE, has been instituted the “VI Action Community Programme in Environmental Matter”. The environmental protection of the soil from the pollution and the reclamation of the contaminated soil represent a fundamental subject of the community environmental politics and of the Members States. It expects to present a community strategy for the soil in regard to the principles of precaution, prevision and environmental responsibility. At community level, is attached great importance to the reclamation of contaminated soil, with the purpose to rehabilitate them for urban and productive uses. Another important aspect is the problem about the environmental liability in matter of prevention and reparation of the environmental damage, faced with the Directive 2004/35/CE. It has been the first community act based on the “polluter pays” principle, with the aim to prevent and repair damage caused at the animals, plants, natural habitats and water resources, as well as damages caused at the soils. It is defined by the government to compel responsible parties to clean up their sites or help cover the costs.

According to the Directive, the environmental damage is defined as the damage, direct or indirect, caused at the aquatic habitat covered by the community law in water management matter, at the species and natural habitats protect by community directive in matter, and the contamination, direct or indirect, of the lands which create a significant risk for the human health.

I.2 ***The Italian Environmental Legislation***

In the last decades the Italian government has adopted a significant range of environmental measures aimed at improving the quality of the environment and of the human life.

The regulatory system concerning the remediation of contaminated sites began to emerge in the Eighties with a series of specific measures but without an organic legislation.

Initial steps were included in Law No. 349 of 8 July 1986 ("Establishment of the Ministry of Environment and rules on environmental damage") where was sanctioned for the first time the civil liability for environmental damage (Article 18, paragraph 1). Another measure was taken by the Decree Law No. 361 of August 31, 1987 ("Urgent provisions for the disposal of waste”), with the Article 5 in which the Regions were appointed to take their inventory of the contaminated sites with the planning and the regular update of "Plans for remediation of the polluted areas". The decree, then converted into Law No. 441 of October 29, 1987, was followed by another Ministerial Decree (No. 185 of May 16, 1989) where the criteria and guide lines to plan the Reclamation Regional Plans were given;

The first systematic approach to the issue of reclamation matter can be found in the Legislative Decree of the 5th February 1997, nr. 22, “Waste Management Act” that represented the new general policy law, playing a foundation role into the pollution protection matter. It is based on the polluter pays principle and sets the main criteria to develop safety measures and carry out contaminated sites restoration. The Waste Act regulates private and public liabilities with respect to land remediation and provides a legislative framework for the following technical issues (Ferguson, 1999):

- acceptable limits for contaminant concentrations in different environmental media as a function of land use;
- guidelines for sample collection, preparation and analysis;
- general criteria for project design and remedial actions.

The close relationship between contaminated site remediation and waste management was here highlighted since one of the primary sources of contamination is the disposal of waste onto or into the land, or any non-controlled or inadequately controlled deposit of waste onto or into the land. Now this connection is even stronger because, in the case of off-site remediation, once the contaminated soil is removed, although it has its own specific characteristics, it constitutes waste and it must be managed as such.

I.2.1 ***The Ministerial Decree 25 October 1999, n. 471***

In accordance with the article 17 of the Legislative Decree 22/97, the executing Ministerial Decree 471/99 (“Regulation concerning criteria, procedures and ways to make sites safe, to drain and to reclaim the polluted sites”) was drafted. It was the first technical regulation for remediation of contaminated sites, incorporating and harmonizing previous laws and clearly defining for the first time:

a) criteria for estimating soil and site quality;
b) level of contamination accepted for multiple use;
c) strategies for planning and performing site surveys and remediation;
d) responsibilities of site owners, industries responsible for the contamination, new owners of the site or of the industry, etc.

In case of contamination the law required to remove the contaminant in order to reach the acceptable concentration limit (ACL) values which are considered safe for the human health and the natural environment. The objective of the remediation was to reach the limits or build a permanent containment. These acceptable levels had to be achieved without having to perform a site-specific risk assessment that instead was envisaged only for particular situations, the cleaned-up with safety measures. The effects of the D.M. 471/99 were that during the first five years the activities were mainly dedicated to the characterization of the existence of contaminated sites. The remediation activities performed have been the dig and dump or the confinement because of the low price of the landfill disposal and the delay in the application of the Landfill Directive and waste acceptance criteria. In addition the stringent limit values were not seen as feasible with current treatment technologies.

I.2.2 ***The Sites of National Interest***

Regarding the planning of remediation at the national level, with the Law 426/98 is processed a first national program of environmental remediation and restoration of contaminated sites; in accordance with its article 1 the Ministerial Decree n. 468 of September 18, 2001 (Regulation on the "National Plan for Restoration and Environmental Clean-up"), lists the first fourteen Sites of National Interest (SNIs) to undergo restoration, defines prioritising actions, criteria to identify beneficiaries, financing measures, monitoring and check legislation. Besides identifying further sites of national interest, law 179/02 (Environmental annex of 2002 financial law) introduced new measures on the implementation of restoring actions in contaminated areas. Law 266/05 included two new sites of national interest and promoted negotiating procedures between the parties concerned, to be enforced in order to convert contaminated sites of relevant public interest into industrial areas (Ministry for the Environment, Land and Sea, 2009).

The SNIs are selected on the basis of:

- site general features;
- type and degree of contamination;
- environmental impact in terms of health and ecological hazard;
- impact on cultural and environmental heritage.

SNIs comprise Italy's most important industrial areas: among these, petrochemical plants in Porto Marghera, Brindisi, Taranto, Priolo, Gela; urban and industrial areas of East Napoli, Trieste, Piombino, La Spezia, Brescia, Mantova; waste landfills. There are many places highly contaminated for instance by vinyl chloride monomer, polychlorinated biphenyl (PCB), chlorinated pesticides, dioxins and furans (as Porto Marghera); Casale Monferrato is contaminated by asbestos of the factory Eternit, Taranto by polycyclic aromatic hydrocarbons (PAHs), lead, dioxins, PCBs and carbon monoxide because of the steel industry; Brindisi by the illegal dumping of industrial wastes of petrochemical, Gela by sewage sludge containing mercury and by discharges into the sea of water process of refineries and petrochemical plants. Contamination is a quite complex issue, since in most cases industrial activities with different source and intensity have followed one another over decades, thus remarkably compromising the use of landscape and environmental resources.

Concerning Sardinia two sites of national interest are included: the Sulcis Iglesiente Guspinese area and the industrial area of Porto Torres.

In total the National Remediation Plan includes 57 SNIs (Figure I.1) (last added at the end of 2008, “La Maddalena”) surveyed by the Ministry of National Remediation Programme, based on the characteristics of the area, the amount and type of pollutants and the severity of the health and environmental risks. It is 639,414 hectares (more than 600,000 football fields) of polluted land, some of which, the "megasites” (as Casale Monferrato: 74,325 hectares; Litorale Domizio Flegreo: 140,755 hectares; Sulcis: 356,353 hectares), with levels and extensions of the contamination of soil and groundwater that suggest no less than 25 years for a total recovery (APAT Environmental Data Report 2006).

To these it needs to add thousands of sites of interest and regional expertise: 15,000 potentially contaminated and more than 4,000 those determined to be reclaimed.

In Figure I.2 the partitioning of sites indicated in the Regional Registers is shown according to the progress of remediation.

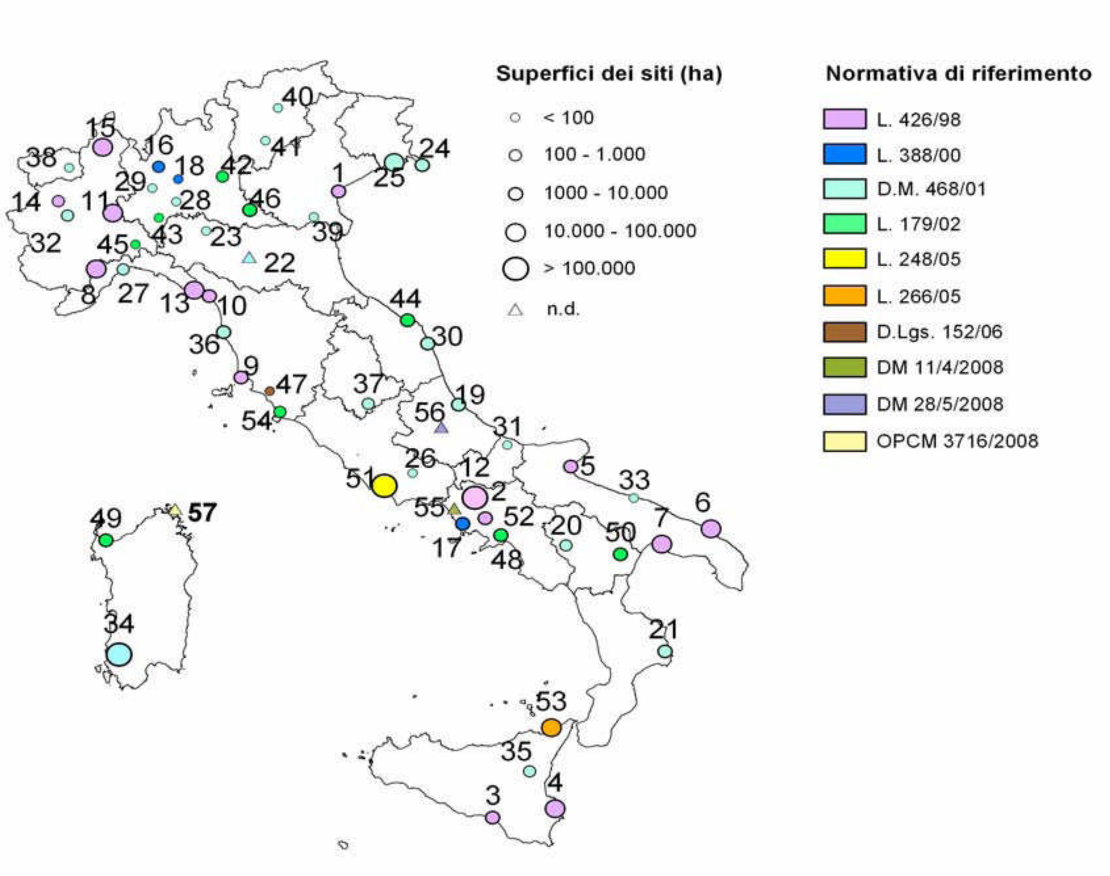


Figure I.1 *Sites of National Interest (D'Aprile L. and Romano E., 2009)*

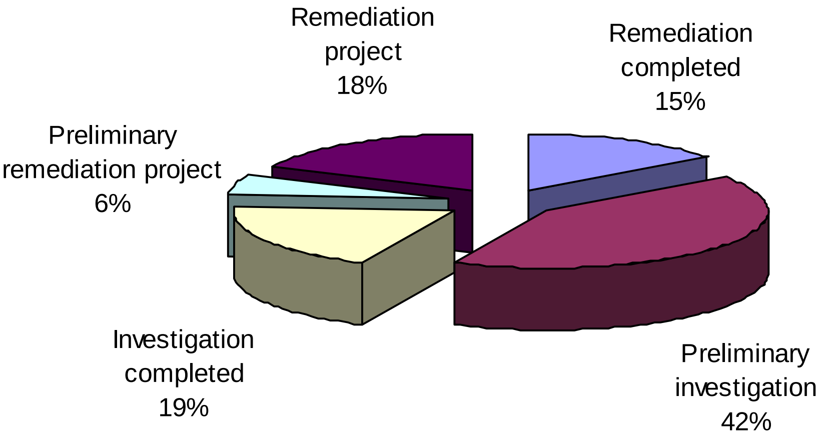


Figure I.2 *Sites included in the regional registers. Data from Regions, ARPA/APPA (2006)*

According to some estimates, SNIs identified cover about 3% of the national territory. Level and nature of pollution greatly vary and require differentiated actions. Frequently, in the SNIs the actions of securing (especially the pump and treat of groundwaters) have been adopted without a deep knowledge of the local situation and the existing real risk; the remediation technologies were lowly applied and this strategy has caused a waste of money on interventions which didn't solve the problems.

Table I.1 *Sites of National Interest, by region, land and sea surface, and main contamination type (2008)*
Source: Ministry for the Environment, Land and Sea, 2009

Region Site name (SIN)	Surface (hectares) Ground surface	 Surface at sea	Main contamination types
Piemonte			
Casale Monferrato	74,325		Asbestos
Balangero	317		Asbestos
Pieve Vergonte	12,242		Chemical
Basse di Stura	163		Iron and steel Landfills
Serravalle Scrivia	74		Chemical Landfills Waste
Valle d'Aosta			
Emarese	15		Asbestos
Lombardia			
Sesto San Giovanni	256		Iron and steel
Pioltello - Rodano	85		Chemical Landfills
Cerro al Lambro	6		Landfills Waste
Milano - Bovisa	43		From gas production Hydrocarbon stocks
Brescia - Caffaro	263		Chemical Landfills
Laghi di Mantova e Polo chimico	1,03		Petrochemical

Region Site name (SIN)	Surface (hectares) Ground surface	 Surface at sea	Main contamination types
			Refinery
			Chemical
Broni	14		Asbestos
Trentino-Alto Adige			
Bolzano	26		Chemical
Trento nord	24		Chemical
Veneto			
Venezia Porto Marghera	3,221	2,566	Petrochemical
			Chemical
			Electric
Mardimago - Ceregnano	57		Manufacturing
			Landfills
Friuli Venezia Giulia			
Trieste	502	1,196	Iron and steel
			Refinery
			Landfills
Laguna di Grado and Marano	4,198	6,831	Petrochemical
			Iron and steel
			Landfills
Liguria			
Cengio and Saliceto	22,387		Chemical
			Waste
Pitelli	338	1,571	Landfill
			Waste
			Shipyard industry
Cogoleto - Stoppani	46	168	Chemical
Emilia Romagna			
Sassuolo - Scandiano	1		Manufacturing
Fidenza	25		Chemical

Region Site name (SIN)	Surface (hectares)		Main contamination types
	Ground surface	Surface at sea	
Toscana			
Piombino	931	2,12	Iron and steel Landfills
Massa and Carrara	1,648	1,891	Iron and steel Abestos
Livorno	656	1,423	Landfills Electric Refinery Hydrocarbon stocks
Orbetello	64	2,646	Chemical
Landfill Le Strillaie	53		Landfills Waste
Umbria			
Terni - Papigno	655		Iron and steel Landfills
Marche			
Basso Bacino del fiume Chienti	2,641	1,191	Manufacturing
Falconara Marittima	108	1,164	Refinery
Lazio			
Frosinone	2		Landfills
Bacino del fiume Sacco	117,086		Chemical Manufacturing
Abruzzo			
Fiumi Saline e Alento	1,137	778	Manufacturing Landfills Waste
Bussi sul Tirino	234		Chemical Landfills Waste

Region	**Surface (hectares)**		**Main contamination types**
Site name (SIN)	**Ground surface**	**Surface at sea**	
Molise			
Campobasso - Cuglionesi II	4		Waste
Campania			
East Napoli	834	1,433	Petrochemical Refinery Hydrocarbon stocks
Litorale Domizio Flegreo and Agro Aversano	157,025	22,412	Landfills Waste
Napoli Bagnoli - Coroglio	945	1,494	Iron and steel
Litorale Vesuviano areas	9,615	6,698	Landfills Waste
Samo river hydrographic basin	42,664		Manufacturing Waste
Pianura	156		Landfills Waste
Puglia			
Manfredonia	304	853	Chemical Landfills
Brindisi	5,733	5,59	Petrochemical Electric
Taranto	4,383	6,991	Iron and steel Manufacturing Refinery
Bari - Fibronit	15		Asbestos
Basilicata			
Tito	315		Asbestos Waste
Industrial area in Val Basento	3,33		Chemical Asbestos

Region **Site name (SIN)**	**Surface (hectares)**		**Main contamination types**
	Ground surface	**Surface at sea**	
Calabria			
Crotone - Cassano - Cerchiara	868	1,452	Chemical Iron and steel Landfills
Sicilia			
Gela	795	4,563	Petrochemical Landfills
Priolo	5,815	10,085	Petrochemical Refinery Electric
Biancavilla	330		Asbestos
Milazzo	549	2,19	Petrochemical Refinery Landfills
Sardegna			
Sulcis - Iglesiente - Guspinese	61,918	89,121	Petrochemical Chemical Electric
Industrial areas in Porto Torres	1,844	2,762	Petrochemical Iron and steel Electric

The remediation of soil and water and the restoration of degraded areas are complex operations requiring specific technical and scientific know-how, including knowledge of the methodologies and tools required to tackle problems arising during the different phases of the remediation process (Mariani et al., 2008). There are many issues inherent in managing contaminated or potentially contaminated sites that should always be taken into consideration: physical-chemical behaviour and toxicological properties of the pollutant chemical species involved; geology and hydrogeology of the area under examination; engineering of environmental remediation projects and workers' health and safety.

To this regard, health and environmental risk assessment is a well-consolidated procedure applied at European and extra-European level for the management of contaminated sites. This assessment tool allows to:

- quantify the risks to human health and the environment associated with contaminated sites and determine the concentration limit values for environmental matrices subject to contamination, corresponding to an acceptable level of risk and according to the specific conditions of the individual site;
- plan environmentally compatible remediation interventions with economically sustainable solutions while driven by the principle of environmental system conservation.

As mentioned before the D.M. 471/99 did not counted a site-specific risk assessment.

I.2.3 *The Legislative Decree 3 April 2006, n. 152*

On 29th April 2006 the Legislative Decree dated 3 April 2006 n. 152 "Environment Regulation" was adopted by the Italian Government. The Environmental Consolidation Act was designed to "rationalize and coordinate the whole legislation on environmental matters" and was divided up into the following chapters:

- procedures for strategic environmental assessments (SEA), environmental impact assessments (EIA) and integrated pollution prevention and control (IPPC);
- preservation of soil, prevention of desertification, water pollution protection and water resources management;
- waste management and remediation of contaminated sites;
- air protection and reduction of atmospheric pollution;
- environmental damage.

The Title V under section 4 deals with contaminated sites clean-up activities.

This legislation aims at reducing or eliminating pollution sources, identifies principles and application fields of restoration-related legislation and describes procedures, criteria and operation modes to carry out the necessary actions for area clean-up, in accordance with European principles and measures.

The most important change regarding the reclamation project procedures was the need of a site-specific risk-based approach to calculate the site specific target levels (SSTLs), i.e., the levels of contamination of the saturated and unsaturated soil, which, if exceeded, require safety measures and remediation and to determine the remediation project objectives.

Moreover a cost-effective analysis was required to evaluate the remediation solutions and the application of BAT (Best Available Technology) had to be favoured as defined on 97/61/CE Directive.

A fundamental step in applying the procedure of risk assessment is the reconstruction of the Conceptual Site Model (CSM) (Figure I.3).

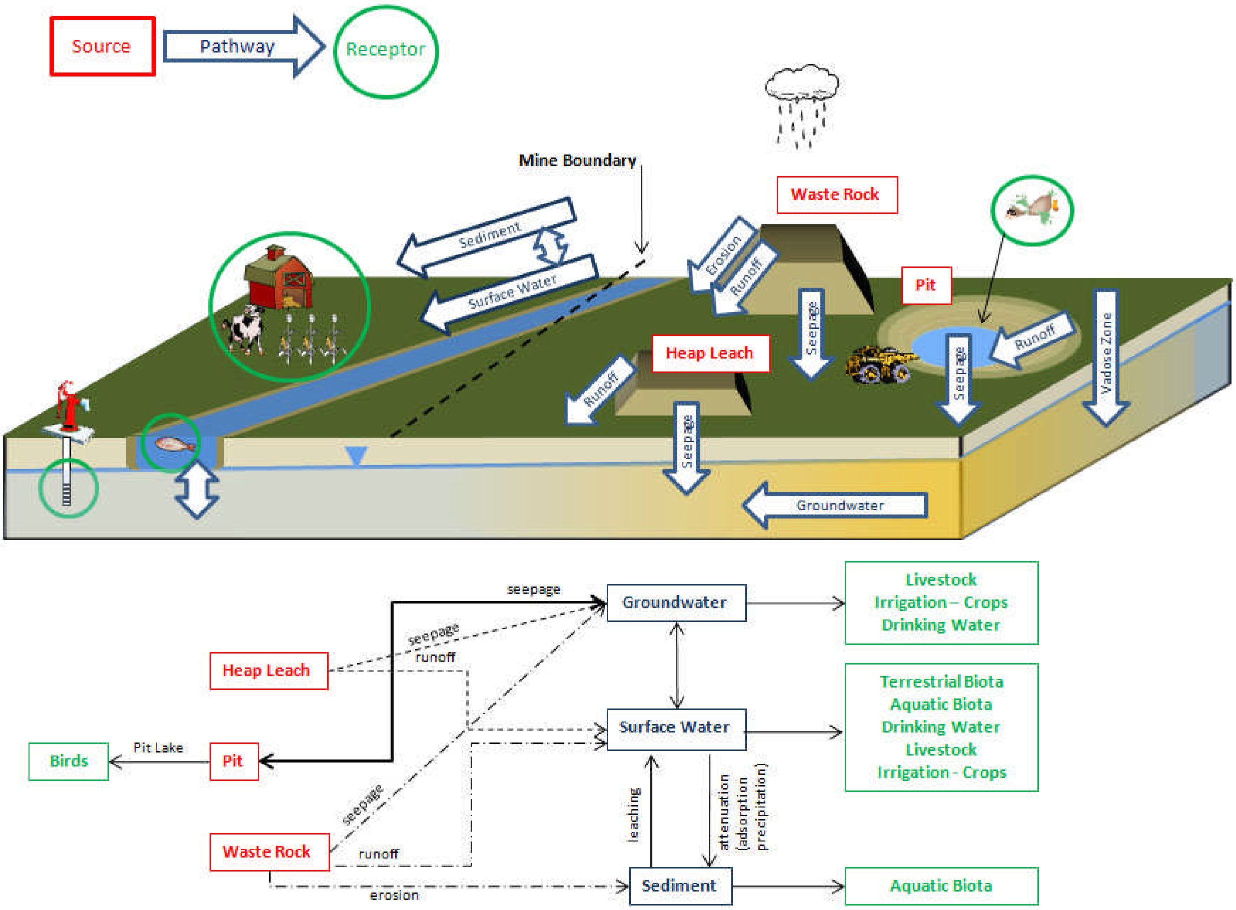


Figure I.3 *Scheme of the Conceptual Site Model*

In essence, this consists in reconstructing the characteristics of three main elements of the risk assessment procedure (Mariani et al., 2008):

Source => Pathway => Receptor

- *source* - by correctly defining the geometry, representative concentration value and the physical-chemical and toxicological properties for each chemical of concern identified;
- *pathway* - by identifying all possible migration routes by which the pollutants reach potential receptors and the criteria for assessing transport factors, including the ones for determining the site-specific parameters necessary to calculate them;
- *receptor* - by identifying the possible receptors of contamination, both on-site and off-site, and by defining the site-specific values to be attributed to the corresponding exposure factors.

Once the CSM has been fully developed, by applying specific criteria it is possible to estimate the risk associated with the specific site and/or to calculate the SSTLs for each secondary contamination source identified (surface soil, deep soil and groundwater).

The risk assessment may be performed in two modes, forward and backward. In forward mode, the health and environmental risk associated with the contaminated site can be assessed on the basis of the concentrations observed in the source by way of sampling and analysis. Italian Ministerial Decree 471/99 required the application of risk assessment in forward mode to verify the acceptability of the risk of residual concentrations identified using the best available techniques (BATs). In backward mode it is possible to estimate, on the basis of a risk threshold considered acceptable, the maximum acceptable concentration values corresponding to the source of contamination. Legislative Decree 152/06 requires the application of risk assessment in backward mode in order to identify the SSTLs (Mariani et al., 2008).

Another significant difference is that the new decree has exceeded the simple approach of tabular comparison of the previous legislation; indeed while the D.M. 471/99 set the limit values of concentration of the different substances beyond which the site was considered as contaminated, the more recent law refers to two possible levels of contamination:

- a contamination surveillance limit named threshold concentration of contamination (TCC);
- a risk-based values named threshold concentration of risk (TCR).

Introducing the risk analysis, it is possible to distinguish between potentially contaminated sites for which it is obligatory to proceed with the preliminary environmental characterization to define the state of pollution, and contaminated sites, which must be immediately cleared.

More precisely if a substance in soil or water is above the surveillance limit during the preliminary investigations the site is called "potentially contaminated" and an extend site investigation plan must be carried out. If after the site-specific risk assessment $C < TCC$ only a monitoring plan must be performed, whilst if $C > TCR$ a reclamation project is necessary. The solution chosen has to reach the remediation objectives (the TCR), to produce as less waste as possible and to be chosen through a decision process based on cost-effectiveness and cost-benefit analysis.

Therefore also the definition of contaminated site is changed; in the previous regulation a contaminated site is defined as a site where the pollutant concentrations are higher than the Acceptable Concentration Limit (ACL). The last regulation defines as contaminated site a site where the pollutant concentrations are higher than the site specific risk-based values (TCR).

The threshold contamination concentrations and the threshold risk concentrations in the soil and subsoil in relation to the specific purpose of use of the sites to be remediated (expressed in mg/kg of substance) are set out in D.Lgs. 152/2006, Part IV, Title V, divided in sites for public, private and residential green areas and in sites for commercial and industrial use (Table I.2) whilst the contamination concentration thresholds in underground water are expressed in mg/l as shown in Table I.3.

Table I.2 *Limits of major contaminants in soil for public, private and residential green areas (column A) and for commercial and industrial use (column B) (D. Lgs. 152/2006)*

Contaminant	Column A public, private and residential green areas	Column B commercial and industrial use
	$mg \cdot kg^{-1}$	
As	20	50
Cd	2	15
Cr_{tot}	150	800
Hg	1	5
Ni	120	500
Pb	100	1000
Cu	120	600
Zn	150	1500

Table I.3 *Limits of major contaminants in underground water (D. Lgs. 152/2006)*

Contaminant	TCC in underground water ($mg \cdot l^{-1}$)
Cd	5
Cr	50
Hg	1
Ni	20
Pb	10
Cu	1000
Zn	3000

The Law 152/06 has been partially modified through various legal acts until the adoption of a final Decree containing some consolidated modifications to the initial legislative text. The Government approved on 21 December 2007 the Legislative Decree containing the consolidated modifications to Legislative Decree n. 152/2006, namely the Legislative Decree n. 4/2008, the so-called "*Decreto Correttivo Unificato*", which was published on the Ordinary Supplement n. 24 to *Gazzetta Ufficiale* n. 24 of 29 January 2008. The new Decree is in force from 13th of February 2008. The main changes introduced by the new Legislative Decree, concern the environmental impact assessment (EIA), strategic impact assessment (SIA), air and waste sectors. In the waste matter, along with a bureaucratic simplification for the small industries, it revises the Italian legislation to make it more consistent with the EC law requirements (Montini, 2008).

The introduction of art. 252-bis (Sites of relevant public interest for industrial reconversion) within Legislative Decree 4/08 envisages public financing and several elements to provide maximum speed to polluted areas reuse procedures by private subjects; this could lead to increased development of restoration activities and to productive restoration of old hazardous sites for industrial use.

CIPE (Interministerial Committee for Economic Planning) deliberation of December 21, 2007 on the implementation of consistent regional, European and national policy as defined in the National Strategic Reference Framework 2007-2013, envisaged the drafting of the Special Strategic Plan (SSP) also called "National special programme for the economic-productive restoration of contaminated industrial sites", subsequently approved by CIPE deliberation of April 2, 2008, n. 61. The SSP main objective is to increase competitiveness of economic-productive systems and capacity of attracting investors by working on quality and economic-environmental efficiency of contaminated industrial sites through their restoration, with the final aim of renewed industrialisation. SSP envisages two main priorities: 1) conversion for industrial purpose and environmental restoration; 2) technical assistance and related actions. In order to comply with SSP, regions have submitted a list of sites that should undergo restoration and reuse for industrial purposes and be monitored (Ministry for the Environment, Land and Sea, 2009).

I.3 *The reclamation of abandoned mining areas*

Mining is the activity with the greatest environmental impact. Today the potential environmental impacts that can occur due to mining activities are minimized but there are many abandoned sites around the world that continue to adversely affect the environment.

The soil and rock excavated to expose the materials of interest (i.e. coal, metal ores, non-metallic ores), in addition to the waste rock and tailings formed during the processing of valuable minerals, often contain sulfide minerals such a pyrite (FeS_2) that when exposed to air and water, will oxidize and release large quantities of iron and sulfate into solution. In addition, H^+ ions are liberated during the oxidation process producing an acidic solution that readily weathers and releases other trace minerals (i.e. copper and zinc) into solution. The acidic solution formed is called acid mine drainage (AMD). The environmental impact of AMD can be severe because of high content of metals and sulfate and low pH, affecting both surface and groundwater. Indeed water becomes easily contaminated at mine sites when it comes into contact with waste rock and tailings. AMD can lower the pH of surrounding surface water, making it corrosive and unable to support many forms of aquatic life and vegetation. Humans may also be affected by consuming water and fish tissue with a metal content.

Erosion represents another environmental issue for mine sites. When material is moved in significant quantities, as it is in the mining process, large quantities of sediment, containing toxic heavy metals such as arsenic, lead, and other, are transported by water erosion and can affect surface water and wetlands. It results in the movement of soil, including topsoil and nutrients, from one location to another, adversely affecting soil organisms and vegetation.

Abandoned mine sites include areas where mining or processing activity is determined to have ceased. They can produce AMD for more than 100 years and, consequently, pose significant risks to surface water and ground water. Therefore they present serious threats to human health and the environment and the attention to this issue is becoming increasingly important.

Sardinia was affected by intense mining, especially in the territory of Sulcis-Iglesiente-Guspinese, where the highest concentration and extent of mine areas is present. The long mining history of Sardinia ended when the exploitation of the Sardinian ores became uneconomic. This was due to the exhaustion of resources, and the extreme competition of other mining districts in the world.

The poor management of these sites has led to intense heavy metal contamination over large areas. Actually, scenarios of potential environmental risk, in particular due to the heavy metal pollution, characterize these abandoned mining sites.

The execution on disused mining areas of the characterization plans as required by the Ministerial Decree 471/99 has highlighted the difficulties to make reclamation interventions or permanent security measures on large volumes of waste dumped on the mining areas. Indeed solutions for reducing the concentrations to below the legal limits are not economically or technically feasible, therefore safety measures are required to ensure source isolation and containment.

The peculiarity of mining sites compared to other industrial areas has led to the definition of specific procedures for their rehabilitation. Considering the criticality of the interventions required for the remediation and restoration of abandoned mining areas, due to the variability of characteristics and the extent of the sites, in addition to national legislation, regional guidelines have been defined; they indicate contamination characteristics and provide the guidance for the implementation of plans for characterization and remediation projects.

Moreover, following the example of other European countries where the remains of the mining activities are now remarkable sources of culture and income, several activities for a revaluation and reconversion of the historical, industrial, naturalistic and human heritage are in progress in different areas of Sardinia. To this regard several significant abandoned mining areas in Sardinia are included in the Environmental and Mining Historical Geopark of Sardinia, sponsored by the UNESCO. One of the aims of the Geopark is to ensure the reclamation of the lands where the ceasing of mining activities caused an environmental degradation and the abandonment of large lands. Indeed, potential environmental risks are present in these areas, in particular due to the heavy metal pollution.

I.3.1 *The mining area of Baccu Locci*

The Baccu Locci Pb – As abandoned mine is located in the Sarrabus-Gerrei mining district, near the village of Villaputzu (south-east Sardinia). It represents a peculiarity in the metallogenesis of the island thanks to an unusual primary paragenesis made up of about equal proportions of galena and arsenopyrite. About a century (1873-1965) of exploitation for Pb and As has produced visible environmental impact, mainly due to the unwise practice of discharging tailings from the flotation plant, built in 1949, directly into the Baccu Locci stream that drains the mined area. This has caused wide scattering of highly contaminated materials over the whole catchment as far as the coastal plain located about 10 km downstream of the mine (Frau et al., 2009).

Arsenic contained in waste-rock materials mainly occurs as arsenopyrite and scorodite, or as sorbed species on Fe(III)-hydroxides. Tailings produced by the flotation plant were discharged directly into the Baccu Locci stream waters and transported downstream and arsenic is released to surface waters mainly by desorption from ferrihydrite contained in tailings/sediments along the course of the stream. Arsenic heavily affects water quality with dissolved concentrations up to and over 1 mg/L (Frau and Ardau, 2004). The chemical analysis of samples collected in the Baccu Locci mining area showed As concentration values ranging from 3.000 mg/Kg to 50.000 mg/Kg, with an average of about 20.000 mg/Kg. Recalling the limits imposed by D.Lgs. 152/06, 20 and 50 mg/kg depending on the intended use of sites, it is clear that the 20.000 mg/kg in this area defining a serious situation.

A sample of this soil has been tested during the experimentation.

Chapter II

Soils and contaminants

The soil is a complex heterogeneous three-phase medium comprising mineral and organic solids, aqueous and gaseous components. The minerals present are usually weathering (chemically decomposing) rock fragments and secondary minerals such as phyllosilicates or clay minerals, oxides of Fe, Al and Mn and sometimes carbonates (usually $CaCO_3$). The solid components are usually clustered together in the form of aggregates, thus creating a system of interconnected voids (pores) of various sizes filled with either water or air. The solid components have the ability to adsorb ions, but this differs between materials and is strongly influenced by the prevailing pH and redox conditions and the relative concentrations of the ions present in the aqueous soil solution (Alloway, 1995).

Being a dynamic system, subject to short term fluctuations, such as variations in moisture status, pH and redox conditions and also undergoing gradual alterations in response to changes in management and environmental factors, also the potential metals mobility could change as soil properties or conditions change. Hence these changes need to be considered in decisions on the management of polluted soils.

A brief description of main properties that play an important role in the chemical behaviour of metals in soils is given in the following paragraphs.

II.1 ***Soil pH***

The hydrogen-ion activity or pH is the most important chemical property of soil and it is the pre-eminent factor controlling the chemical behaviour of metals. Indeed the pH affects several chemical processes such as adsorption/desorption, precipitation/dissolution and oxidation/reduction. Soil pH is also affected by the changes in redox potential: reducing conditions generally cause a pH increase and oxidation brings about a decrease.

Hydrogen ions are strongly attracted to the negatively charged surfaces of the soil particles and they have the power to replace most other cations. In general heavy metal cations are most mobile under acid conditions and increasing the pH usually reduces their bioavailability. However proper anions become more available with increasing pH.

Figure II.1 presents solubility curves for various metals as a function of pH.

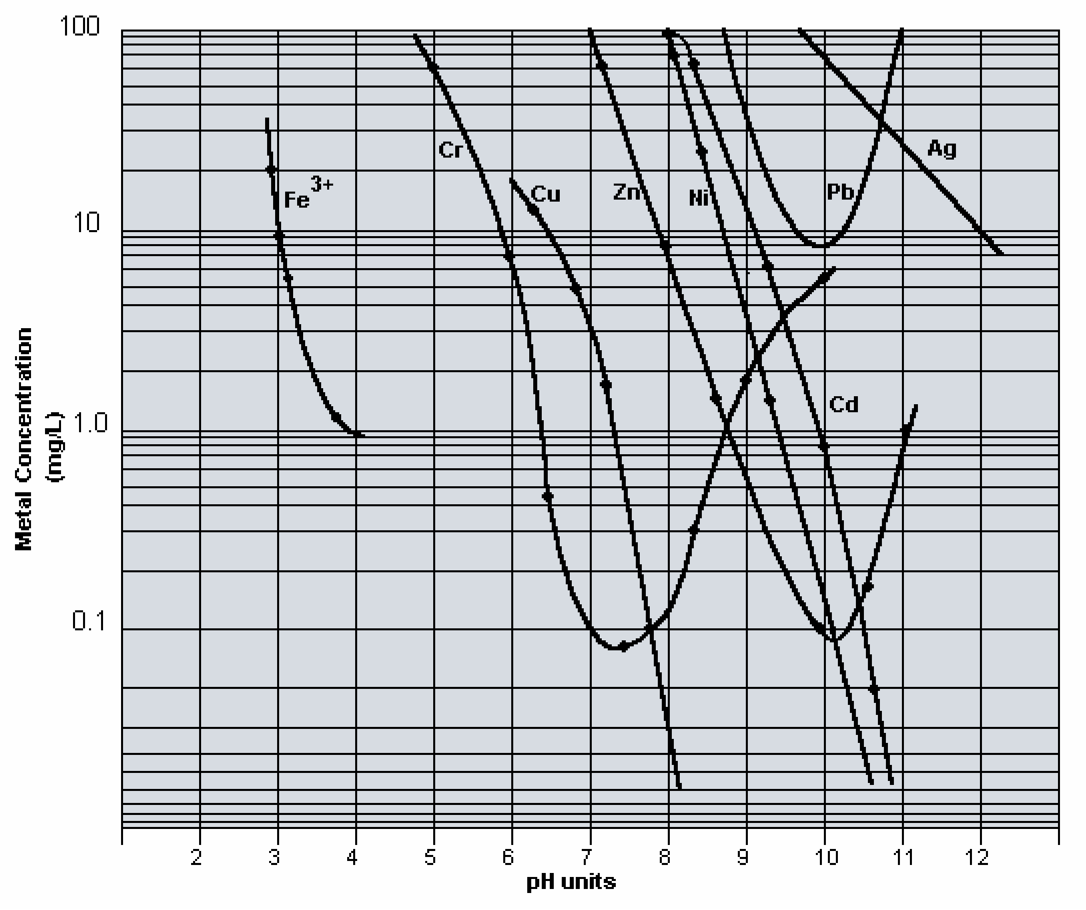


Figure II.1 *Solubility curves of common heavy metals as function of pH*

II.2 *Clay minerals*

Clay minerals are products of rock weathering and have marked effects on both the physical and chemical properties of the soils. Their contribution to soil chemical properties results from their comparatively large surface area and permanent surface negative charge (Selinus, 2005). Clays are ultra fine grained, normally considered to be less than 2 micrometres in size; they are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations.

Like all phyllosilicates, clay minerals are characterised by two-dimensional *sheets* of corner sharing SiO_4 and AlO_4 tetrahedra. These tetrahedral sheets have the chemical composition $(Al,Si)_3O_4$, and each tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two-dimensions, whilst the fourth vertex is not shared with another tetrahedron; all of the unshared vertices are on the same side of the sheet.

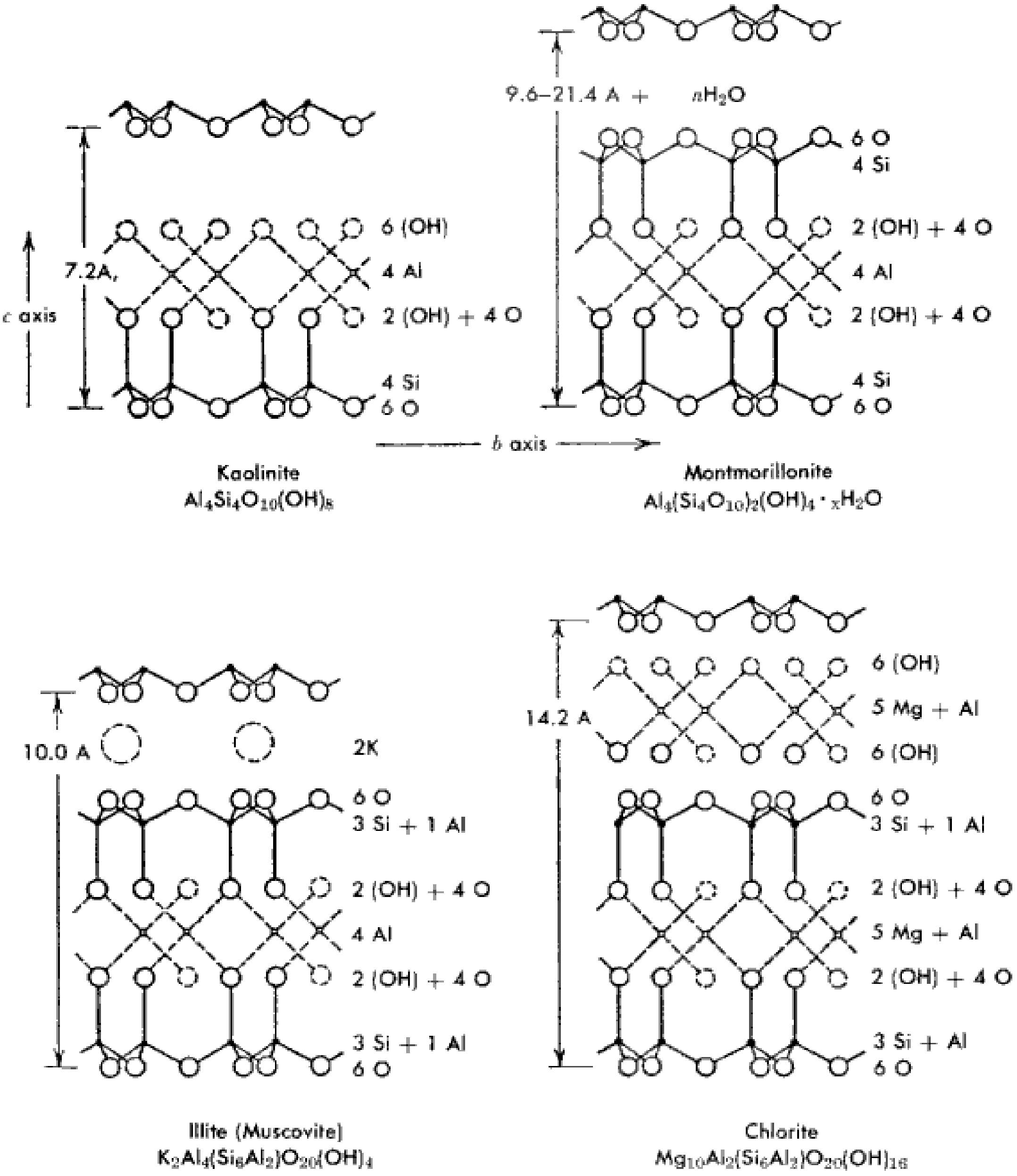
The tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminium or magnesium, coordinated by six oxygen atoms.

Clays can be categorised depending on the way that tetrahedral and octahedral sheets are packaged into *layers*: the clay is known as a 1:1 clay if there is only one tetrahedral and one octahedral group in each layer; the 2:1 clay has two tetrahedral sheets with the unshared vertex of each sheet pointing towards each other and forming each side of the octahedral sheet.

Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge or will have a net negative charge. If the layers are charged this charge is balanced by interlayer cations such as Na^+ or K^+. In each case the interlayer can also contain water. The crystal structure is formed from a stack of layers interspaced with the interlayers.

Clay minerals are divided into four major groups:

- the kaolinite;
- the montmorillonite/smectite;
- the illite;
- the chlorite group.



Kaolinite
$Al_4Si_4O_{10}(OH)_8$

Montmorillonite
$Al_4(Si_4O_{10})_2(OH)_4 \cdot {}_xH_2O$

Illite (Muscovite)
$K_2Al_4(Si_6Al_2)O_{20}(OH)_4$

Chlorite
$Mg_{10}Al_2(Si_6Al_2)O_{20}(OH)_{16}$

Figure II.2 *Clay layer structures*

II.3 ***Oxides of iron, manganese and aluminium***

The oxides of Fe, Al and Mn which are commonly referred to as hydrous oxides, play an important role in the chemical behaviour of metals in soils. They occur in the clay size (< 2 μm). Hydrous Fe oxide minerals tend to be the most abundant of all the oxides in soils. Gibbsite is a common form of Al hydroxide but is much less abundant than the Fe oxides as the most common goethite.

With regard to the dynamics of heavy metals in soils, Fe and Mn oxides coprecipitate and adsorb cations including Co, Cr, Cu, Mn, Mo, Ni, V and Zn, anions, such as HPO_4^{2-} and AsO_4^{3-}, from solution. This is due to a pH-dependent charge which, generally, is negative in alkaline conditions and positive in acid conditions; the pH at which there is no net charge, called the PZC (point of zero charge), varies for different hydrous oxide minerals. In pure form, the PZC values for Fe oxides are in the range 7-10, and those for Al oxides 8-9.4; however mixing with clays in soils, the PZC values are usually much lower (Alloway, 1995).

Variation in redox conditions have a profound effect on both the quantities of hydrous oxides present in a soil and also on the adsorptive capacity of that soil for a wide range of cations and anions.

The combined effect of E_h and pH conditions on the form Fe are best illustrated by an E_h/pH diagram, as shown in Figure II.3. It can be seen that the oxides of Fe can be dissolved by either decreasing pH or E_h; small changes in E_h or pH can give rise to either extensive dissolution or precipitation of Fe oxides. When reducing conditions cause the dissolution of hydrous Mn, Al and Fe oxides, their co-precipitated metals are released into the soil solution.

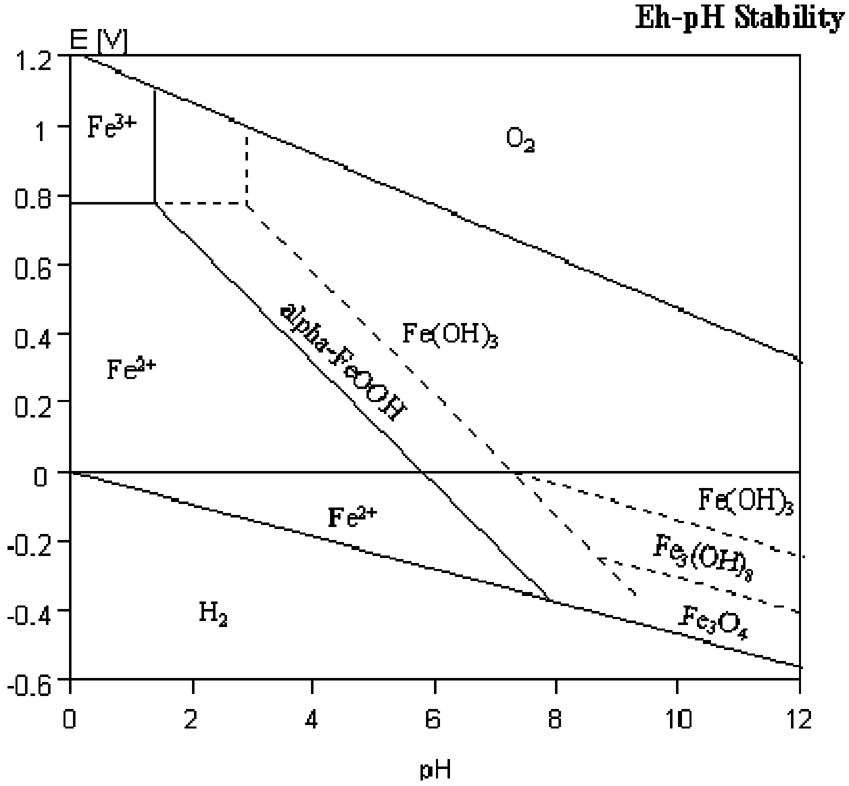


Figure II.3 *Eh-pH stability diagram*

II.4 *Soil organic matter*

All soils contain organic matter, derived from soil biomass, although the amount and type may vary considerably. Colloidal soil organic matter has a major influence on the chemical properties of soils and can be divided into "non-humic" and "humic" substances. The non-humic substances comprise unaltered biochemicals such as amino acids, carbohydrates, proteins, lipids and organic acids, released by the decay of plant, animal and microbial tissue. Humic compounds are a series of acidic polyelectrolytes, formed by secondary synthesis reactions involving microorganisms. They have a wide variety of functional groups, including carboxyl, phenolic hydroxyl, carbonyl, ester and methoxy groups. The elemental composition of humus is tipically 44-53% C, 3.6-5.4% H, 1.8-3.6% N and 40-47% O (Selinus, 2005).

Soil organic matter affects the physical, chemical and biological conditions in soils: an increase in organic carbon cause an increase in adsorption characteristics.

II.5 *Cation exchange capacity*

The cation exchange capacity (CEC) of a soil indicates the capacity of that soil for ion exchange of cations between the soil and the soil solution. For instance, clays are aluminosilicates in which some of the aluminium and silicon ions have been replaced by elements with different valence or charge; when aluminium (Al^{3+}) is replaced by iron (Fe^{2+}) or magnesium (Mg^{2+}), it leads to a net negative charge.

Because of the typical negative charged surfaces of soil particles and in order to maintain the electroneutrality, cations as Na^+, Ca^{2+}, Mg^{2+} and others form the diffuse double layer. These cations can be replaced by one another. There is some selectivity or preference for one ion over another by the adsorbent, giving to a replacing order amongst the cations, determined by their valency and degree of hydration: if the valency of an ion is high, its replacing power will be greater; H^+ ions behave like polyvalent ions and the greater degree of hydration corresponds to lower replacing power.

The CEC differs from soil to soil depending on clay content, clay types and organic content: the CEC is higher in soils that contain high clay content and high organic content, increasing the difficulty of removal of cationic contaminants adsorbed on soil surfaces during a remediation process.

II.6 *Anion exchange capacity*

The anion exchange capacity (AEC) is the capacity of soil to adsorb and exchange anions. In general the AEC is lower than CEC since the soil must be charged positively and this occurs only in low-pH conditions or for broken bonds on broken surfaces of clay minerals.

II.7 *Contaminant characteristics*

II.7.1 *Chromium (Cr)*

Chromium is one of the less common elements in earth's crust with an average concentration of 100 ppm and occurs only in compounds, due to erosion of Cr-containing rocks.

Chromium enters the air, water and soil in the Cr(III) and Cr(VI) forms through natural processes and human activities. The main human activities that increase the concentrations of Cr(III) are steal, leather and textile manufacturing. The main human activities that increase Cr(VI) concentrations are chemical, leather and textile manufacturing, electro painting and other Cr(VI) applications in the industry.

Chromium is mined as a primary product and is not recovered as a by-product of any other mining operation. The main source of chromium is the mineral chromite ($FeCr_2O_4$). Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakihstan and the Philippines and others unexploited deposits are in Greenland, Canada e USA.

The toxicity and carcinogenic properties of the hexavalent Cr form have been known for a long time, while the International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (the agent is not classifiable as to its carcinogenicity to humans).

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. For most people eating food that contains Cr(III) is the main route of chromium uptake, as Cr(III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Cr(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes; anyway the uptake of too much Cr(III) can cause health effects as well, for instance skin rashes.

Adverse effects of the Cr(VI) on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of Cr(VI) compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

As chromium compounds were used in dyes and paints and the tanning of leather, these compounds are often found in soil and groundwater at abandoned industrial sites, now needing environmental cleanup and remediation treatments.

For a better understanding of the Cr behaviour, especially in EK system, it is necessary to consider that the two chromium oxidation states that are encountered under soil conditions, Cr(III) and Cr(VI), exhibit migration and adsorption characteristics different from each other and explain the complexity of Cr EK removal. The relation between Cr(III) and Cr(VI) strongly depends on pH and oxidative properties of the site, but in most cases, the Cr(III) is the dominating species and the oxidation state +3 is the most stable.

More details on the behaviour of chromium during an electrokinetic process can be found in the section IV.1, "*Electrokinetic treatments applied on contaminated soils by Cr or As".*

II.7.2 ***Arsenic (As)***

Arsenic is one of the most widespread toxic contaminants of concern in environmental cleanup. It can be found naturally on earth in small concentrations. It occurs in soil and minerals and it may enter air, water and land through wind-blown dust and water run-off. Arsenic in the atmosphere comes from various sources (e.g. vulcanoes) but human activities are responsible for much more: thousands of tonnes of arsenic per year are released by the burning of fossil fuels. In addition to natural (usually volcanic) sources, other sources of arsenic in the environment include metals smelting (usually copper), pesticides, herbicides, insecticides, fungicides, defoliants, wood preservatives and a variety of industrial processes. In general As is mainly emitted by the Cu producing industries, but also during Pb and Zn production and in agriculture.

Arsenic is a component that generally is extremely hard to convert to water-soluble or volatile products but, due to human activities, mainly through mining and melting, naturally immobile arsenic has also mobilized.

Arsenic occurs in a wide variety of mineral forms and most arsenic is found in conjunction with sulfur in minerals such as arsenopyrite ($FeAsS_4$) which is the main commercial ore of As worldwide. Arsenic compounds are not mined as such because they are recovered as a by-product of refining the ores of other metals, such as copper, lead and zinc. Mining of these deposits can produce As pollution, often due to unsatisfactory disposal practices of flotation tailings.

The predominant forms found in soil are arsenate As(V) and arsenite As(III): the As(V) prevails in oxidizing conditions of the soil ($E_h > 200$mV; pH 5-8), whilst As(III) is the dominant form in reducing conditions. Arsenites and arsenates are the most important inorganic compounds of As in soil because they are very soluble in water and can change oxidation state depending on the pH and redox conditions.

The reactions that govern the behaviour of arsenic in the soil-solution are essentially those of precipitation/dissolution and adsorption/desorption. Indeed the presence of phyllosilicates, oxides and hydroxides of Fe, Al, Mn influence the solubility and oxidation state; they are potentially the most important As adsorbents.

Fe hydroxides have high isoelectric points of about 8.6 and possess net positive charges in most geological environments, showing high affinities for As species. Both As(III) and As(V) are strongly chemisorbed. Adsorption affinity is higher for As(V) at lower pH values and for As(III) at higher pH values. Pierce and Moore (1982) reported that As(V) is preferentially sorbed to Fe hydroxides between pH 4 and 7 with an optimal adsorption pH of about 4, whereas As(III) is preferentially sorbed onto Fe hydroxides between pH 7 and 10 with an optimal adsorption pH of about 7. The sorption of As(III) and As(V) to Fe (hydro)oxides contributes to As immobilization in soils. Under neutral or mildly acidic conditions, As sorption to Fe hydroxides and the formation of ferric arsenate precipitates may effectively decrease As concentrations in mining affected waters.

Al (hydro)oxides are ubiquitous in acidic soils and aquatic environments. Amorphous $Al(OH)_3$ has an isoelectric point of 8.5, and thus is an extremely efficient adsorbent to immobilize As. It has been reported that the adsorption of As(V) increases up to pH 7 by amorphous $Al(OH)_3$ and crystalline $Al(OH)_3$ (gibbsite) and decreases significantly at higher pH values. Although As(III) can be strongly adsorbed from pH 6 to 9.5, this decreases at higher pH values.

Mn (hydro)oxides in soils are often of poor crystallinity and mixed oxidation states. Mn hydroxides have an isoelectric point about 2.3, and therefore carry a net negative charge at the common natural pH range of 3–9, which suggests that they would not adsorb As anions. It was observed that the negatively charged As(V) species, $H_2AsO_4^-$, was adsorbed negligibly onto the negatively-charged birnessite surface at a pH range of 4–7.

However, desorption and remobilization of the sorbed As from the (hydro)oxides may occur when the site biogeochemical conditions change with time. Significant As(V) remobilization from Fe hydroxides can occur at pH values of approximately pH 8 and higher, due to the increase of electrostatic repulsion on the negatively charged oxide surface, and the rate of As(V) desorption can be quite high. Moreover, in reducing soils, As sorbed on Fe(III) hydroxides can be remobilized and released into groundwater as a result of the reduction of Fe(III) to Fe(II) and the reduction of As(V) to As(III). Therefore reduction of arsenate to arsenite can promote arsenic mobility because arsenite is generally less strongly adsorbed.

Arsenic adsorption can be affected by the presence of competiting ions; for instance phosphate and arsenate have similar geochemical behaviour and as such compete for sorption sites.

The presence of arsenic in the environment can pose a risk to human health. Humans may be exposed to arsenic through food, water and air or through skin contact with soil or water that contain arsenic. Exposure to inorganic arsenic can cause various health effects: it has been linked to a variety of cancers, cardiovascular disease, diabetes, and anemia, as well as having reproductive, developmental, immunological, and neurological effects (U.S. Environmental Protection Agency, 2003). In October 2001, the USEPA revised the arsenic standard for drinking water from 50 µg/L to 10 µg/L (effective as of 2006) sparking substantial research into cost-effective methods to reduce arsenic concentrations in drinking water and increasing attention to remediation of arsenic in both water and soil systems.

Due to its toxic nature and relative abundance, there is a growing need for cost-effective arsenic treatment. In general arsenic is troublesome concerning mobility and treatment. Traditionally, remediation of arsenic-contaminated soils is achieved by excavation and *ex situ* treatment (most typically solidification/stabilization) and/or disposal. However, the high cost of such practices has stimulated the development of *in situ* alternatives for remediation of contaminated soils that are less disruptive and, often, less costly than conventional treatment (Martin and Ruby, 2003).

II.7.3 *Copper (Cu)*

Copper is a naturally occurring element that exists in the environment as the free metal, and in the (I) and (II) oxidation states. Copper is an essential element in plants and animals (including humans), which means it is necessary for us to live. Therefore, plants and animals must absorb some copper from eating, drinking, and breathing. Precise levels of intake are often not known, even for animal diets. Because the biological availability and toxicity of copper are related to the copper(II) oxidation state, the Agency for Toxic Substances and Disease Registry (ATSDR, 1990) has focused on that form of copper. Little information is available regarding the toxicity of ingested copper to humans. Case reports of adverse effects following ingestion of large amounts of copper(II) in contaminated water or as suicide attempts include acute gastrointestinal distress, acute hemolytic anemia in a young child, hepatic micronodular cirrhosis in two infant siblings, hepatic centrilobular necrosis in adults, renal tubular necrosis or clinical evidence of renal tubular damage in a child and in adults.

Copper compounds are commonly used in agriculture to treat plant diseases like mildew, for water treatment and, as preservatives for wood, leather, and fabrics. Hydrated copper sulfate ($CuSO_4 \cdot H_2O$), also known as blue vitrol, is the best known copper compound, used as an agricultural poison, as an algicide in water purification and as a blue pigment for inks. Cuperic chloride ($CuCl_2$), another copper compound, is used to fix dyes to fabrics. Cuprous chloride ($CuCl$) is a poisonous white powder that is chiefly used to absorb carbon dioxide (CO_2). Copper cyanide ($CuCN$) is commonly used in electroplating.

The industrial use of Cu combined with the associated burning of coal, wood and certain wastes contribute to source pollution of the environment with Cu. Soil management of Cu is a difficulty in numerous areas of the world because if the pH is not maintained at a proper range the availability of Cu could be a problem. Cu is mainly retained in soils through exchange and specific adsorption mechanisms. Like As, Cu retention and partitioning in soils is related to the presence of organic matter, Fe and Mn oxides, and clay minerals (Balasoiu et al., 2001).

Chapter III

Remediation technologies applied on metal-contaminated soils

Contamination by metals is a common problem at hazardous waste sites. The metals most frequently identified are lead, arsenic, chromium, cadmium, nickel, copper and zinc. Choosing the most suitable technology is the most important element for the effectiveness of remediation in reducing the concentration and for costs, but it is often limited by its applicability to different and specific environmental situations.

Remediation treatments are usually described as *in situ* or *ex situ* and this last is further described as *on-site* or *off-site***:**

- in-situ techniques use processes without moving or removing materials from the site;
- ex-situ on-site techniques are applied to excavated soil or to extract groundwater with handling and processing of materials, but within the same site;
- ex-situ off-site operations occur with handling and processing of materials off-site, to a licensed landfill site or treatment centre.

In general, in situ treatments are capable of providing cost savings (when compared with traditional treatment methods), reducing environmental impacts and are suggested by legislation more frequently for contaminated sites remediation. However, they require longer cleanup time and relatively few alternatives exist for the in situ treatment of metals. The main advantage of ex situ treatments (on site/off site) is that they generally require shorter cleanup time periods, and there is more certainty about the uniformity of treatment because of the ability to screen, homogenize, and continuously mix the soils. Ex situ processes, however, require excavation of soils leading to increased costs and engineering for equipment, possible permitting, and materials handling worker safety issues. For example e*x situ* remediation of contaminated sites by heavy metals is usually followed by soil washing process: the post-treatment of the extracted solution and the recovery of the soil after treatment are the major concerns when using this process.

However, a particularly significant problem about reclamation matter is often that of non-application of in situ remediation techniques. The statute provides to favour the treatment of contaminated soils on site to avoid all possible risks arising from the transport of contaminated land, besides the difficulty of managing hazardous waste landfills and finding the areas needed. But technologies such as direct treatment of readily biodegradable organic pollution and volatile or chemical oxidations which have found wide application at the international level, in Italy they have so far met with opposition from government and local communities for fears on the safety, effectiveness and control.

The remediation technologies can be divided into four types:

- *biological* processes involve the introduction of microbes and nutrients into the soil to destroy or transform contaminants, utilizing micro-organism degradation capacities;
- *chemical* methods such as solvent extraction and treatment walls, can treat a variety of pollutants, modifying chemical structures to generate compounds less toxic or more separable than original compounds;
- *physical* methods promote the phase transfer of the contaminants or their separation from the solid soil matrix, and can be used to treat both organic and inorganic pollutants;
- *thermal* carried out by processes which induce pollutant separation by volatilization or desorption or to fix with solid matrix, or some more to destroy thermally.

Nowadays the most popular techniques are excavation and off-site disposal, containment by slurry walls or clay capping and bioremediation. Innovative technologies are emerging from funded research projects into industrial applications.

Since metals cannot be destroyed, remediation of metal-contaminated soil consists primarily of manipulating the mobility of metal contaminants to obtain a treated soil that has an acceptable total or leachable metal content.

According to USEPA report (2002), available *in situ technologies* for treating soil contaminated with metals include electrokinetic remediation, phytoremediation, solidification/stabilization, chemical fixation, vitrification and soil flushing.

In next paragraphs a brief description of these technologies is given whilst a more detailed report about the electrokinetic remediation and the reactive barrier technology is shown in the III.6 and III.7, respectively.

III.1 *Phytoremediation*

Phytoremediation is the use of plants to extract, degrade, contain or render harmless environmental contaminants in soil, groundwater and other contaminated media. The various mechanisms of phytoremediation can treat a wide range of contaminants, including metals, volatile organic compounds (VOCs), PAHs, petroleum hydrocarbons, radionuclides, and munitions, although not all mechanisms are applicable to all contaminants. Plants can be used in site remediation, both to mineralize and immobilize toxic organic compounds at the root zone and to accumulate and concentrate metals and other inorganic compounds from soil into aboveground shoots.

The phytoremediation mechanisms used to treat contaminated soils in situ are:

- phytoextraction uses hyperaccumulating plants to uptake contaminants from soil into aboveground plant tissues, which are periodically harvested and treated;
- phytostabilization immobilizes contaminants, mainly metals, at the interface of roots and soil limiting their migration; contaminants are immobilized by adsorption of metals to plant roots, precipitation of metal ions (e.g., due to a change in pH), formation of metal complexes, or a change to a less toxic redox state;
- rhizodegradation is essentially “plant-assisted bioremediation” in that the root zone enhances microbial activity, increasing the breakdown of organic contaminants;
- phytodegradation involves the uptake of contaminants, like phytoextraction; however, the contaminants are subsequently broken down through metabolic processes within the plant;
- phytovolatilization is the uptake of a contaminant into a plant and its subsequent transpiration to the atmosphere, or the transformation or phytodegradation of the contaminant with subsequent transpiration of the transformation or degradation product(s) to the atmosphere.

Phytoremediation is best used to treat large areas of shallow contamination. Because high levels of contaminants may be toxic to plants and inhibit their growth, phytoremediation is best applied to low and moderate levels of contamination, used in conjunction with other treatment methods, or used as a final polishing step in site remediation. It requires longer treatment times for remediation compared with other technologies but it has the potential to be less expensive than excavating and treating large volumes of soil ex situ.

Another limitation is that its application is limited to depth of plant root growth, hence the depth of the contamination requiring treatment must be within this range; in addition the treatment depends on the contact of contaminants with the root zone so phytoremediation is limited by the rate of root growth. Slower growth rates increase the time required to treat a site.

III.2 ***Solidification/stabilization (S/S)***

Solidification and stabilization refer to closely related technologies that use chemical and/or physical processes to treat radioactive, hazardous and mixed wastes. It is a common technology used for the in situ treatment of contaminated soils containing metals. Solidification technologies encapsulate the waste to form a solid material that may be a monolithic block, a clay-like material or a granular particulate.

Stabilization technologies reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile or toxic forms (e.g., Cr(VI) to Cr(III)) without necessarily to change the physical nature and handling characteristics of the waste.

Chemical stabilization relies on the reduction of contaminant mobility by physical or chemical reactions with the contaminant, rather than the contaminant matrix (e.g., soil or sediment), as is done with solidification. The mobility of organic and inorganic compounds can be reduced through various precipitation, complexation and adsorption reactions. Commonly applied inorganic stabilization agents include soluble silicates, carbon, phosphates and sulfur-based binders (USEPA 1997).

The S/S process can be accomplished using either inorganic or polymer binders. The most common inorganic binders are Portland cement, pozzolans (siliceous or aluminous materials that can react with calcium hydroxide to form compounds with cementitious properties), and cement/pozzolan mixtures that are effective for a range of inorganic cations and anions.

III.3 ***Chemical fixation***

In situ chemical fixation represents a promising and potentially cost-effective treatment alternative for metal-contaminated soils.

This treatment is designed to react contaminated soils directly with chemical solutions to cause the formation of insoluble metal-bearing phases and thereby to decrease the metals mobilization.

III.4 ***Vitrification***

In situ vitrification is a thermal treatment that involves the electric melting of contaminated soil to convert it in a stable glass and crystalline solids. The stable glass that is formed immobilizes any non volatile contaminants, including metals and radioactive materials. They are subject to physical and chemical incorporation into the vitreous product, formed by high concentrations of silica (50-80%) and low levels of alkali oxides (1-5%), which results in permanent immobilisation and in an extremely durable and highly leach resistant product.

There are two methods for producing heat for melting the contaminated soil. The older method uses electrodes and electrical resistance to vitrify materials, while the emerging technique uses plasma arc technology.

This technology is applicable to sites with high clay and moisture content, although treatment costs increase with increasing moisture content.

III.5 ***Soil flushing***

Soil flushing is a physical/chemical treatment that involves flooding a zone of contamination with an appropriate solution to remove the contaminant from the soil. Water or liquid solution is injected or infiltrated into the area of contamination. The contaminants are mobilized by solubilization, formation of emulsions or a chemical reaction with the flushing solutions. After passing through the contamination zone, the contaminant-bearing fluid is collected and brought to the surface for disposal, recirculation or on-site treatment and reinjection. Application of soil flushing relies on the ability to deliver, control the flow, and recover the flushing fluid.

Flushing solutions may be water, acidic aqueous solutions, basic solutions, chelating or complexing agents, reducing agents, cosolvents or surfactants. Water will extract water-soluble (hydrophilic) or water-mobile constituents. Acidic solutions may be used to remove metals or basic organic materials. Basic solutions may be used for some metals, such as zinc, tin, or lead, and some phenols. Chelating, complexing and reducing agents may be used to recover some metals. Cosolvents are usually miscible and are effective for some organics. Surfactants can assist in the removal of hydrophobic organics (USEPA 1991).

III.6 *Electrokinetic remediation*

Among the technologies for in situ soil treatment, the electrokinetics applied to remediation relies on the application of low intensity direct currents across electrodes placed in the soil to generate an electric field for mobilization and extraction of contaminants and for bio-geochemical modifications of polluted soils and slurries.

Laboratory experiments have shown the efficiency of the process for the removal of a wide variety of heavy metals (Lageman et al., 1989; Acar and Alshawabkeh, 1993; Probstein and Hicks, 1993, Li et al., 1997, Chung and Kang, 1999), radionuclides (Acar and Alshawabkeh, 1993, Schwartz et al., 1997) and organic compounds (Röhrs et al., 2002; Probstein and Hicks, 1993) by various media such as clays, sediments and saturated or unsaturated soils.

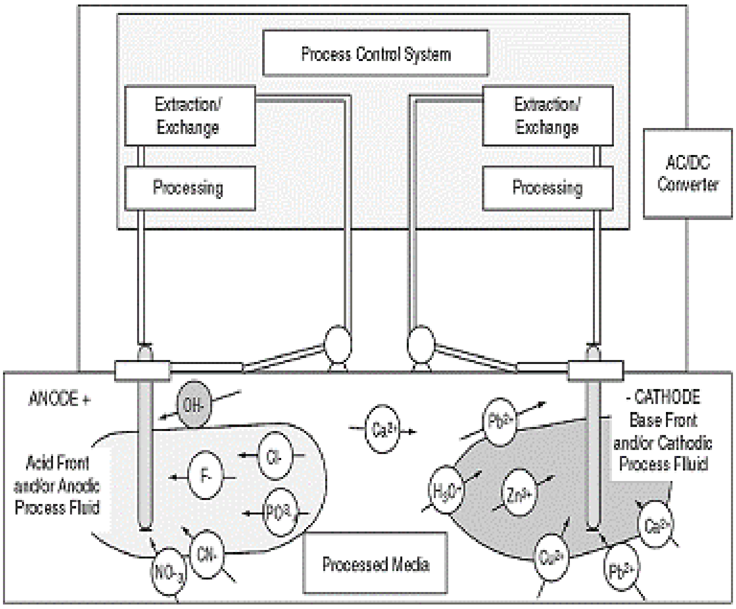


Figure III.1 *Electrokinetic process for soil remediation (Sardinia 2009)*

In an electrokinetic treatment, contaminants in the soil are mobilized under electric fields in the form of charged species, particles or ions by the following transport processes coupled with electrolysis and geochemical reactions:

- electroosmosis, transport of pore fluid under an electric gradient;
- electrophoresis, movement of charged particles under an electric gradient;
- electromigration, transport of charged chemical species under an electric gradient;
- diffusion consists in the spreading of contaminants due to a concentration gradient.

The electromigration and electroosmosis represent the basic mechanisms in the electrokinetic removal of contaminants from the soil. The phenomenon of electrophoresis has less importance, since it involves the transport of colloids or particles of a certain size, usually towards the anode, with a relatively long time; usually in the application of electrokinetics to a fine and very compacted medium the electrophoresis does not occur. Also diffusion is slow if compared to the electromigration rate; it depends on the porosity and tortuosity of the porous medium and the molar concentration of the species. During electrokinetic remediation it does not have a significant role in transporting the contaminants.

The fundamental electrokinetic processes are described in next paragraphs.

III.6.1 *Electroosmosis*

The electroosmosis is the advective movement of water through a porous medium under an electric field.

To better understand the phenomenon should make some observations on the nature of solid-liquid interface. The surfaces of soil particles due to isomorphic substitutions, broken edges or imperfections in the crystal structure, are not electrically neutral but have a net electrical charge, positive or negative. For example, due to isomorphous substitution as Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}, is produced what is called a "permanent structural charge." The replacement of one ion with another less positive value in the crystal lattice determines the development of a negative electrical charge. Other reasons for charge deficiency are broken edges or the existence of natural organic species (such as humic acids) in the soil mass. Most clay minerals have a net negative charge and the total electrical charge per unit surface area (surface charge density) increases as the specific surface (surface area per unit weight) of the soil mineral increases. For example, the surface charge density increases in the following order: sand < silt < kaolinite < illite < montmorillonite.

The natural tendency to neutralize the excess of charge causes an accumulation of opposite charged ions at the interface mineral / solution, resulting in what is called "electrical double layer" as shown in Figure III.2; it consists of two layers:

- Stern layer, consisting of ions linked by electrostatic bonds to the atoms on the surface of the particle;
- Gouy layer or diffuse layer, where ions are not bound but free to move in solution. In this layer the electrical disparity between cations and anions decreases exponentially away from the surface of the particle.

The neutrality of charge in the pore fluid is maintained by the equivalent concentration of anionic and cationic species elsewhere.

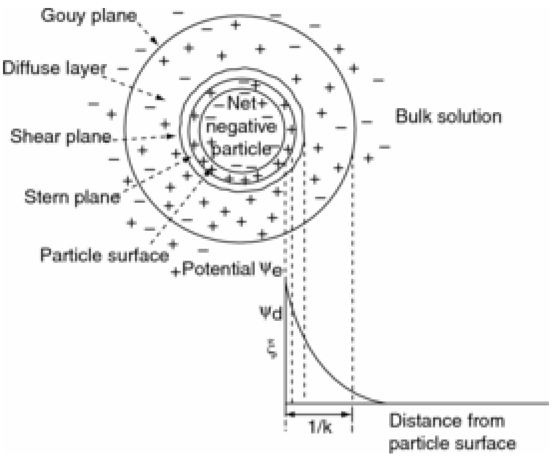


Figure III.2 *Schematic representation of the electric double layer*

Several theories are established to describe and evaluate water flow by electroosmosis. Helmholtz-Smoluchowski model is the most common theoretical description of electroosmosis and is based on the assumption of fluid transport in the soil pores due to transport of the excess positive charge in the diffuse double layer towards the cathode.

When an electric field is applied along the capillary, the excess cations close to the surface move towards the cathode, causing, through the viscosity of the pore fluid, the drag of water layers adjacent and determining a pore fluid flux towards the cathode called electroosmotic flow.

The thickness of the diffuse double layer depends upon the magnitude of the charge density on the soil surface, the concentration of the ions in the pore fluid, the valence of the cations, and the dielectric properties of the pore fluid. When the ionic concentration increases, the thickness of the diffuse double layer and the extent of the strain field resulting in pore fluid flow will be reduced and the electroosmotic pore fluid flux will be confined more to the periphery of the capillary (Acar et al., 1995).

A great interest lies in its ability to induce a significant flow of water even in soils with low permeability; in fact, initially, the electrokinetics has been used mainly for dewatering of low permeability clay soils, for geotechnical purposes, and only in the last thirty years attention has been focused on the effect on organic and inorganic pollutants, following the observation that the flow of water extract could be characterized by significant concentrations of these. This led, therefore, application of this technology for the remediation of porous media.

Electro-osmotic flux (m^3/s) can be calculated from the follow equation:

$$Q = k_e A \frac{dV}{ds}$$

where *A* is the cross sectional area of soil (m^2), *dV/ds* is the voltage gradient (V/m) and k_e is the electroosmotic permeability (m^2/Vs) which depends on several variables.

The rate of electro-osmotic flow is controlled by the coefficient of electroosmotic permeability of the soil (ke), which is a measure of the fluid flux per unit area of the soil per unit electric gradient as follows:

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

where ζ is the zeta potential (V), *D* is the dielectric constant of the fluid (80 for water), ε is the permittivity of vacuum (8.854×10^{-12} F/m), *n* is the effective porosity of the medium, τ is the tortuosity and η is the viscosity of the fluid (Pa s). The value of the electro-osmotic permeability ke (m^2/Vs) is assumed to be a function of the zeta potential of the soil-pore fluid interface, the viscosity of the pore fluid, soil porosity and soil electrical permittivity. These parameters vary with temperature and concentration with the exception of porosity, which can be considered a constant.

Electro-osmotic flow velocity (m/s) can be determined from the Helmholtz-Smoluchowski equation:

$$v = \frac{Q}{A} = k_e \frac{dV}{ds}$$

where *A* is the cross sectional area of soil (m^2) and *dV/ds* is the voltage gradient.

The zeta potential depends on the point of zero charge (PZC) or what is called the iso-electric point, which refers to the pH at which the net charge of a solid particle is zero. For pH values higher than pH_{PZC} the particle has a net negative charge (zeta potential negative) and the electroosmotic flow occurs from anode to cathode, in contrast to values lower than the particle pH_{PZC} has net positive charge (zeta potential positive) and the electroosmotic flow occurs towards the anode. The electro-osmotic flow can virtually be eliminated at the iso-electric point. The value of pH_{PZC} can be measured experimentally by detecting the time at which the particles cease to move in the presence of an applied electric field.

Therefore the reversal of the electroosmotic flow may occur because the net charge of a solid particle may vary due to changes in pH; to better understand the phenomenon, please note that a net charge can also be generated through chemical reactions between ions in solution and those on the solid surface. For example, the formation of OH^- hydroxyl groups at the solid/solution is important because they are highly reactive sites that allow the exchange of H^+ between the solution and the surface of the particle. The bond with H^+ ions (protonation reaction) favoured in acid conditions, leads to an excess of positive charge, while the removal of protons (deprotonation reaction), favoured in alkaline medium, leads to an excess of negative charge.

III.6.2 *Electromigration*

The electromigration is the transport of charged ions and ion complexes in solution towards the electrode of opposite charge, under an electric field: the cations, positively charged, will move to the negatively charged cathode and anions, negatively charged, to the positively charged anode. It is the main mechanism by which electrical current flows through the soil. The parameters that most influence the electromigration are the strength of the applied electric field, the intensity of current, ions concentration and the ionic charge of species, the ion mobility, the porosity and the tortuosity of the soil.

Electromigration is quantified by the ionic mobility (m^2/Vs), which is defined as the velocity of the ion in the soil under the influence of a unit electrical potential gradient (1 V/m). Ion mobility in free solution is defined as:

$$u = \frac{D_i z F}{RT}$$

where D_i is the diffusion coefficient of species i in dilute solution (m^2/s), z is the ionic charge, F is the Faraday constant (96487 C/mol), R is the gas constant (8.314 J K^{-1} mol^{-1}), and T is the absolute temperature (K).

Ionic mobility will be in general an order of magnitude greater than the electroosmotic permeability. Heavy metal ionic mobilities at infinite dilution are in the range of 10^{-4} cm^2/Vs. Accounting for soil porosity and tortuosity, the effective ionic mobility is in the range of 10^{-4} to 10^{-5} cm^2/Vs.

The effective ion mobility in a soil matrix is defined as:

$$u^* = un\tau$$

where n is the porosity of soil and τ is the tortuosity. The electromigration velocity in soils is typically about 4.7 times less than that in free solution (Acar and Alshawabkeh, 1993).

The ion migration velocity can be calculated from:

$$v = u^* \frac{dV}{ds}$$

where dV/ds is the voltage gradient, the strength of the electric field, volts V across the length of the soil s.

III.6.3 *Electrolysis*

Application of direct electric current through electrodes immersed in water induces electrolysis reactions at the electrodes. These reactions generate oxygen gas (O_2) and hydrogen ions (H^+) due to oxidation of water at the anode, and hydrogen gas (H_2) and hydroxyl ions (OH^-) due to reduction at the cathode, as described by the following electrolysis reactions:

$$2\,H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \qquad \text{(anode)}$$

$$4\,H_2O + 4e^- \rightarrow 2H_2 \uparrow + 4OH^- \qquad \text{(cathode)}$$

The prevailing of electrolysis reactions at the electrodes depends on the availability of chemical species and the electrochemical potentials of these reactions. Within the first few days of processing, electrolysis reactions drops the pH at the anode to below 2 and increase it at the cathode to above 10, depending upon the total current applied (Acar et al., 1990; Acar and Alshawabkeh, 1993).

While the acid generated at the anode advances through the soil toward the cathode by ionic migration and electroosmosis, the base developed at the cathode initially advances toward the anode by diffusion and ionic migration. The advance of the base front is slower than the advance of the acid front because of the counteracting electro-osmotic flow and also because the ionic mobility of H^+ is about 1.76 times that of OH^-. As a consequence, the acid front dominates the chemistry across the specimen leading to temporary acidification of the treated soil. The advance of the acid front from anode toward the cathode assists in the desorption and dissolution of metal precipitates whilst formation of the high pH zone near the cathode results in immobilization to precipitation of metal hydroxides.

In general, during electrokinetic remediation other geochemical reactions can occur in the soil, enhancing or retarding the process. The variation of pH, redox potential, concentration, variety and value of the pollutants may cause phenomena of adsorption/desorption or precipitation that may affect the ionic migration. In these cases to optimize the process and prevent immobilization of metals "enhancing" agents can be used including acids, bases, complexing/chelating agents.

III.6.4 *Electrolyte Enhancement*

Several procedures have been proposed to enhance electrokinetic remediation of heavy metals and radionuclides. Indeed, geochemical reactions as precipitation and sorption of heavy metals may prevent their transport and thus limit extraction.

Some of these procedures attempt to control production of hydroxyl ions at the cathode; other attempt to enhance complexation of heavy metals to enhance extraction at the anode. A proper selection of the enhancing agents is fundamental:

- they have to prevent the formation of insoluble salts and even to form polar complexes with metals which may migrate to the electrodes;
- they should not increase the level of toxicity of the porous medium or produce toxic liquid waste;

- they should bind preferentially to the pollutants and not to the minerals of the treated soil;
- they do not have to change irreversibly the initial matrix of the soil;
- they should be biodegradable and, if properly selected, environmentally safe.
- if possible they should be regenerated.

Certainly a careful assessment of the costs is required.

III.6.4.1 *Catholyte neutralization*

One way on controlling the catholyte pH is to proceed with a chemical conditioning using acids such as HNO_3 and CH_3COOH, thus avoiding the development of alkaline conditions produced by electrolysis. This operation limits the formation of metal hydroxide near the cathode (would give rise to a low conductivity zone) and improves the solubility of metals.

It was often found experimentally that, because of precipitation, a layer of reaction products deposited on the electrode can polarize it: the polarization tends to decrease the intensity of the electric field, limiting the efficiency of the process.

It is better to avoid the use of strong acids (e.g. HCl) that can destroy the crystalline structure of the matrix treated and pose a health hazard; for example the use of hydrochloric acid may increase the chloride concentration in the groundwater, promote the formation of some insoluble chloride salts (e.g., lead chloride) and if it reaches the anode compartment, chlorine gas will be generated by electrolysis.

III.6.4.2 *Enhancement of anolyte pH*

An excessive acidification of the soil, especially in soils with low buffering capacity, can neutralize the excess positive charge on soil particles and to reverse the electroosmotic flow, which prevailing on electromigration, may hinder the removal of the contaminant. In addition a strong acidification may cause uncontrolled dissolution of soil minerals resulting in an excessive release of some element as Si and Al. Therefore, it may be necessary to control acid production using enhancement agents to solubilize the contaminants without acidification.

III.6.4.3 *Ion-selective membranes*

Another procedure to control hydroxyl ions and enhance the transport of cationic metals towards the cathode is the use of ion selective membranes to separate the catholyte from the soil. These membranes are insoluble in most solvents and chemically resistant to strong oxidizing agents and strong bases. Anyway this technique is limited if compared to catholyte neutralization because precipitation and accumulation of heavy metals on them results in a significant increase in the electrical resistivity of membrane requiring continuously their clean to reduce the energy cost of this technique.

III.6.4.4 *Chelating or complexing agents*

Because of the high buffer capacity of some soils often the use of acids may not be effective to solubilize the contaminants; Reddy et al. (1997) showed that soils that contain high carbonate buffers, such as glacial till, hinder the development and advance of the acid front. In this case complexing agents may be used to induce desorption of metal ions and formation of new species that can move under electromigration (if charged) or drag by the electroosmotic flow (Wong et al., 1997).

Chelating or complexing agents, such as citric acid and ethylendiamine tetraacetic acid (EDTA), have been demonstrated to be feasible for the extraction of different types of metal contaminants from fine-grained soils. The enhancement agents should form charged soluble complexes with the metal contaminants. It was shown that chelating agents such as EDTA form strong bonds with metals and are highly effective in the decontamination of soils contaminated by heavy metals (Lo and Yang, 1999; Kim et al., 2003). The use of EDTA as an enhancement agent has also been demonstrated for the removal of lead from a calcareous soil characterized by a high buffering capacity (Yeung et al., 1996; Amrate et al., 2005) and lead from sand (Wong et al., 1997).

III.6.5 *Electrodes*

Electrodes are typically constructed of carbon, graphite, or platinum, because, being inert materials, no more contaminants will be introduced in the treated soil as a result of the process. Instead metallic electrodes may dissolve as a result of electrolysis and introduce corrosion products into the soil.

The electrodes must be installed to ensure proper contact with the ground and can be fitted vertically or horizontally. A simple one-dimensional configuration consists of parallel rows of electrodes, simple to install, but which may involve the presence of inactive areas of the electric field between the electrodes of the same polarity; to minimize this problem two-dimensional configurations can be used, such as hexagonal, square, triangle. In this case the electric inactive areas are smaller than the one-dimensional configurations (Figure III.3).

The main factors affecting the choice of configuration to be adopted in a real application are:

- location and size of the possible areas of field inactive;
- number and cost of the electrodes per unit area to be treated;
- time required for the remediation process.

The choice of the spacing of the electrodes depends on the costs and time required by the treatment. Decreasing the spacing the area of inactivity of the electric field can be minimized with the increase of costs. On the other hand a greater spacing reduces the number of electrodes and the costs but increases the time required by the treatment.

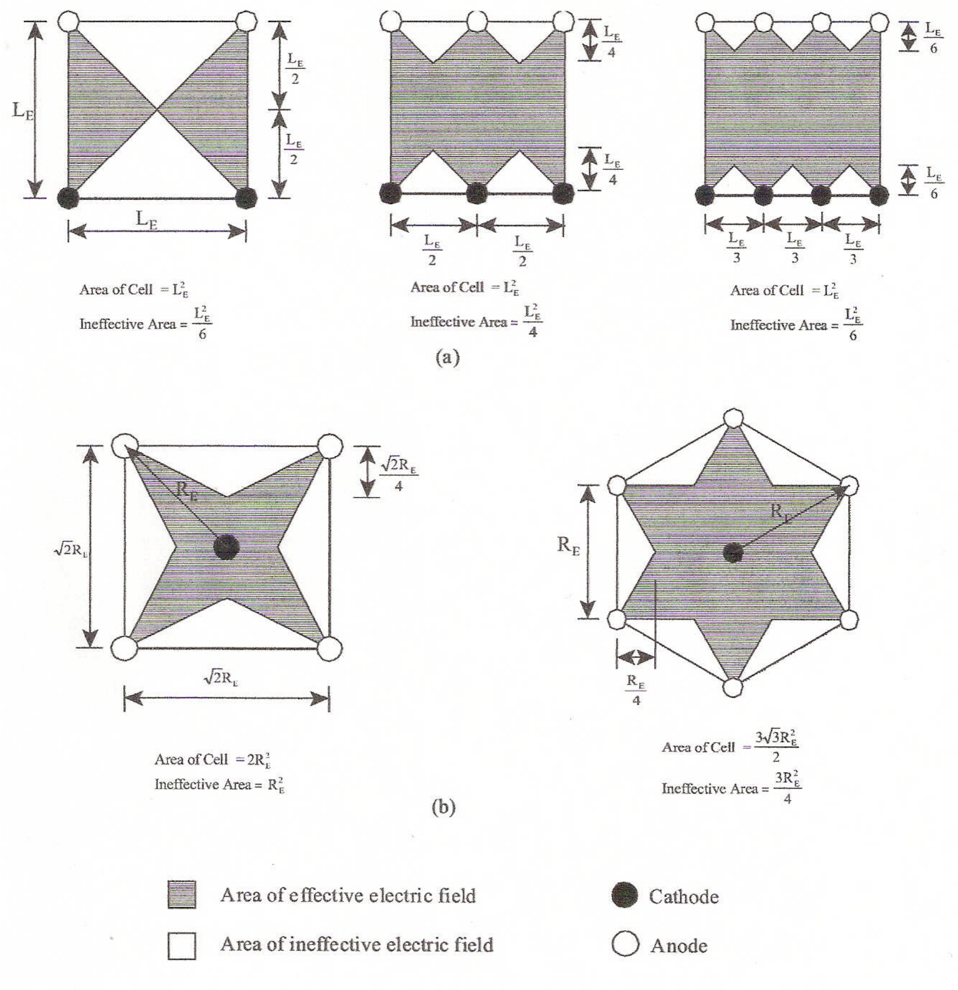


Figure III.3 *Schematic inactivity areas (in white) for one (a) and bi-dimensional (b) electrode configurations (Alshawabkeh, 2001)*

III.6.6 *Advantages and limiting factors of the process*

The major advantages of the technology include:

- implementation in situ with minimal disruption;
- suitable for fine-grained, low-permeability and heterogeneous media, where other techniques such as pump-and-treat can be ineffective;
- applicable for a wide range of contaminants;
- accelerated rates of contaminant transport and extraction may be obtained.

The second point is very significant because in situ remediation of low permeability clayey soils that exhibit sorption capacity is a difficult task in managing contaminated sites; indeed the low permeability of such soils limits extraction of the pore fluid or contaminants by hydraulic gradients; in addition the sorption capacity prevents solubilization of the contaminants and therefore their bioavailability or their transport (Alshawabkeh, 2001).

Regard to the ability of electrokinetics to remove contaminants uniformly from a heterogeneous media, as a contaminated soil containing interlayers of sand and clay, the hydraulic conductivities can vary many orders of magnitude (e.g. 10^{-3} m/s for sand and 10^{-9} m/s for clay). If pump-and-treat is used to remediate such a heterogeneous soil, most of the fluid flow induced will occur in the sandy layer whilst the clayey layer will be practically untreated. Conversely, electric conductivities of these soils are within an order of magnitude; hence the electric field strengths in the different soil layers will be similar with similar ionic migration rates of contaminant transport, resulting in a more homogeneous cleanup.

On the other hand, the limiting factors in the electrokinetic process are:

- type of bond between the pollutant and the solid matrix and subsequent solubility;
- physical abnormalities: the presence in the field of metallic or insulating materials can alter the electrical conductivity;
- moisture content: the efficiency is strongly reduced if content is less than 10%;
- corrosion of the electrodes: their choice is important depending on the pH conditions;
- the process is not efficient if the concentration of ions to be removed is rather low and that of ions that you have no interest to mobilize is high;
- redox reactions can cause the formation of undesirable products such as chlorine gas.

It is clear that the effectiveness of an electrokinetics process is highly dependent on soil properties (buffering capacity, mineralogy, organic matter content) and chemical behaviour of contaminants. The best efficiencies are obtained in the treatment of soils characterized by high water content, low salinity, low ionic strength and low cation exchange capacity; if the porosity of the soil is low, the energy expenditure is great. Highly plastic soils, such as illite, montmorillonite, or soils that exhibit high acid/base buffer capacity require excessive acid and/or enhancement agents to desorb and solubilise contaminants (Alshawabkeh et al., 1997), requiring excessive energy.

III.6.7 ***Costs of the electrokinetic treatment***

The treatment costs depend on the volume of the site and soil characteristics to be decontaminated, the type and concentration of contaminants, the spacing of the electrodes as mentioned in paragraph III.6.5.

Should consider the costs for the energy needs, for the purchase and installation of the electrodes, for any chemical conditioning, to treat extracted flow and other variable costs.

The concentration of enhancement solutions should be optimized to reduce overall costs. Moreover the electrokinetic treatment can be cost-effective by careful choice of applying the lowest current or voltage to achieve cleanup objectives. The spacing between electrodes will also determine the number of wells to be constructed. The system is not cost effective if a large number of wells are needed.

The variable costs include costs for security and monitoring.

III.6.8 *Electrokinetic fencing*

Electrokinetics can be used not only to remediate a contaminated soil but also in order to slow or prevent migration of contaminants into un-polluted ground due to diffusion or a hydraulic gradient by configuring cathodes and anodes in a manner that causes contaminants to flow toward the center of a contaminated area of soil. The practice has been named “electrokinetic fencing”.

Containment technologies like slurry walls, sheet pile cut-off walls and grout curtains are relatively expensive to construct and may require the use of specialised equipment (Narasimhan and Ranjan, 2000).

Electrokinetic fencing can be a better alternative. It represents a containment technique, which exploits the transport processes as electroosmosis and electromigration to create a barrier since the combined effect can be withstand the hydraulically-generated movement of pollutants (Figure III.4).

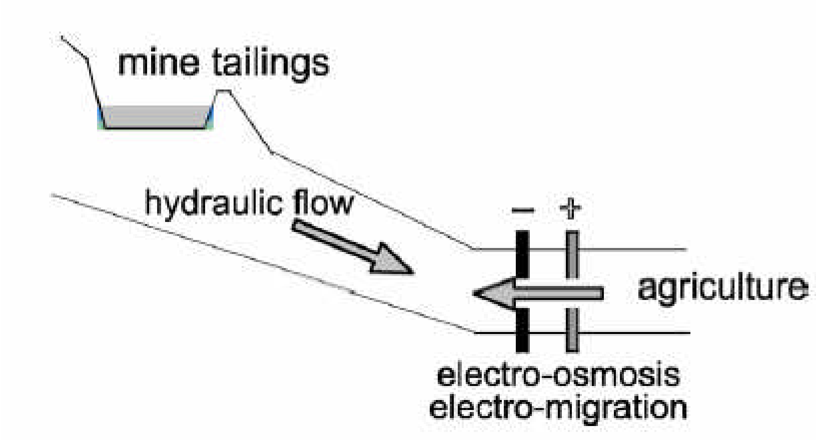


Figure III.4 *Scheme of an electrokinetic barrier to prevent heavy metals contamination of agricultural soil (Lynch et al., 2007)*

The idea of using an electrokinetic barrier was conceived for the first time by Lageman et al. (1989) who have successfully tested this system to prevent dispersal of contaminants such as lead, copper, zinc and cadmium from an abandoned industrial site.

The barrier will be effective to prevent the movement of heavy metal cations if the hydraulic velocity (v_{HYD}) through the soil is not greater than the sum of the electromigration velocity (v_{ION}) plus the electroosmosis velocity (v_{EOF}):

$$v_{HYD} < v_{ION} + v_{EOF}$$

Darcy's velocity is the velocity of the flow across the cross-section due to hydraulic gradient:

$$v = Ki = \frac{Q}{A}$$

where *K* is the hydraulic conductivity of the soil (m/s) and *i* is the hydraulic gradient defined from:

$$i = \frac{dh}{ds}$$

where *dh* is the difference in potential head and *ds* the length of the soil. *A* is the cross-section area of soil (m^2) and *Q* is the flow rate (m^3/s).

In a porous medium, as the soil, the flow must move around the particles through the voids, so the cross-section available is much lower and the pore fluid velocity is higher for a given flow rate. The real velocity of the front is defined as:

$$v_f = \frac{v}{n}$$

where *n* is the porosity of the soil and *v* is the Darcy's velocity.

The efficiency of the barrier depends strongly on the types of soils and ions present in the treatment. In coarse grained soils, the barrier works essentially by electromigration, whilst in fine grained soils, the barrier works both electromigration and electroosmosis, blocking the ions by the combination of their effects and slowing up the water flow.

Unlike the electrokinetic contaminant removal, in the case of the barrier it is not necessary the pH conditioning of the solutions at the electrodes, because the precipitation contaminants aid to increase the barrier efficiency reducing the pore volume and hindering the contaminant flow.

The system works optimally when the contamination is characterized by only one type of charged ions. For example when the anode is placed down gradient of the cathode the migration of cations can be effectively controlled by the electrokinetic barrier but to control the migration of anions the polarity of the electrodes should be reversed. Doing so will make the electro-osmotic flow take place in the same direction as that of the ground water movement and will increase the advective transport of the contaminant. To solve this problem an additional row of cathodes should be installed on the downstream side of the anode. Therefore, to contain the dispersion of pollutants, the placement and configuration of the electrodes is strictly related to the type of contamination and carefully designed: if the contaminant of interest is either a cation or an anion, a simple double row of anode and cathode electrode arrangement could serve as an effective barrier; conversely, if the contaminant includes both anions and cations, then a triple-row configuration of electrodes need to be implemented (Narasimhan and Ranjan, 2000).

III.7 R*eactive barriers (RBs)*

The reactive barrier technology is an in situ remediation treatment consisting in an emplacement of reactive materials where a contaminant plume must move through it and treated water exits on the other side. Usually the RBs work as permeable ones in porous media where convective transport of contaminants is spontaneous, typically under its natural gradient, and it is more properly known as permeable reactive barrier (PRB) technology; thus it is characterized by the passive interception and designed to degrade or immobilize dissolved contaminants in groundwater as it flows through the barrier (Figure III.5).

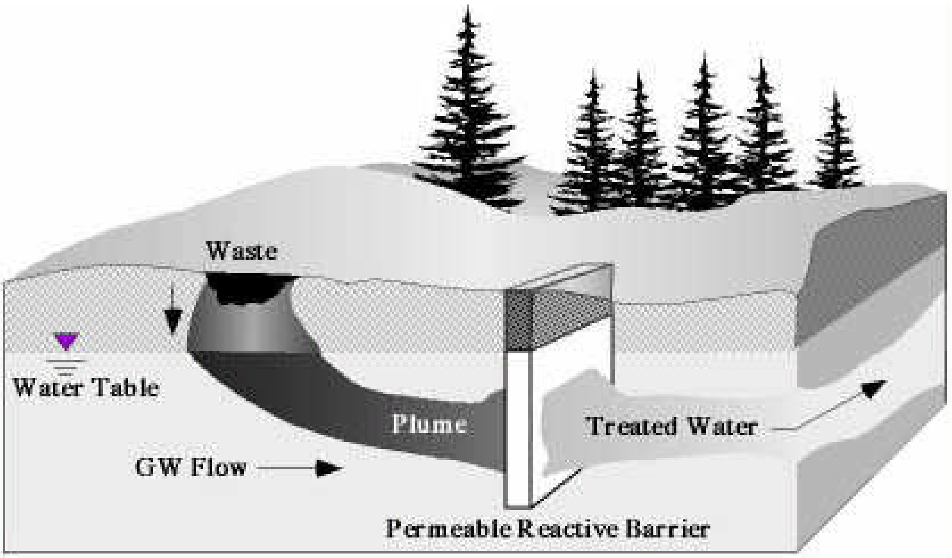


Figure III.5 *Schematic of a permeable reactive barrier (from USEPA, 1998c.)*

Various configurations of in-situ PRBs systems have been constructed:

- in a *continuous PRB* (Figure III.6) configuration the treatment material is distributed across the width of the contaminated groundwater plume. The continuous PRB has been the most common configuration used;
- a *funnel and gate* (Figure III.7) configuration uses an impermeable section (funnel) to direct the captured groundwater flow towards the permeable treatment section (gate); this configuration allows better control over reactive cell placement and plume capture.

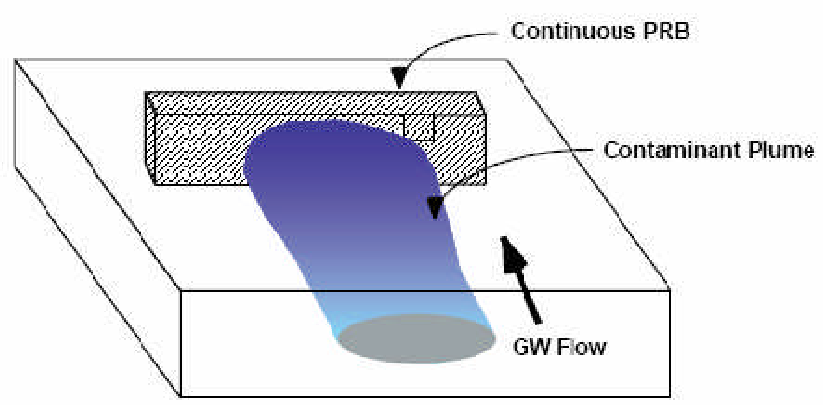


Figure III.6 *Basic configuration of a Continuous PRB (Powell et al., 1998)*

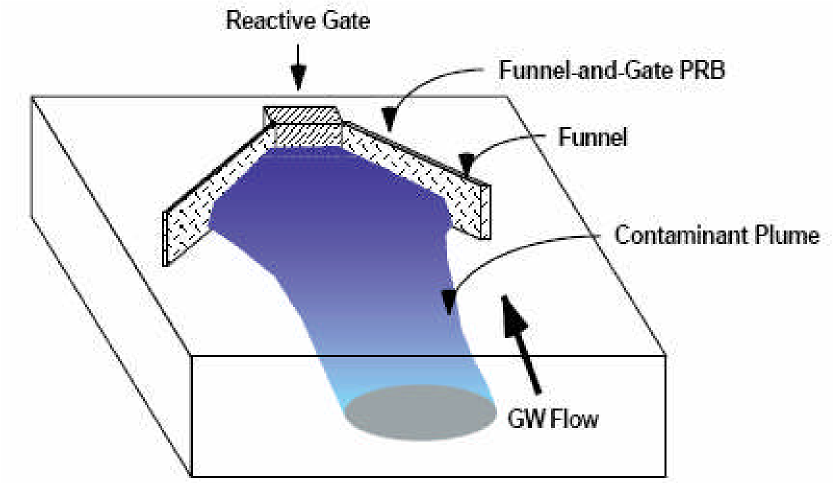


Figure III.7 *Basic configuration of a Funnel-and-Gate PRB (Powell et al., 1998)*

The reactive barriers could be used in porous media that are not characterised by high permeability, providing external energy for instance by the electrokinetic technique in order to make possible the flow of the contaminants through the reactive barrier. They must be installed in a position such that all plume passes through the reactive system and by means of physical, chemical or biological reactions an acceptable treatment of the contamination is achieved. The residence time required and the ground-water velocity through the RB are used to determine the size of RB needed to achieve the desired treatment level.

III.7.1 *Reactive materials*

The reactive media used in RBs must be designed to degrade or immobilize contaminants without rapidly clogging up with precipitates or quickly losing its reactivity; the materials should be compatible with the subsurface environment, without cause counterproductive reactions, toxic intermediary products, detrimental effects; they should not interrupt the flow by not having excessively small particle size, should be low cost and should have a long service life (it should not be readily soluble or depleted in reactivity).

In general, the reactive materials used for the construction of RBs and PRBs may change pH or redox potential conditions, cause precipitation, have high sorption capacity or release nutrients/oxygen to enhance biological degradation.

Reactive media remove contaminants through sorption, precipitation and degradation processes. The sorption process causes removal of contaminants by physically sorbing them onto the surfaces of reactive media as zeolites and activated carbon whilst the chemical state is not altered. The precipitation causes immobilization of contaminants by formation of insoluble compounds that fall out within the barrier. A degradation process involves chemical or biological reactions to break down contaminants into harmless compounds.

Obviously the selection of material is closely correlated to the type of contaminant to be treated. Organic contaminants can be broken down into innocuous elements and compounds, conversely, inorganic contaminants cannot be destroyed but can only change speciation. Therefore remediation strategies must focus on transforming inorganics into forms that are non-toxic, not bioavailable and immobile, or capable of being removed from the subsurface (Ott, 2000).

The materials that have shown the best success with a wide range of contaminants are zero-valent iron, calcium carbonate (limestone), zeolites and organic material (including activate carbon).

III.7.1.1 *Zero-Valent Iron*

Much of the installed RBs use zero-valent metals, especially metallic or granular iron, as reactive medium for the treatment of chlorinated organic compounds. Zero-valent iron (Fe^0) donates the electrons necessary to reduce the contaminants, and becomes oxidized to Fe^{2+}

or Fe^{3+}. This ability can also be exploited to reduce inorganic anions that are more toxic and mobile in higher oxidation states, such as Cr^{6+} (Powell et al., 1997).

This material is favoured because it is relatively inexpensive and easy to obtain in huge quantities.

III.7.1.2 *Calcium carbonate (calcite, limestone)*

Calcite [$CaCO_3$(s)] is a common mineral phase in many limestone aquifers. The use of limestone has been proposed for sites with metals contamination because, increasing the pH, the precipitation of inorganics is achieved being the solubility of many metals reduced in neutral/slightly basic conditions.

III.7.1.3 *Zeolites*

Zeolites are minerals that have very high ion-exchange, adsorbing, catalytic, molecular sieving capacities and make them potentially useful as treatment mineral for use in the RBs. As the mineral is anionic (negatively charged), it can be used to remove cations from aqueous solutions. Several hundred zeolitic materials exists, both natural and synthetic; Clinoptilolite, a natural zeolite, is a potential material for remediation of aqueous solutions since it demonstrates strong affinity for several toxic heavy metals and can selectively adsorb some radionuclides.

III.7.1.4 *Organic materials*

Organic materials can be very effective at removing nitrate, sulphate, dissolved organics, and dissolved metals from groundwater (Striegel et al., 2001).

Granular activated carbons are highly suitable being chemically stable materials with a high adsorption capacity for many organic and inorganic contaminants largely due to its high surface area (about 1000 m^2/g) and the presence of different types of surface functional groups (hydroxyl, carbonyl, lactone, carboxylic acid, etc.).

III.7.2 *Design of the barrier*

In the design of the barrier, two key parameters have to be considered: the amount of reactive medium in the barrier and the thickness of the barrier. The length and the depth of reactive barriers are a function of the hydrogeological characteristics of the aquifer.

The amount of medium depends on specific interactions between contaminants and reactive material and it must be such that the complete degradation of the contaminant is guaranteed.

With regard to the thickness it must allow that the reaction is complete: if the contaminated flow is characterized by the presence of a mixture of contaminants the thickness will be evaluated depending on the speed of the slower reaction.

III.7.3 *Advantages and disadvantages*

The RB technology, especially in the permeable configuration, represents an effective alternative to conventional approaches for groundwater remediation such as the pump-and-treat (P&T) method where water is extracted, cleaned and then possibly injected. Moreover the P&T technology is not applicable when the contamination resides in fine-grained soils as clayey or silty soils, being hindered by low hydraulic conductivities of these soils.

RBs have significant advantages:

- RBs can degrade or immobilize contaminants in situ without any need to bring them up to the surface;
- they tend to treat less volume of water as there is no active pumping, and so reducing the load on the treatment;
- they can be modified to treat several different types of contaminants;
- after the installation the above ground can be re-used for other purposes, because there are limited above ground structures, except to provide external energy;

On the other hand different factors may limit the effectiveness of the RB and have to be considered:

- finite treatment capacity, limited by the chemical characteristics of the barrier, including the total mass of reactive material and rate of reaction within the barrier;

- physical changes into the barrier, including decreases in porosity and permeability may limit barrier life, requiring periodic replacement of the reactive medium after its reactive capacity is exhausted or it is clogged by precipitants and/or microorganisms; the reactive materials are generally used up very slowly and have the potential to treat contaminated flow for several years or decades;
- treatment time longer than other active remediation methods;
- possibility of plume bypassing the RB as a result of changes in flow regime.

III.7.4 ***Costs associated to RB technology***

The RB technology provides treatment at costs that are competitive with other groundwater remediation systems especially if work as permeable, under a natural gradient, because, being an in situ remediation technology, there is no need to excavate and dispose contaminated soils or to pump and treat contaminated groundwater.

Costs associated with the implementation of a RB treatment system include the initial costs associated with the design, installation, and site rehabilitation, and the continuing costs of monitoring the barrier performance. Costs to provide external energy in order to create the contaminated flow through the RB should be considered, whilst the passive nature of PRB technology makes operating costs lower. Costs may also be associated with the recovery and disposal of the reactive material following the completion of the treatment program.

Chapter IV

Literature Review

IV.1 *Electrokinetic treatments applied on contaminated soils by Cr or As*

In this chapter a brief qualitative overview of experiences about the electrokinetic remediation of chromium (Cr) and arsenic (As) contaminated soils is given.

Cr and As are reported to be among the more difficult elements to remove by electrokinetics (Ottosen et al. 2009). An analysis of the data obtained during several studies underlines that the efficiency of unenhanced EK removal of Cr falls between 3-64%, with the majority of the considered experiments resulting in removal lower than 35% (Gent et al., 2004; Wieczorek et al., 2005; Ottosen et al. 2009). The complexity of Cr EK removal is mainly due to its presence in soils as two different forms: hexavalent Cr(VI) and trivalent Cr(III). Hexavalent Cr exists as oxyanions which are soluble, remain in solution over a wide range of pH values and in an EK system migrate towards the anode. Under subsurface conditions, trivalent Cr generally occurs as cation Cr^{3+} as well as cationic, neutral and anionic hydroxo complexes. In acidic environment and at relatively low redox potentials, Cr(III) exists as cation and cationic complexes which electromigrate towards the cathode. Within the pH range 6.8-11.3, Cr(III) precipitates as hydroxides, whilst at higher pH values it may form anionic complexes which electromigrate towards the anode (Reddy and Chinthamreddy, 1999). EK removal of Cr(III) cation and cationic complexes is significantly hindered by adsorption on the negatively charged soil particles and by precipitation. Although Cr(VI) is characterised by higher EK removal efficiency with respect to the trivalent form, it may be reduced to Cr(III) in presence of ferrous iron, sulphide and the soil organic matter content itself. Moreover, while attempting EK removal, reduction to Cr(III) has been observed even in the absence of any reducing agent due to the redox reactions which occur at the electrodes during water electrolysis (Reddy and Chinthamreddy, 1999). For the provided reasons, *EK removal of Cr(VI) is considered difficult without a proper enhancement* capable of limiting reduction to Cr(III) and allowing the development of alkaline conditions; although the research on this issue is still relatively limited (Ottosen, 2009).

Electrokinetic treatment has had limited use to treat soil, groundwater and industrial wastes containing arsenic (USEPA 2002).

The unenhanced EK removal efficiency of As is also reported to be rather limited, with a peak of about 60% achievable only over long treatment periods of 120 days and more (Ribeiro et al., 1998; Maini et al., 2000; Ottosen et al., 2000; Ricart et al., 2005; Ottosen et al. 2009). The chemistry of As is significantly different with respect to the other metals. The predominant forms found in soil are arsenate As(V) and arsenite As(III), under high redox and slightly reducing conditions, respectively; arsenate are present in the form of oxyanions ($H_2AsO_4^-$ $HAsO_4^{-2}$ and AsO_4^{3-}); As(III) can be found as oxyanion ($H_2AsO_3^-$) but also as uncharged specie (H_3AsO_3) which is not removed by electromigration (Ottosen et al., 2000). A possible enhancement for arsenite consists of adding an alkaline solution (NaOH or ammonia) to ensure that As(III) is present as charged species (Ottosen et al., 2009).

The obvious conclusion is that Cr and As are difficult to remove without enhancement because the alkaline front is not sufficient to obtain the contaminant desorption. Typically, in order to obtain better results with lower final concentrations in the soil, reagents addition or a combination of different techniques are used. However the research on enhancement is very limited.

As far as arsenate is concerned, mobilization enhancing methods have been studied which foresee control or limitation of the development of the acid front, as arsenate is scarcely mobile under acidic conditions and, conversely, mobile under alkaline conditions where most of the heavy metals are not.

Baek et al. (2009) investigated the feasibility of electrolyte conditioning with strong or alkaline solution on electrokinetic remediation of arsenic-contaminated mine tailing. The mine tailing contained calcium oxide of more than 50%. At alkaline condition arsenic was precipitated with calcium and formed very stable solid, calcium arsenate. The precipitate of arsenic could not be moved by electromigration which decreased overall arsenic removal in electrokinetic process. Catholyte conditioning with strong acidic solution prevented increase in pH and the ionic arsenic was removed by electromigration from cathode to anode. Catholyte conditioning with strong acidic solution and anolyte conditioning with strong alkaline solution showed similar efficiency to remove arsenic. The maximum removal efficiency of arsenic was 62% after 28 days operation with catholyte conditioning with 0.1M nitric acid; however the remaining As in soil still exceeded the regulated level and to meet the regulation criteria further treatment needed to be applied.

Positive results were obtained on soils spiked with arsenate and Cr(III) by adding sodium hypochlorite in order to oxidize Cr(III) to Cr(VI) and to promote the development of the alkaline front which enhances the removal of both arsenate and Cr(VI) (Le Hecho et al., 1998). Further results were obtained by using potassium phosphate and sodium hydroxide as cathodic electrolytes for the removal of As from a spiked kaolinite and an arsenic-bearing tailing-soil, respectively (Kim et al., 2005); bench-scale tests demonstrated that the potassium phosphate was effective in extracting arsenic from the kaolinite sample probably due to anion exchange of arsenic species by phosphate, whilst the sodium hydroxide boosted the level of hydroxide ions in the system which, in turn, enhanced the ionic migration of arsenic species through the anion exchange of arsenic as well as the dissolution of arsenic-bearing minerals; moreover, in order to further enhance the EK removal of As, the development of acidic conditions was prevented by adopting sodium carbonate as anolyte capable of neutralizing the hydrogen ions. Arsenic was successfully mobilized also by adding ammonia (Ottosen et al., 2000) and ammonium citrate (Ottosen et al., 2003) to the EK system, or adding to the soil an oxidizing agent as $K_4P_2O_7$ to oxidize the As(III) species to As(V) (Ribeiro et al., 1998). In another experiment, the efficiency as enhancing agent of chemical reagents as ethylendiamine tetraacetic acid (EDTA), citric acid and the cationic surfactant CPC (cetylpyridinium chloride) was compared under potential gradient of 2 to 3 V/cm for 5 days treatment (Yuan and Chiang, 2008), and the best results were attained with EDTA due to its capability of scavenging metals without inducing strong acidification of the medium. Anyway the authors concluded that a further investigation needed to be conducted to achieve higher removal efficiency.

Another way to improve the removal efficiency is to manipulate the electric field in order to reduce the concentration gradients generated during the process with a constant electric field, or decrease the heavy metal migration distance, or improve desorption (Ottosen et al., 2009). To this regard, several research experiences have studied the application of cyclic or pulsed electric fields (to minimize or eliminate concentration gradients that could form during the application of DC electric) (Reddy and Saichek, 2004; Hansen and Rojo, 2007) or mobile anodes and bipolar electrodes to reduce the migration distance (Chen et al., 2006; Hansen et al., 2007), as well as the combination of electrokinetics with others technologies such as soil washing, phytoremediation, ultrasound, reactive barriers, although some of these methods were never applied for the removal of As or Cr but for Cd, Cu or organic compounds and are cited here for completeness on enhancing methods of electrokinetics.

Specifically by the combination of EK treatment with soil washing process, each individual treatment can take advantage; indeed the electrokinetics could be applied for the treatment of fine-grained materials (Page and Page, 2002), whilst the soil washing that is less complex and less expensive, is more appropriate to decontaminate the coarse fractions. In addition the application of enhancement solutions is easy in this application. On the other hand, in this combined treatment the benefits of in situ technology are lost.

The use of ultrasound in EK remediation has been evaluated, to enhance the desorption and dissolution of contaminants, valid option especially in soils that are contaminated with heavy metals and organics (Chung and Kamon, 2005; Sandoval-Gonzales et al., 2007).

With regard to the present work, the EK remediation coupled with reactive barriers (RBs) is also a possible way in order to enhance EK removal of metals from low permeability soils.

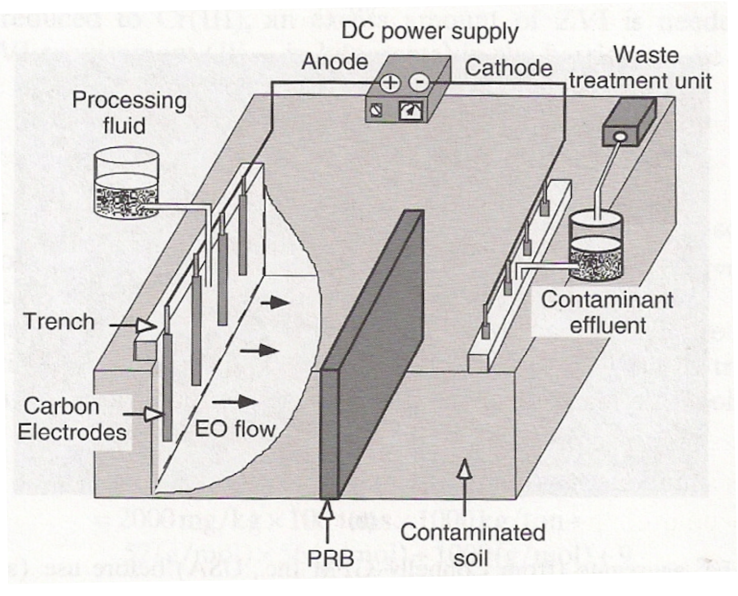


Figure IV.1 *Schematic diagram of coupled EK-PRB for in situ soil remediation (Weng, 2009)*

Recently, a limited number of laboratory experiments have been carried out on in-situ treatment of arsenic or chromium contaminated soils integrating PRBs into the EK process, in which different reactive materials have been tested for immobilizing a variety of contaminants (Weng et al., 2006; Weng et al., 2007; Yuan and Chiang 2007; Chung and Lee 2007; Yuan et al., 2009; Cang et al., 2009) but results have often been variable and inconclusive as reported in the literature. Weng et al. (2006) were the first to introduce the EK coupled with PRBs constituted by Fe(0) and sand, installated either near the cathode or anode or in the middle of the soil specimen. They reported that the position of the barrier had an impact on the electroosmotic flow but not on the Cr(VI) reduction. Up to 60 to 71% total Cr removal was achieved for the process with a zero-valent iron (ZVI) barrier with respect to only a 28% removal efficiency for the process without barrier. Weng et al. (2007) continued to study this subject installing a barrier 1:1 w/w ratio of granular ZVI and sand in the center of the specimen. The transport of the acid front was retarded by the strong opposite migration of anionic chromate ions and, as result, an alkaline front was developed promoting the desorption of Cr(VI). Moreover they observed a reverse electroosmotic flow, mainly attributed to the migration of anionic chromate towards the anode.

Enhancement of Cr(VI) removal was attained also by Cang et al. (2009) when a ZVI reactive barrier (RB) was incorporated in an electrokinetic system. Results showed that loading ZVI-PRBs in different locations of soil column strongly affected the EK performance. A removal efficiency of 71.5% was achieved when two ZVI-PRBs were loaded at the two ends of the soil column.

Yuan and Chiang (2007) proposed a remediation system of electrokinetic process coupled with iron permeable reaction barrier of ZVI granular and FeOOH to treat arsenic contaminated soil. They found the best performance in system with barrier filled with FeOOH than with ZVI located in the middle of electrokinetic cell. This was largely because of higher surface area of FeOOH adsorbing more anionic As(V) as $HAsO_4^{2-}$ and AsO_4^{3-} ions and because of the moving of $HAsO_4^{2-}$ to the anode side by electromigration effect was inhibited by the electroosmotic flow. Overall As(V) removal efficiency was 27% at 5 days of treatment for the process without barrier, increasing to 51% and 60%, respectively for the ZVI and FeOOH fillings installed at the center of the specimen. Results indicated that the removal of

As in EK/PRB systems was much more contributed by surface adsorption/precipitation on PRB media (ZVI and FeOOH) than by EK process.

Chung and Lee (2007) investigated the feasible use of atomizing slag as an inexpensive PRB reactive material coupled with the EK processes in order to remediate contaminated ground, with either inorganic or organic substances, of low permeability soils. Experimental results showed that the removal efficiencies for trichloroethylene (TCE) and cadmium (Cd) both achieved approximately 90%. The removal rate of Cd from the soil specimen was higher due to the additional effects of electromigration for its positive charge.

Yuan et al. (2009) investigated an enhanced EK remediation process coupled with PRB of carbon nanotube coated with cobalt (CNT-Co) for As(V) removal from soil under potential gradient of 2.0 V/cm for 5 days treatment. Results showed that removal efficiency of As(V) was greater than 70% in EK/CNT-Co system with EDTA as processing fluid, which was enhanced by a factor of 2.2 compared to EK system and EK/CNT systems. A better removal performance in EK/CNT-Co system was attributed to higher sorption of As(V) onto CNT-Co than onto CNT. Among EK processes, As(V) removal was dominated by electroosmosis flow and electromigration in EK/CNT-Co system with groundwater and EDTA as processing fluid.

A further method of generating an iron electrokinetic barrier was proposed by Cundy and Hopkinson (2005) and Faulkner et al. (2005) using low cost sacrificial iron electrodes to build up a low permeability iron-rich layer. The so-called FIRS (Ferric Iron Remediation and Stabilisation) technique involves the application of a low voltage gradient (typically less than 0.2 V/cm) between two or more sacrificial, Fe-rich, electrodes emplaced in, or either side of, a contaminated soil or sediment. The electric potential is used to generate a strong pH gradient within the soil column and force the precipitation of an Fe-rich barrier or ‘‘pan’’ in the soil between the electrodes. The remobilised contaminants are concentrated onto or immediately adjacent to a well-defined electrokinetically-generated Fe-rich band, forming a localised area of high contaminant concentration which can be removed for disposal or further treatment. Arsenic, in particular, seems highly amenable to the FIRS treatment, due to its solubility under the high pH conditions generated near to the cathode, and its marked geochemical affinity with the freshly precipitated Fe oxides and oxyhydroxides in the Fe barrier.

Generally, in this approach, zero-valent iron has mainly been used to fix either arsenic or chromium although using low-cost reactive materials, such as some industrial residues and derived products should contribute to improve economics of combined treatments and their environmental friendliness. In the view of an EK-RB combined treatment of soils contaminated by arsenate and chromate, red mud (RM), a by-product of bauxite refinement for alumina production through the Bayer process, is a suitable material, after a proper treatment to obtain what is called transformed red mud (TRM). For more details on this material see section IV.3.

Most of the research done up until now has been limited to the use of electrokinetic technology in situ clean-up. However the electrokinetic could be used as barrier to prevent the migration of contaminants as described in Chapter III.

IV.2 ***Experiences about electrokinetic fencing***

The idea of using an electrokinetic barrier was conceived for the first time by Lageman et al. (1989) who have successfully tested this system to prevent dispersal of contaminants such as lead, copper, zinc and cadmium from an abandoned industrial site.

Yeung and Mitchell (1993) investigated the migration of sodium chloride through a one-dimensional column for different lengths of time. A hydraulic gradient of 50 (hydraulic head of 500 cm applied to a sample of 10 cm length) was applied continuously whilst an electrical potential gradient of 1 V cm^{-1} was applied across the samples for 1 h per day in a direction to cause electro-osmotic flow opposite to the hydraulic flow. Experimental results showed that the electrokinetic barrier completely retards the migration of cations Na^{2+} even after 25 days; on the other hand the migration of chloride ions was enhanced by the application of the electrical potential gradient. Indeed when the contaminants include both negatively charged and positively charged ions, an additional row of cathodes should be installed on the downstream side of the anode.

Narasimhan and Ranjan (2000) published a model for simulating the contaminant migration in soil under coupled hydraulic, electrical and chemical gradients.

Lynch et al. (2007) investigated the efficiency of an electrokinetic barrier carrying out one-dimensional (1D) tests to prevent cadmium from polluting an uncontaminated sample, and two-dimensional tests to avoid the migration of copper due to hydraulic flow. Results of 1D tests indicated that the barrier can prevent or significantly reduce heavy-metal contamination from spreading against a hydraulic gradient of 7. In 2D tests, with two rows of electrodes inserted in a horizontally flat soil tank, was found that an electric field of 125 V m^{-1} was sufficient to prevent significant copper incursion from a contaminant flow under a hydraulic gradient of 1.3. Similar tests to 1D described above were also performed to prevent zinc migration: when a gradient voltage of 1.25 V cm^{-1} was applied the transport of zinc down-gradient was severely reduced, whilst at lower applied voltages, 0.5 V cm^{-1} and 0.85 V cm^{-1}, some pollution was observed (Ruggeri, 2005).

IV.3 *Red mud production*

Red mud (RM) is the waste by-product of bauxite processing for alumina production in the Bayer Process. Bauxite, the most important ore of aluminium, contains only 30-54% alumina, Al_2O_3, the rest is a mixture of silica, various iron oxides and titanium dioxide.

During the Bayer process, bauxite is digested by washing with a solution of sodium hydroxide, NaOH, at high temperature (200-250 °C) and pressure (25 atm); in these conditions, a soluble compound is obtained ($NaAl(OH)_4$) while the other components of bauxite do not dissolve and are separated by filtering. The hydroxide solution is cooled and pure $Al(OH)_3$ is precipitated as a white, fluffy solid, then calcined (heated to 1050°C) to produce oxide (Al_2O_3), from which the Al metal is finally recovered. The remaining mixture of iron, titanium, sodium, silica and other impurities is discarded and represents a waste product known as red mud, a dry red solid due to its oxidised iron content and, since it has been subjected to sodium hydroxide treatment, is highly caustic, having pH values higher than 13. RM is a complex material that differs due to the different bauxites used and the different process parameters. Anyway each RM has specify characteristics, such:

- produced during the Bayer process
- water suspensions and highly alkaline
- mainly composed of iron oxides and have a variety of elements and mineralogical phases
- relatively high specific surface/fine particle size distribution

Red mud represents one of the prime concerns of aluminium/alumina industry from the point of view of resource conservation and protection of the environment (Kumar et al., 2006). It is, therefore, a problematic material whose global annual production accounts for some 70 million tonnes and whose indefinite storage in huge tailing dams, often close to the coast, represents an environmental problem. The disposal of RM remains a major problem. In a research by Hind *et al.* (1999), it is reported that conventional disposal methods have revolved around the construction of clay-lined dams or dykes, into which the RM slurry is pumped and allowed to dry naturally. However the potential impact on the surrounding groundwater and environment is high. As an alternative, dry disposal of bauxite residue, involving enhanced dewatering and evaporative drying, has also been found to further decrease environmental risks and lower overall disposal costs (Cooling and Glenister, 1992). It is reported that out of 84 alumina plants all over the world, only seven are still practising the sea disposal in a planned manner because of scarcity of land (www.redmud.org).

Because of their high caustic nature a careful management is required to avoid for example the contamination of water resources by percolation from the basin. In addition, the management of the basin increases the costs of the entire process of alumina production.

Below, on the left a picture from a red mud disposal lake in the vicinity of Kashipur region of Orissa (India) is shown (Figure IV.2). On the right, a landfill where dry disposal has been taking place is shown (Figure IV.3) (source: www.redmud.org).

Figure IV.2 *Red mud disposal lake*

Figure IV.3 *Red mud dry disposal in landfill*

IV.3.1 *Reuse of red muds*

It is estimated that for every tonne of alumina produced, 1-1.5 t of red muds are generated as a waste (Kumar et al., 2006); because of their highly caustic nature, red muds are classified as hazardous waste and as such are required to be neutralised prior to transport, even if they are to be reused (Bertocchi et al., 2006). Recently, the issue represented by proper and environmentally sound management of red mud waste has been intensively studied. Most of the studies focused so far on dehydrating red mud waste to reduce its detrimental effects on the environment, or on extracting all or some of the compounds which can be found in this waste in order to allow for their use in civil engineering, metallurgy and chemical processes. However, many of the proposed solutions proved to be costly, so the research on this issue is still needed. In addition, the costs for disposal, due to the construction and management of the basin, for the recovery site and for the restriction of land use, are such as to justify an interest in reuse of red mud. it would reduce drawbacks of environmental and economic nature, saving on the entire production cycle. For this purpose, utilisation of red mud has been a subject of major scientific research.

An elevated number of potential uses has been reported in the literature. The various uses include metallurgical ones (iron and steel production, titania, alumina and alkali, minor constituents recovery), production of building materials (constructional brick, light weight aggregates, bricks roofing and flooring tiles, cements etc), catalysis, ceramics (pottery, sanitary ware, special tiles and glasses, glazes, ferrites) and other various direct uses (in waste treatment, as a filler, as a fertiliser, etc). Be considered that for successful recovery of major or minor constituents of RM the economic are still not favouring and in most cases a disposal problem for the remaining quantity of RM still remains. On the utilisation of red mud for building materials production the use of RM in these processes would be beneficial and the bulk production of building materials could eliminate the disposal problem. In this way an added value would be given to RM, being a raw material, and the economical aspects regarding industrial realisation would be more favourable.

The use of red muds can occur after a proper process of transformation to improve its characteristics.

The transformation of the red mud characterized by pH 13 into a useable and saleable product having pH of about 9 would be surely advisable and is considered by the European Commission a best available technology (BAT) for a proper management (European Commission, 2004). To this regard, a process was developed by an Australian company (Virotec International), whereby red mud is transformed through the BASECON^{TM} process into BAUXSOL^{TM} (or transformed red mud), following mixing with calcium chloride salt and magnesium chloride brine derived from local solar salt plants. The transformed red mud (TRM) consists mainly of micron-sized sodium hydroxide etched aggregates of hydrated-iron oxides (hematite and ferrihydrite, 35 wt%) and hydrated alumina (boehmite and gibbsite, 20 wt%). These are impregnated by newly formed and more or less soluble alkaline minerals, mainly sodalite (15 wt%,), calcium hydroxides, hydroxycarbonates and calcium alumino silicates (portlandite, calcite, cancrinite, hydrocalumite and aluminohydrocalcite, 15 wt%), magnesium hydroxides and magnesium alumino silicates (brucite and hydrotalcite, 4 wt%) (Table IV.1). However the exact composition depends on the composition of the bauxite used at each refinery, operational procedures at the refinery, neutralization processing of the caustic red mud, and the blends chosen. Because it is prepared from an industrial residue, the TRM is relatively inexpensive. The production process can rely on a large availability of raw materials at low cost and on a procedure that does not generate dangerous wastes to the environment. This 'green' reuse of a waste product, economically sustainable, also lightens the trouble of industrial waste disposal, partly resolving the issue with the management and disposal of red muds.

In the view of a EK-RB combined treatment of soils contaminated by arsenate and chromate, as presented in this work, the TRM is a suitable material having a high acid neutralising capacity (2.5 to 7.5 moles of acid/kg), a very high metal trapping capacity (greater than 1.000 milliequivalents of metal/kg); it also has a high capacity to trap and bind phosphate and some other chemical species, and although more of 80% of TRM particles are < 10 µm, it is largely insoluble and non-dispersive in water showing an excellent flocculant property.

Table IV.1 *TRM Mineralogy*

Major minerals (in decreasing order of abundance)	
Hematite	Fe_2O_3
Boehmite	γ-AlOOH
Gibbsite	$Al(OH)_3$
Sodalite	$Na_4Al_3Si_3O1_2Cl$
Quartz	SiO_2
Cancrinite	$(Na,Ca,K)_8(Al,Si)_{12}O_{24}(SO_4,CO_3)\cdot 3H_2O$
Other minerals (in alphabetical order)	
Anatase	TiO_2
Aragonite	$CaCO_3$
Brucite	$Mg_3(OH)_6$
Diaspore	β-$Al_2O_3 \cdot H_2O$
Ferrihydrite	$Fe_5O_7(OH) \cdot 4H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Hydrocalumite	$Ca_2Al(OH)_7 \cdot 3H_2O$
Hydrotalcite	$Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$
P-aluminohydrocalcite	$CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$

IV.3.2 *Applications of the transformed red mud*

The TRM is used in numerous situations of metal contamination as:

- treatment of waste water;
- contaminated groundwater (by arsenic or other metals);
- soils, sludge and residues contaminated with metals;
- removal of phosphates from water;
- treatment of effluents from tanneries (acid and enriched by chromium);
- treatment of mine tailings and acid sulphate soils.

Therefore this material can be used to remediate metal contaminated waters (like the acid mine drainage, common in mining areas) and soils, allowing the achievement of a double environmental goal: ***the solving of an environmental problem by reusing a waste industrial***

by-product. The use of TRM to treat contaminated waters allows to achieve the best "quality of treated water/cost of treatment" ratio: the active treatment is usually performed by dispersing the product in the form of slurry by means of pumps on the surface of the basin to be treated, in amounts determined on the basis of concentrations of metals and acidity of the water (www.virotec.com). Its application to treat acid rock drainage and sulphidic waste rock and tailings provides another new options for managing some difficult environmental problems at both abandoned and active mine sites. Indeed the management of acid mine water is a common problem in mining and processing, particularly for the removal of As, Cu, Cr, Fe, Ni, Mn, Pb, U and Zn.

Figure IV.4 *Escaping of water from a basin of mining waste (by Virotec)*

IV.3.3 *Adsorption capacity of TRM*

Based on previous studies conducted in the laboratories of DIGITA on the capacity of the TRM for the removal of chromium from contaminated water, the decreased efficiency of Cr adsorption with increasing pH was observed. The optimal value of pH for Cr(VI) adsorption on the hematite in the TRM was obtained at pH 5.5, corresponding to a TRM adsorption capacity for Cr(VI) of 1.6 mg/g, whilst the ANC (Acid Neutralization Capacity) tests showed an acid neutralizing capacity of app. 4 mole/kg(TRM) (Mureddu, 2006).

With regard to As, laboratory tests conducted by Virotec underlines that the TRM can not be used effectively to remove As if the pH is above 7 (www.virotec.com). A solution is to wash the material with acid to remove minerals that provide the solid alkalinity, thereby increasing the proportion of positive surface charges on particles, obtaining better As removal capacities (up to 3.5 g As /kg of acid washed TRM). Another method to improve the adsorption capacity of red mud is to submit it to heat treatment. For example Genc et al. in preliminary tests used TRM to remove As(V) from nearly neutral water and although high removal efficiencies were achieved, the amount of adsorbent required was high, suggesting that TRM could be only used for pre-treatment of As or that its adsorption capacity needed to be increased; its activation was possible using a combined acid and heat treatment method and high As(V) removal efficiencies were reported also in presence of competing anions, such as phosphate, silicate, bicarbonate and sulphate (Genc et al., 2004).

Transformed red muds have been investigated for the removal of anions as phosphate, arsenite, arsenate and fluoride from aqueous media; several studies conducted to test red mud waste as an alternate arsenic adsorbent demonstrated the excellent efficiency of this material for As removal from aqueous solutions by adsorption, confirming as the adsorptive capacity of red mud can be increased by acid treatment (Altundogan et al., 2002; Altundogan et al., 2003). Another important aspect is that once the As is bound to TRM it can not be removed to any significant extent unless the pH of the leaching solution is raised above 10.5. This suggests that the spent TRM may be left on site after its capacity for arsenate has been exhausted.

In conclusion the data derived from literature indicate that the TRM used in this research has excellent potential for use as an unconventional adsorbent that is comparable with commonly used pure adsorbents (e.g. Fe- and Al-hydroxides). As far as contamination due to oxyanions is concerned such as arsenate and chromate, the removal efficiency of TRM is a function of the solution pH and the highest efficiencies are achieved under slightly acidic conditions (Altundogan et al., 2002; Genç et al., 2003); therefore, when using TRM in order to immobilize metal-oxyanions, preliminary off or on site acidification is usually required.

Chapter V

Materials and Methods

V.1 *Materials*

V.1.1 *Soils*

The experiments of first part were carried out with four soil samples using:

- a spiked illitic-kaolinitic soil;
- a spiked kaolinitic soil;
- a mine tailing soil;
- an industrial site soil.

The choice was motivated by two needs: to find soils whose characteristics are similar or comparable to those of the materials commonly used in other experiments found in literature and to work with soils available in Sardinia, a region in which there are many cases of contamination by heavy metals.

The illitic-kaolinitic soil was provided by the company Svimisa SpA, sampled at a clay quarry in Escalaplano (Sardinia, Italy); the soil fraction passing through a 2 mm sieve was used for the tests. The kaolinitic soil was produced by mixing 80% by weight of sand (washed and sieved < 2 mm) and 20% of pure kaolinitic clay (commercialized by Carlo Erba). The mine tailing soil was collected from the Baccu Locci mining area located in the South-East of Sardinia. The last soil was collected from an industrial site in the central Italy.

Concerning the work carried out in the laboratory of Cambridge University, fine sand of 90-150 µm (grade E) mixed with 10% or 20% of silt, also know as silica flour, was used as a test soil. Sand and silt were both provided by David Ball Group plc, Cambridge, UK.

V.1.2 *Contaminants*

With regard to spiked soils, potassium dichromate crystals ($K_2Cr_2O_7$, Carlo Erba) and sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, Carlo Erba) were used for Cr(VI) and As(V) contamination, respectively.

Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was used in experiments on electrokinetic fence to prepare the contaminated solution (1000 mg/l of Cu).

V.1.3 *Reactive materials*

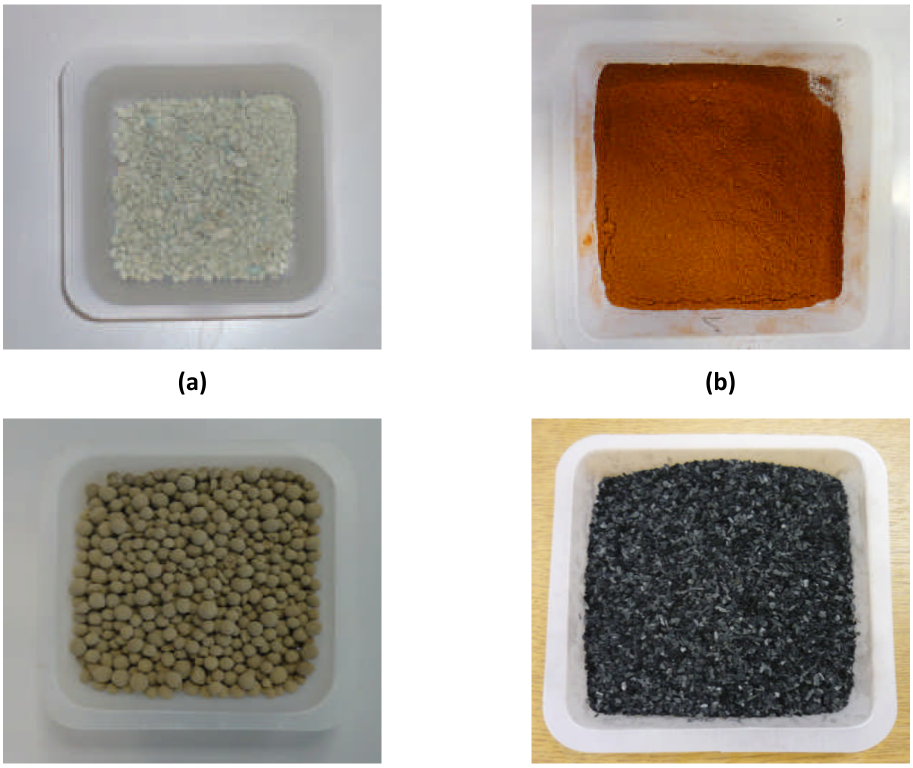
Sodium-treated granular zeolite, transformed red mud (TRM), granular magnesium oxide (MgO) and biochar were selected as reactive materials (Figure V.1). The selection of these materials was based on efficiency to treat heavy metals, on their commercial availability, environmental compatibility and safety.

Natural zeolite was provided as slurry by Kentish Minerals, Westerham, Kent (UK). It was transformed in granular material in order to establish a porosity that ensured the permeability of the medium. Slurry was dried at 105 °C for 72 hours, then was ground using a manual mortar and sieved in order to obtain a 1mm – 4mm particle size range. The sodium-treated zeolite was obtained treating 90 g of granular natural zeolite in 600 ml of NaCl 2M for 24 hours (Curkovic at al., 1997). After washing, the granular material was dried at 105 °C for 24 hours.

The TRM was provided by the company Virotec Italia Srl (Rome, Italy), experimentally produced starting from the residue of the bauxite refinery owned by the company EurAllumina SpA (Portoscuso, Sardinia, Italy); the production process foresees mixing of 20% by weight solid waste suspension with calcium chloride salt and magnesium chloride solar salt plant brine until pH reached 8.9.

Natural magnesite is the raw material used most commonly for industrial grades of MgO. Magnesite ($MgCO_3$) can be calcined to produce highly reactive MgO generally known as Caustic Calcined Magnesite (CCM); at higher reaction temperatures the resultant magnesium oxide is considerably less reactive. Mainly due to the high cost of pure magnesium oxide, which is 8 to 10 times more expensive for example than the same grade of lime, the use as PRB filler is feasible only if low-grade MgO is used. MgO was provided by Richard Baker Harrison Ltd, Ilford, Essex (UK) in 2mm – 5mm particle size range.

Biochar is charcoal made from biomass which is a biological material derived from living, or recently living organisms. It is produced by burning up the biomass in absence or limited amount of oxygen through carbonisation, pyrolysis or gasification (Brown, 2009). Currently there is no specific standard that distinguishes biochar use for agronomic and environmental management with those of charcoal produced as fuel. Biochar in the form of activated carbon has been the main acceptable method for several soil and groundwater remediation techniques. Biochar was provided by Bioregional Charcoal Company Ltd, Wallington, Surrey (UK). It was ground using a manual mortar and sieved in order to obtain a 1 mm – 4 mm particle size range.


(a) (b)

(c) (d)

Figure V.1 *Reactive materials: (a) granular natural zeolite; (b) transformed red mud; (c) granular magnesium oxide; (d) biochar*

V.2 *Contamination procedure*

The soils were singly spiked dissolving the reagent in distillated water and adding the liquid phase to the soil in order to obtain Cr or As concentrations of approximately 1000 and 100 mg kg^{-1} dry soil, respectively. Homogenization with a mixer provided with stainless steel blades was performed in order to grant a uniform contaminant distribution, which was checked by analysis of several samples taken before the EK treatment. The soils were allowed to settle for about one month to allow the adsorption of contaminant.

V.3 *Physical, chemical and mineralogical characterization: analytical methods*

V.3.1 *Granulometric analysis and classification USDA and UCSC*

The analysis of the particle size distribution was conducted using several sieves. The initial sample was divided into quartiles to obtain smaller samples.

The USDA classification system (The United States Department of Agriculture) identifies three distinct classes depending on the size of the particles:

- sand: 2 – 0.05 mm;
- silt: 0.05 – 0.002 mm;
- clay: < 0.002 mm.

A more comprehensive system is the USCS method (United Soil Classification System). The classification is based on the amount of passing the n. 200 mesh ASTM sieve and on the values of Atterberg limits. Data on the Atterberg limits were provided by the geotechnical laboratory of the Department.

V.3.2 *Specific weight of grains*

The specific weight was conducted using a helium pycnometer (Accupyc 1330, Micrometrics). The measurement was made through a two-step procedure:

- mass measurement using an electronic scale to the fourth decimal place;
- volume measurement using a double chamber of known volume, in which a fixed volume of gas (helium) expands from one to another.

Determined these two values the specific weight was calculated by the equation density = mass / volume.

V.3.3 *Hydraulic permeability*

The permeability test and the experimental determination of the hydraulic permeability K_i, was conducted from hydraulic experiments using Darcy's law using the same cell used in the electrokinetic treatment.

The soil sample was first saturated, then the water was allowed to flow through the soil under a steady state head condition while the quantity (volume) of water flowing through the soil specimen was measured over a period of time. By knowing the quantity Q of water measured, the length L of specimen, the cross-sectional area A of the specimen, the time t required for the quantity of water Q to be discharged, and the head h, the hydraulic conductivity has been calculated using the Darcy's law and solving for K:

$$Q = \frac{AKht}{L}$$

V.3.4 *Cation exchange capacity*

The cation exchange capacity (CEC) was assessed by mixing 25 g of dry soil with 50 ml of 1M ammonium acetate at pH 7 according to the Method III.1 in D.M. 13/09/99 (chemical analysis performed at Department of Chemical Engineering of the University of Cagliari).

V.3.5 *Buffering capacity*

The buffering capacity was determined by experimental titration curves, which relate the soil pH with the amount of acid or strong base added (chemical analysis performed at Department of Chemical Engineering of the University of Cagliari).

V.3.6 *Moisture content, pH, electrical conductivity and redox potential*

In order to determine the moisture content, the sample was weighed, dried at 105°C for 24 hours and weighed again. The pH value was assessed by mixing dried soil samples with deionized water according to a 5:2 liquid/solid (L/S) ratio (Method III.1 in D.M. 13/09/99) and recorded using a Crison GLP 22 pHmeter. The electrical conductivity (EC) was determined by mixing dried soil samples with deionized water according to a 2:1 L/S ratio (Method IV.1 in D.M. 13/09/99). The redox potential (Eh) was measured by mixing dried soil samples with deionized water according to a 5:1 L/S ratio and using Hanna Instruments HI 4221 pH/ORP.

V.3.7 *Metals content*

In order to determine the total As content, 0.5 g of dry soil was digested in acid solution in a microwave oven, according to the USEPA 3051A method. Total Cr was determined by acid digestion of 1 g of dry soil in accordance with the USEPA 3050 method, whilst Cr(VI) was determined by alkaline extraction of 2.5 g of dry soil (USEPA 3060A method). The Cr(III) concentration was then calculated by subtracting the Cr(VI) concentration value from the total Cr concentration value. Total Cr and As concentrations were measured by Inductively Coupled Plasma (ICP) optical emission spectrometer (Varian, Model 710-ES), whilst Cr(VI) concentration was measured by UV/Vis spectrophotometer (Unicam Helios Alpha). All measurements were performed in triplicate and in each batch of analysis two blanks and two samples spiked with Cr/As standard solution were included to guarantee the reliability of the analytic results.

In order to assess the total Cu content 2 g of dry soil from each sample were digested in 20 ml of 1 M HNO_3 for 18 hours on a shaking table. Total Cu concentration was then measured by using an ICP mass spectrometer (Perkin Elmer Model Optima 7000 DV).

V.3.8 *Arsenic sequential extraction*

To assess the As distribution in the solid phase of real contaminated soils, a fractionation scheme presented by Wenzel et al. (2001) was used. This sequential extraction scheme targets the most abundant forms of As in the soil solid phase and determines five operationally defined fractions: (1) ammonium sulphate extractable, (2) ammonium dihydrophosphate extractable, (3) oxalate buffer soluble, (4) oxalate buffer–ascorbic acid extractable and (5) residual. The authors of this scheme provided evidence that, within the inherent limitations of chemical fractionation, these fractions are primarily associated with: (1) non-specifically sorbed, (2) specifically-sorbed, (3) amorphous and poorly-crystalline hydrous oxides of Fe and Al, (4) well-crystallized hydrous oxides of Fe and Al and (5) residual phases. The residual fraction was operationally defined as that solubilized by HNO_3/HCl digestion, similarly to the method used for total concentration of As in soils.

The sequence and composition of extracting solutions are given in Table V.1.

Table V.1 *Sequential extraction procedure adopted*

Fraction	Extractant	Extractant conditions	Wash step
1	$(NH_4)_2SO_4$ (0.05 M)	4 h shaking, 20°C	
2	$(NH_4)_2H_2PO_4$ (0.05 M)	16 h shaking, 20°C	
3	NH_4-oxalate buffer (0.2 M); pH 3.25	4 h shaking in the dark, 20°C	NH_4-oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark
4	NH_4-oxalate buffer (0.2 M)+ ascorbic acid (0.1 M); pH 3.25	30 min in a water basin at 96±3°C in the light	NH_4-oxalate (0.2 M); pH 3.25 SSR 1:12.5; 10 min shaking in the dark
5	HNO_3-HCl	Microwave digestion	

Soil (1 g) was placed in 50 ml centrifugation tubes and 25 ml of the extraction reagents were added sequentially. After each extraction step, extracting solutions were separated by centrifugation for 15 min at 3000 rpm, filtered through 0.45 µm cellulose acetate filter paper and stored in the refrigerator (20 °C) until analysed. The residual soil was used for the subsequent extraction steps. The residues after extraction steps 2 and 3 were washed according to the published procedure (Wenzel et al., 2001), then centrifuged again. Washing solutions were combined with the corresponding extracts (Table V.1). In all fractions, extracted As was determined by ICP-OES. All extractions were performed in duplicate.

V.3.9 *CHN analysis*

The material was characterized by CHN analyzer (LECO CHN-1000) in order to identify the percentage of the elements carbon (C), hydrogen (H) and nitrogen (N) present in the soil.

V.3.10 *TOC/IC analysis*

The total organic carbon (TOC) and the inorganic carbon (IC) contents were determined using the analyzer Shimadzu TOC-V Series and the solid sample combustion unit SSM-5000A.

V.3.11 *Mineralogical characterization*

The material was characterized by X-ray diffraction (XRD, Rigaku) in order to identify qualitatively different mineralogical components in the soil.

V.4 *Adsorption tests*

Batch adsorption tests were performed by placing the material (soil or reactive medium) in contact with solutions of As or Cu at different concentrations for a specific interval of time. The amount of pollutant removed from solution by each material was evaluated.

Arsenic solutions at concentrations of 20, 10, 5, 2 and 1 mg/l were prepared by dissolving in distilled water appropriate amount of sodium arsenate dibasic ($Na_2HAsO_4 \cdot 7\ H_2O$), previously dried at 45 °C and stored in desiccator. Suspensions of 10 g/l were prepared and placed in a shaking agitator for 24 hours. At the end of the test the suspensions were centrifuged and filtered and the eluate was analyzed to determine the residual content of arsenic. The tests were performed with and without pH control, maintaining the pH of the suspension to values similar to the original material by adding known amounts of 0.1 M HCl.

Batch equilibrium adsorption tests were performed in order to identify the experimental equilibrium isotherm for adsorption of Cu on TRM and on granular MgO. It was carried out mixing a known volume of copper solution (V_l) characterized by concentration c_0 with a known mass of dry material (m_s) for 24 hours. The resulting slurry was allowed to settle and the supernatant was analysed to determine the equilibrium pore water concentration (c). The mass of the solute adsorbed, normalized with respect to the mass of dry material was determined as follows:

$$q = \frac{(c_0 - c)V_l}{m_s}$$

This procedure was repeated for different initial solute concentrations to cover the range of concentrations expected in the field. The results were plotted on a graph of c versus q known as a batch equilibrium isotherm, and were fitted with a batch equilibrium isotherm equation. For relatively low concentrations, the slope of c versus q is linear and is given by the distribution coefficient, $K_{d,}$ which was determined as follows:

$$K_d = \frac{q}{c}$$

V.5 *Leaching tests*

The leaching tests were performed according to the method UNI EN 12457.

The contaminated soil sample was dried and then crushed to make it as smooth as possible. The leaching tests were performed using as eluent distilled water, sodium hydroxide (NaOH) and potassium dihydrogen phosphate (KH_2PO_4) solutions at concentration values of 0.1 M, 0.2 M and 0.5 M adopting three different liquid/solid (L/S) ratios of 2, 5 and 10. The samples, after shaking for 24 hours, were centrifuged at 30 rpm for 15 minutes and then filtered (0.45 µm). The eluate was analyzed to determine the total content of arsenic by ICP/OES. The solid residue was dried to be subjected to the extraction of metals as described in the paragraph V.3.7 "Metals content".

V.6 *Electrokinetic treatment*

V.6.1 *Experimental set-up for electrokinetic remediation runs*

The electrokinetic tests were conducted in a one-dimensional plexiglass cylindrical cell, 30 cm long and 6.2 cm in diameter, fitted with platinized titanium electrodes at both ends. A 30 V constant voltage was applied, resulting in a voltage gradient of 1 VDC cm^{-1}. The general scheme of the experimental apparatus is shown in Figure V.2.

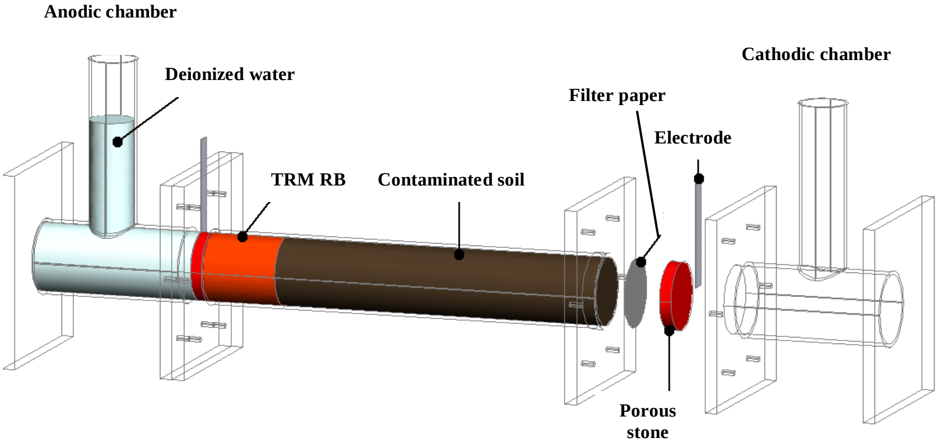


Figure V.2 *Scheme of the experimental apparatus*

The anodic and cathodic compartments were separated from the soil by means of 20-25 µm filter paper and porous stone. Vents allowed for evacuation of the electrolysis gases generated at the cathode (H_2) and anode (O_2). The anodic and cathodic chambers were filled with deionized water or proper conditioning agents and the hydrostatic levels were kept constant during the experiment.

After 30 days from the artificial contamination, both clean and contaminated soils were loaded into the cell and compacted with a standard procedure, that is dropping 20 times a 0.5 kg steel hammer from a 40 cm height on each about 300 g soil layer loaded into the cell.

As for the soil contaminated with Cr, 5/6th of the cell volume was filled with contaminated soil. The remaining 1/6th of cell volume adjacent to the anodic chamber was filled with clean soil (control tests) or clean soil mixed with TRM. Filter paper (20-25 µm) was placed between the contaminated and the uncontaminated soil.

In the case of soil contaminated with As, 4/6th of the cell volume was filled with contaminated soil. The remaining 2/6th of the cell volume was filled with clean soil (close to the cathode) and with clean soil or clean soil mixed with TRM (close to the anode).

In the case of mine tailing and industrial site soils, 5/6th of the cell volume was filled with contaminated soil and the remaining 1/6th of cell volume adjacent to the anodic chamber was filled with clean soil (control tests) or clean soil mixed with TRM.

In order to neutralize the anodic acid production, the required amount of TRM to be used in the RB was estimated on the base of the moles of hydrogen ions produced at the anode during the corresponding control run, taking into account the TRM acid neutralizing capacity of app. 4 $mmole \cdot g^{-1}$. The moles of H^+ produced were calculated according to Faraday's Law by dividing the current intensity (I) integrated over time (t), that represents the total electron charge produced, by the amount of charge in 1 mole of electrons (F), obtaining the total moles of electrons, which are equivalent to the total moles of hydrogen ions (H^+) produced at the anode during the test:

$$H^+ = \frac{\int (I \bullet t)}{F}$$

During the tests the electric intensity as well as the pH and the electrical conductivity (EC) in both the anodic and cathodic chambers were measured once a day. Daily, the aqueous solution from the anode and cathode compartments was sampled in order to assess the Cr or As concentration. Water levels in the anode and cathode compartments were monitored in order to determine the electroosmotic flow and when necessary water level was adjusted to avoid any hydraulic gradient. After the treatment, the soil specimen was manually extruded from the cell and sliced into 6 sections in order to determine the water content, the final pH as well as the Cr or As concentrations.

V.6.2 *Experimental electrokinetic remediation runs*

Firstly two runs were performed on uncontaminated soil named as “blank” tests, indicated as BLK 6 and BLK 12 to evaluate the behavior of the soil without contaminants during the EK process (not reported in the Table V.2). Secondly, three series of electrokinetic experiments were performed: in the first, the illitic-kaolinitic soil was contaminated with Cr(VI) and following the promising results of the treatment of the chromate-contaminated soil, the same type of soil was spiked with As(V) as contaminant; in the second one the kaolinitic soil was contaminated by As(V). Thus, a total of fourteen runs were performed on the two different soils (illitic-kaolinitic and kaolinitic) artificially contaminated by Cr or As, singly added, comparing systems with anodic TRM RB and without (the latter named as control runs), and varying the duration of the tests. Different concentrations of Cr and As were added after the preliminary As-adsorption tests performed on the illitic-kaolinitic soil because the low adsorption capacity of the soil required a low initial arsenate concentration to avoid that an excess of arsenate remained in solution and not adsorbed on the soil.

The third series of tests was performed on natural contaminated soils, a mine tailing soil and an industrial site soil, despite the serious difficulties in finding natural soils characterized by low permeability (suitable for the electrokinetic treatment) and contaminated with Cr and/or As. The use of conditioning agents was chosen to obtain preliminary information on mobilization of contaminant and to joint its use to that of the reactive barrier for enhancing further the whole process.

A summary of the different applied conditions is reported in Tables V.2, V.3 and V.4.

Table V.2 *Schematic summary of the applied treatment conditions on spiked soils*

▒ contaminated soil ☐ clean soil ▦ clean soil + barrier (A) anode (C) cathode

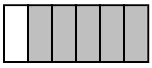
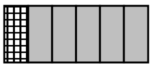
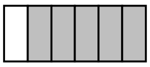
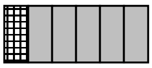
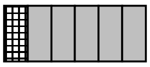
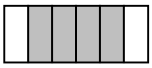
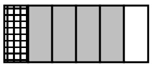
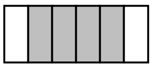
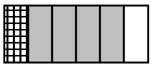
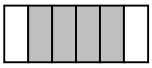
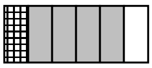
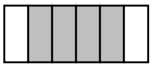
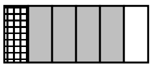
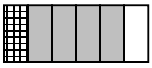
	Run	*Soil Contamination (mg kg^{-1} $_{dry\ soil}$)*	*Duration (days)*	*TRM content in the slice adjacent to the anode (% wt.)*	*Experiment scheme*
Cr	6Cr_BLK	1000	6	0	A  C
	6Cr_TRM		6	6	A  C
	12Cr_BLK		12	0	A  C
	12Cr_TRM		12	12	A  C
	12Cr_TRMplus		12	50	A  C
As	6As_BLK	100	6	0	A  C
	6As_TRM		6	8	A  C
	12As_BLK		12	0	A  C
	12As_TRM		12	16	A  C
	6As_BLK_K		6	0	A  C
	6As_TRM_K		6	2.5	A  C
	12As_BLK_K		12	0	A  C
	12As_TRM_K		12	6	A  C
	16As_TRM_K		16	10	A  C

Table V.3 *Schematic summary of the applied treatment conditions on contaminated mine tailing soil*

▒ contaminated soil □ clean soil ▦ clean soil + barrier (A) anode (C) cathode

Run	*Catholyte*	*Anolyte*	*Duration (days)*	*TRM content in the slice adjacent to the anode (% wt.)*	*Experiment scheme*
1R	DW	DW	16	_	A □▒▒▒▒▒ C
2R	KH_2PO_4 0.2M	DW	23	_	A □▒▒▒▒▒ C
3R	NaOH 0.2M	DW	25	_	A □▒▒▒▒▒ C
4R	DW	DW	25	30	A ▦▒▒▒▒▒ C
5R	NaOH 0.2M	DW	25	50	A ▦▒▒▒▒▒ C

Table V.4 *Schematic summary of the applied treatment conditions on contaminated industrial soil*

▒ contaminated soil □ clean soil ▦ clean soil + barrier (A) anode (C) cathode

Run	*Catholyte*	*Anolyte*	*Duration (days)*	*TRM content in the slice adjacent to the anode (% wt.)*	*Experiment scheme*
6R	DW	DW	15	_	A □▒▒▒▒▒ C
7R	DW	DW	15	20	A ▦▒▒▒▒▒ C

V.6.3 *Experimental set-up for electrokinetic fence and PRB runs*

Tests on electrokinetic fence and PRB were performed in a two-dimensional system using a plexiglass flat tank with a total soil compartment of 40 cm wide, 30 cm long and 5.5 cm deep, divided in two equal cells by a plastic division fixed with silicon to avoid any leaks between the soil cells (Figure V.3).

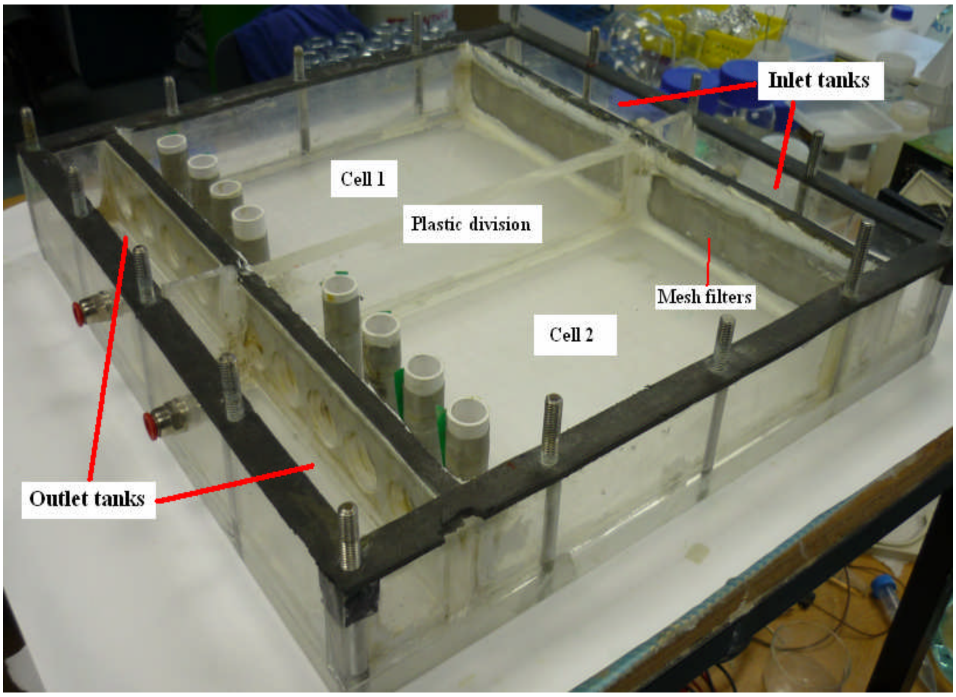


Figure V.3 *Experimental apparatus used*

In the inlet tanks the copper solution was stored and with the use of a peristaltic pump a constant hydraulic head was kept; in the outlet tanks two separated collection systems were connected. The soil was held back into the soil compartment by stainless steel mesh filters of 50 µm porosity which allow water but not soil to pass through.

The scheme of the experimental apparatus is shown in Figure V.4.

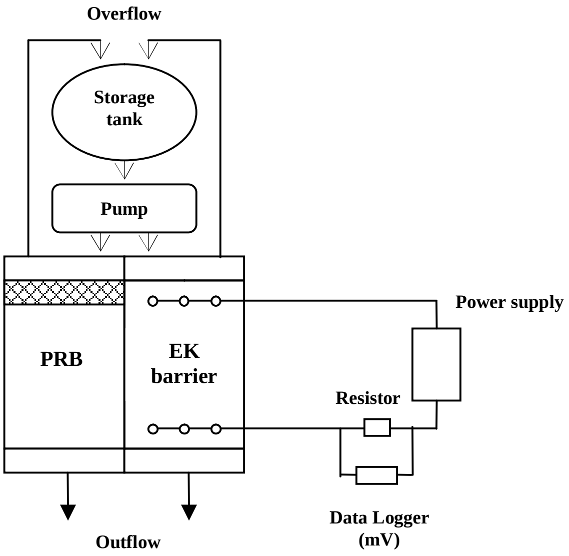


Figure V.4 *Scheme of the experimental setup used in electrokinetic fence runs*

In order to achieve a uniform flow across the cross-section of the cell, the soil, before adding into the cell, was fully saturated with deionized water and placed into a desiccator to ensure maximum air bubbles removal. The tank was filled with wet soil and left overnight to consolidate.

The electrokinetic barrier was activated inserting two rows of oppositely charged graphite electrodes (6 mm diameter) and connecting them with the power supply by crocodile clips. It was arranged with the cathode line (negative electrode) on the top side of the barrier and the anode line (positive electrode) on the bottom side of the barrier, with a cathode to cathode spacing of 7 cm and a cathode to anode spacing of 20 cm.

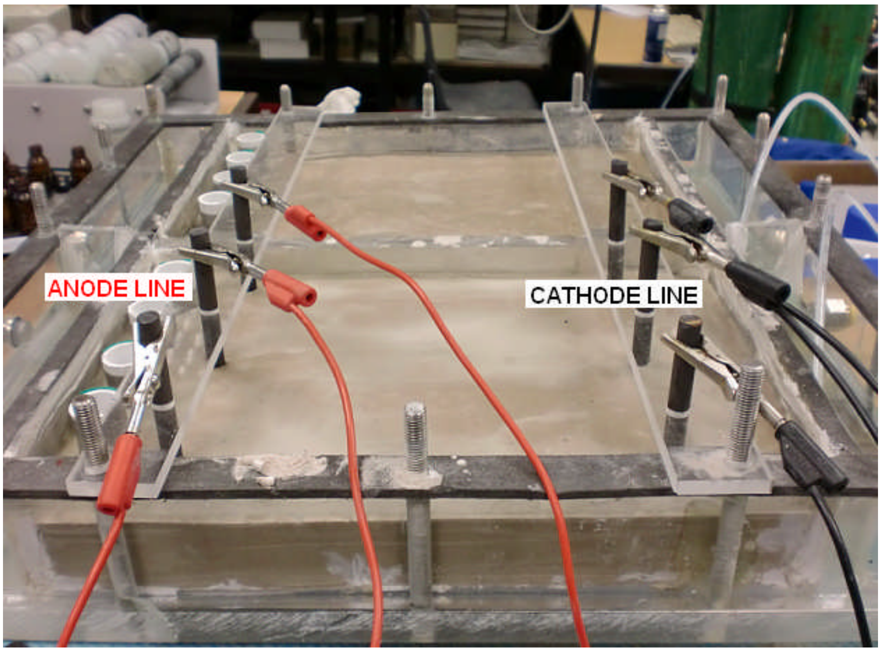


Figure V.5 *General view of the electrokinetic barrier configuration*

The electric potential gradient induces a net water flow towards the cathode due to electroosmosis. At the same time, electromigration gives rise to an inward motion of cations (positive ions) and to an outward motion of anions (negative ions).

Periodically in one cell a permeable reactive barrier was put in. The reactive material, mixed with soil, was installed in a 20 cm wide, 6 cm long and 4 cm deep on the top of the tank.

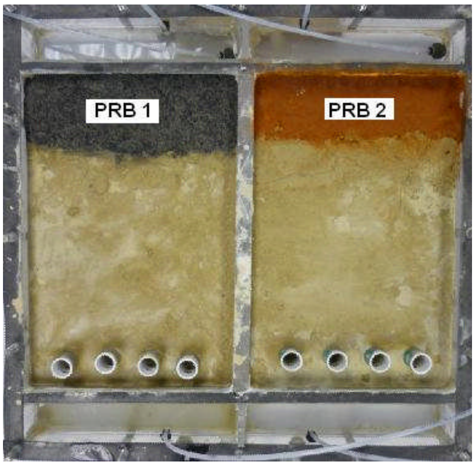


Figure V.6 *Example of two PRBs installed*

The tank was tilted at a proper degree relative to the horizontal (3° - 5°) to create a hydraulic gradient that has transported a copper plume into the uncontaminated soil. Due to the use of a peristaltic pump connected with the inlet tank, the hydraulic head was kept constant between the tanks. In the outlet tanks the discharge of the outflow into a bucket was allowed through a drainpipe connected to a plug.

Initially deionised water was allowed to flow through the soil, so as to measure the flow rate. It was then drained from the inlet and outlet tanks, and replaced by the copper-polluted water.

Electrokinetic barrier runs were performed with a constant voltage of 30 V. Measurement of the current was collected by data logger and flow rate was measured periodically in the outflow tanks.

Outflow water samples were collected from each cell in order to check for breakthrough of copper. Regard to this, a system of wells has been set up in the soil immediately before the outlet tanks to avoid dilution of copper concentration. Every well was totally covered by a stainless steel mesh, porosity 50μm, in order to avoid the soil's passage through. The detail is shown in Figure V.7. A syringe was used to extract the samples from the wells.

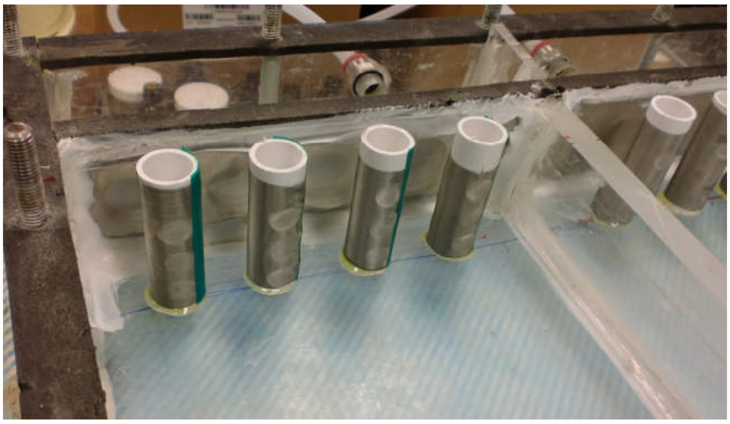


Figure V.7 *Detail of wells set up before the outlet tanks*

At the end of the experiment soil samples were collected according a grid of 4 x 5 samples and analyzed to determine the final copper concentration profile and the final pH profile; an interpolation program (Surfer) was used to produce the 3D plot of the copper concentration and of the pH in the soil.

After each experiment the cell was rinsed with acid to remove any traces of copper before the following run.

V.6.4 *Experimental electrokinetic fence and PRB runs*

Experiments were performed using two mixtures of quartz sand (grade E) and silt (known as silica flour) in order to obtain a similar flow rate of about 30 – 40 ml/h:

- soil A, 90% sand (grade E) and 10% silica flour;
- soil B, 80% sand (grade E) and 20% silica flour.

A slope of three degrees, correspondent to an hydraulic gradient of 0.05, was chosen to transport a copper plume into the uncontaminated soil. The electrokinetic barrier test (EKB) was performed using a constant voltage of 30 V. Different reactive materials were fixed in a permeable reactive barrier.

A summary of the different applied conditions is reported in Table V.5. The different durations are correlated to the "breakthrough time" which was different for every run.

Table V.5 *Schematic summary of the applied treatment conditions on EKB and PRB tests*

Test	Soil	PRB	Hydraulic gradient	Duration (h)
BLANK	B	_	0.05	40
EKB	A	_	0.05	144
BIOCHAR	B	5 %wt biochar	0.05	75
Na-ZEOLITE	A	25 %wt sodium-treated granular zeolite	0.05	105
TRM	B	2.5 %wt transformed red mud	0.05	130
MgO	A	26 %wt granular magnesium oxide	0.05	144

V.6.5 *Construction of the breakthrough curve*

The copper concentration of the solution collected from the monitoring wells during each test was used to draw a breakthrough curve. It is a graph of concentrations versus time that is useful for showing the breakthrough time which is the time that it takes for half of the initial concentration of the contaminant to reach the monitoring wells. Usually a breakthrough curve has a S-shape as shown in Figure V.8.

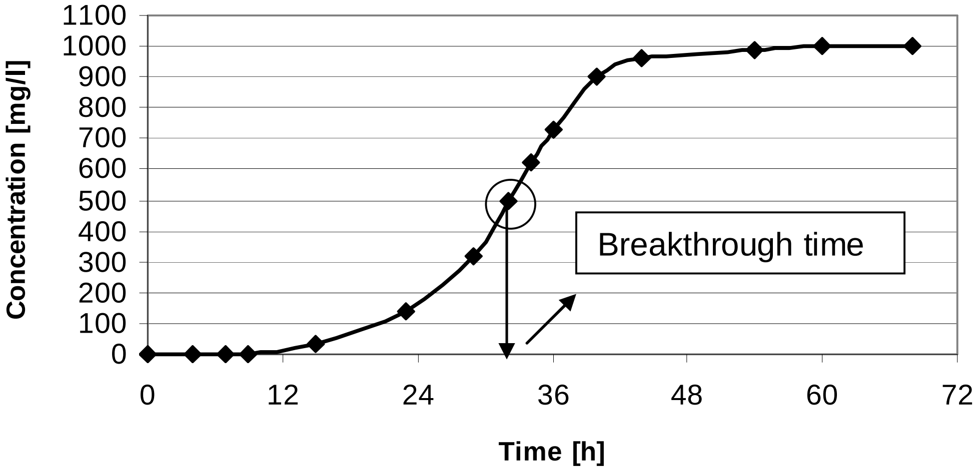


Figure V.8 *Typical S-shaped breakthrough curve*

In order to compare the breakthrough curve of the different barriers and to calculate the retardation factor, a normalization has been necessary because each test was characterized by a slightly different flow rate. Therefore, Number of Pore Volumes (NPV) instead of time was used as x-axis magnitude.

The NPV has been obtained from the volume of the soil, the porosity of the soil and the flow rate. Volume of the soil (V_t) and flow rate (v) were easily calculated. The porosity, n, was experimentally determined as follows:

$$n = \frac{V_v}{V_t}$$

where V_v is the volume of the voids and V_t is the total volume of the soil. The volume of the voids was determined weighing a fully saturated soil sample, drying it in a oven at 105°C for

24 hours, to allow water to evaporate, and weighing the dry soil sample. The difference between the two weights is equal to the volume of voids because the density of the evaporated water is 1000 Kg·m^{-3} .

The time to take one Pore Volume (*1PV*) was obtained as follows:

$$1PV = \frac{V_t n}{v}$$

Finally, the NPV was defined from the time (*t*) and the time to take *1 PV* as follows:

$$NPV = \frac{t}{1PV}$$

Chapter VI

Results and Discussion

VI.1 Soils and reactive materials

VI.1.1 *Soils*

The chemical-physical characteristics of the used spiked illitic-kaolinitic and kaolinitic soils are summarized in Table VI.1.

Table VI.1 *Mineralogical and chemical-physical characteristics of the used spiked soils*

Property		ILLITIC-KAOLINITIC SOIL	KAOLINITIC SOIL
Particle size distribution	Sand	38%	80%
	Silt	34%	0%
	Clay	28%	20%
Density	kg m^{-3}	$2.69 \cdot 10^{3}$	$2.58 \cdot 10^{3}$
Hydraulic conductivity	m s^{-1}	$5.3 \cdot 10^{-8}$	$8.6 \cdot 10^{-8}$
pH	- -	5.4	7.1
CEC*	cmol kg^{-1}	18.59	9.27
Buffering capacity*	mol l^{-1}	40 ***	0
Electrical conductivity	µS cm^{-1}	340	105
Atterberg limits**	Liquid limit	23%	11.4%
	Plastic limit	12.4%	2.2%
	Plasticity index	10.6%	9.2%
USCS classification		CL	SC

* analysis performed at Department of Chemical Engineering of the University of Cagliari
** analyses provided by the geotechnical laboratory of the DIGITA of the University of Cagliari
*** pH related to the maximum buffer capacity: 5

The mineralogical composition of the illitic-kaolinitic soil was obtained qualitatively by the X-ray diffraction pattern, shown in Figure VI.1.

According to the information contained in the technical assistance provided with soil by the company Svimisa SpA, the mineralogical composition of the soil was illite, kaolinite, quartz and feldespar.

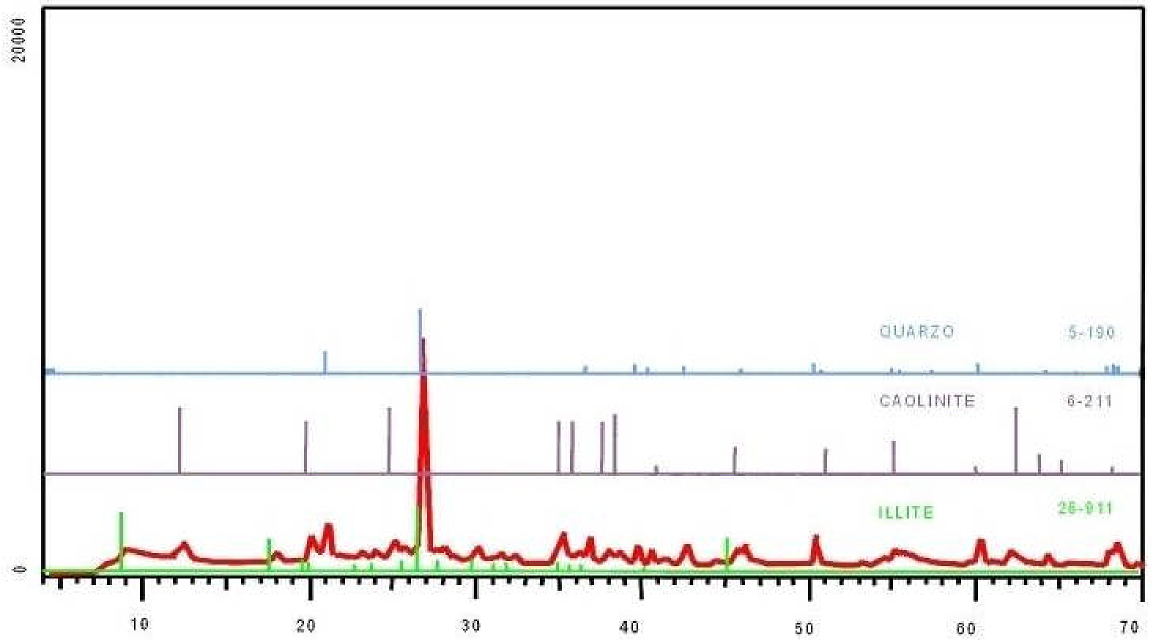


Figure VI.1 *X-ray diffraction of the illitic-kaolinitic soil*

The Svimisa company provided also the following information on the main chemical components of the soil: SiO_2 57% wt., AlO_3 26.2% wt., Fe_2O_3 2.6% wt., CaO 0.2% wt., MgO 0.7% wt., K_2O 3.4% wt. and TiO_2 1.3% wt..

With regard to the mine tailings and the industrial soil, the particle size distributions are shown in Table VI.2 and VI.3, respectively.

The granulometric analysis of the mine tailing soil revealed a size of grains larger than those usually treated with an electrokinetic treatment; that of industrial soil is less large. Anyway only the soil fraction passing through a 2 mm sieve was used for the electrokinetic tests.

Table VI.2 *Grain size analysis of the mine tailings*

Grain size class	Mass (%)
+ 11.2	13.92
- 11.2 + 4	33.65
- 4 + 2	17.57
- 2 + 1.4	8.85
- 1.4 + 0.355	17.29
- 0.355	8.72
Total	100.00

Table VI.3 *Grain size analysis of the industrial soil*

Grain size class	Mass (%)
+ 4	17.05
- 4 + 2	21.55
- 2 + 1	17.75
- 1 + 0.5	20.72
- 0.5 + 0.25	13.33
- 0.25 + 0.125	3.91
- 0.125 + 0.063	2.43
- 0.063	3.26
Total	100.00

The mineralogical compositions of the mine tailings and the industrial soil are shown in Figure VI.2 and Figure VI.3, respectively. The mine tailing soil was mostly characterized by the presence of quartz, illite and muscovite; there were also minerals such as halloysite, scorodite, goethite, ferrihydrite and hematite. Unlike what was expected, minerals such as blenda and galena were not present.

The industrial soil was mainly characterized by quartz, illite, kaolinite and feldspar (albite and anorthite); in lower proportions muscovite, gypsum, anhydrite, goethite and hematite were present.

The chemical-physical characteristics of the used natural contaminated soils are summarized in Table VI.4. The buffering capacity was qualitatively assessed by mixing 1.5 g of dry soil with 30 ml of distillated water according the procedure used by Yeung et al. (1996); daily a small amount of nitric acid 1M was added and after shaking for 24 hours the pH was measured.

Table VI.4 *Chemical-physical characteristics of the used natural contaminated soils*

Property		MINE TAILING SOIL	INDUSTRIAL SOIL
Density	kg m^{-3}	$2.90 \cdot 10^{3}$	$2.87 \cdot 10^{3}$
Hydraulic conductivity	m s^{-1}	$2.3 \cdot 10^{-6}$	$1.9 \cdot 10^{-7}$
pH	- -	4.47	7.04
Electrical conductivity	mS cm^{-1}	18	12
Redox potential	mV	80	120
Buffering capacity	- -	Low	Low

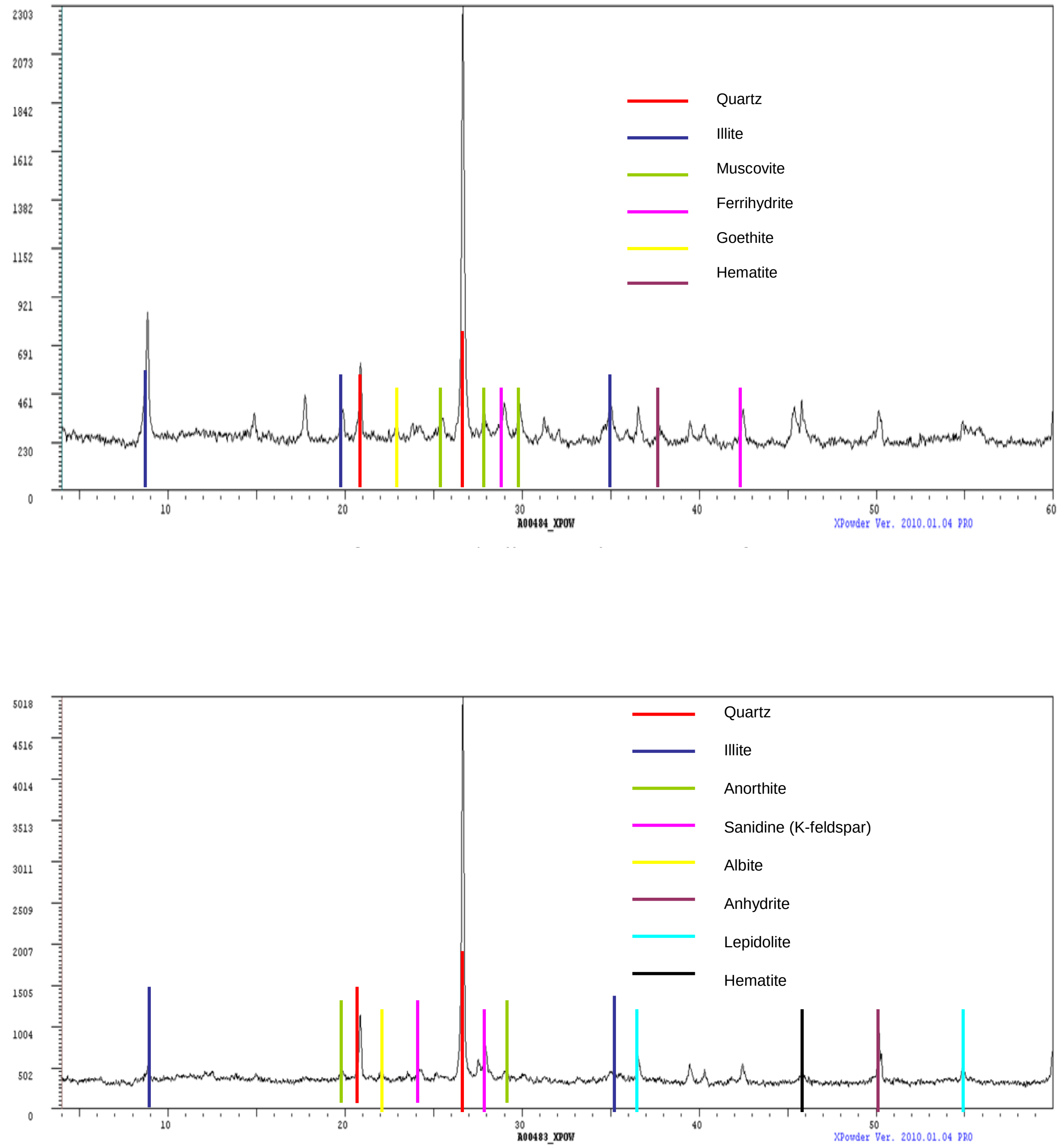


Figure VI.3 *X-ray diffraction of the industrial soil*

The total metals content of the mine tailings, shown in Table VI.5, was determined on following fractions:

- $2 < \Phi < 4$ mm;
- $1.4 < \Phi < 2$ mm;
- $0.355 < \Phi < 1.4$ mm;
- $\Phi < 0.355$ mm.

Table VI.5 *Total metals content of mine tailings (mg/kg)*

Fraction	As	Ni	Cd	Cr	Zn	Cu	Pb
$2 < \Phi < 4$ mm	28533.3	12.2	4.4	23.7	194.6	271.4	9199.2
$1.4 < \Phi < 2$ mm	26600.0	15.1	6.5	26.4	299.6	296.5	11676.8
$0.355 < \Phi < 1.4$ mm	32200.0	11.7	4.2	19.7	193.1	266.4	11410.1
$\Phi < 0.355$ mm	34403.2	16.1	6.8	28.2	520.7	629.5	13928.2

The contamination is consistent with the mining activity that characterized the mining site of Baccu Locci, based on the exploitation of deposits of galena (PbS) and especially arsenopyrite (FeAsS). As might be expected, the concentration values of most metals increase with decreasing particle size. In the finer fraction can be observed a contamination of about 34.000 ppm of As, 14.000 ppm of Pb, 500 ppm of Zn and 630 ppm of Cu; lower concentrations in Cr, Ni and Cd. From studies conducted in the same area, arsenic was mainly bound to ferryidrite ($FeOOH \cdot 0.4H_2O$) which is de-adsorbed as a function of pH and for the presence of competing ions in solution; other phase containing arsenic which contributes to raising the level of contamination is the scorodite ($FeAsO_4 \cdot 2H_2O$).

The total metals content of the industrial soil was determined on all granulometric fractions as shown in Table VI.6. The concentration values of most metals increase with decreasing particle size. In the finer fraction can be observed a contamination of almost 12.000 ppm of As, 18.000 ppm of Pb, 3.000 ppm of Zn and 2.200 ppm of Cu; lower concentrations in Ni, Cd and Cr.

Table VI.6 *Total metals content of industrial soil (mg/kg)*

Fraction	As	Ni	Cd	Cr	Zn	Cu	Pb
$2 < \Phi < 4$ mm	907.69	108.77	5.48	172.80	1252.61	465.79	584.73
$1 < \Phi < 2$ mm	1834.24	90.52	5.65	151.34	1087.31	489.63	3584.61
$0.500 < \Phi < 1$ mm	2265.10	108.61	5.26	153.98	1002.44	422.72	2790.46
$0.250 < \Phi < 0.500$ mm	2098.87	86.58	5.17	167.52	973.50	402.55	3037.76
$0.125 < \Phi < 0.250$ mm	5011.91	71.08	9.25	171.14	1815.09	1035.54	6341.98
$0.063 < \Phi < 0.125$ mm	7742.35	53.66	12.17	76.11	2533.88	1833.66	14783.87
$\Phi < 0.063$ mm	11706.20	50.75	13.43	67.70	2995.73	2186.64	18317.07

Results of CHN analysis performed on the two natural contaminated soils are shown in Table VI.7. The soils were characterized by low organic carbon content (TOC < 0.4%).

Table VI.7 *CHN analysis results*

	C (%)	H (%)	N (%)
Mine tailing soil	1.260 ± 0.149	0.850 ± 0.077	0.025 ± 0.016
Industrial soil	0.989 ± 0.010	0.772 ± 0.018	0.037 ± 0.010

VI.1.2 *As fractionation in experimental soils*

The partitioning of As in the mine tailings and in the industrial soil among the five fractions of the sequential extraction procedure (SEP) is shown in Figure VI.4 and VI.5, respectively. In general, it is in accordance with expectations. Indeed, it is evident that As is primarily associated with amorphous and crystalline Fe oxides, whilst minor proportions of As are associated to residual phase.

Regard to mine tailing soil, the percentage of As related to non-specifically adsorbed fraction is lower than 1% of the total As and therefore it is not appreciable in the figure while the fraction of As extracted in the second step (specifically-sorbed) represents about 6% of total As. These results are interesting in providing a relative assessment of environmental risk due to As mobilization. Despite the high total soil As concentration, the contribution of potentially mobile, non-specifically adsorbed As (fraction 1) was low, usually remained much below 1% of total As. These results confirm the crucial role of Fe and Al oxides in immobilizing high amounts of As. The amounts of As extracted in fractions 3-4 accounted for

32-47% of total soil As. The appreciable contribution of residual fraction (15-20% of total) should be considered as beneficial from the standpoint of environmental risk.

The amounts of As in fraction 2, indicative of surface-bound As species and inner-sphere surface complexes of As ranged from 5% (in the soil fraction < 1.40 mm) up to 6.5% (in the soil fraction < 0.35 mm) of total soil As.

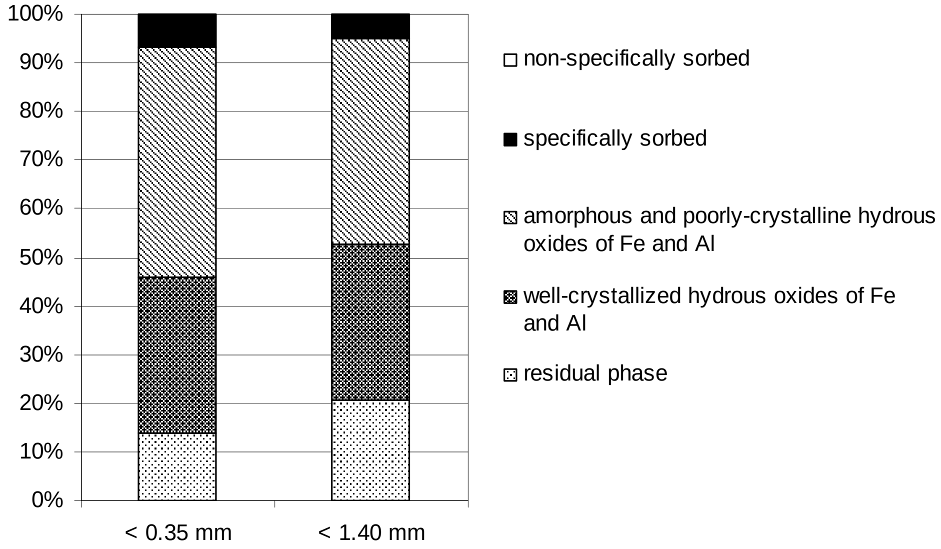


Figure VI.4 *Partitioning of As in the fractions of mine tailing soil Φ < 0.35 mm and Φ < 1.40 mm*

The accuracy of adopted SEP was tested by comparing the sum of the five fractions (As_{sum}) against the total As (As_{tot}) concentration determined by acid digestion using a microwave technique (Table VI.8 and Table VI.9).

Table VI.8 *Partitioning of As among the five fractions (mg/kg) and accuracy of SEP for the mine tailing soil*

	Step 1	Step 2	Step 3	Step 4	Step 5	Sum of fraction 1-5	Total As	Accuracy (%)
Fraction soil < 0.35 mm	21.58	1232.31	8882.26	6005.73	2616.10	18757.97	20352.04	92.17
Fraction soil < 1.40 mm	23.22	949.12	8097.85	6136.16	3960.62	19166.98	21454.32	89.34

Considering the industrial soil, similar results were obtained with a percentage of As related to non-specifically adsorbed fraction of about 1.3% of the total As for fraction Φ > 0.500 mm and 0% for Φ > 0.125 mm and therefore they are not appreciable in the figure. The fractions of As specifically-sorbed ranged from 15% (in the soil fraction + 0.125 mm) up to 20% (in the soil fraction + 0.500 mm) of total As. Despite the results obtained on the mine tailing soil, in this case a higher As concentration could be potentially mobilized. Anyway the Fe and Al oxides, as amorphous and crystalline, immobilize high amounts of As, accounted for 33–50% of total As. No As was found in the residual fraction.

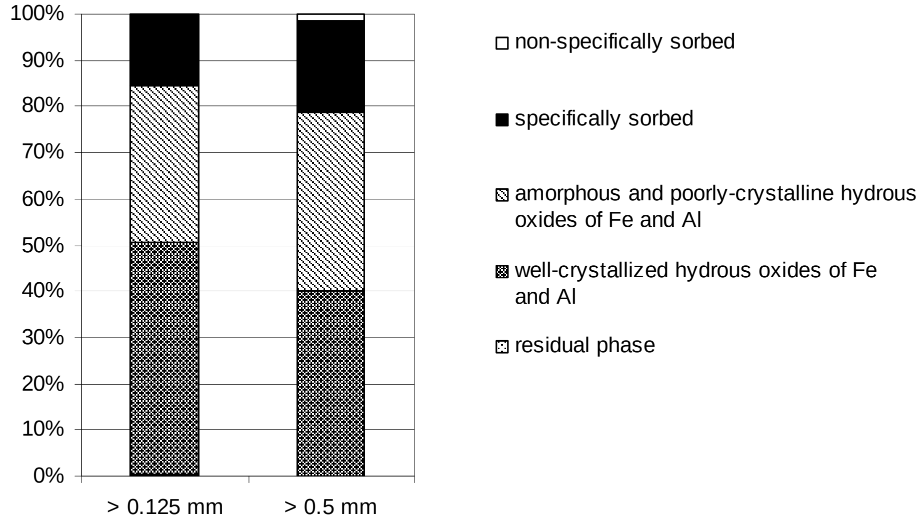


Figure VI.5 *Partitioning of As in the fractions of industrial soil Φ > 0.125 mm and Φ > 0.500 mm*

Table VI.9 *Partitioning of As among the five fractions (mg/kg) and accuracy of SEP for the industrial soil*

	Step 1	Step 2	Step 3	Step 4	Step 5	Sum of fraction 1-5	Total As	Accuracy (%)
Fraction soil > 0.125 mm	0.38	867.94	1879.28	2779.90	11.74	5539.24	5194.39	106.64
Fraction soil > 0.500 mm	31.41	458.92	953.75	906.06	0.00	2350.15	2265.67	103.73

VI.1.3 *Reactive materials*

Natural zeolites was provided by S&B Industrial Minerals (Athens, Greece). It is a calcium hydrated aluminosilicate containing a minimum of 85% clinoptilolite and a maximum of 15% feldspar, micas and clays, characterized by specific density 2.16 g/cm^3, pH 6.5 and cation exchange capacity 180 meq/100g. The chemical composition and the physical characteristics are given in Table VI.10. In first test it was used 100% as slurry, then it was transformed in granular material in order to establish a porosity that ensured the permeability of the medium.

The mineralogical and chemical-physical characteristics of the TRM are shown in Table VI.11. The chemical composition of granular magnesium oxide is given in Table VI.12.

Table VI.10 *Natural zeolite typical chemical composition and physical characteristics (Kentish Minerals)*

Chemical component	% wt
SiO_2	71.12
Al_2O_3	11.69
K_2O	3.88
CaO	3.00
Fe_2O_3	0.75
MgO	0.71
Na_2O	0.62

Colour	greenish-ivory
pH	6.5 – 7
Humidity	max 8%
Solubility	insoluble
Apparent bulk density	0.85 – 1.1 g/cm^3
Pore volume	0.34 cm^3/cm^3
CEC	min 180 cmol/Kg
LOI	8.23

Table VI.11 *Characteristics of the TRM*

Characteristic TRM		
Mineralogy		
		Hematite, ferrihydrite: 35% Boehmite, gibbsite: 20% Sodalite: 17% Quartz: 7% Other: 21% [*]
Particle size distribution		
	Sand	0%
	Silt	30%
	Clay	70%
Density	kg m^{-3}	$3.2 \cdot 10^3$
pH	- -	8.40
Atterberg limits		
	Liquid limit	55%
	Plastic limit	30%
	Plasticity index	25%
USCS classification		CH

[*] Other minerals: Cancrinite, Anatase, Brucite, Hydrotalcite, Aragonite, Calcite, Diaspore, Gypsum, Hydrocalumite

Table VI.12 *Main chemical components of the magnesium oxide*

Chemical component	% wt
MgO	69.94
CaO	4.66
SiO_2	8.20
Fe_2O_3	2.60
Al_2O_3	2.51

VI.2 *Adsorption tests*

In Tables VI.13 and VI.14 the results of As-adsorption tests carried out on the illitic-kaolinitic soil are given; in the second test the pH was maintained at values close to the natural soil pH by adding quantities recorded of 0.1 M HCl. The removal efficiency was calculated as a percentage of As removed from the solution with respect to the one initially present.

The final pH of the samples in the test without pH control increases with increasing initial concentration of As: this is reasonable since the solutions at different concentrations were prepared using a basic salt of arsenic (sodium arsenate dibasic, $Na_2HAsO_4 \cdot 7\ H_2O$) .

The removal efficiency increases with decreasing initial concentration of arsenic. The best removal efficiency was achieved in both cases at the minimum value of initial concentration of As (1 mg/l), almost 50% and 70% in tests with and without pH control, respectively. The best efficiencies, with the same initial concentration, were obtained for higher pH values with the only exception of the sample characterized by the higher initial concentration (20 mg/l) for which the removal efficiency was better at pH 5.58 than at pH 7.23.

The illitic-kaolinitic adsorption capacity for Cr(VI) at natural pH of soil (5.4), experimentally determined in previous studies (Mureddu, 2006), was 0.7 mg Cr(VI)/g soil; for As(V) it was lower, equal to 0.3 mg As(V)/g soil.

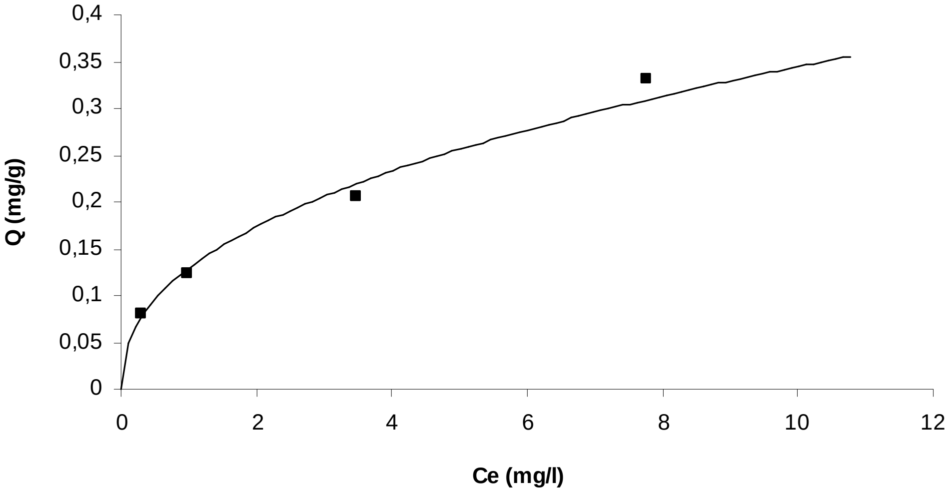


Figure VI.6 *Experimental equilibrium isotherm for adsorption of As(V) on illitic-kaolinitic soil*

Table VI.13 *Adsorption test results of As on illitic-kaolinitic soil without pH control*

Sample	Initial As concentration	Residual As in solution	Final pH	As removal	Removal efficiency (%)
	[mg/l]	[mg/l]		[mg/kg]	
20	20	20.00	7.23	0	0
10	10	7.76	6.95	224	22.4
5	5	3.47	6.67	153	30.6
2	2	0.98	5.76	102	51
1	1	0.30	5.79	70	70

Table VI.14 *Adsorption test results of As on illitic-kaolinitic soil with pH control*

Sample	Initial As concentration	Residual As in solution	Final pH	As removal	Removal efficiency (%)
	[mg/l]	[mg/l]		[mg/kg]	
20	20	19.19	5.58	81	4.0
10	10	9.54	5.56	46	4.6
5	5	4.20	5.74	80	16
2	2	1.60	5.49	40	20
1	1	0.52	5.60	48	48

The adsorption results on kaolinitic soil, carried out using a solution of As with a pH that has been previously brought to a value close to the original material by the addition of 0.1 M HCl, are given in Table VI.15. The results showed a minor influence of the initial concentration on As removal efficiency, compared to that observed for illitic-kaolinitic soil: indeed the difference between the minimum and maximum removal efficiency is only 10 percentage points.

Table VI.15 *Adsorption test results of As on kaolinitic soil*

Sample	Initial As concentration	Residual As in solution	Final pH	As removal	Removal efficiency (%)
	[mg/l]	[mg/l]		[mg/kg]	
20	20	14.08	8.1	592	29.6
10	10	6.78	7.2	322	32.2
5	5	3.19	6.9	181	36.3
2	2	1.32	6.7	68	34.1
1	1	0.62	6.3	38	38.2

The results of batch equilibrium adsorption capacity of TRM for arsenate (Qe, mg/g) at given final solution concentrations (Ce, mg/L) after 5 days of contact and with final solution pH of 5.6 is shown in Figure VI.7. Adsorbent concentration of 10 g/L and initial arsenate concentrations of 20, 10, 5 and 1 mg/L were used. Best fit Langmuir isotherm with maximum adsorption capacity (Qmax) of 1.04 mg/g, Langmuir constant K of 0.33 and coefficient of determination R^2 of 0.92 were obtained.

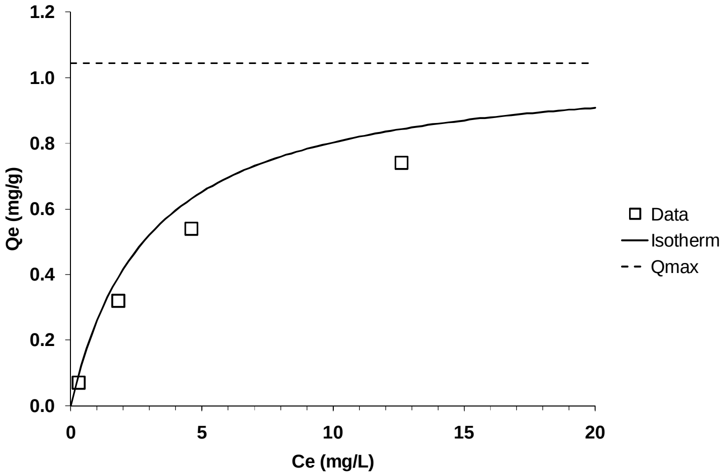


Figure VI.7 *Batch equilibrium adsorption capacity of TRM for arsenate*

The batch equilibrium adsorption tests performed in order to evaluate the adsorption of Cu on TRM and on granular MgO are reported in the Section VI.8 *"Experimental electrokinetic barrier and PRB runs*", pages 161 and 164.

VI.3 *Leaching tests*

The leaching tests were conducted to determine if a suitable chemical extractant, appropriate for electrokinetic experiments, could be found to assist eventually the desorption of the arsenic during the EK/RB treatment. Despite the information available in literature about more common conditioning agents, it was decided to evaluate the same soil tested for electrokinetic runs.

The results of leaching tests performed on the mine tailing soil for 2, 5 and 10 L/S ratios are given in Table VI.16 where also the final pH is reported. Results show that in general when the L/S ratio increases also the As concentration in the leachate increases, whilst the pH remain relatively constant. The leaching tests performed using distillated water as eluent have released the lower and negligible percentages of As; although the As concentrations released are very low, they appear to decrease probably due to the increase of dilution. In oxidizing conditions, characteristic of the considered soil, arsenic is stable and the species is strongly adsorbed on clays, oxides and hydroxides of Fe and Al, whilst the solubility is low. Studies using soils or pure Fe hydroxides have shown that the mobility of As(V) increases with increasing pH.

An increase in the concentration of the extractant, with the same L/S ratio, has always resulted in higher efficiency of extraction, whilst an increase in the L/S ratio, with the same concentration of the extractant, has not determined significant increase of the removal efficiency.

The most significant results were obtained with the sodium hydroxide solution in which the Fe, Al-oxides were solubilizated, confirmed also by the final brown-black colour of the solution. Sorption of As is usually reduced significantly at high pH and its mobilisation can occur under these conditions: indeed the pH of the sodium hydroxide solutions changed the most reaching the final higher value of about 12.5. The phosphate solution did not eluate significant amount of arsenic compared to the sodium hydroxide. The final pH values for the phosphate solutions ended at a similar pH to the natural pH of the soil (about 4.40) and the soil has shown a low potential for elution at acidic pH.

Of all the solutions tested 0.5 M sodium hydroxide extracted the greatest amount of arsenic for every L/S ratio tested.

Table VI.16 *Leaching test results of the mine tailing soil*

L/S ratio, Leaching agent, Concentration	Final pH	As [mg/l]	Release [%]
2 DW	3.80	0.60	0.08
5 DW	3.63	0.52	0.07
10 DW	3.70	0.38	0.05
2 KH_2PO_4 0.1 M	4.12	28.34	3.92
5 KH_2PO_4 0.1 M	4.08	42.12	5.82
10 KH_2PO_4 0.1 M	3.98	35.07	4.85
2 KH_2PO_4 0.2 M	4.14	22.34	3.09
5 KH_2PO_4 0.2 M	4.24	34.25	4.73
10 KH_2PO_4 0.2 M	4.08	37.26	5.15
2 KH_2PO_4 0.5 M	4.27	33.56	4.60
5 KH_2PO_4 0.5 M	4.45	58.73	8.12
10 KH_2PO_4 0.5 M	4.30	50.91	7.04
2 NaOH 0.1 M	11.43	1008.44	54.98
5 NaOH 0.1 M	11.72	998.76	54.45
10 NaOH 0.1 M	11.99	1147.10	62.54
2 NaOH 0.2 M	12.23	1274.23	69.47
5 NaOH 0.2 M	12.48	1304.20	71.11
10 NaOH 0.2 M	12.45	1305.16	71.16
2 NaOH 0.5 M	12.52	1485.63	80.99
5 NaOH 0.5 M	12.47	1574.32	85.83
10 NaOH 0.5 M	12.57	1581.50	86.22

VI.4 *Experimental electrokinetic remediation runs on spiked illitic-kaolinitic soil*

VI.4.1 *Tests on the Cr contaminated soil*

VI.4.1.1 *Current intensity*

The current intensity profiles as a function of time are shown in Figure VI.8 for all the tests.

During BLK6 and BLK12 tests, carried out with illitic-kaolinitic uncontaminated soil, peak values of, respectively, 20 and 25 mA were achieved with a subsequent slow decrease and stabilization over time, as a result of gradual depletion of solutes and precipitation of non-conductive solids (Acar et al., 1993; Acar et al., 1995; Weng et al., 2007).

In the 6Cr_BLK and 12Cr_BLK runs, in absence of the reactive barrier, the current intensity increased during the first 24 h and stabilized around 17 and 11 mA, respectively. In the presence of TRM RB (6Cr_TRM and 12Cr_TRM tests) the current intensity peaked at nearly the same values for both the tests (25 and 26 mA respectively) and decreased more sharply than in BLK6 and BLK12 runs, reflecting an increase in the electric resistance. The decrease in current intensity with time is generally due to a decrease in the concentration of dissolved ionic species, which is caused by the formation of precipitates near the cathode such as $Fe(OH)_3$ and $Cr(OH)_3$. The decrease was also probably due to the enhanced migration of Cr towards the anode and its accumulation outside the cell, in the anodic compartment, with a consequent decrease of the ionic strength of the circulating pore solution.

No appreciable differences regard to the trends of current intensity were evident between the two different durations of the homologous tests (BLK6 and BLK12, 6Cr_BLK and 12Cr_BLK, 6Cr_TRM and 12Cr_TRM).

In the 12Cr_TRMplus test a different behavior was observed: it represents the most concentrated adopted TRM in which the neutralizing capacity of part of the TRM was first destroyed by means of hydrochloric acid treatment and the TRM content in the RB was increased to 50% wt.: due to this attempt it was probably that the ionic strength of the pore solution was higher than in 6Cr_TRM and 12Cr_TRM runs in which the contaminant migrated outside the material and accumulated into the anolyte. As a result, the current intensity value was high until the 7th days of test.

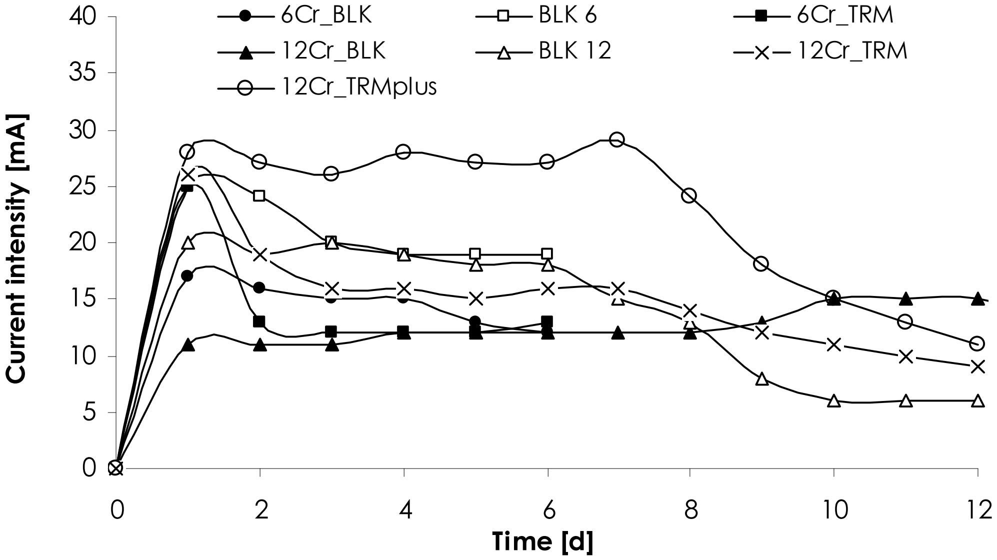


Figure VI.8 *Current intensity as a function of treatment time for Cr illitic-kaolinitic runs*

VI.4.1.2 *Electroosmotic flow*

Figure VI.9 shows the cumulative electroosmotic (EO) flow collected in the cathode compartment for all the tests performed. It is possible to notice that in the absence of the reactive barrier (6Cr_BLK and 12Cr_BLK runs) the EO flow was greater than in tests performed with TRM RB. This effect could be caused by the enhancement of anionic Cr(VI) migration towards the anode, hence in the opposite direction with respect to the EO flow. This feature has been reported also in others studies: Weng et al. (2007), while treating hyper-Cr(VI) contaminated clay (around 2500 mg/kg), found a completely reversed EO flow (towards the anode) as a results of anodic Cr(VI) migration. Reddy et al. (2001), while attempting EK remediation of different contaminants, found that in the tests with anionic contaminants the migration of these species towards the anode may have caused a reduced EO flow with respect to the tests carried out on soil contaminated by cationic species as nickel and cadmium.

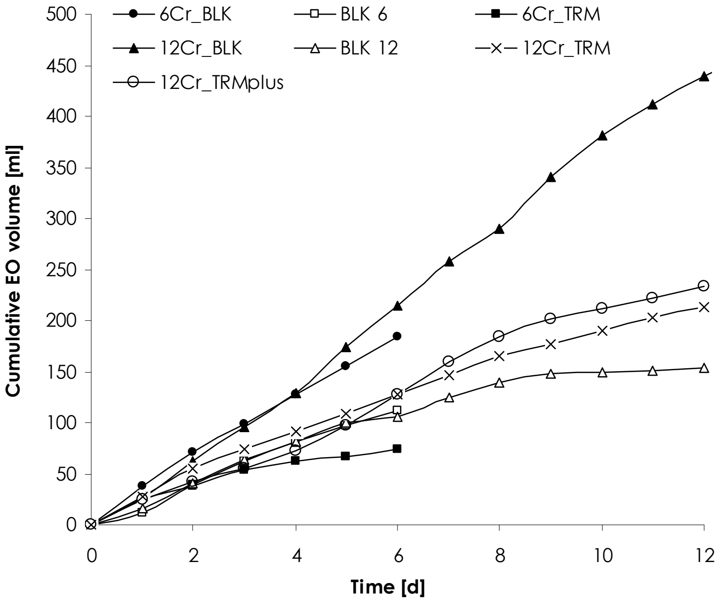


Figure VI.9 *Cumulative electroosmotic (EO) flow as a function of treatment time for Cr illitic-kaolinitic runs*

The coefficient of EO permeability K_e ($cm^2/V·s$), which is a measure of the flow per unit area per unit electric gradient, was calculated by the equation:

$$Q = k_e A \frac{dV}{ds}$$

where Q represents the EO flow ($ml·d^{-1}$), A the cross-section area of the cylindrical cell (cm^2) and dV/ds the applied gradient electric ($V·cm^{-1}$). The obtained K_e values, shown in Figure VI.10, are in agreement with the literature data of $1·10^{-7}$ to $4·10^{-5}$ $cm^2/V·s$ for all soils (Weng et al., 2007). The slightly higher K_e values were observed for the runs without TRM RB, in particular for the control run 12Cr_BLK characterized by low fluctuations.

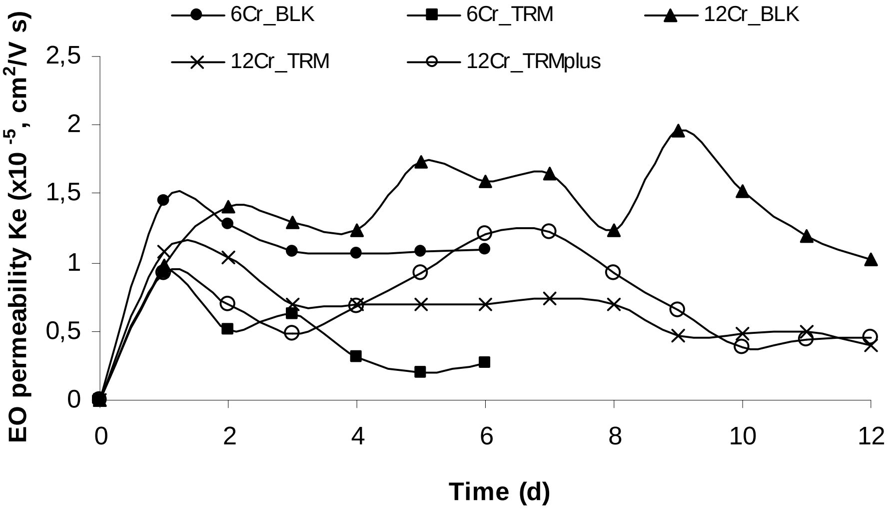


Figure VI.10 *EO permeability towards cathode as a function of treatment time for Cr illitic-kaolinitic runs*

VI.4.1.3 *Chromium concentration and soil pH*

Data on total Cr concentrations in the soil specimen before and after the treatment are shown in Figure VI.11 (b), plotted as ratio between the final and the initial concentration (C/C_0). In the same figure, pH profiles, as assessed before and after the runs, are also shown (Figure VI.11 (a)). Figure VI.12 reports the residual Cr(III) (a) and Cr(VI) (b) concentrations in the soil as percentage of total Cr, after the electrokinetic treatment. The initial content in each of the 5 contaminated sections is considered equal to 20% of the overall pollutant mass, thus assuming an initial uniform distribution.

In the control runs 6Cr_BLK and 12Cr_BLK a noticeable accumulation of total Cr in the middle sections of the specimen was observed; the same issue is reported also in Cang et al. (2007) with regard to Cr unenhanced EK removal. For a better understanding of this distribution, it is necessary to consider that the two chromium oxidation states that are encountered under soil conditions, namely Cr(III) and Cr(VI), exhibit migration and adsorption characteristics different from each other. The migration of Cr(VI) oxyanions towards the positively charged anode results in encountering regions of lower pH and high redox potential near the anode where it may be reduced into Cr(III), in particular when the soil contains electron donors such as Fe^{2+} and organic matter (the total carbon content of the soil was 0.2% and it was essentially inorganic). When EK alone is applied, generally oxidizing conditions exists only in the soil close to the anode reservoir, while a reductive environment prevails throughout most of the specimen (Weng et al., 2007). Experimental evidence of substantial Cr reduction in a large portion of an electrokinetic cell has been reported in Weng et al. (2007) and Reddy and Chinthamreddy (2004). In the present study the Cr(III) profile (Figure VI.12 (a)) suggests that newly formed cationic Cr^{3+} species precipitated as $Cr(OH)_3$ when the pH increased, hindering chromium removal. Indeed, though Cr^{3+} electromigration should have been aided by the electroosmotic flow from anode to cathode, no chromium was detected in the cathode reservoir.

Electromigration towards the anodic compartment of the Cr still remained in the form of Cr(VI) (run 6Cr_BLK) was hampered by the acidic conditions in the portion of soil near the anode. In fact, Cr(VI) adsorption on soil particles is known to increase when pH decreases and vice versa; in particular, it has been reported that whilst at neutral to alkaline conditions Cr(VI) exists as CrO_4^{2-}, which is characterized by negligible adsorption on deprotonated soil, at lower pH values it is present as $HCrO_4^-$, which adsorption onto protonated soil particles may be much more significant (Reddy et al., 1997). Therefore, although chromium appeared to migrate towards the anode, most of the chromium remained within the soil during tests without TRM RB.

During the electrokinetic runs performed with the TRM RB incorporated (12Cr_TRM and 12Cr_TRMplus in particular) mobilization and migration of Cr towards the anode were noticed, in contrast to the control runs (Figure VI.11 (b)). Figure VI.11 (a), showing the pH variation in the soil, demonstrates how the presence of the TRM RB always suppressed the development of an acidic front. The relatively high pH strongly limited the reduction of Cr(VI) into Cr(III) (Figure VI.12) and, presumably, the protonation of the soil, therefore decreasing the adsorption capacity of the soil for Cr(VI), thus enhancing the desorption, mobilisation and electromigration of the anionic chromate towards the positively charged anode.

Similar results were obtained also in other experiments. Chromium mobilization was significantly enhanced by avoiding acidification of the medium and limiting Cr(VI) reduction to Cr(III) through the addition of phosphate buffer and NaClO, respectively (Cang et al., 2007). As far as studies focusing on combined application of EK removal and reactive barriers are concerned, in another experiment the control exerted on the pH of the anolyte allowed a significant mobilization of Cr(VI) and its subsequent trapping onto an adsorbent material fitted at the anode consisting of tannin chemically incorporated into cellulose: 83% wt. of the initial Cr(VI) content was mobilized with respect to 44% wt. in the EK-alone test (Sawada et al., 2004).

In the present study, a substantial depletion of the initial Cr in the soil slices closer to the cathode and a subsequent accumulation in the anodic slice containing the RB were observed, for run 12Cr_TRMplus in particular. In this run, in which the Cr mobilization and anodic migration were much more evident, the advancement of the basic front, the most extended among all the performed tests, was probably due to the greater amount of circulating species, mirrored by the higher current intensity values, and, thus, to a greater OH^- production, according to Faraday's law for the electrolytic decomposition of water at the electrodes and as reported by others authors (Altin and Degirmenci 2005, Buchireddy et al. 2009, Pomes et al. 1999, Genc et al. 2009). Moreover the greater H^+ ions production during this run was completely controlled by the RB, whilst in the previous runs (6Cr_TRM and 12Cr_TRM) the amount of TRM resulted to be slightly underestimated due to the measured current intensity values which were higher than expected.

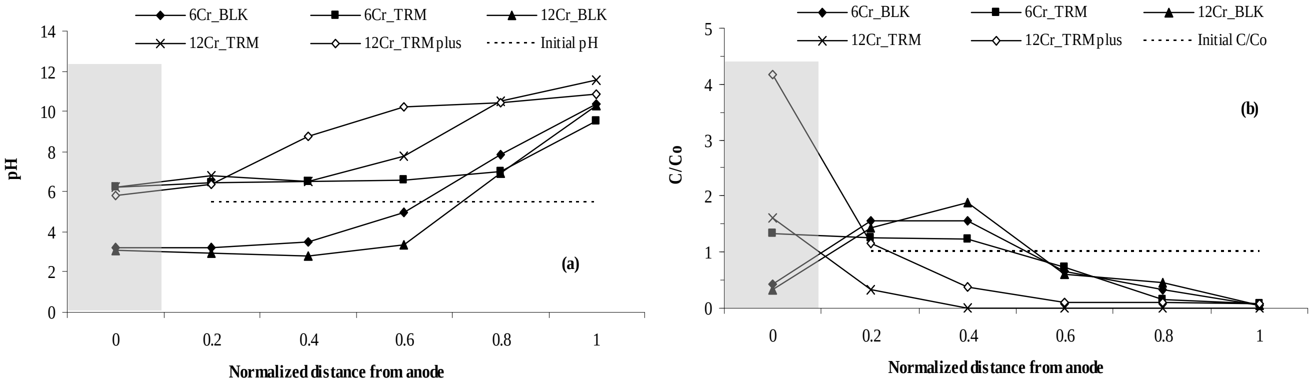


Figure VI.11 *pH profiles (a) and distribution of total Cr (b) in the soil after the electrokinetic treatment as a function of the normalized distance from anode (shaded area: TRM RB in runs 6Cr_TRM, 12Cr_TRM and 12Cr_TRMplus; clean soil slice in control runs 6Cr_BLK and 12Cr_BLK)*

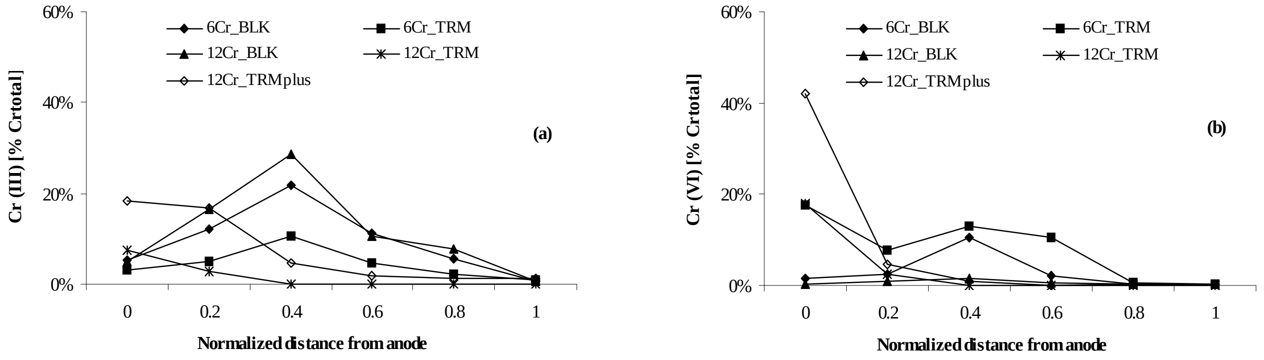


Figure VI.12 *Residual Cr (III) (a) and Cr (VI) (b) concentration in the soil as percentage of total Cr after the electrokinetic treatment*

Figure VI.13 shows the total Cr concentration found in the anolyte: it can be seen that in the presence of TRM RB more Cr was accumulated in the anodic chamber and the migration began before.

Table VI.17 summarizes the experimental results and presents the mass balances. The efficiency of the TRM RB can be evaluated either in terms of Cr mobilization or trapping. The incorporated TRM RB increased Cr mobilization towards the anode; 19.4% wt. of the initial total Cr was found in the anodic chamber after 6 days of treatment in presence of the RB (run 6Cr_TRM) as compared to 8.8% wt. of the initial total Cr in run 6Cr_BLK. The comparison between two of the runs carried out for 12 days (runs 12Cr_BLK and 12Cr_TRM) again underlines that the presence of the TRM RB enhanced Cr migration towards the anode: 60.8% wt. of the initial total Cr was found in the anolyte in presence of the RB as compared to 9.1% wt. of the initial total Cr without the reactive barrier.

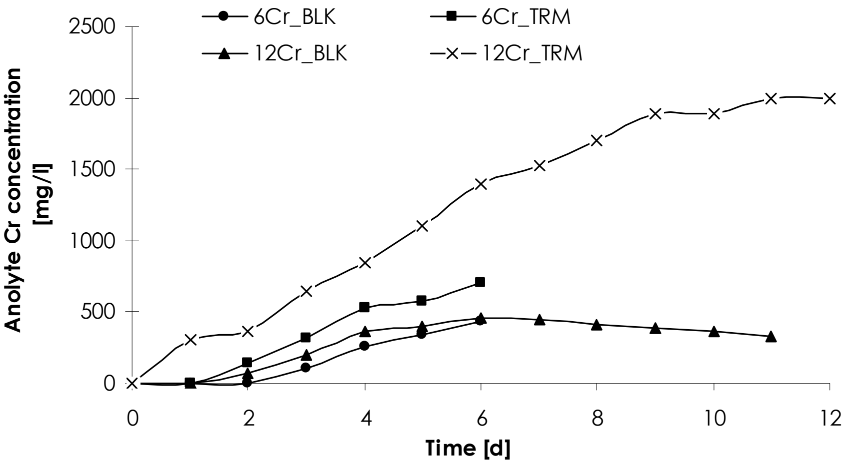


Figure VI.13 *Concentration of total Cr accumulated over time in the anodic chamber*

In terms of Cr immobilization, the TRM RB trapped 20.6% wt. and 25.5% wt. of the total initial Cr after 6 and 12 days of treatment, respectively, whilst 6.6% wt. and 5.3% wt. of the initial total Cr was found in the slice closest to the anode at the end of control runs 6Cr_BLK and 12Cr_BLK. However, the above mentioned data on Cr mobilization and trapping underline that a significant part of the mobilized total Cr was not captured by the RB, but moved into the anodic chamber. It thus appears that the quantity of TRM to be used for H^+ ion neutralization was not sufficient for adsorption of the entire Cr mass eventually mobilized, as is desired in order to prevent contamination of the anolyte and its treatment. Therefore, in the 12Cr_TRMplus run in which the TRM content in the RB was increased to 50% wt. from the 12% wt. of run 12Cr_TRM and part of the TRM content was first acid neutralized by means of hydrochloric acid treatment, more adsorption capacity was added (but not more neutralization capacity); the aim of this test was the immobilization of the chromium in the TRM RB slice, without migration in the anodic chamber: consequently 60.6% wt. of the initial total Cr was trapped in the anodic RB (95.4% wt. of the mobilized total Cr) and no Cr was found in the anodic chamber anymore. At the end of run 12Cr_TRMplus the pH of the RB was 5.8 (Figure VI.11 (a)), very close to the optimal value (5.5) for Cr(VI) adsorption on the hematite in the TRM of the RB as observed in previous adsorption tests performed in the laboratory (personal communication). Indeed, it can be noticed from Table VI.17 that the mobilized Cr mass was similar in the 12Cr_TRM and

12Cr_TRMplus runs, slightly higher in the latter, as expected due to the same run duration. However, when efficiency is defined as percentage of the total initial mass that is mobilized, one can notice that it is higher in 12Cr_TRM due to the lower initial Cr content of run 12Cr_TRM.

Table VI.17 *Summary of the results of the treatment of the Cr-contaminated soil and mass balances*

Test	**Initial Cr_{tot} (mg)**	**Cr_{tot} after electrokinetic treatment**				**Cr_{tot} mobilized**		**Anodic slice/RB (% initial Cr_{tot})**	**Anode reservoir (% initial Cr_{tot})**	**Mass balance (%)**
		Anodic slice/RB (mg)	Soil (mg)	Anode reservoir (mg)	Cathode reservoir (mg)	Mass (mg)	Mass (% initial Cr_{tot})			
6Cr_BLK	1481.20	97.46	1107.72	130.19	0.00	463.17	31.27	6.58	8.79	90.15
6Cr_TRM	1188.88	245.27	656.89	231.00	0.00	526.54	44.29	20.63	19.43	95.31
12Cr_BLK	1102.05	58.41	849.24	99.85	0.00	321.91	29.21	5.30	9.06	91.42
12Cr_TRM	1085.26	276.21	57.24	660.00	0.00	936.21	86.27	25.45	60.82	91.54
12Cr_TRMplus	1558.62	943.80	494.06	0.00	0.00	989.15	63.46	60.55	0.00	92.25

NOTE: the mobilized Cr mass has been calculated taking into account also the mobilization internal to the contaminated soil; it represents the sum of three components: the mass found in the anodic specimen slice, the mass found in the anolyte and/or catholyte, the mass which accumulated in specimen slices (others than the anodic one) with respect to the initial content (the latter is not reported in Table).
The relative mass balance errors are less than 10% and these differences could be attributed to the non-uniform contaminant distribution within the samples subjected to chemical analysis.

In Figure VI.14 the distribution of total Cr in presence of the TRM RB and the total Cr accumulated in the anodic reservoir is shown with respect to the initial condition; increasing the treatment duration and the content or TRM as adsorbent at the anode, the removal efficiency was improved and the soil was almost completely cleaned up.

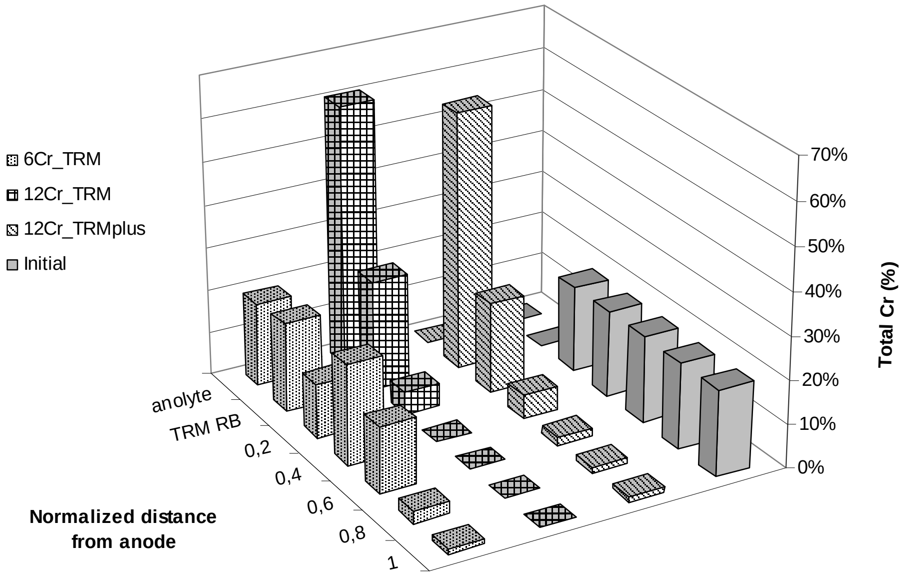


Figure VI.14 *Distribution of total Cr in the presence of the TRM RB*

VI.4.2 *Tests on the As contaminated soil*

Following the promising results of the treatment of the chromate-contaminated soil, similar tests were performed on the same type of soil spiked with arsenate as contaminant.

The current intensity profiles are shown in Figure VI.15. In all the tests the current intensity initially increased rapidly, then decreased and finally stabilized at a constant value. As might be expected due to the low level of soluble salts in the sample and the low ionic strength of soil solution, the current intensity values remained rather low for the duration of the tests, with the highest value of 25 mA achieved after 24 hours during the 12As_TRM run. These results are consistent with those recorded under similar operating conditions and on soils with similar characteristics, reported in the literature. For example, Lynch et al. (2007) reported intensity current values lower than 25 mA in an electrokinetic cell containing the same type of illitic-kaolinitic soil contaminated with cadmium, under a constant voltage of 25 V. In all tests the current has reached its peak within 72 hours after its start.

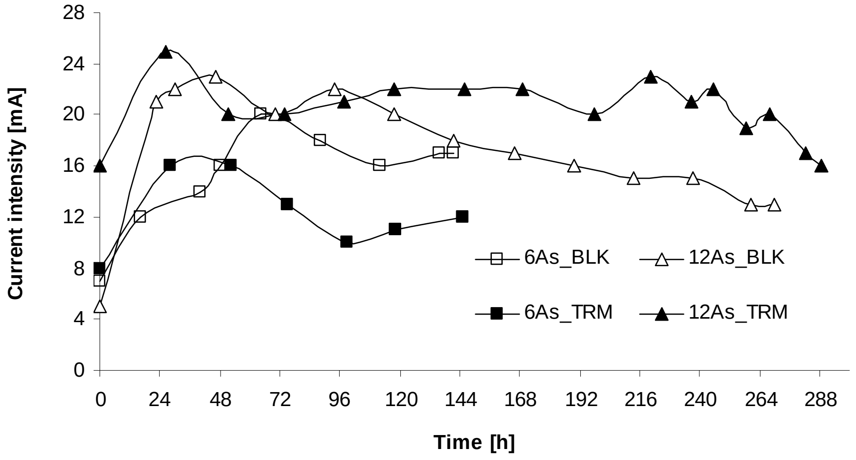


Figure VI.15 *Current intensity as a function of treatment time for As illitic-kaolinitic runs*

The pH profiles (a) and the distribution of total arsenic in the soil (b) as a consequence of the treatment are shown in Figure VI.16.

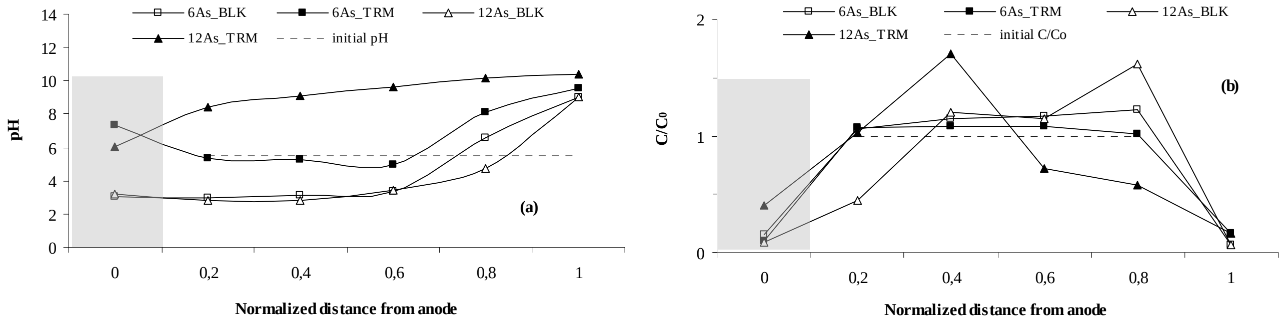


Figure VI.16 *pH profiles (a) and As distribution in the soil (b) after the electrokinetic treatment as a function of the normalized distance from anode (shaded area: TRM RB in runs 6As_TRM and 12As_TRM; clean soil slice in control runs 6As_BLK and 12As_BLK)*

It appears that electromigration of arsenate oxyanions (e.g. $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) towards the anode is much less pronounced than obtained with Cr. Arsenic was not detected in the anolyte and the distribution profiles show that relatively small fractions of app. 6 and 13% wt. (control runs) and 16 and 29% wt. (runs performed with TRM RB) were mobilized from the soil after 6 and 12 days, respectively, with a maximum entrapment into the TRM RB of app. 10% wt after 12 days.

Comparing the results of the 12 days EK treatment without and with TRM RB, one notices that in the former case approximately 15% wt. of total arsenic has been moved from the anodic to the cathodic half of the soil specimen, whilst in the latter case approximately 20% wt. of total arsenic moved in the opposite direction from the cathodic to the anodic half of the specimen.

A certain transport of arsenic towards the negatively charged cathode, opposite to the direction of expected anion electromigration, is suggested for control run 12As_BLK, like it was also reported by Baek et al. (2009) when adding sodium hydroxide to the anolyte and by Buchireddy et al. (2009) while treating CCA contaminated soil. Migration of As towards the cathode could be explained to be a consequence of the EO flow, which relative importance increased as soil was less acid during the EK treatment; it is likely that the direction and magnitude of the EO flow can influence the transport of the arsenic species. In Figure VI.17 the cumulative EO flow collected in the cathode compartment is shown: the electroosmotic volumetric flow of the 12As_TRM run (420 ml) was indeed almost twice as high as that of the more acid 12 days control run (180 ml). Therefore, despite the poor overall results, the TRM RB has certainly improved EK arsenate treatment as it caused a clear electromigration of arsenic towards the anode despite the probable considerably increased electroosmotic transport towards the cathode. In addition it must be considered that arsenic which exists as arsenate can be removed as anionic species before to be reduced to arsinite; indeed the migration of As(V) oxyanions towards the anode could cause, coming across regions of lower pH and high redox potential near the anode, the reduction into As(III), in particular when the soil contains electron donors such as Fe^{2+}, as seen in the case of Cr(VI). As(III) can be found not only as anionic charged species ($H_2AsO_3^-$) but also as uncharged one (H_3AsO_3) which is not removed by electromigration but transported by the electroosmotic flow. This would explained the increase in the As concentration from the anode to the cathode in control run 12As_BLK.

Moreover, although in most cases the electromigration seems to be the dominant transport process of charged species, in this work, as it depends on concentration of ionic species in solution, the low As mobilization was probably not capable of significantly supporting electromigration, whilst the EO flow played a main role, influencing the transport of the mass fraction of arsenic that was mobilized. Being the electromigration the main mechanism of electrokinetic removal at high concentrations and electroosmosis at lower concentrations, the different behaviour observed for As-runs with respect to the Cr-runs could has been influenced also by the lower As initial concentration (100 ppm vs 1000 ppm).

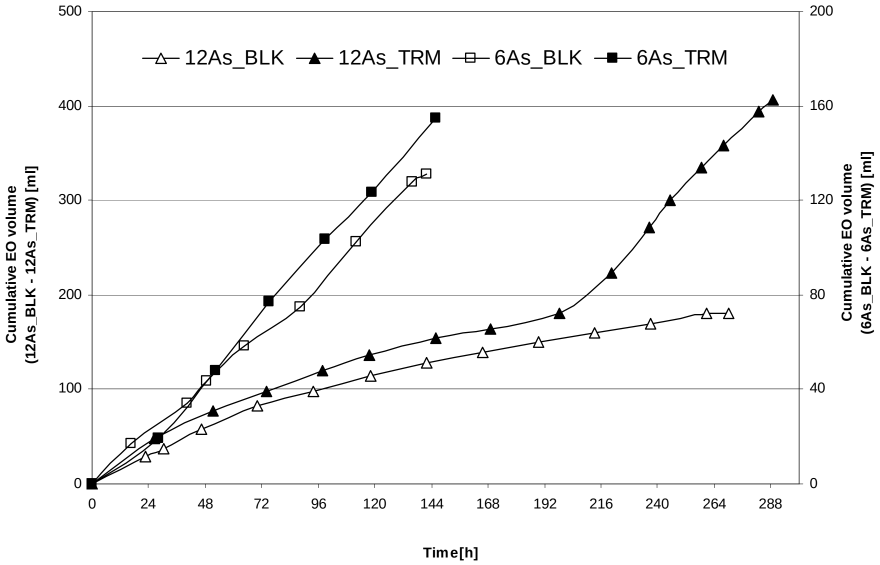


Figure VI.17 *Cumulative electroosmotic (EO) volume as a function of treatment time for As illitic-kaolinitic runs*

The coefficient of electroosmotic permeability K_e, shown in Figure VI.18, ranged from $9.7 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$ $cm^2/V \cdot s$.

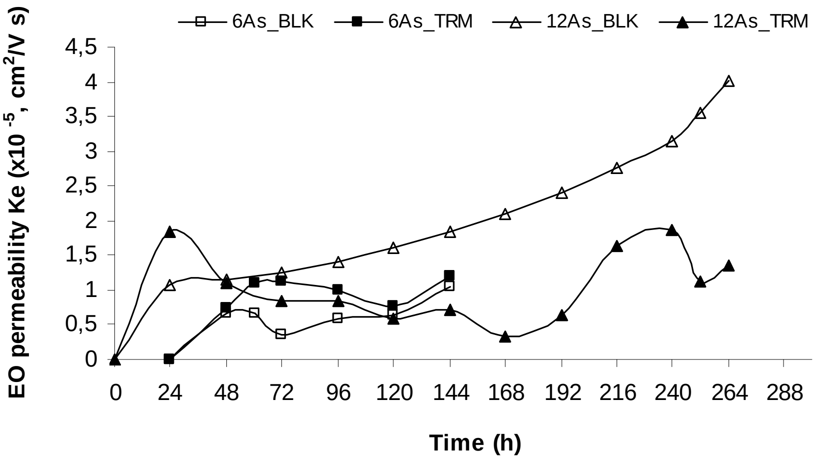


Figure VI.18 *EO permeability towards cathode as a function of treatment time for As illitic-kaolinitic runs*

In Figure VI.19 the profile of electrical conductivity in soil samples at the end of the electrokinetic test, as a function of the normalized distance from the anode, is shown. As for the 6As_BLK and 12As_BLK runs, the EC is higher in the central sections probably due to the combined effect of electromigration and transport by electroosmosis; the test 6As_TRM is characterized by a slight peak in the central sections, but the highest value is at the anode and the same behaviour is more pronounced in the test 12As_TRM. This is probably due to the different composition of the anodic section, consisted of uncontaminated soil and TRM.

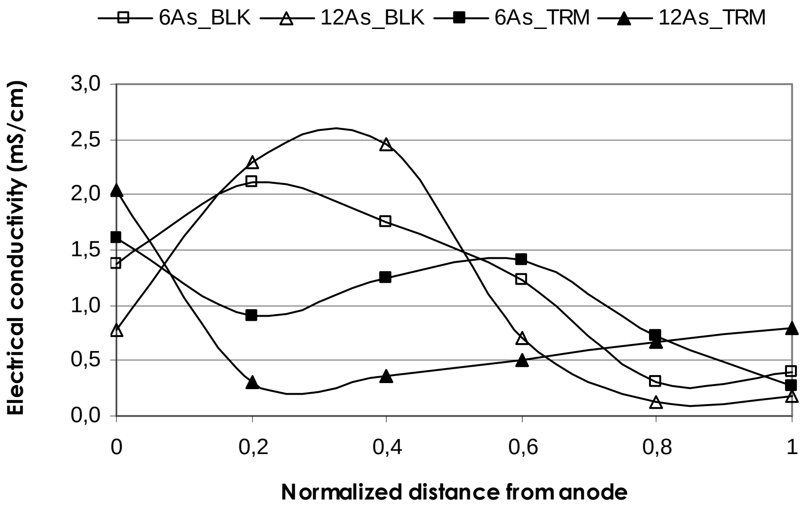


Figure VI.19 *Electrical conductivity after the As illitic-kaolinitic runs as a function of the normalized distance from anode*

The poor removal of arsenic from soil during the EK experiments might be explained to some extent, apart from the relative importance of electroosmotic flow, by several other effects. Firstly, acidification by the anode during the control runs caused protonation of the arsenate anion and decreased its electromigration rate towards the anode, whilst the presence of the TRM RB, suppressing the development of an acidic front, would favour the migration of As(V). Additionally, the protonation of abundant soil particles with respect to the relatively low concentration of arsenate caused immobilisation of a relatively large fraction of arsenate due to adsorption. In particular the iron oxy-hydroxides in the soil (Fe_2O_3 2.6% wt.) have high affinity for arsenate (Kim et al., 2005; Pierce and Moore, 1982) in function of pH (Pierce and Moore, 1982; Wang and Mulligan, 2006; Garcia- Sanchez et al., 2002), with preferentially adsorption for pH values between 4 and 7 with an optimum pH of approximately 4 (Yuan and Chiang, 2008; Pierce and Moore, 1982). Secondly, it can be argued that acidification of the soil down to pH = 3 could mobilize cations such as $Fe^{2+/3+}$ and Al^{3+}, which electromigrate towards the cathode, scavenging arsenate, transporting it against the direction of its electromigration and releasing it only near the cathode as pH increases and cations precipitate as hydroxides. This effect might be noticeable if arsenate concentration in the soil is low.

Thus it appears that the poor and relative inconclusive results of the arsenic EK tests are due to a too low concentration of added arsenate, masking the positive effect of the TRM RB on oxyanions electromigration towards the anode.

Table VI.18 *Summary of the results of the treatment of the As-contaminated soil and mass balances*

Test	**Initial As_{tot} (mg)**	**As_{tot} after electrokinetic treatment**				**As_{tot} mobilized**		**Mass balance (%)**
		Anodic slice/RB (mg)	Soil (mg)	Cathodic slice (mg)	Anodic and cathodic reservoirs (mg)	Mass (mg)	Mass (% initial As_{tot})	
6As_BLK	98.00	3.81	95.08	1.57	0.00	6.04	5.60	102.51
6As_TRM	97.80	2.17	93.83	3.96	0.00	14.02	12.80	102.20
12As_BLK	104.92	2.22	102.74	1.78	0.00	19.19	16.00	101.73
12As_TRM	103.43	9.33	88.89	4.98	0.00	30.66	28.90	99.78

Note: since most of the mobilization occurred within the contaminated soil, mass of mobilized As is defined also by the mobilization internal to the contaminated soil.

Since the experimental data reported in the present research only relates to the final total arsenic content and therefore it has not been possible to better explain the results with respect to the individual arsenic species, the more probable As speciation according to the Eh/pH conditions has been considered in the discussion of the results. To this regard also in studies available in literature about As electrokinetic remediation the same approach has been adopted, as reported for instance by Le Hecho et al. (1998), Kim et al. (2005), Yuan and Chiang (2007), Baek et al. (2009), Buchireddy et al. (2009).

To confirm the difficulties in the desorption of the contaminant, it is interesting to observe the sequential extraction of arsenic performed on the middle sections before and after the EK/RB treatment 12As_TRM; as shown in Figure VI.20 before the treatment the As is not mainly associated with easily exchanged sorption sites that is the non-specifically sorbed fraction, but much of the As is specifically adsorbed (33% wt.) and adsorbed on the amorphous and poorly crystalline Fe and Al oxides (34% wt.).

The speciation of contaminant after the EK/RB treatment showed that significant change did not occur: it can be observe the decrease of the non-specifically sorbed fraction (8% wt. vs 18% wt. before treatment) and the slight increase of the percentage associated with the amorphous and poorly crystalline Fe and Al oxides (46% wt. vs 34% wt. before treatment), whilst the percentage associated with the well-crystallized Fe and Al oxides did not change (app. 15% wt.).

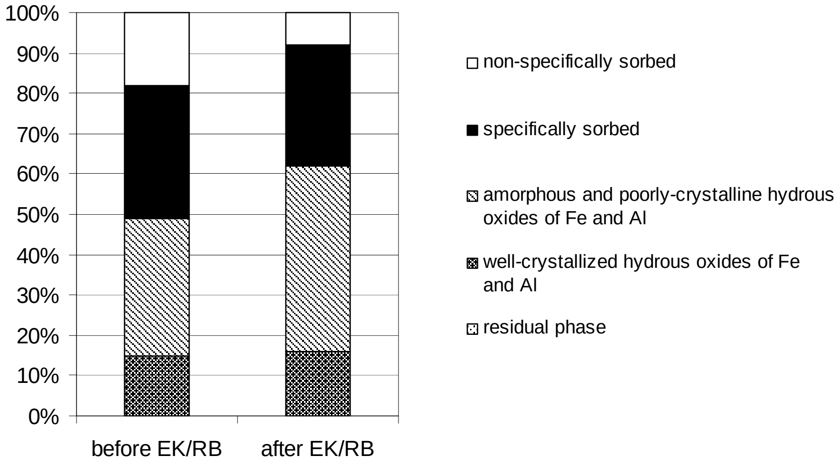


Figure VI.20 *Partitioning of As before and after the 12As_TRM run*

VI.5 *Experimental electrokinetic remediation runs on spiked kaolin*

VI.5.1 *Current intensity and electroosmotic flow*

The evolution of the current intensity over time as assessed during the four tests performed on the As-spiked kaolin is shown in Figure VI.21. In general, the measured values were relatively low, reaching the maximum of 10 mA within 24 hours in test 12As_TRM_K. Low current intensity values were expected because of the low concentration of mobile ions in the soil, even if spiked.

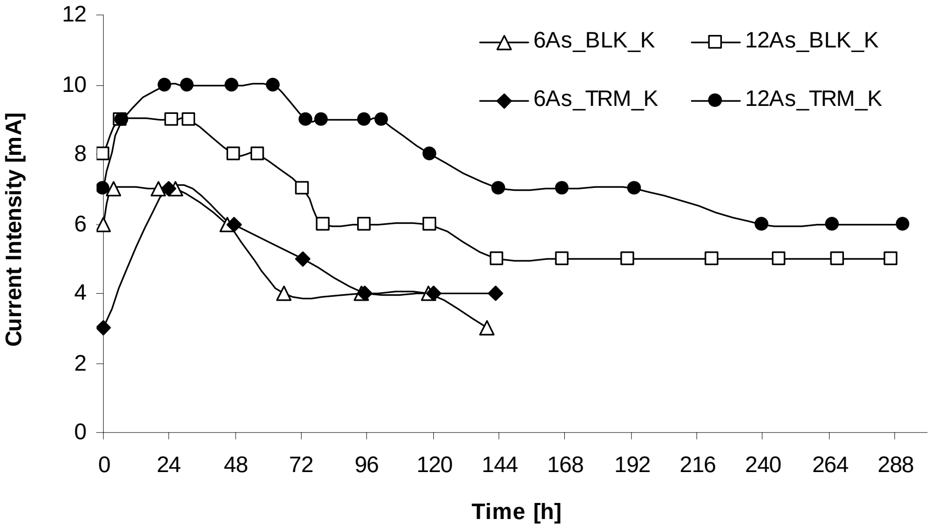


Figure VI.21 *Variations of current intensity over time for As kaolinitic runs*

Figure VI.22 shows the cumulative electroosmotic (EO) volumes collected in the cathode compartment. The highest volume (530 ml) was collected during the 12As_BLK_K run, three times greater than during 6As_BLK_K (150 ml). It can be observed that in the absence of the reactive barrier (6As_BLK_K and 12As_BLK_K) the EO flow was slightly greater than in 6As_TRM_K and 12As_TRM_K runs, considering the same treatment duration. The reduction of the EO in presence of the reactive barrier could have been caused by the enhanced migration of anionic As forms towards the anode, that is in the opposite direction with respect to EO flow itself, as explained for Cr(VI). In general, in soils contaminated by anionic contaminants the migration of these species towards the anode may cause a slight decrease of the EO flow with respect to the values that would be assessed in a soil polluted by cationic species.

The coefficient of electroosmotic permeability K_e, shown in Figure VI.23 ranged from $5.7 \cdot 10^{-7}$ to $0.5 \cdot 10^{-5}$ $cm^2/V \cdot s$. It can be noticed the extreme variability of the rate of electroosmotic flow and the significant reduction of the K_e value in presence of the TRM RB.

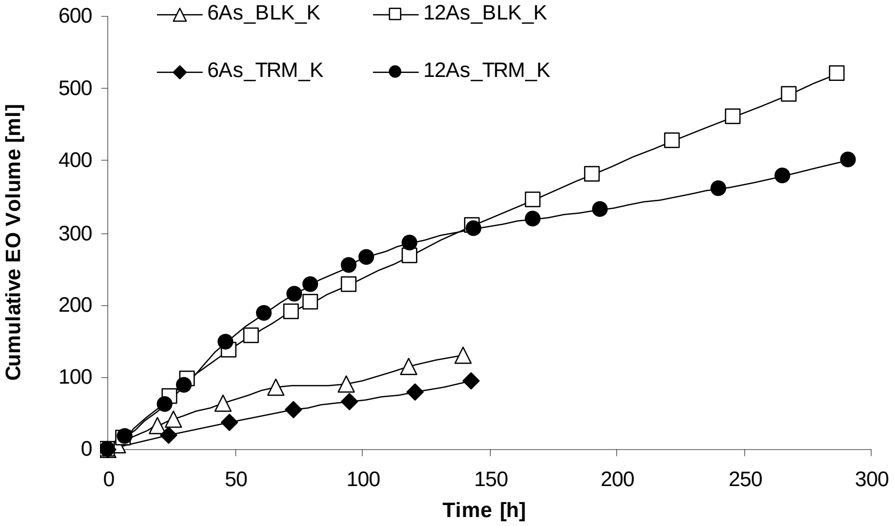


Figure VI.22 *Cumulative electroosmotic volume over treatment time for As kaolinitic runs*

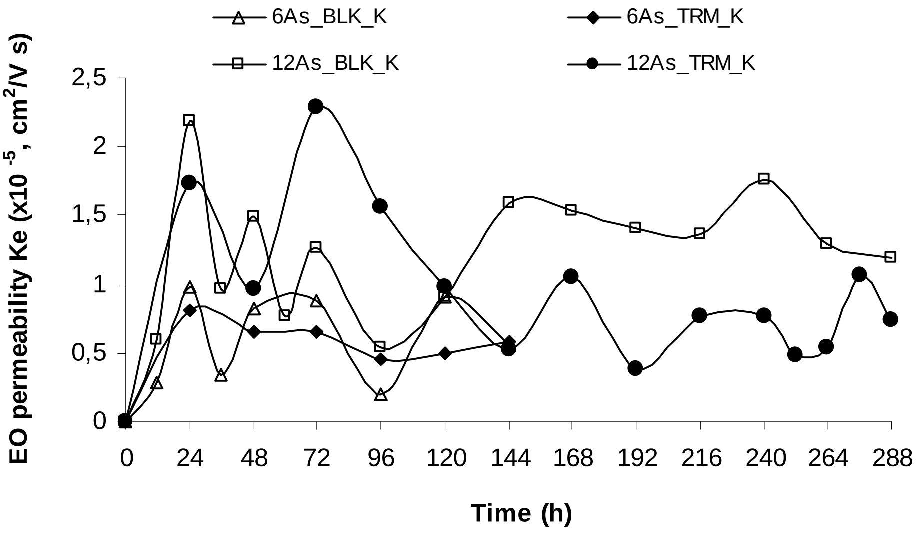


Figure VI.23 *EO permeability towards cathode as a function of treatment time for As kaolinitic runs*

VI.5.2 *Soil pH*

The soil pH profiles for all the tests are shown in Figure VI.24, on the left the runs of duration 6 days, on the right those of 12 days. In general, low pH values near the anode and high pH values near the cathode, as compared with the pH of the untreated soil (pH = 5.2), were found in systems without the TRM RB. Comparing the profile of 6As_BLK_K run with that of 6As_TRM_K run and the profile of 12As_BLK_K run with that of 12As_TRM_K run (that is same treatment duration, but with and without TRM RB), it can be observed that the presence of the reactive barrier resulted in a remarkable increase of the pH near the anode (from about 4 to 8); doubling the duration of the test did not modify the pH profiles (see 6As_BLK_K vs 12As_BLK_K and 6As_TRM_K vs 12As_TRM_K).

The pH monitoring of the anolyte and catholyte has showed a similar trend to the one of tests performed on illitic-kaolinitic soil, with the establishment of strongly acidic conditions in the anodic chamber and strongly alkaline in the cathodic chamber, because of the water electrolysis reactions at the electrodes.

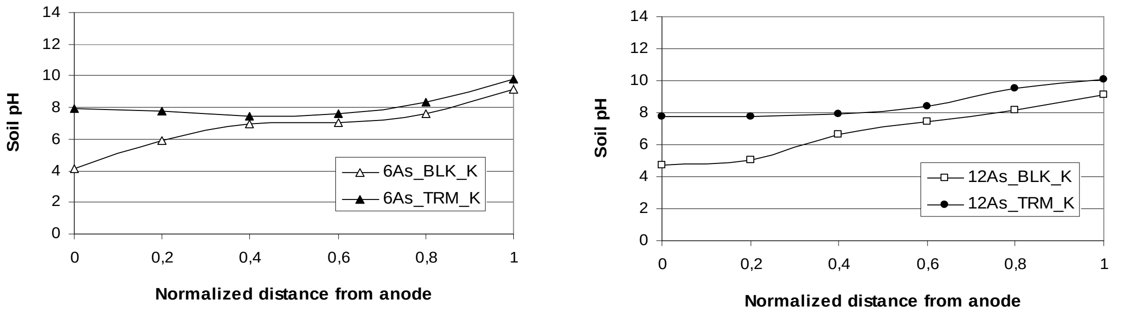


Figure VI.24 *pH profiles in the EK treated specimens as a function of the normalized distance from anode; the "0" slice is the TRM RB in 6As_TRM_K and 12As_TRM_K*

For these tests the electrical conductivity is not reported being the measured values lower than obtained during the tests performed on the illitic-kaolinitic soil; this is understandable because the illitic-kaolinitic soil is a real clay soil, while the kaolinitic matrix was prepared in the laboratory by mixing pure kaolin and sand washed and sieved to 2 mm, practically free of charged species that could influence the trend of electrical conductivity.

VI.5.3 *Concentration profiles*

Data on the concentration of total As assessed in the soil before and after the treatment are shown in Figure VI.25. In the control tests (6As_BLK_K and 12As_BLK_K runs) only a slight mobilization towards the anode was observed. In comparison, 6As_TRM_K and 12As_TRM_K runs showed that the presence of the anodic TRM RB enhanced the anodic electromigration of As, presumably due to the control of the acidic front and, thus, the increase of pH into the soil which, in turn, resulted in the onset of conditions favourable to the mobilization of the anionic pollutant. Given the presence of the reactive barrier, arsenic migration resulted to be proportional to the duration of the treatment (6As_TRM_K vs 12As_TRM_K runs).

Indeed, 30% wt. of total As was accumulated onto the anodic RB after 6 days (6As_TRM_K run), whilst 58% wt. of total As content was accumulated onto the RB after 12 days of treatment (12As_TRM_K run). The EO flow did not support As electroosmotic transport towards the cathode, but electromigration towards the anode prevailed resulting the dominant transport mechanism. However, As was not found into the anodic chamber solution, suggesting that the RB was capable of effectively trapping the mobilized pollutant and that, provided that the mass of reactive material is properly defined on the basis of the mass of pollutant to be trapped, treatment of an As-polluted anolyte may not be required.

Therefore it may be noted that during these runs a significant mobilization of arsenic was obtained as comparison with previous tests; if the interference with iron oxides was a reason of the low efficiency assessed while attempting As decontamination on the illitic-kaolinitic soil, in this case the absence of a significant iron content in the soil as well as a good advancement of the basic front allowed the desorption and the mobilization of the arsenic from the kaolinitic soil.

The results obtained showed that electrokinetic As removal was enhanced by the presence of the TRM RB, which suppressed the formation of the acidic front and that mobilized arsenate was effectively adsorbed onto the iron-oxide rich TRM RB, avoiding transport into the anodic chamber and the need of treating an As-polluted anolyte.

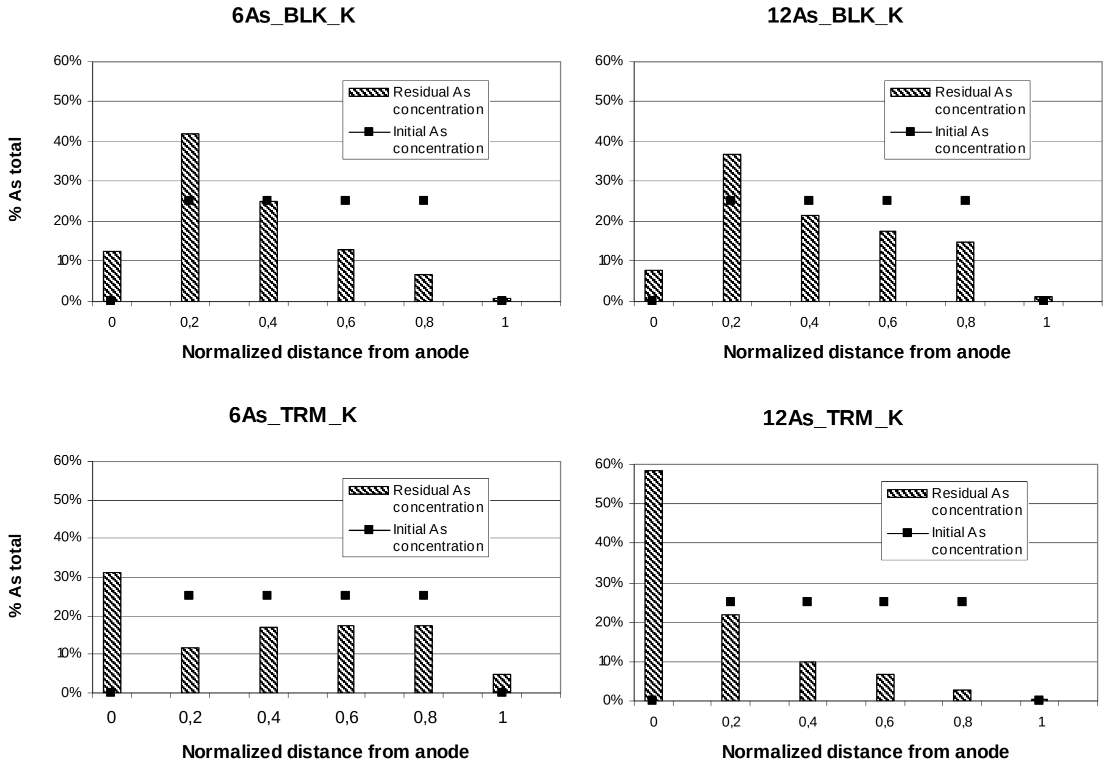


Figure VI.25 *Arsenic content in the soil specimen sections before and after the treatment (as %wt with respect to the total pollutant content); the "0" slice is the TRM RB in 6As_TRM_K and 12As_TRM_K*

Figure VI.26 presents a comparison between the residual arsenic concentration after 12As_TRM_K in five previously polluted soil sections (from anode to cathode) and the regulatory threshold limits established by current Italian regulation on contaminated soils (Legislative Decree 3 April 2006, n. 152). The post-treatment concentration values accomplished the limit established for industrial and commercial areas in all the sections but in that close to the anodic RB. The graph does not describe the concentration value for the anodic section, since, in view of a future in situ application of this technique, this section represents the reactive barrier, intended to be excavated and removed after treatment.

Nevertheless, the assessed behaviour over time of the process suggests that the above mentioned limit could be accomplished by simply increasing the duration of the treatment. Indeed the efficiency of contaminants removal achieved in 16As_TRM_K after 16 days has been increased, ensuring the regulatory threshold limits established for industrial sites in all sections of the decontaminated specimen (Figure VI.27).

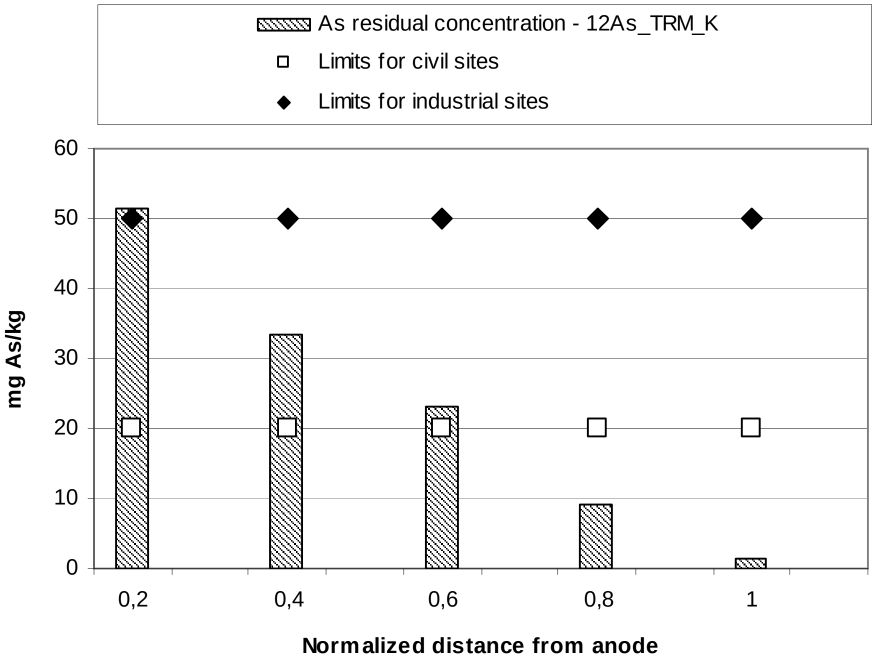


Figure VI.26 *Comparison between arsenic concentration after the treatment (12As_TRM_K run) in five soil sections and the regulatory threshold limits established by current Italian regulation on contaminated soils. The TRM RB section is not represented*

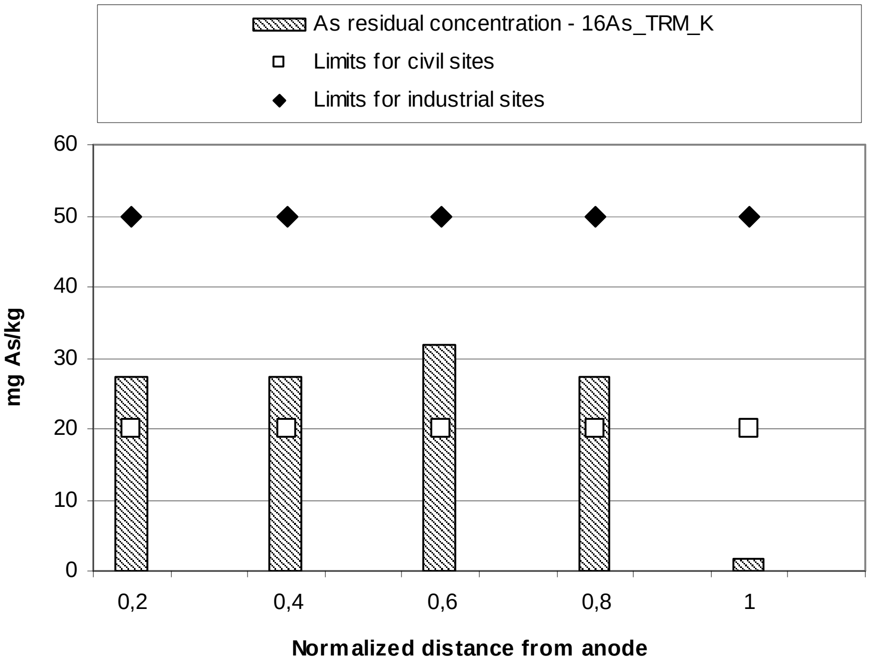


Figure VI.27 *Comparison between arsenic concentration after the treatment 16As_TRM_K run. The TRM RB section is not represented*

With only four more days of treatment, 75% wt. of total As was accumulated onto the anodic RB after 16 days (16As_TRM_K run) and all sections of the specimen were decontaminated, as shown in Figure VI.29. Also in this case the presence of the reactive barrier has allowed a significant increase of the pH along the specimen (Figure VI.28). In Figure VI.30 the summary of results obtained as trapping into the anodic slice/RB for all tests is shown.

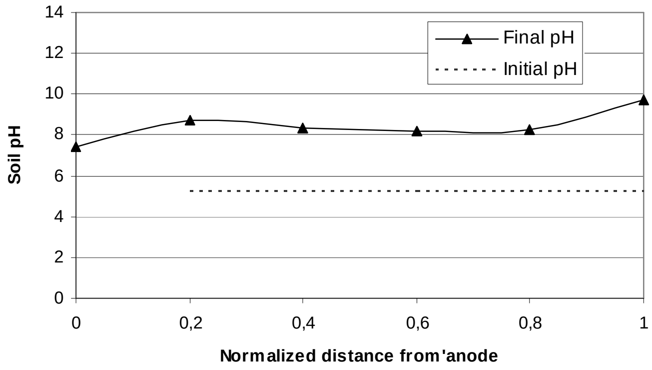


Figure VI.28 *Soil pH profile after the 16As_TRM_K run; the "0" slice is the TRM RB*

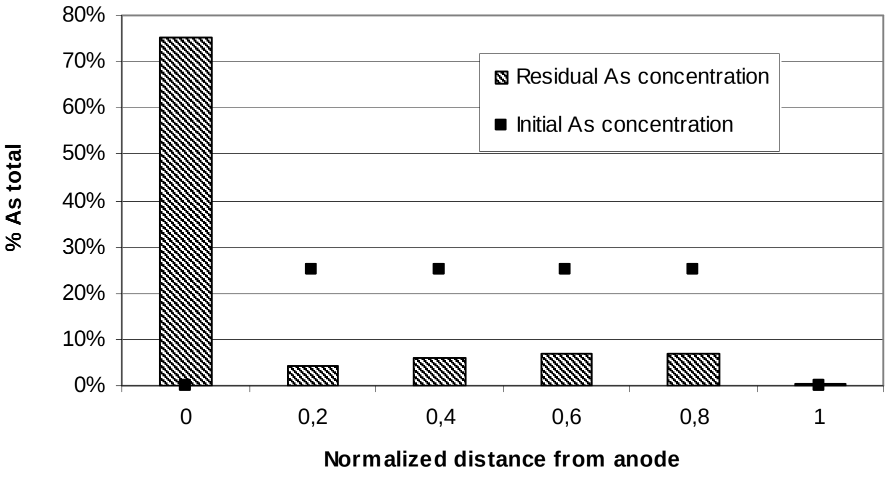


Figure VI.29 *Arsenic content in the soil specimen sections before and after the 16As_TRM_K run as a function of the normalized distance from anode; the "0" slice is the TRM RB*

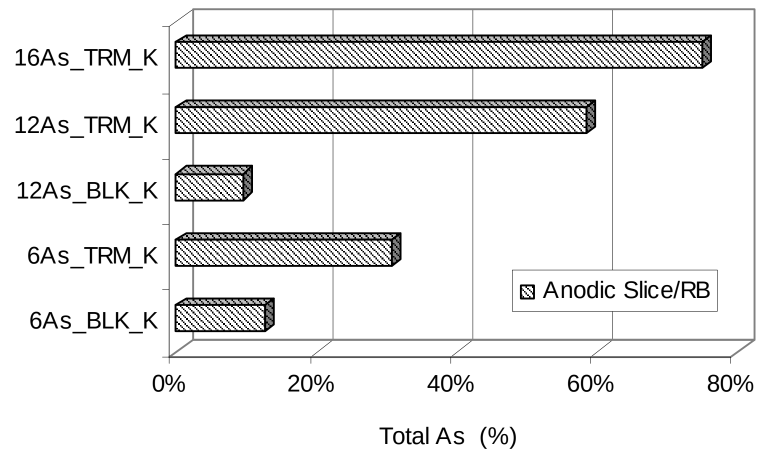


Figure VI.30 *Arsenic content in the anodic slice/RB after the treatment (as %wt with respect to the total pollutant content)*

In Table VI.19 the summary of the results of the treatment of the As-spiked kaolinitic soil and mass balances are given.

Table VI.19 *Summary of the results of the treatment of the As-spiked kaolinitic soil and mass balances*

Test	Initial As_{tot} (mg)	As_{tot} after electrokinetic treatment				Anodic slice/RB	Mass balance (%)
		Anodic slice/RB (mg)	Soil (mg)	Cathodic slice (mg)	Anode reservoir (mg)	(% initial As_{tot})	
6As_BLK_K	73.76	9.25	56.56	0.62	0.00	12.54	90.06
6As_TRM_K	84.28	25.73	55.96	4.40	0.00	30.53	102.15
12As_BLK_K	97.87	8.75	92.85	1.49	0.00	9.42	105.33
12As_TRM_K	93.45	54.46	37.36	0.41	0.00	58.28	98.69
16As_TRM_K	127.12	95.00	31.09	0.40	0.00	74.73	99.50

Although the reactive barrier could be excavated and removed at the end of treatment, to leave it in situ would be economical; with this aim the anodic reactive barriers of the 12As_TRM_K run, in which 58% wt. of total As content was accumulated, and of 16As_TRM_K run, in which 75% wt. of total As was accumulated, have been studied to assess the release of arsenic, fifteen days after the end of electrokinetic treatment. The tests were conducted by mixing TRM RB with distilled water according to L/S ratio 10, shaking for 24 hours. The samples were filtered (0.45 µm) and the eluate subjected to chemical analysis. The reactive barrier of the 16As_TRM_K run was divided in four sections (Figure VI.31 (a)) to assess the concentration profile (Figure VI.31 (b)). The release was measured from the more contaminated section (Bx3).

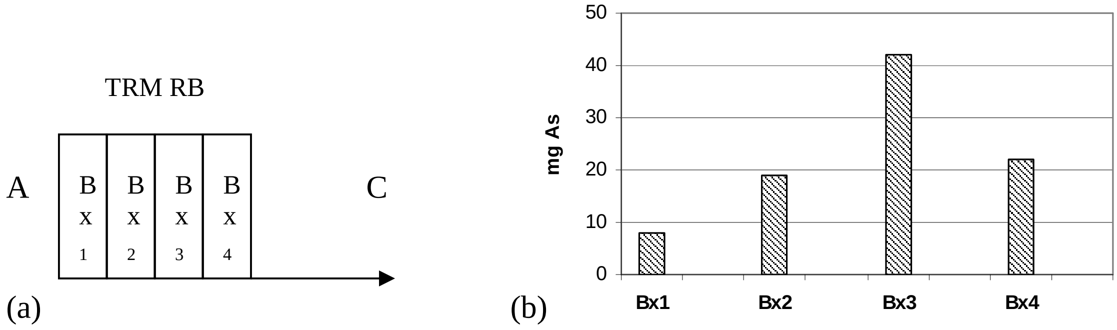


Figure VI.31 *As mass in the TRM RB (b) (divided in four sections (a)) at the end of the 16As_TRM_K run*

The As release from the reactive barrier of the 12As_TRM_K run is resulted about 1.9 mg/l, equal to 9.6% of As adsorbed, whilst studying the barrier of the 16As_TRM_K run a smaller amount of arsenic (1.4 mg/l) has been released, less than 3.5% of the amount adsorbed during the EK/RB treatment (both at about pH 7); in subsequent wash cycles it was found the release of small and negligible quantities of arsenic. Performing the leaching test with acetic acid to determine the potential of material to release chemical contaminants into a landfill environment (Italian Interministerial Committee Deliberation July 27, 1984), only a very small amount of 0.03 mg/l (for both runs), less than 0.5% of total As, was released by acetic acid leaching at pH 5. Therefore the analysis of dried spent TRM RB indicated that bound As is not readily leachable, allowing the spent media to be disposed safely in a landfill. Anyway, considering these results and the fact that the release may change over time depending on the variability of environmental conditions of the site as pH and redox, the removal of the barrier would be appropriate; hence the barrier would have to be built in such a way that the worn out reactive material can be extracted easily (Day et al., 1999).

VI.6 *Experimental electrokinetic remediation on mine tailing soil*

It is important to clarify that the choice of this soil was not related to find a solution to the problem of contamination of the specific mining area of Baccu Locci, from which the soil comes from, but the objective of the study was to investigate the application of the EK-RB process for the remediation of natural arsenic-contaminated soil (do not artificially contaminated), though aware that it was a type of contamination very difficult.

The mine tailing soil was chosen since it is highly contaminated with arsenic and the arsenic-bearing tailings are potential sources of arsenic contamination. The aim was to determine if As could be effectively moved through the soil using the electrokinetics improved by the presence of the TRM RB.

Five runs were carried out to evaluate the removal of arsenic, as reported in Chapter V "Materials and Methods", section V.6.2 *"Experimental electrokinetic remediation runs"*. Three tests were conducted without the installation of the reactive barrier using distillated water as electrolytes solution in one run and investigating in the other two tests the effectiveness of two enhancing agents (used in previous leaching tests) as cathodic electrolyte, 0.2 M potassium phosphate (KH_2PO_4) and 0.2 M sodium hydroxide (NaOH) to overcome the problem of the strong adsorption of As onto the iron oxy-hydroxides.

The phosphate solution was selected due to its anion exchange capacity with arsenic species. Based on the results further two tests were performed coupling the use of EK technique with the TRM RB, using at first distillated water as electrolytes solution and, in the second test, distillated water as anodic solution and 0.2 M NaOH as cathodic solution. Periodically each electrolyte solution was refreshed to reduce the effect of water electrolysis reactions with the aim to control the pH along the specimen.

VI.6.1 *Current intensity and cumulative electroosmotic volume*

The current intensity profiles as a function of time are shown in Figure VI.32 for all the tests.

In general the current intensity values are stabilized at higher values with respect to tests performed on artificially contaminated soil, due to the major ionic strength of the circulating pore solution, indicating that there were more species available to migrate across the specimen during the process.

In general the current intensity values were recorded higher in presence of the enhancing agents, especially when NaOH was present, with (5R run) and without (3R run) the RB, remaining high until the end of the treatment.

The maximum current density was 3.3 mA/cm^2.

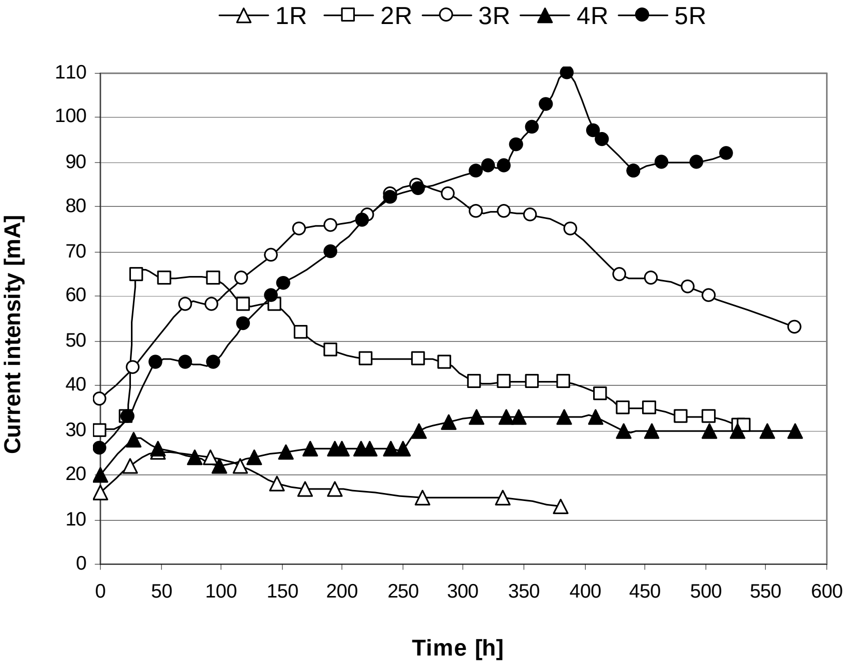


Figure VI.32 *Profile of current intensity over treatment time (1R – 5R runs)*

The transported water volume by electroosmosis collected in the cathode compartment in all tests performed is shown in Figure VI.33. It is possible to notice that the larger EO flow was recorded in presence of the reactive barrier (4R run); in presence of the conditioning agents potassium phosphate (2R run) and sodium hydroxide (3R run) the electroosmotic flow was slightly lower. The normal electroosmotic flow from anode to cathode was not maintained in 5R run in which during the 12th day a reverse electroosmotic flow was registered, although the acidification of the soil was not occurred. The relatively explanation of this observation remains uncertain because generally is the low pH in the soil that can reverse the polarity of zeta potential, whilst the high pH condition within the specimen reinforced the normal electroosmosis towards the cathode, retarding the electromigration of arsenic towards the anode. Anyway also Yeung et al. (1996) observed a reverse electroosmotic flow at a soil pH much higher than the pH at which polarity reversal of zeta potential occurs. Moreover, sorption of hydrolysable metal ions such as Co^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} onto the clay particle surface can also change the charge of soil (West and Stewart, 1995). Also Mewett (2005) in his experiments observed that the electroosmotic flow ceased for some time and it was explained by the addition of large amounts of salt to the system. Anyway the reverse EO flow could be positive because it may enhance the removal of anionic species and it may promote the development of a high pH environment in the soil because assists the advancement of the basic front.

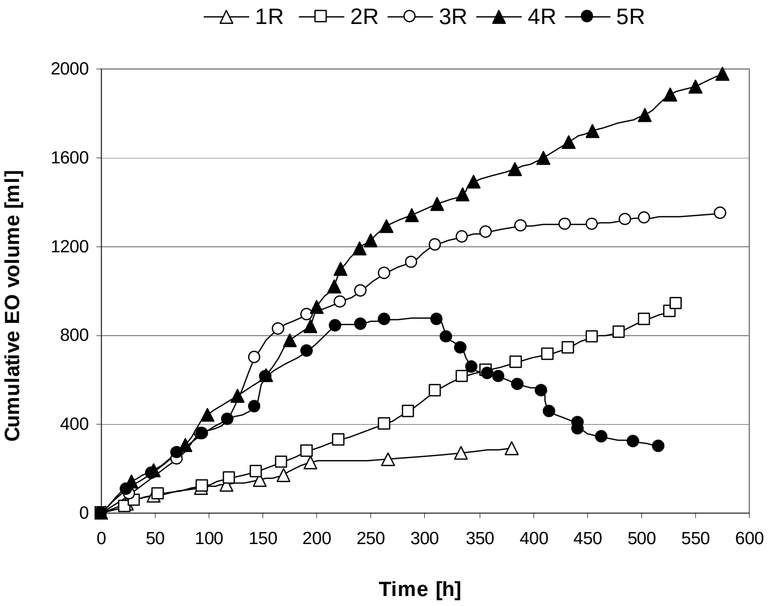


Figure VI.33 *Cumulative electroosmotic volume over treatment time (1R – 5R runs)*

VI.6.2 *Soil pH, electrical conductivity and redox potential*

The pH profiles assessed at the end of the electrokinetic runs are shown in Figure VI.34. Without reactive barrier the acid front can move towards the cathode more easily, resulting in a decrease of the final pH with respect to the initial value for most of the specimen (1R and 2R runs). In addition in test 2R the production of hydroxide ions at the cathode was counteracted by the addition of the acid phosphate solution, resulting in the lowest overall pH. During the 3R run the addition of alkaline NaOH solution into the catholyte contributed to increase the pH of the cathodic side. The use of TRM RB permitted to not acidificate the whole soil bed, maintaining the pH values slightly higher than the initial one, whilst the joint application of the RB and conditioning of the electrolyte solution allowed the highest final pH profile.

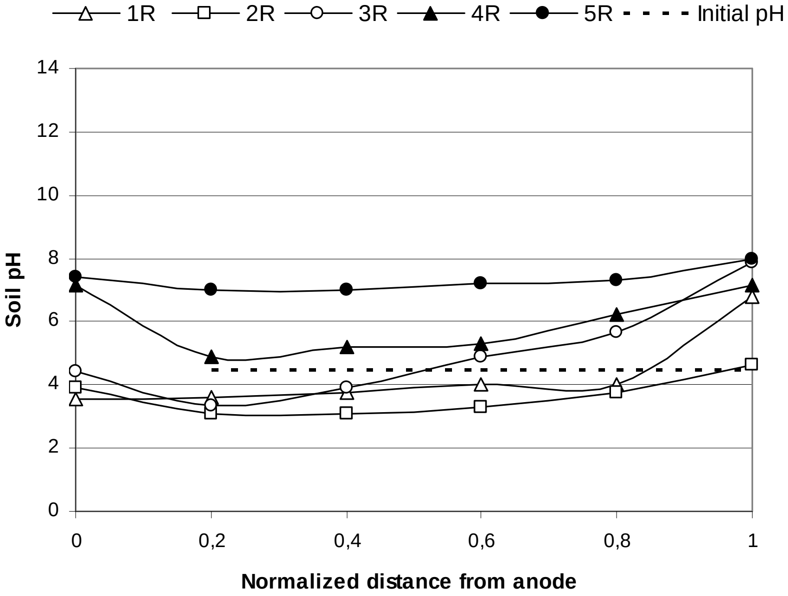


Figure VI.34 *pH profiles in the EK treated specimens;* the "0" slice is the TRM RB in runs 4R and 5R

In general, because of the water electrolysis reactions, the anolyte pH was strongly acid, below the value of 2, whilst the production of hydroxide ions at the cathode resulted in an increase in pH above 12 for the entire duration of tests. Using enhancing agents the pH of catholyte decreased to the value of 5 during the 2R run due to the use of phosphate solution which is acid; indeed in this test also the final soil pH was the lowest.

In Figure VI.35 the profile of electrical conductivity assessed at the end of the electrokinetic tests is shown. The values ranged from 10 mS·cm^{-1} to 33 mS·cm^{-1}. In 2R and 3R runs, the EC is slightly higher in the central sections, whilst in 5R run the opposite behaviour was observed, with increasing values towards the anode and towards the cathode.

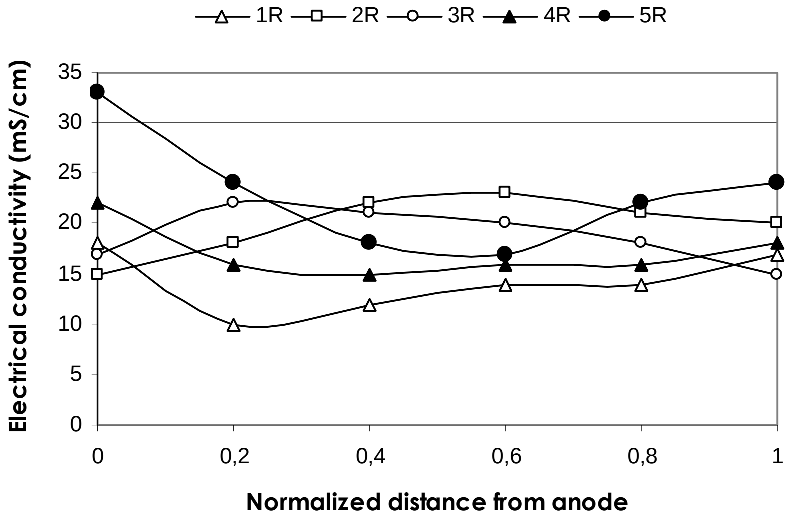


Figure VI.35 *Electrical conductivity after the 1R – 5R runs as a function of the normalized distance from anode; the "0" slice is the TRM RB in runs 4R and 5R*

Figure VI.36 shows the variations of redox potential profiles along the cell.

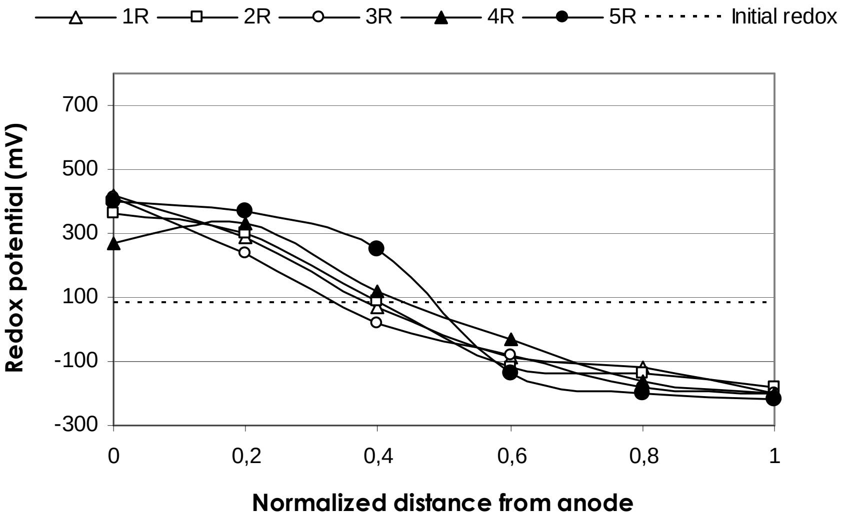


Figure VI.36 *Redox potential distribution in the soil specimen after the 1R – 5R runs as a function of the normalized distance from anode; the "0" slice is the TRM RB in runs 4R and 5R*

In general because of the electrolysis reactions, for all performed runs, at the anode an oxidative environment occurs whilst the cathode is characterized by reducing conditions, that extend for more than half of the sample; it seems that redox potential profile is not substantially affected by the presence of the TRM RB. Also the redox potentials measured at the electrodes are in agreement with the redox reactions associated with the water electrolysis reactions (figure not shown).

Therefore the reductive environment and the low values of pH are likely to encourage the As(V) reduction. Nevertheless, As(III) is usually less strongly adsorbed and more mobile than As(V); moreover in reducing soils, As sorbed on Fe(III) hydroxides can be remobilized and released as a result of the reduction of Fe(III) to Fe(II) and the reduction of As(V) to As(III). Therefore reduction of arsenate to arsenite can promote arsenic mobility.

VI.6.3 *Concentration profiles*

With regard to the As concentration profiles (Figure VI.37) the distribution of residual As in absence of reactive barrier and without electrolyte conditioning did not change substantially (1R run): most of the arsenic was not able to be moved and concentrated in a defined zone. During the 2R test, characterized by a major electroosmotic flow respect to the 1R run a slight accumulation next to the cathode has been observed, whilst using NaOH as catholyte solution (3R run) a mobilization towards the anode was occurred, probably due to the anion exchange of the hydroxide ions and a partial dissolution of arsenic-bearing Fe-oxyhydroxides. Indeed, as shown by the sequential selective extraction performed on the mine tailing soil, the As species were mainly associated with the Fe-oxyhydroxides and they can be severely leached under an extremely alkaline condition. As reported also by Ko et al. (2003), about a sequential extraction analysis on mine tailings in Korea, the largest fraction of As in the samples was the NaOH-extractable fraction. It suggested that the NaOH solution could be effective in extracting and mobilizing arsenic species in tailing soil.

Good results were not obtained using the KH_2PO_4 solution despite the known anion exchange capacity of phosphate ion with arsenate; As and P have similar electron configuration and form triprotic acids with similar dissociation constants: at equal concentrations, phosphate outcompetes arsenate for adsorption sites in soils because of smaller size and higher charge density of phosphates. Although the chemical behaviour of arsenate is similar to that of phosphate and other studies have demonstrated that the presence of phosphate could suppress the adsorption of arsenate and displace adsorbed arsenate from soils, the desorption of arsenate is also dependent on the soil type. For example soils rich in variable charge minerals as Al or Fe oxides do not release arsenate easily and only large additions of phosphate to high anion-fixing soils (Smith at al., 1998) and alkaline pH or Fe or Al oxide dissolution may affect arsenate solubility.

Based on the poor results, the use of this agent was not combined with the use of reactive barrier, also to avoid the adsorption of phosphates into the RB.

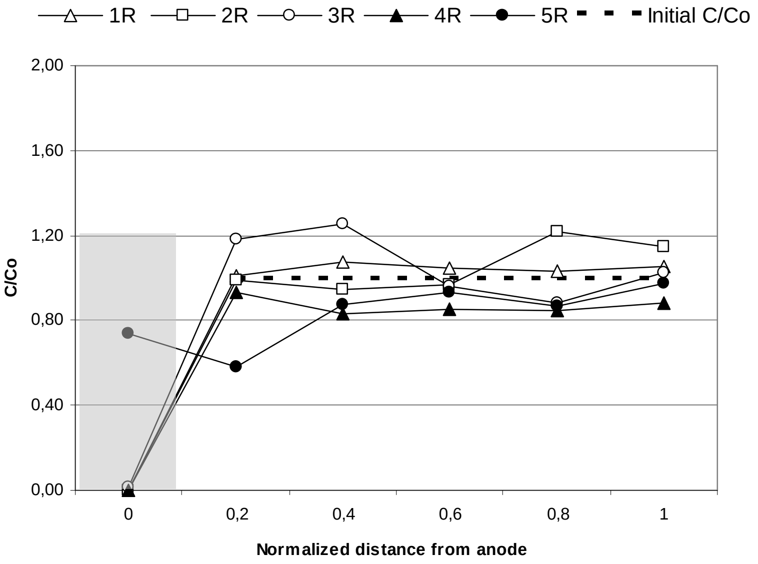


Figure VI.37 *Residual As concentration in the soil after the electrokinetic treatment as a function of the normalized distance from anode (shaded area: TRM RB in runs 4R and 5R; clean soil slice in control runs 1R, 2R and 3R)*

To better understand the mobility of As, it should be considered that under high redox conditions the predominant form found in soil is arsenate As(V), whist under slightly reducing conditions arsenite As(III) is present: these arsenic species are dominantly present in the form of oxyanions (As(V) → $H_2AsO_4^-$ $HAsO_4^{-2}$ and AsO_4^{3-}; As(III) → $H_2AsO_3^-$); As(III) can also be found as uncharged H_3AsO_3 which is not removed by electromigration but it could be transported by the electroosmotic flow; a possible enhancement for arsenite consists of adding an alkaline solution as NaOH to ensure that As(III) is mainly present as negatively charged species in the alkaline environment (Ottosen et al., 2000 and 2009).

Therefore at the cathode, under high pH values, arsenic is likely to become a negatively charged species and move towards the anode, whilst under the low pH values at the anode the arsenic is more likely to become a neutral species due to the protonation of arsenate and tend to be transported by the EO flow; whereas this, the presence of TRM RB, neutralizing the H^+ produced at the anode, should contribute in removing As-oxyanions by electromigration. The As mobilization towards the cathode could also be due to the formation of positively charged species such as a metal arsenate complex ($MeH_2AsO_4^+$).
Specifically, if the Eh/pH diagram is observed (Figure VI.38), it can be noticed that arsenates predominate at high pH for a large range of Eh values (above the thick line in figure) whilst at lower pH and Eh values lower than 0.6 V arsenites predominate (under the thick line in figure). In particular As is always present in anionic forms under extremely high pH (AsO_4^{3-}, AsO_3^{3-}, $H_2AsO_3^-$ and $HAsO_3^{2-}$) or for a range of pH values in oxidizing conditions ($H_2AsO_4^-$ and $HAsO_4^{2-}$), whilst in a large area of Eh/pH values As can be also present in stable uncharged form (H_3AsO_3).

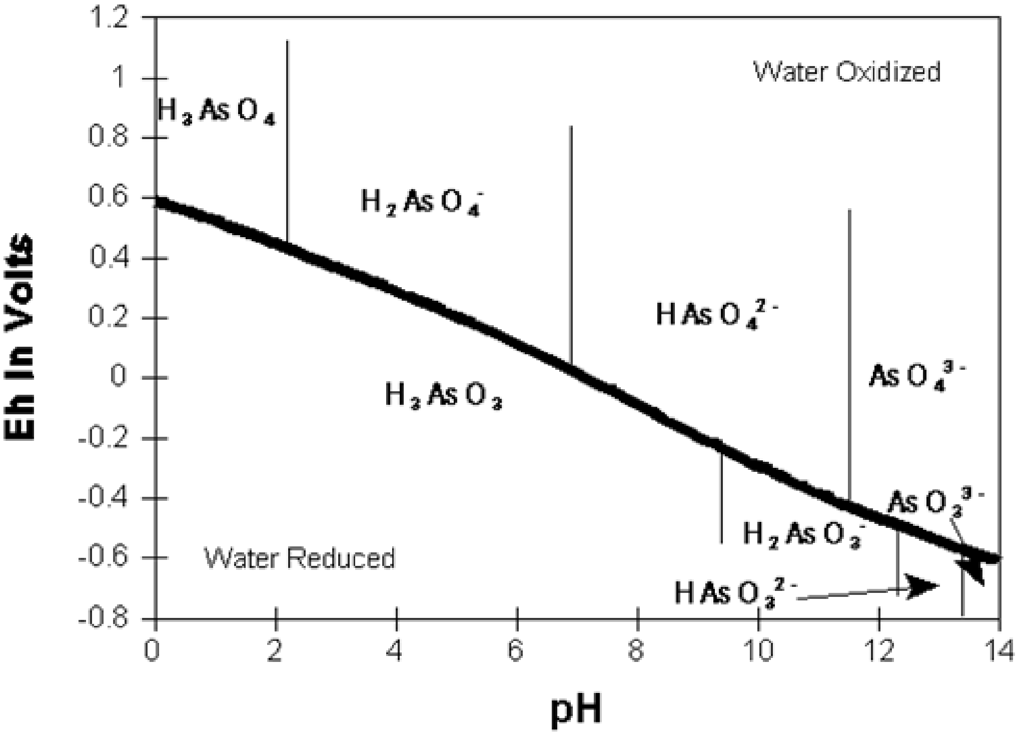
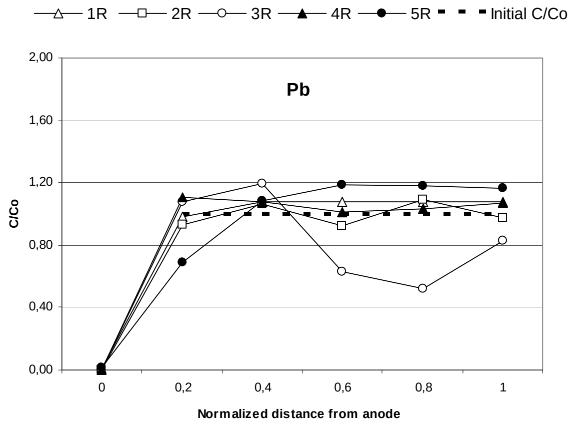
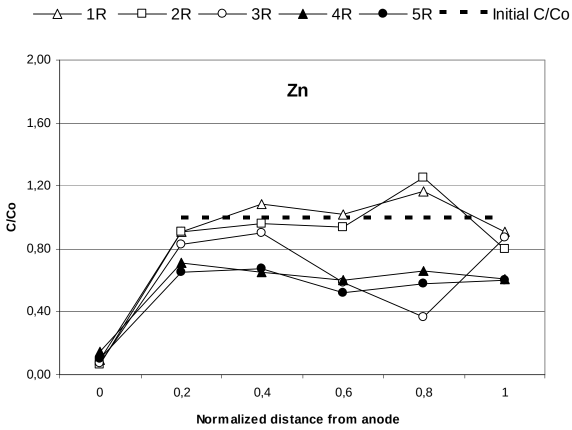


Figure VI.38 *Simplified Eh/pH diagram for As speciation in water system*

In addition it must be considered that the simultaneous presence of different contaminants can make difficult the removal of all pollutants: for instance As has low mobility under acidic conditions, whilst it is more mobile under alkaline one where most heavy metals are not easily transportable. Moreover in presence of contamination by other metals is likely that at high pH values, i.e. near the cathode, hydroxide ions bind heavy metals as Pb^{2+} and Cu^{2+} and precipitate as hydroxides. The precipitation of contaminants may impair the removal efficiency of electrokinetic extraction and causes that the hydroxide ions are less available to desorb the As. If these interactions are not properly taken into consideration, erroneous interpretation of results obtained may ensue (Yeung et al., 1997). Indeed this reactions could reduce leaching and desorption of arsenic under the alkaline front.

Observing the residual concentration of metals present in major concentrations, which are lead, zinc and copper (Figure VI.39) it can be noticed a large depletion along the specimen for Zn and Cu, especially during the 4R (total removal 32.4% wt. and 42.8% wt. respectively) and 5R runs (total removal 37.7% wt. and 41.9% wt. respectively) and an accumulation in the cathodic reservoir; the residual concentration of Pb is similar to the initial content except during the 3R run (total removal 15% wt.). As known the leaching of metals is pH-dependent and the solubility of heavy metal hydroxides such as lead, zinc and copper is minimal within pH range 9-11 (Chimenos et al., 2000). As shown in Figure VI.34 the performed treatment forces the pH towards high values but not enough to minimize the solubility of heavy metals: indeed pH lower than 8 does not allow the precipitation of divalent metal hydroxides.





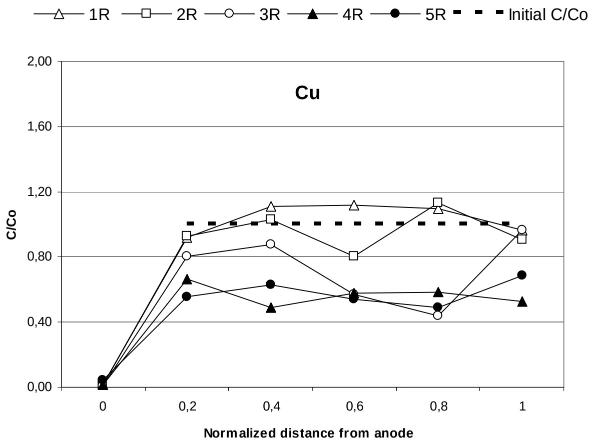


Figure VI.39 *Residual Pb, Zn and Cu concentration in the soil after the electrokinetic treatment as a function of the normalized distance from anode*

As shown in the previous Figure VI.37, concerning the residual As concentration in the soil after the EK treatments, in the runs 4R and 5R a slight lack of As compared to the initial content was observed; in particular during the test 5R, in which the alkaline condition was overwhelming due to the use of TRM RB at the anode and the addition of NaOH solution into the catholyte, the residual As concentration was the lowest and the cathodic solution was observed to became brown, highlighting the presence of iron, as confirmed by the analysis of electrolytes. Therefore the partial dissolution of Fe oxides could have released subsequently As in a more soluble form. As reported in literature, the increase in solubility of As in reducing conditions is associated with the dissolution of oxides and hydroxides of Fe; there is a significant correlation between dissolved Fe and mobility of As to confirm that these soil components are the major agents of adsorption of pollutant (Masschelyn et al., 1991). A general increase in As solubility was also possible in the alkaline conditions reached during this test and by anion exchange between sodium hydroxide and arsenic species; also the reverse electroosmotic flow may enhance the removal of anionic and uncharged As species. Indeed, as explained before, in the reducing conditions and for a large range of pH the primary form of As is expected to be the As(III) that forms a uncharged stable specie (H_3AsO_3) not mobile for electromigration but portable by the reverse electroosmotic flow.

If the behaviour of 3R and 5R runs is observed, the effect of the presence of the TRM RB can be evaluated, showing an improvement of the process in terms of mobilization and migration of species.

As better shown in Figure VI.40, during the EK run performed with the TRM RB and NaOH as cathodic conditioning agent (5R run), mobilization and migration of As towards the anode was noticed: the TRM RB trapped 14% wt. of the total initial As and a low concentration of As (3.4% wt. of the initial total As) was found in the anodic chamber.

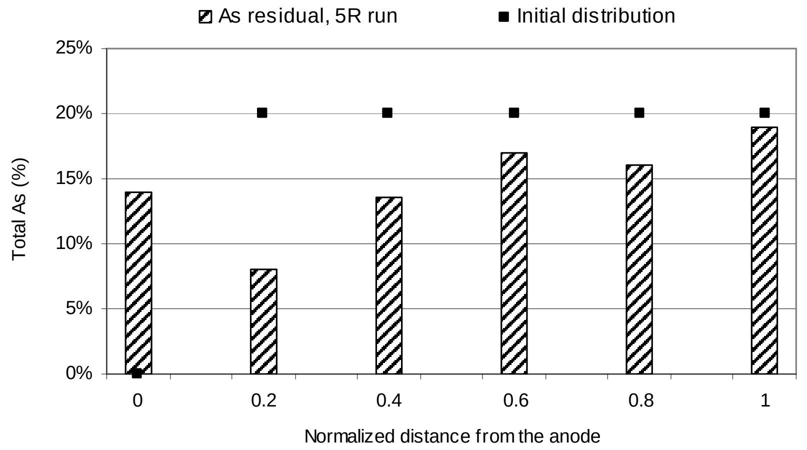


Figure VI.40 *Residual As concentration in the soil at the end of the 5R run as a function of the normalized distance from anode (the '0' slice is the TRM RB)*

Table VI.20 summarizes the experimental results and presents the mass balances. The low quantities of As found in the cathodic reservoir (less than 7%) at the end of 4R and 5R runs were probably due to the formation of positively charged species and to the transport by EO flow of stable uncharged species as $H_3AsO_3^0$. The total As removal achieved in 5R run was 24% wt. of the total initial As (sum of mass accumulated into the TRM RB, in the anolyte and in the catholyte).

Table VI.20 *Summary of the results of the treatment of the mine tailing soil and mass balances*

Test	**Initial As_{tot}**	**As_{tot} after electrokinetic treatment**				**Anodic slice/RB**	**Anode reservoir**	**Mass balance (%)**
	(mg)	Anodic slice/RB (mg)	Soil (mg)	Anode reservoir (mg)	Cathode reservoir (mg)	**(% initial As_{tot})**	**(% initial As_{tot})**	
1R	24113.57	14.59	25575.31	0.00	0.00	0.06	0.00	106.12
2R	15563.51	3.39	15233.21	0.00	0.00	0.03	0.00	97.90
3R	13496.39	31.84	13548.87	7.43	0.00	0.24	0.06	100.68
4R	19876.99	5.49	19232.26	0.00	1125.40	0.03	0.00	102.45
5R	24482.38	3394.65	17374.21	825.66	1645.60	13.87	3.37	94.93

In conclusion, the mine tailing soil studied was a very acidic material and it was composed by a significant percentage of iron. Extremely high concentrations of As were found and sequential extraction confirmed that much of the As was strongly bound to Fe and Al oxides, whilst the contribution of potentially mobile and surface-bound As forms was very low.

During the electrokinetic experiments it has been very difficult to maintain an appropriate pH to reach the most favourable remediation conditions. The only use of conditioning agents did not have any significant effect. The best result was achieved using, additionally to the 0.2 M NaOH electrolyte, the anodic TRM RB (run 5R) confirming the improvement of its use.

With regard to the tests carried out on industrial soil a brief outline is given on the first two tests, since the research is still ongoing.

The final pH values assessed at the end of experiments are shown in Figure VI.41 (a); it can be noticed the positive effect of the presence of TRM RB to control the pH.

The residual As concentration in the soil after the electrokinetic treatments is given in Figure VI.41 (b). In both runs there was not significant change in total arsenic content across the soil.

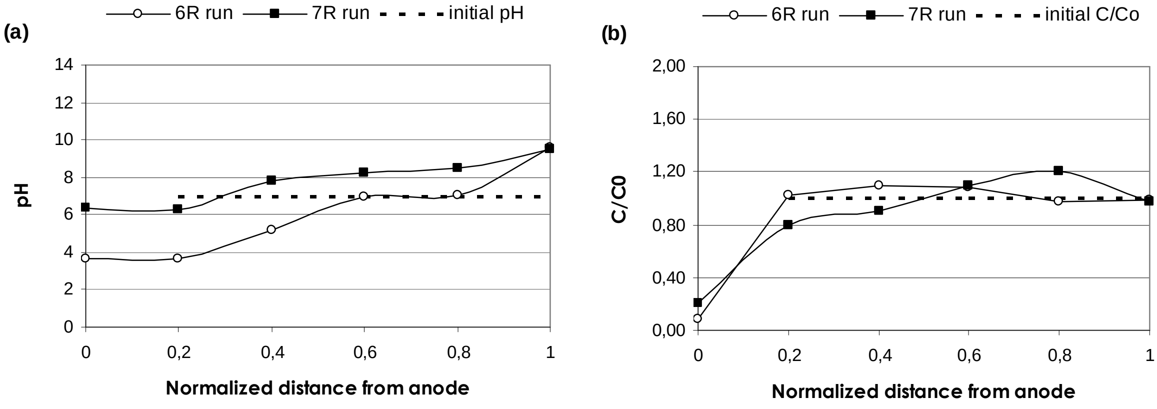


Figure VI.41 *Final pH profile (a) and residual As concentration (b) in the soil after the electrokinetic treatment as a function of the normalized distance from anode;* the “0” slice is the TRM RB in run 7R

In general the study carried out has revealed the difficulty to treat the As-contamination and highlights the complexity of As behaviour in soil; moreover the assessment of applicability of the technology to a natural contaminated soil is particularly difficult because of its complex nature, due to the age of the contamination, to the presence of several pollutants and to the numerous interactions between soil and contaminants, whilst a spiked soil is often more easily to be treated.

Although further investigations could be necessary for a detailed interpretation of the obtained results, in the case of As contamination the presence of oxides and hydroxides of Fe and Al and their strong adsorption capacity can justify the lower efficiency of the process with respect to the process for the removal of Cr. Indeed the soils and in particular the natural contaminated soils had a high iron content which binds the As, assisting in its stabilisation. Certainly if on the one hand the strong bond of As to Fe and Al hydroxides makes it difficult to remove the As by electrokinetics, on the other hand it is advantageous with respect to the environmental impact of the arsenic contamination because the environmental risk associated with possible increase in arsenic mobility should be assessed as low, as demonstrated by leaching tests conducted with distillated water. Therefore in terms of the potential environmental impact the natural attenuation of the mobility and reduced availability of the arsenic is beneficial. Anyway it remains an obstacle to low cost electrokinetic removal and in addition changes in environmental conditions such as redox, pH etc. may release the contaminant bound to different fractions, so the monitoring of environmental conditions would appear to be a priority.

VI.7 ***Economic considerations***

In the field of contaminated sites remediation is always difficult to derive reliable information on treatment costs based on lab scale studies, since too many are the elements of influence which are site specific; in general the costs depend on the volume of the soil to be decontaminated (size of area x depth of contamination) and on its characteristics, the type and concentration of contaminants. Therefore, as far as the present study is concerned, only general considerations can be derived from the data obtained.

In general, EK is considered an expensive remediation process and its application conceivable only when other process would be ineffective, for instance on soils characterized by low permeability and significant presence of clay and lime; therefore, costs for EK remediation are usually compared with those for excavation and disposal of contaminated soil as hazardous waste (Reddy and Cameselle, 2009).

The main elements of cost for an EK remediation system are energy consumption, purchase and installation of the electrodes, eventual chemicals for an enhanced process, treatment of the liquid phase (electrolytes). The EK-RB combined treatment would be characterized also by the cost for TRM supplying; to this regard, the TRM is relatively cheaper than other reactive materials such as zero-valent iron or zeolite (roughly 300 US$ vs 500 US$).

In electrokinetic treatment, costs associated with the consumption of energy are estimated to be only about 15% of the total cost whilst it is estimated that the costs of site installation and operations have the largest variability. Standard EK metal treatment systems cost little to install but require high operating costs to manage pH and extracted metal-laden wastes (Athmer, 2009). In addition possible costs associated with the recovery and disposal of the reactive material following the completion of the treatment must be added, plus cost associated with the characterization of the site, costs for security and monitoring post-operam.

Another important factor affecting overall costs is the time requirement of the process, because if there is some limitation the EK system will operate more aggressively requiring greater electrode placement densities or smaller distances between electrodes increasing costs for power consumption, whilst if time is not a primary concern the overall cost can be optimized (Athmer, 2009).

As far as the comparison object of the present study is concerned, the energy consumption, E_u (kWh/m^3), related to each of the bench-scale laboratory tests, is shown in Tables VI.21 and VI.22 and was calculated as follows:

$$E_u = \frac{1}{V_s} \int VI \ dt$$

where V_s represents the volume of treated soil (m^3), V the applied voltage (V), I the current intensity (A) and t the processing time (h). For the process keeping a constant-voltage condition the energy expenditures were related to the time integral of the current across the soil specimen (Weng et al., 2007).

In Table VI.21 is also reported the percentage of total contaminant removal, whilst the runs listed in the Table VI.22 were not characterized by significant removal efficiencies.

In general the E_u values increased when the processing time doubled from 6 to 12 days whilst the presence of the TRM RB did not affect the energy expenditure except during the run 12Cr_TRMplus where the most concentrated RB was adopted (50% wt. vs less than 12% wt. in the other runs); on the basis of the lab-scale performed on spiked soils, the higher efficiency in terms of Cr removal achieved by combining EK and TRM RB would entail a higher treatment cost. However, it has to be underlined that, in the view of this EK/RB combined treatment, if most of the mobilized contaminant is effectively trapped in the RB, the cost for the treatment of a polluted liquid phase (anolyte) would be saved: indeed, comparing the 12Cr_TRM and the 12Cr_TRMplus, this latter characterized by higher energy consumption and lower removal percentage, the anolyte treatment was avoided whilst in the 12Cr_TRM run 60.8% wt. of total Cr was found in the anodic reservoir, requiring proper treatment, the cost of which must be added. The energy consumption was also affected by the use of conditioning agents during the 2R, 3R and 5R runs.

Table VI.21 *Contaminant removal and energy cost for EK/RB treatment*

Run	**Total Cr removal (%)**	**Energy consumption (kWh/m^3)**	**Run**	**Total As removal (%)**	**Energy consumption (kWh/m^3)**
6Cr_BLK	15,37	70	6As_BLK_K	12,54	25
6Cr_TRM	40,06	69	6As_TRM_K	30,53	25
12Cr_BLK	14,36	125	12As_BLK_K	9,42	60
12Cr_TRM	86,27	143	12As_TRM_K	58,28	77
12Cr_TRMplus	60,55	434	16As_TRM_K	74,73	91

NOTE: The total contaminant (Cr/As) removal (%) is the sum of mass accumulated into the anodic/RB slice and in the anolyte.

Table VI.22 E*nergy cost for EK/RB treatment*

Run	Energy consumption (kWh/m^3)	Run	Energy consumption (kWh/m^3)
6As_BLK	80	1R	233
6As_TRM	65	2R	816
12As_BLK	172	3R	1301
12As_TRM	207	4R	558
		5R	2636

Assuming a current electricity fee in Italy of approximately € 0.15 per kilowatt hour (for industrial use), the entrapment of 60.6% wt. of total Cr would cost (relatively to energy need) about 65 €/m^3.

Unfortunately only limited data are available on the costs associated with EK remediation technology and, at the moment, there is still a lot of resistance to using this relatively unknown process: as more installations will be employed the confidence in estimate of costs will increase. Indeed laboratory studies may not provide an accurate cost estimate as compared with field pilot-scale or full-scale applications.

Just to give a general idea, it is estimated that the costs of commercial full-scale electrokinetic treatment for typical installation range from \$115 to \$400/m^3 of soil if it is contaminated with inorganic pollutants and \$90 to \$275/m^3 of soil if it is contaminated with organic pollutants with an average cost of \$200/m^3 equates to about \$90 per ton of saturated loamy soil (Athmer, 2009; Reddy and Cameselle, 2009). These estimated costs are generally less than the cost of excavation and disposal as hazardous waste.

VI.8 *Experimental electrokinetic fence and PRB runs*

First experiments were carried out in order to find out the optimal set-up and several configurations were tested before finding the best one.

The silica flour soil was not used alone because of its low permeability that did not allow the water to go through; using only grade E quartz sand the flow rate was excessive due to its high permeability. Therefore, different mixtures were tried to obtain a flow rate of about 30 – 40 ml/h and two mixtures were chosen, named soil A and soil B. As reported in the Chapter *"Materials and methods"* the soil A was 90% sand (grade E) and 10% silica flour, the soil B was 80% sand (grade E) and 20% silica flour.

A similar reasoning was undertaken in order to detect the optimal slope and hydraulic gradient. A slope of five degrees (correspondent to an hydraulic gradient of 0.09) was excessive as it caused a quick copper's breakthrough. Hence, a slope of three degrees (correspondent to an hydraulic gradient of 0.05) was chosen.

The BLANK test, carried out using the soil B, without any barrier arranged, was conducted in order to determine the breakthrough time (time taken for half of the initial contaminant concentration (500 mg/l) to reach the monitoring wells). A 40 ml/h average flow rate was measured and, as showed in Figure VI.42 (a), after around 18 hours the breakthrough was occurred. The time to take one Pore Volume (*1PV*) was 18 hours, which coincided with the breakthrough time, as showed in Figure VI.42 (b).

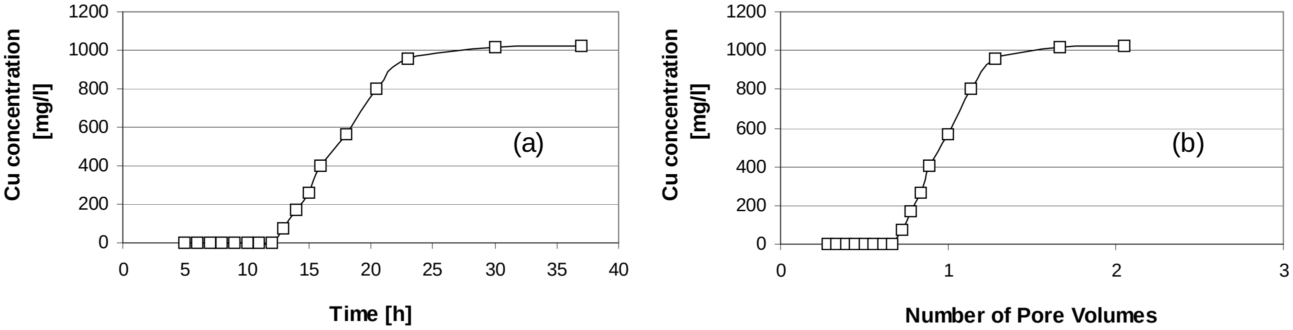


Figure VI.42 *BLANK test breakthrough curve (a) Cu concentration versus time; (b) Cu concentration versus NPV*

Following tests were conducted to look for the configuration which can ensure the best way to counteract pollutant spread due to an imposed hydraulic gradient of 0.05. The aim was to find the arrangement which can delay as possible the copper breakthrough, using the blank test result as comparison.

VI.8.1 *Electrokinetic barrier test*

Electrokinetic barrier test (EKB) was tested in order to evaluate if the electromigration and electroosmosis phenomena could oppose the diffusion of pollutant due to a hydraulic gradient of 0.09 and 0.05. The test was performed using the soil A and a constant voltage of 30 V.

The calculation about electrokinetic permeabilities and ion mobilities indicated that in most cases it should be possible to retain copper ions by a fence against advection by moderate hydraulic gradients. Indeed for preventing the movement of heavy metal cations by means of an electrokinetic barrier, the hydraulic flow velocity of groundwater through the soil (v_{Hyd}) should not be grater than the sum of the electroosmotic velocity (v_{EOF}) plus the electromigration velocity (v_{ion}), assuming diffusion is neglected:

$$v_{Hyd} < v_{ion} + v_{EOF} \qquad (1)$$

This is a simple approach which is not valid for complex situations with multiple pollutant ions, but it may be a simplified explanation valid for single ionic species.

It is possible to estimate the relative average copper ion velocities due to the electroosmotic flow (EOF) and the ion migration.

In the first test, performed using a hydraulic gradient of 0.09, the average flow rate recorded in the tank without electrodes was 250 ml/h; when the voltage was applied the flow rate was reduced to the average value of 200 ml/h. The net flow rate, taking into account the negative EOF contribution, was 50 ml/h.

By literature, the ion mobility of copper in a free solution (u) is given $5.56 \cdot 10^{-4}$ $cm^2/(V \cdot s)$. From Equation (2), the average copper ion velocity due to the electromigration is calculated to be 0.5 cm/h, taking porosity (η) as 0.48 and tortuosity (τ) as 0.35 (Acar and Alshawabkeh, 1993) whilst dV/dL = 1.5 (cathode to anode spacing of 20 cm).

$$v_{ion} = u \,(dV/dL)\, \eta\, \tau \qquad (2)$$

The velocity of copper due to the hydraulic flow (v_{Hyd}) was 3.13 cm/h [(250 ml/h)/(80cm^2)], whilst that due to the electroosmotic flow (v_{EOF}) was 2.5 cm/h [(200 ml/h)/(80cm^2)].

From Equation (1) the daily average velocity of copper is the sum of these three components (v_{Hyd} - v_{EOF} - v_{ion}) and it is equal to 1.13 cm/h. The breakthrough was therefore to be expected through 30 cm of soil at about 26.5 h, if there is no retardation, not just in agreement with that found experimentally (app. 18 h). Indeed using a hydraulic gradient of 0.09 the hydraulic flow was too fast to allow the working of the barrier for greater than this time.

For this reason following runs have been performed using a hydraulic gradient of 0.05 correspondent to a slope of 3 degrees. In this case a 30 ml/h average flow rate was measured; reducing the average hydraulic flow rate a major migration against the hydraulic gradient, from the anode to the cathode, has been observed. The copper breakthrough was detected slightly later than previous test but, however, it was quite quick, as showed in Figure VI.43 (a). The time to take one Pore Volume (*1PV*) was around 24 hours (Figure VI.43 (b)).

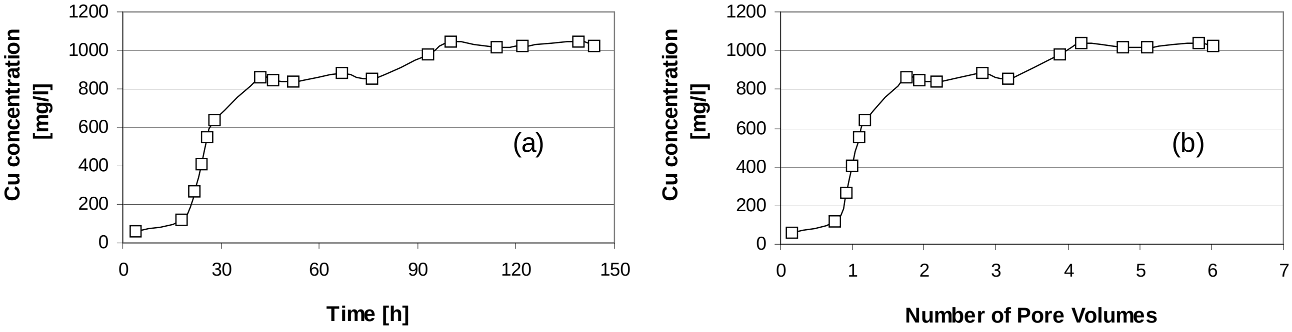


Figure VI.43 *EKB test breakthrough curve (a) Cu concentration versus time; (b) Cu concentration versus NPV*

Figure VI.44 shows the copper soil concentrations measured along the soil sample at the end of the experiment during the electrokinetic barrier test. The contaminated water flow was from the right to the left in the graph. As predicted, the greatest copper concentration values were close to the cathode decreasing towards the anode.

High concentration values at the cathode are also due to brown-black copper oxide precipitates formed in correspondence to the electrodes and collected at the end of tests. Indeed the simplest ion that copper forms in solution is the typical blue hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$, a charged complex that with hydroxide ions forms a neutral complex, insoluble in water that precipitates:

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

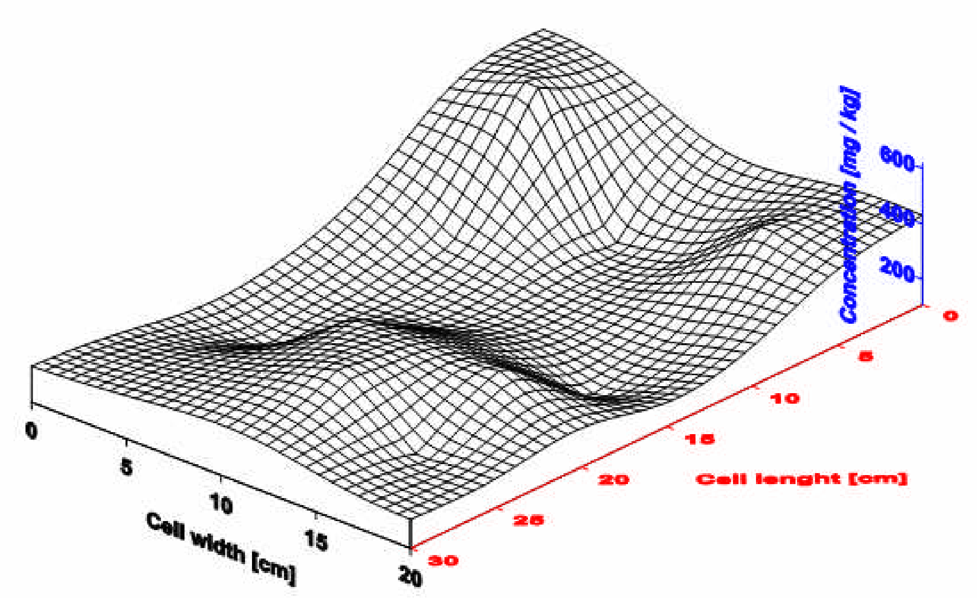


Figura VI.44 *3D plots of copper concentration in the soil after the EKB test*

The pH profile is shown in Figure VI.45, with a higher pH distribution around the cathodes (5 – 5.5) and a lower pH distribution around the anodes (4 – 4.5).

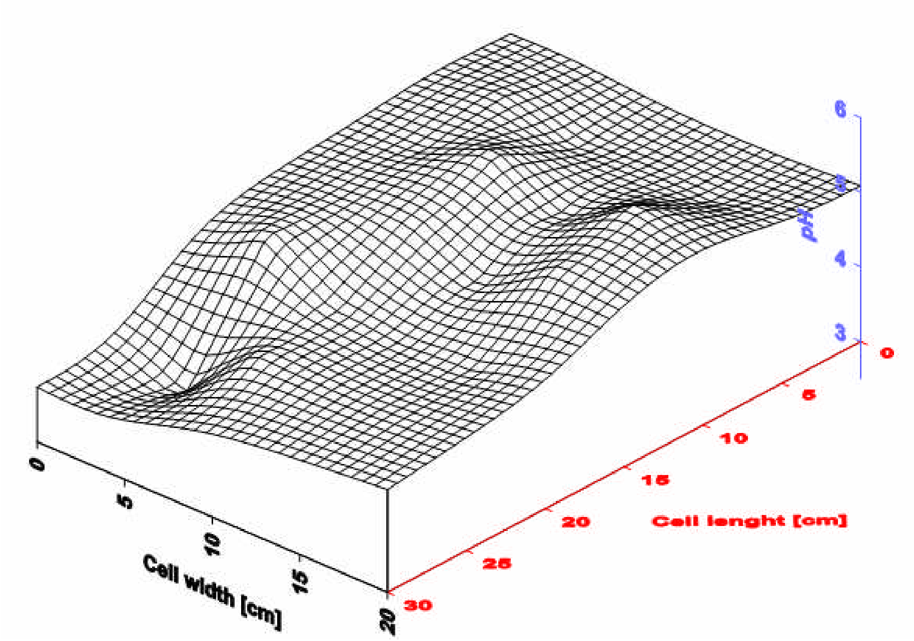


Figura VI.45 *3D plots of final pH distribution in the soil after the EKB test*

The use of electrokinetic barrier was not successful to counteract pollutant spread due to an imposed hydraulic gradient. Indeed, fence could be a possibility under conditions where the natural hydraulic flow is relatively slow, as in fine-grained soils, or, probably, an higher voltage was necessary.

VI.8.2 *Biochar PRB test*

Biochar was tested as adsorbent in a PRB test. The test was performed using soil B and a PRB characterized by 5% wt. of biochar mixed with the soil.

Setting an hydraulic gradient of 0.05, a 32.5 ml/h average flow rate was measured, whilst the time to take *1 PV* was about 22 hours. As showed in Figure VI.46, the copper breakthrough was quite quick, after around 1.3 pore volumes, correspondent to a time of around 28 hours.

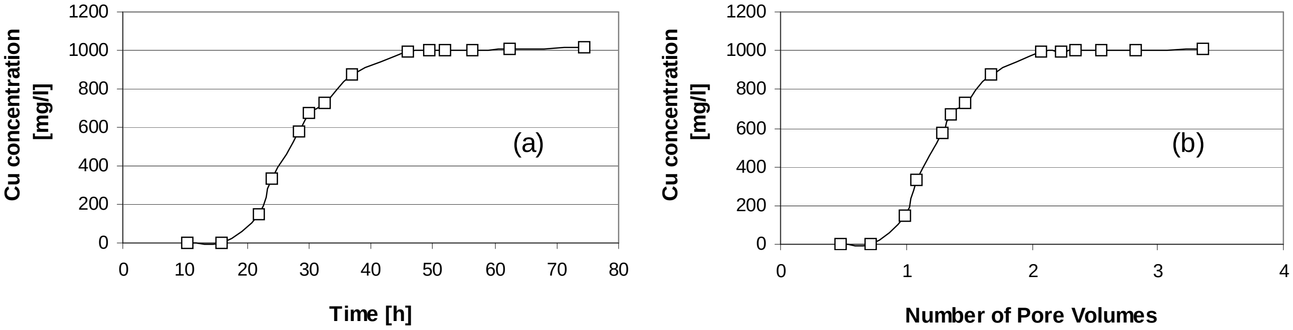


Figure VI.46 *Biochar test breakthrough curve (a) Cu concentration versus time; (b) Cu concentration versus NPV*

The copper concentration profile measured along the soil at the end of the experiment is shown in Figure VI.47. The contaminated water flow was from the right to the left in the graph.

In this test the profile is more constant along the soil after the barrier, showing high values of concentration into it and rapidly decreasing from the inlet tank to the outlet one.

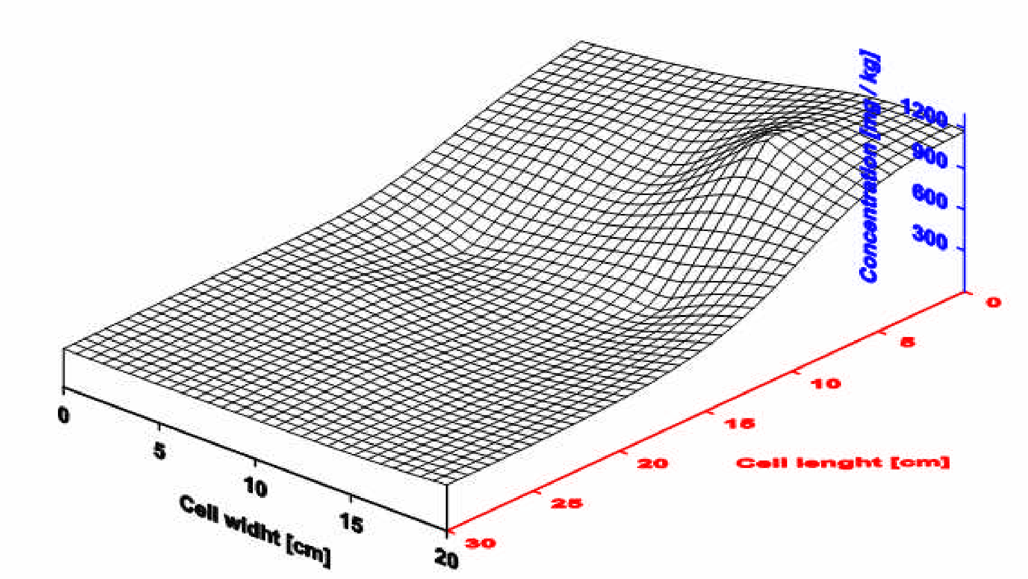


Figure VI.47 *3D plots of copper concentration in the soil after the BIOCHAR test*

The final pH distribution in the soil is shown in Figure VI.48. The pH was approximately 5.2 into the barrier, whilst the average pH value in the rest of the soil was about 4.65.

Even though the final copper concentration in the soil was promising, with a great metal accumulation in the barrier, biochar can not be considered a good copper's adsorbent because the breakthrough was practically as fast as the blank test's one.

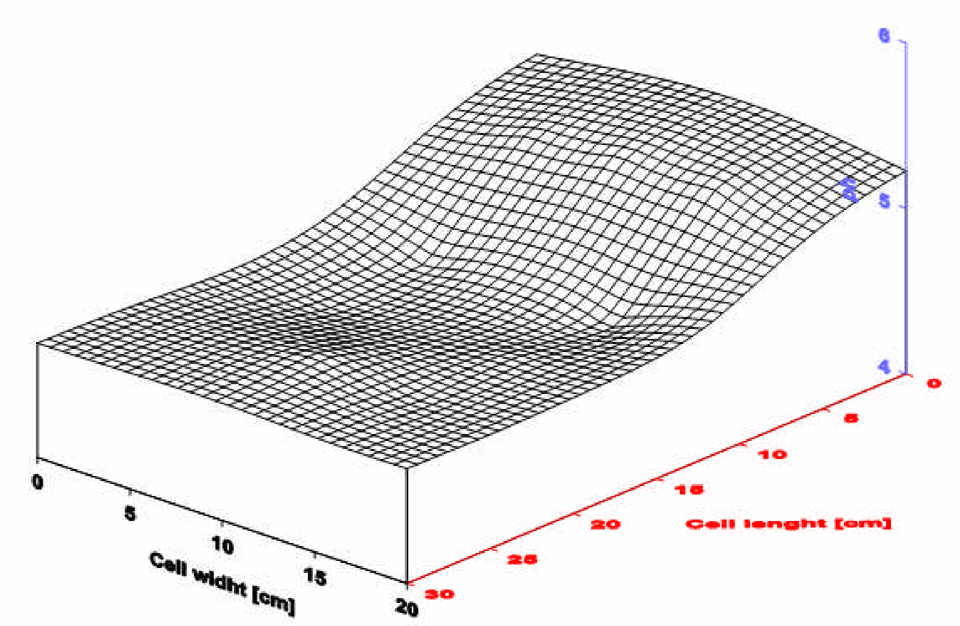


Figure VI.48 *3D plots of final pH distribution in the soil after the BIOCHAR test*

VI.8.3 *Sodium-treated granular zeolite PRB test*

The test was performed using soil A and a PRB of 25% wt. sodium-treated granular zeolite mixed with the soil.

Setting an hydraulic gradient of 0.05, an average flow rate of 35.5 ml/h was measured, whilst the time to take *1 PV* was about 20 hours. As showed in Figure VI.49, the copper breakthrough occurred after approximately 3.5 pore volumes, correspondent to a time of 68 hours. The first part of the breakthrough curve has an unexpected shape, probably due to a residual contamination. After about 2 pore volumes a normal shape of the curve was observed. Therefore, the initial trend was ignored and only the remaining part of the curve was analysed.

By comparison of this result with that blank test one in which the breakthrough occurred after 18 h, sodium-treated granular zeolite could be considered a good reactive materials because it can delay the copper solution's spread across the soil. Indeed the breakthrough occurred 3.8 times later with a flow rate slightly lower. Therefore using the normalization with respect to the number of pore volumes, the retardation factor is 3.5 because 3.5 pore volumes have to be replaced before to obtain the breakthrough of copper.

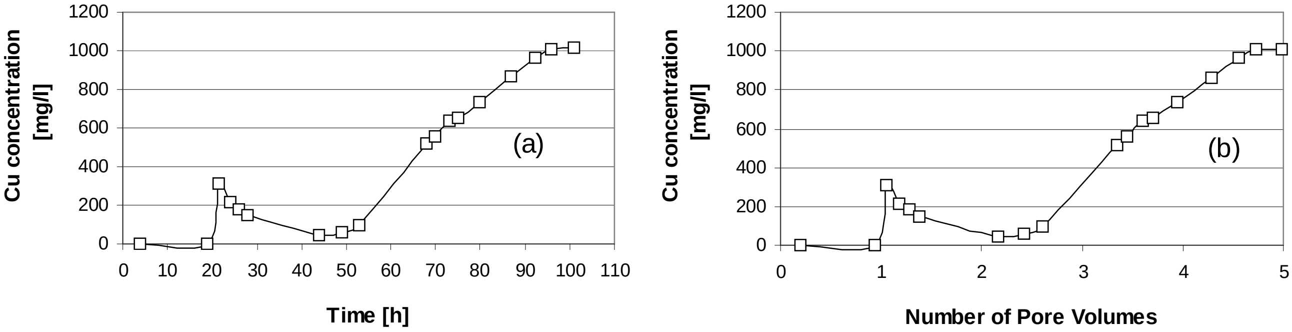


Figure VI.49 *Na-treated zeolite test breakthrough curve (a) Cu concentration versus time; (b) Cu concentration versus NPV*

The copper concentration profile evaluated in the soil at the end of the experiment is given in Figure VI.50. High values of concentration into the barrier were measured, rapidly decreasing along the soil sample from the inlet tank to the outlet one. The copper accumulation in the barrier was considerably greater than that in biochar one (4000 mg/Kg versus 900 mg/Kg).

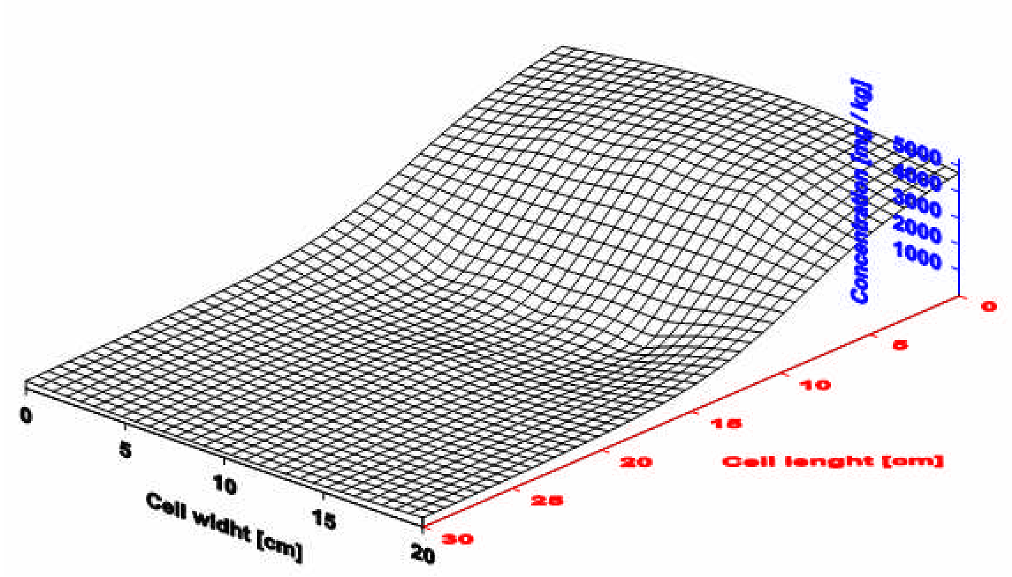


Figure VI.50 *3D plot of final copper concentrations in the soil at the end of the Na-treated zeolite PRB test*

The final pH profile in the soil at the end of the treated zeolite PRB test is shown in Figure VI.51; the pH was roughly constant in the cell with values of about 5.55 – 5.70 along the whole soil, without relevant differences between the barrier and the rest of the cell.

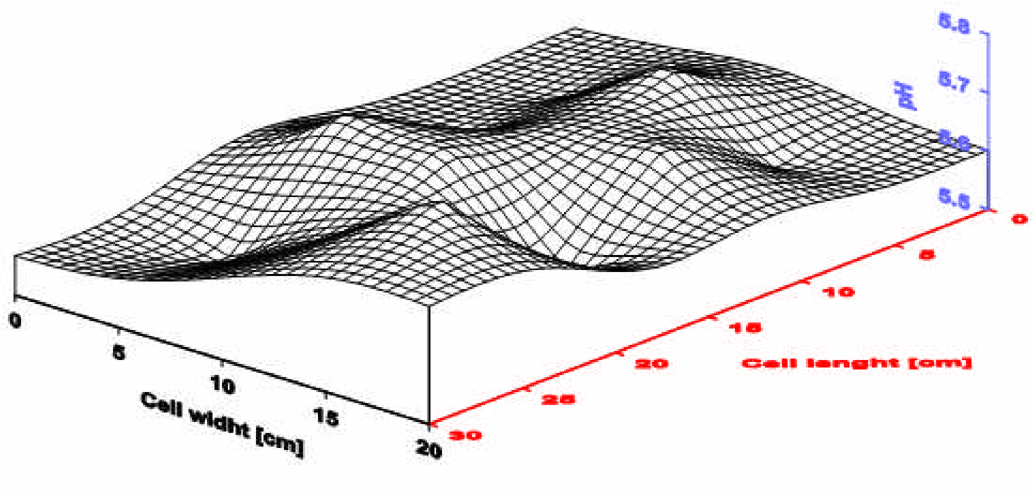


Figure VI.51 *3D plot of final pH profile in the soil after the Na-treated zeolite PRB test*

VI.8.4 *Transformed red mud PRB test*

Before starting the PRB experiment, a batch equilibrium adsorption test was performed in order to identify the experimental equilibrium isotherm for adsorption of Cu on TRM.

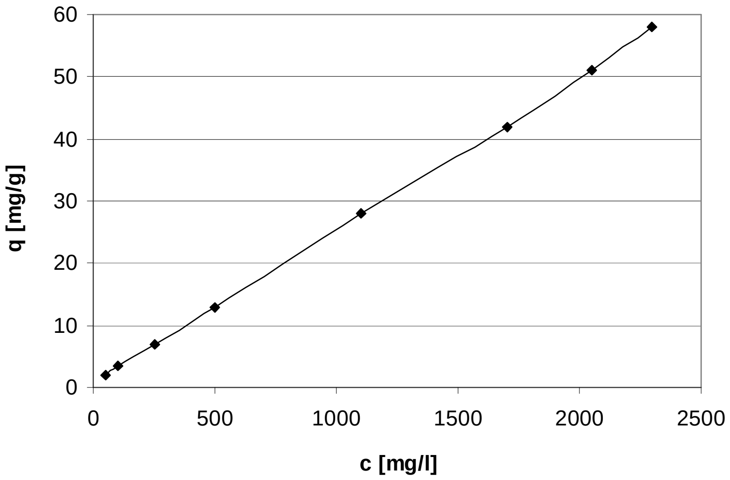


Figure VI.52 *Experimental equilibrium isotherm for adsorption of Cu on TRM*

As shown in Figure VI.52, the experimental equilibrium isotherm for adsorption of Cu on TRM is linear. The graph is not characterized by a plateaux, but the mass of copper adsorbed on TRM, q, increases as the copper's concentration of the solution, c, is made larger. Therefore the transformed red mud can be considered a good adsorbent. The distribution coefficient, K_d, of the TRM is 0.02458 l/g. It can be used to estimate the retardation factor, R_d, which represents the delay in the contaminant migration front due to linear, reversible and instantaneous adsorption to the soil solid phase. The value of R_d depends on the type (e.g., inorganic versus organic compounds) and the form (e.g., complexed versus free metals) of solute species, the type of soil and the soil constituents (e.g., organic matter, metal oxides, etc.) and the chemistry of the pore liquid. As a result, R_d can vary over several orders of magnitude. The retardation factor can be determined as follows (Shackelford, 1997):

$$R_d = 1 + \frac{\rho_d}{\theta} K_d$$

where ρ_d (g/cm^3) is the dry density of the soil, ϑ (-) is the volumetric moisture (water) content and, as told before, K_d (l/g) is the distribution coefficient.

The retardation factor R_d of the TRM was estimated about 107.

The first test was performed using soil B and a PRB of 10% wt. TRM mixed with the soil but not flow across the barrier was recorded. Decreasing the TRM percentage to 5% wt. a better result was not achieved, so the percentage was further decreased to 2.5% wt.

In this way, setting an hydraulic gradient of 0.05, a 36 ml/h average flow rate was measured, whilst the time to take *1 PV* was around 20 hours. As showed in Figure VI.53, the copper breakthrough occurred after 4 pore volumes, correspondent to a time of about 80 hours.

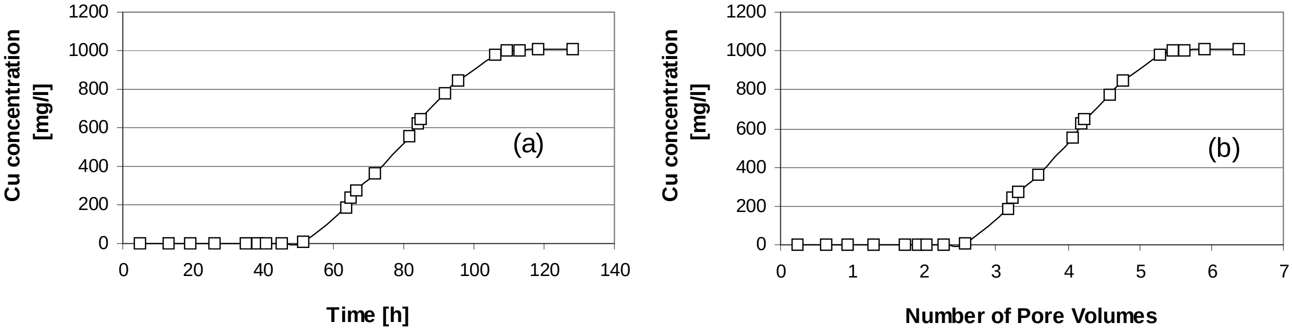


Figure VI.53 *TRM test breakthrough curve (a) Cu concentration versus time; (b) Cu concentration versus NPV*

Using a very low percentage of reactive material, the result achieved was better than that obtained with the 25% wt. sodium-treated zeolite.

In Figure VI.54 the final copper concentration profile measured at the end of the experiment is shown; the copper accumulation in the TRM barrier was remarkable, with an average concentration of 4000 mg/Kg. The final pH profile is given in Figure VI.55.

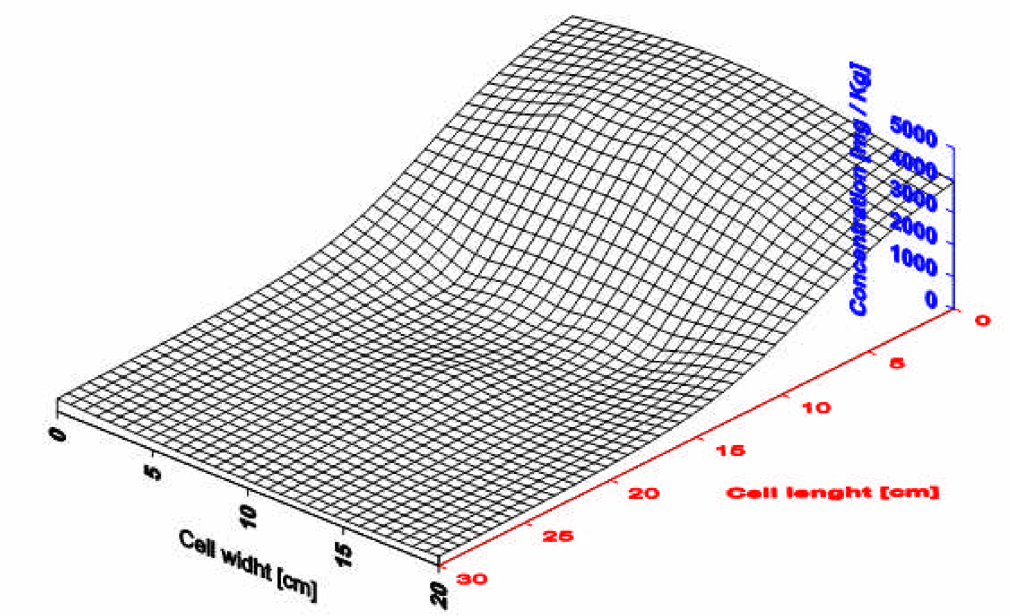


Figure VI.54 *3D plot of final copper concentration in the soil after the TRM test*

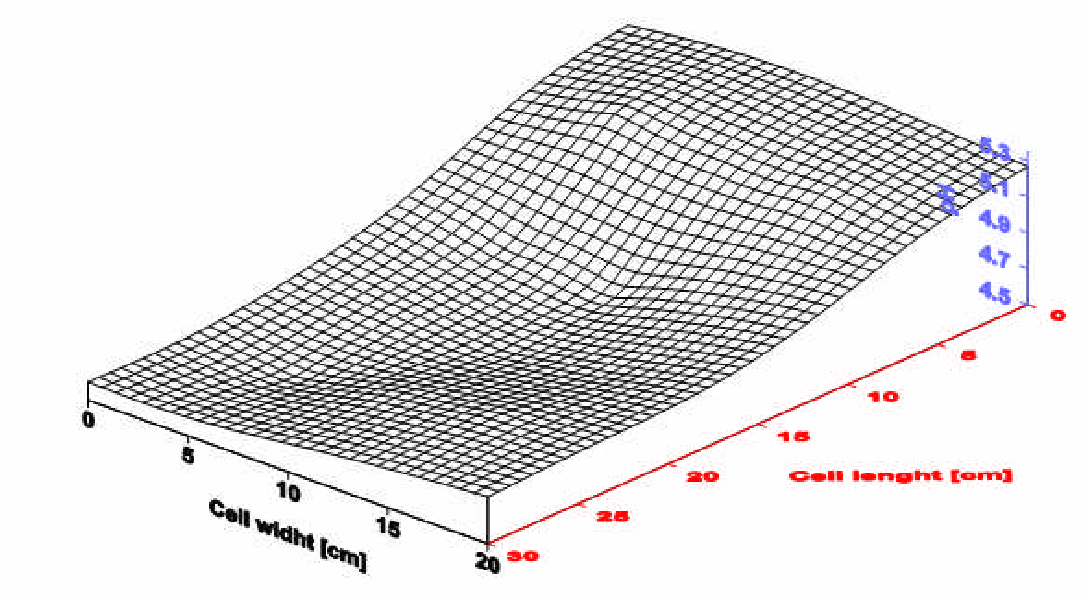


Figure VI.55 *3D plot of final pH profile in the soil after the TRM test*

The theoretical retardation factor of the TRM was 107, significantly greater than 4, the value obtained experimentally. However, the result of the PRB test was appreciable because only a 2.5% of TRM was used, instead of the 100% TRM utilized in the adsorption test.

VI.8.5 *Granular MgO PRB test*

The granular MgO PRB test was performed using soil A and a PRB of granular magnesium oxide 26% wt. mixed with the soil. Before starting, a batch equilibrium adsorption test was performed in order to assess the experimental equilibrium isotherm for adsorption of Cu on granular MgO, but the material was dissolved by the 24 hours mixing, increasing significantly the specific surface area. This result can not reproduce perfectly the conditions in the PRB test where the granular MgO used was not dissolved by the solution flow. The experimental equilibrium isotherm for adsorption of Cu on granular MgO is linear, as shown in Figure VI.56.

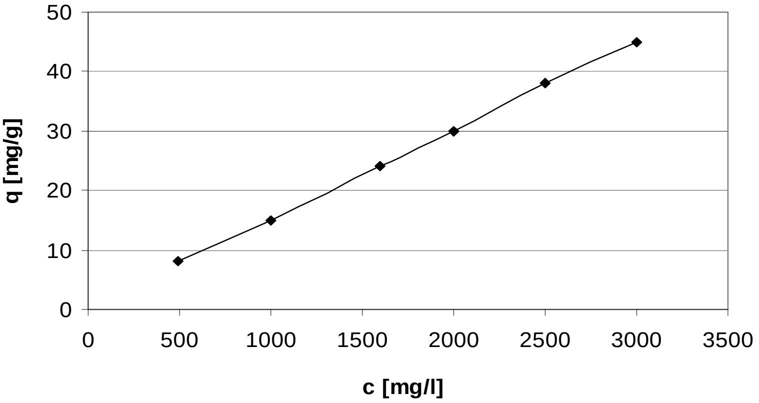


Figure VI.56 *Experimental equilibrium isotherm for adsorption of Cu on granular MgO*

The distribution coefficient K_d of the Magnesium Oxide is 0.01499 l/g while the theoretical retardation factor R_d is about 66.

Setting an hydraulic gradient of 0.05, a 24 ml/h average flow rate was measured, while the time to take *1 PV* was 30 hours. As showed in Figure VI.57 the copper breakthrough occurred after about 3.1 pore volumes, correspondent to a time of 93 hours. This result was quite good, similar to the sodium-treated granular zeolite one and slightly worse than the TRM result.

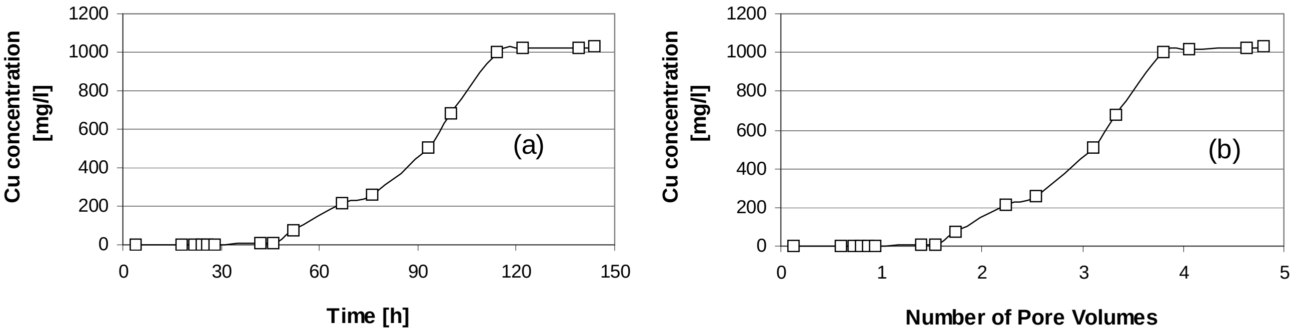


Figure VI.57 *Granular MgO test breakthrough curve (a) Cu concentration versus time; (b) Cu concentration versus NPV*

In Figure VI.58 the final copper soil concentration profile is shown (the contaminated water flow was from the right to the left in the graph). High values of concentration into the PRB that rapidly decrease from the inlet tank to the outlet one can be observed. The copper accumulation in the granular MgO barrier was considerable but slightly lower than the values measured in the treated zeolite and in the TRM barrier (3200 mg/Kg versus 4000 mg/Kg).

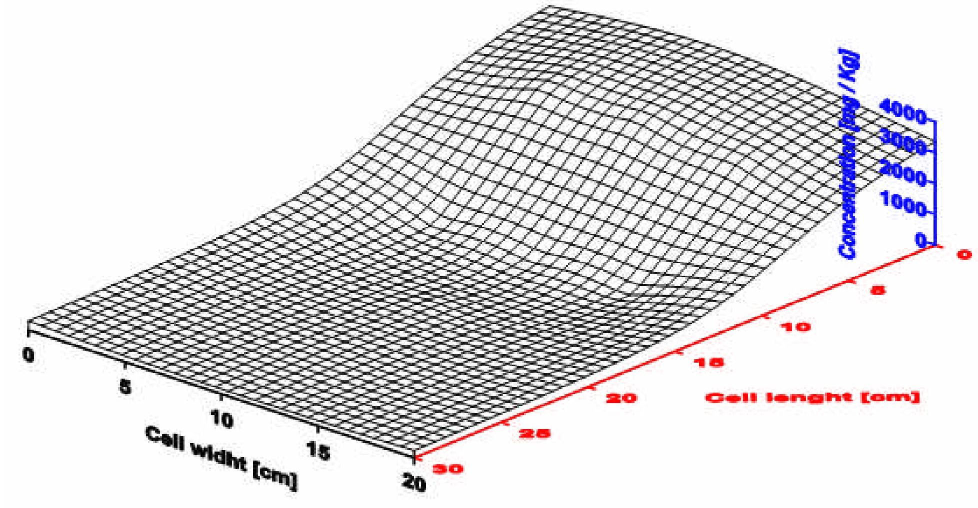


Figure VI.58 *3D plot of final copper concentration in the soil after the granular MgO PRB test*

The final pH profile shows pH values of about 9.3 into the barrier and an average pH value in the soil of about 4.6 (Figure VI.59). The pH of the barrier was influenced by the presence of Magnesium Oxide, being an alkaline material and this has certainly improved the process of adsorption of copper having a minimum solubility at pH of 8.2.

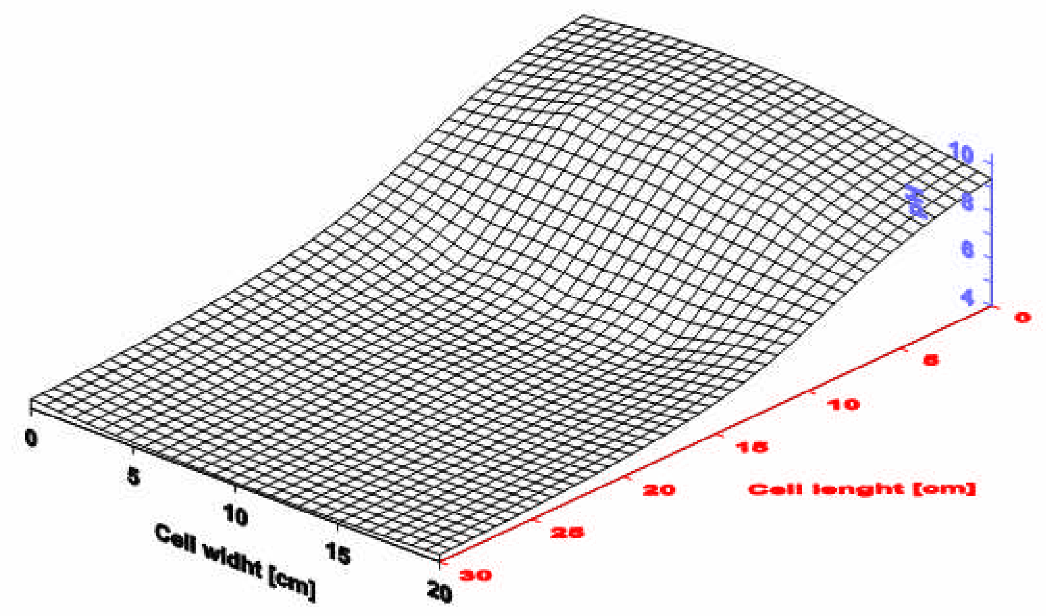


Figure VI.59 *3D plot of final pH profile in the soil after the granular MgO PRB test*

VI.8.6 *Final comparison between EKB and PRB test*

To limit the spread of copper through a soil due to an hydraulic gradient the electrokinetic fence and the PRB technology were tested. The materials needed for such barriers should be reactive (to form an insoluble solid to retain metals), permeable, durable, available and inexpensive (Cortina et al., 2003).

As shown in Figure VI.60, the electrokinetic barrier did not represent the best solution. Comparing the different adsorbent materials put into the PRB, better results were achieved using the transformed red mud.

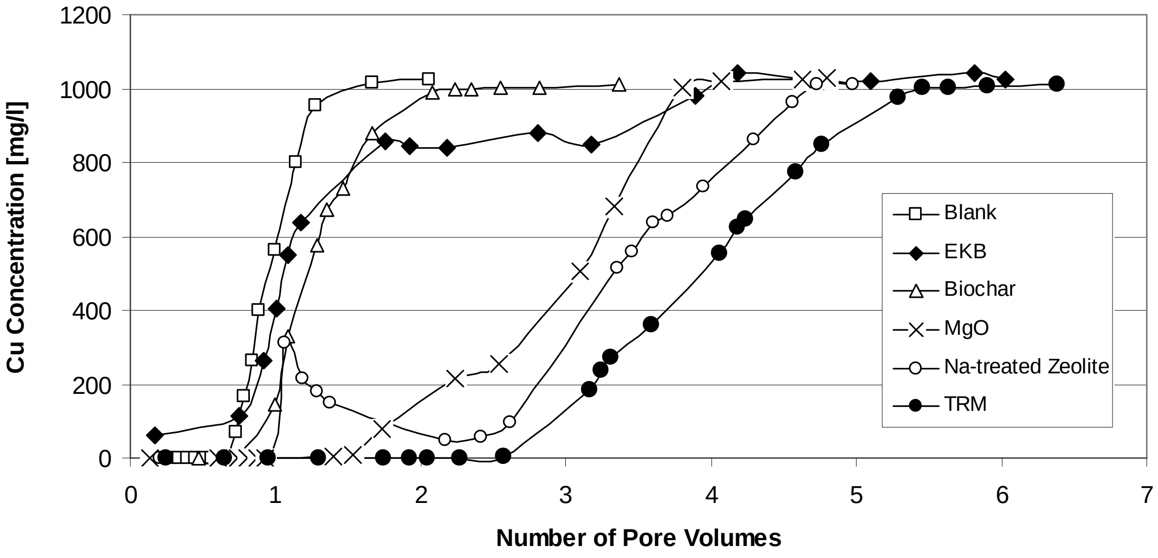


Figure VI.60 *Comparison among the breakthrough curves obtained during the experimentation*

Indeed, using only a 2.5% wt. of TRM, the most delayed breakthrough curve was obtained and the greater experimental retardation coefficient ($R_d = 4$) and distribution coefficient ($K_d = 0.02458$ l/g) were measured. Moreover, another important advantage of TRM is that red mud is a by-product of bauxite refinement for alumina production therefore, thanks to an adequate treatment, a waste can be efficiently recovered as secondary raw material. The major problem connected with TRM is due to its very low permeability which did not allow to use a great percentage of this material. Transformation of TRM in granular material in order to establish a porosity that ensured the permeability of the medium could be considered a possible solution, seeing the good results obtained with the sodium-treated granular zeolite and the granular MgO. Indeed, thanks to their granulated form, an high percentage of reactive material has been used in the PRB, obtaining delayed breakthrough curves and high retardation coefficients.

Figure VI.61 shows the average copper concentration measured in the PRB at the end of each experiment.

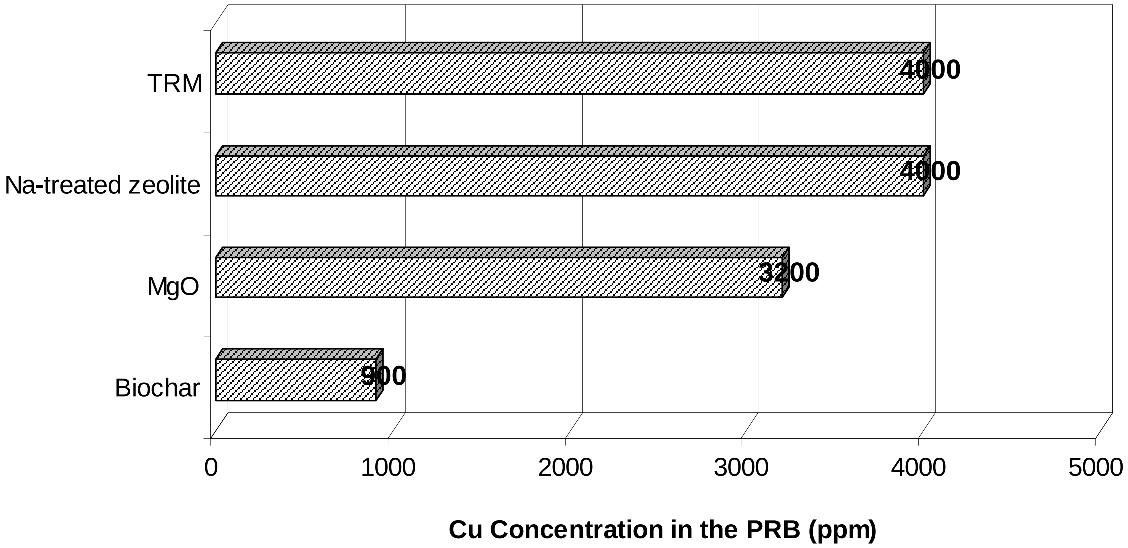


Figure VI.61 *Final copper concentration measured into the different reactive materials in PRB*

Conclusions and Recommendations

The production of waste and the release, continuous or accidental, of hazardous substances into the soil and groundwater and surface water may directly or indirectly cause an environmental contamination, clearly posing risks to human health.

A widely found source of diffuse pollution is represented by the disused mining areas due to the presence of high concentrations of heavy metals and to the large portions of land affected by mining. The abandonment of these areas and their conversion to other uses require the adoption of environmental interventions aimed at to isolate or to contain the sources of pollution, and, if it is economically or technically feasible, to ensure the remediation and recovery of polluted soils. It is estimated that in Sardinia about 70 million m^3 of abandoned metal mining waste require remediation. In this context excavation and operations of transport at great distances to apply *ex situ* treatment (most typically solidification/stabilization) and/or disposal appear inappropriate because they are too costly and because the objective is the rehabilitation of large volumes. Considering that some portions of contaminated mining areas are characterized by low permeability and that relatively small areas have a high value-added the development of *in situ* alternatives for remediation of such contaminated soils, less disruptive and, often, less costly than conventional treatment, appears of particular interest.

The potential of electrokinetic remediation technology has been successfully demonstrated in numerous studies for the remediation of heavy metal-contaminated fine grained soils; it is often applied using various enhancement techniques to improve its effectiveness and to overcome the some specific problems of the process as well as those deriving by the soil characteristics and the interactions between soil and contaminants.

A significant part of this research has been devoted to investigating the possibility of using the Transformed Red Mud (TRM) in a electrokinetics (EK) - reactive barrier (RB) combined system for the treatment of low permeability soils contaminated by arsenate and chromate.

Indeed arsenic and chromium, common soil contaminants found worldwide, are reported to be among the more difficult elements to remove by electrokinetics. Therefore the TRM RB was used with the aim of enhancing the electrokinetic removal, in particular in order to prevent the acidic conditions from developing within the soil by neutralizing the hydrogen ions generated due to the anodic water electrolysis, and of exploiting its metal immobilizing capacity. A significant advantage is that the TRM derives from red muds, an industrial waste by-product of bauxite refinement for alumina production which, thanks to an adequate treatment, can be used as reactive material; since large quantities of industrial residues are produced, their transformation into secondary raw materials for use in other processes is fundamental. Moreover the use of TRM as low-cost reactive material, over the great environmental value, should contribute to improved economics of such the proposed combined treatment and its environmental friendliness.

The electrokinetic experiments conducted on four different soils (a spiked illitic-kaolinitic soil, a spiked kaolinitic soil, a mine tailing soil and an industrial site soil) provided some useful information on the possible application of this coupled technology.

As far as concerns Cr(VI) removal from the spiked illitic-kaolinitic soil, the efficiency of the electrokinetic process was clearly enhanced by the presence of the anodic TRM RB that suppressed the formation of an acidic front, thus decreasing the adsorption capacity of the soil for Cr(VI) oxyanions, increasing the rate of electromigration towards the anode, limiting Cr(VI) reduction by ferrous iron in the soil.

The incorporated TRM RB increased Cr mobilization towards the anode: 19.4% wt. of the initial total Cr was found in the anodic chamber after 6 days of treatment in presence of the RB as compared to 8.8% wt. of the initial total Cr after 6 days without RB. The comparison between the runs carried out for 12 days again underlines that the presence of the TRM RB enhanced Cr migration towards the anode: 60.8% wt. of the initial total Cr was found in the anolyte in presence of the RB as compared to 9.1% wt. of the initial total Cr without the RB. The most concentrated of the adopted TRM RB used in 12Cr_TRMplus run was capable to entrap all the mobilized Cr(VI) before it could enter the anolyte: indeed 60.6% wt. of the initial total Cr was trapped in the anodic RB and no Cr was found in the anodic chamber anymore, thus preventing the necessity of decontamination of the anolyte.

As far as concerns As removal from the same type of soil, the enhancement of the efficiency of electromigration did not result into considerable arsenate removal and its entrapment by the TRM RB, likely due to various counteracting effects brought about by the relatively low concentration of the initially added arsenate, masking the positive effect of the TRM RB on arsenate electromigration towards the anode; indeed, being the electromigration the main mechanism of electrokinetic removal at high concentrations and the electroosmosis at lower concentrations, the different behaviour observed for As-runs with respect to the Cr-runs could has been influenced also by the lower As initial concentration (100 ppm vs 1000 ppm). Moreover, the interference with iron oxides was another reason of the low efficiency assessed while attempting As decontamination: the iron oxy-hydroxides in the soil have high affinity for arsenate in function of pH, with preferential adsorption for pH values between 4 and 7 with an optimum pH of approximately 4. Therefore arsenic seem to be more difficult to remove and further and longer tests are clearly needed.

As comparison, runs on spiked kaolinitic soil were carried out in order to overcome the interference of iron oxy-hydroxides; in this case the absence of a significant iron content in the soil allowed that 30% wt. of total As was accumulated onto the anodic RB after 6 days and 58% wt. after 12 days of treatment. The electroosmotic flow did not support As electroosmotic transport towards the cathode, but electromigration towards the anode prevailed resulting the dominant transport mechanism. In addition As was not found into the anodic chamber solution, suggesting that the RB was capable of effectively trapping the mobilized pollutant and that the treatment of an As-polluted anolyte may not be required. Increasing the treatment duration to 16 days, 75% wt. of total As was accumulated onto the anodic RB and all sections of the specimen were decontaminated, ensuring the regulatory threshold limits established for industrial sites. Although to leave the reactive barrier in situ at the end of treatment would be economical opportune, by the study of As-release from the RB the removal of the barrier would be appropriate considering that the release may change over time depending on the variability of environmental conditions of the site as pH and redox.

When the application of the EK-RB process for the remediation of natural arsenic-contaminated soils (a mine tailing soil and an industrial soil) was investigated, during all electrokinetic tests performed it has been very difficult to maintain an appropriate pH to reach the most favourable remediation conditions. The used mine tailing soil was a very acidic material and it was composed by a significant percentage of iron. Extremely high concentrations of As were found and sequential extraction confirmed that much of the As was mainly associated with the Fe, Al-oxyhydroxides, whilst the contribution of potentially mobile and surface-bound As forms was very low. Being the As species very difficult to mobilize, various electrokinetic experiments were conducted using conditioning agents in addition to the use of the anodic TRM RB. Potassium phosphate and sodium hydroxide solutions were used in an attempt to mobilise the arsenic, but any significant effect was attained. The 0.2 M sodium hydroxide solution mobilised arsenic effectively during leaching tests, but used as catholyte in the electrokinetic system (without RB) did not allow for significant migration towards the electrodes. The best result was achieved using, additionally to the 0.2 M NaOH electrolyte, the anodic TRM RB (run 5R): in this test a slight reduction of the As content, as compared to the initial one, was observed, with 3.4% wt. of the initial total As found in the anodic chamber at the end of treatment and app. 14% wt. entrapped in the TRM RB. In general, the sodium hydroxide was capable of mobilising part of the arsenic from the tailing-soil; this may be explained by the pH increase, as well as by desorption of arsenic species and partial dissolution of the arsenic-bearing minerals which made possible ionic migration; indeed the cathodic solution was viewed to become brown due to the presence of iron, as confirmed by the analysis of the electrolytes.

This research activity has thus revealed the difficulty to treat the As-contamination in soils, highlighting the complexity of As behaviour; the major challenge to overcome during the performed runs was to solubilise the contaminant. It is worth to underline that usually best results are achievable with spiked soils rather than with real contaminated ones where the soil-contaminant interactions are more complex and mobilization of As would be very difficult without extreme changes of soil conditions.

Although further investigations could be necessary for a detailed interpretation of the obtained results, in the case of As contamination considered during the present work, the presence of oxides and hydroxides of Fe and Al and their strong adsorption capacity can be identified as the main reason for the lower efficiency attained with respect to the process for the removal of Cr. Soils and, in particular, natural soils had a high iron content which binds the As, assisting its stabilisation, making remediation difficult but, in the same time, reducing the environmental risk associated with the element mobility.

In general, EK is considered an expensive remediation process and its application conceivable only when other process would be ineffective, for instance on soils characterized by low permeability and significant presence of clay and lime; therefore should be taken into account that costs for EK remediation are usually compared with those for excavation and disposal of contaminated soil as hazardous waste which are generally more expensive (Reddy and Cameselle, 2009). The EK-RB combined treatment would be characterized by the main elements of cost for an EK remediation system (energy consumption, purchase and installation of the electrodes, eventual treatment of electrolytes) and by the cost for TRM supplying, which is relatively cheaper than other reactive materials such as zero-valent iron or zeolite.

In conclusion, the results obtained allow to suggest the following considerations:

- the electrokinetic process can effectively mobilize contaminants from low permeable soils and could be used effectively to remove anionic contaminants from contaminated soil, as seen for chromium;
- hydrogen ions generated at the anode during the EK process have provided the acidity required to increase the capacity of a nearby TRM RB to adsorb oxyanions;
- the acid neutralizing TRM RB has suppressed acidification of the contaminated soil, promoting the desorption of oxyanions under the influence of the alkalinity produced at the cathode and enhancing their electromigration towards the anodic zone where the action of the TRM RB has been improved by the hydrogen ions;
- anyway more tests are needed to establish the feasibility of the use of TRM in combination with electrokinetic treatment of metal oxyanions contaminated soil; these additional tests should establish optimum conditions, stability of the exhausted adsorbent left in the soil and the economic advantage of the investigated technology with respect to comparable enhanced electrokinetic treatments;
- further mobilization and entrapment into the anodic TRM RB could be observed prolonging the treatment duration or the voltage applied; a further improvement of As removal could be attained by adopting other enhancing strategies, for example using stronger conditioning agents as sulphuric acid, aimed at the dissolution of the arsenic bearing minerals, or sodium hypoclorite in order to oxidize As(III) to As(V).

With regard to the electrokinetic fence in comparison with different permeable reactive barriers, the efficiency of electrokinetic barrier has been evaluated low, not capable of preventing the Cu contamination spreading against a hydraulic gradient of 0.09 and 0.05.

Concerning the reactive materials used in the PRB, the best results (in order of increasing efficiency) were guaranteed by the granular MgO that ensured an experimental retardation factor of around 3.1, the sodium- treated granular zeolite with a value of around 3.5 and the TRM with the best experimental retardation factor of around 4. According to the results obtained in the present research, the TRM was found to be suitable and economically feasible to immobilize contaminants. The major problem connected with the use of TRM in permeable configuration is its very low permeability which did not allow to use a greater percentage of this material because it would stop the solution's flow. Transformation of TRM in granular material in order to establish a porosity that ensured the permeability of the medium could be considered a possible solution to the problem. The results obtained are encouraging and hopefully the research into this area will be continued:

- electrokinetic barrier should be tested with lower hydraulic gradients in order to limit, for the same voltage, the influence of the hydraulic velocity, and higher voltages in order to avoid, for the same hydraulic gradient, the pollution spread;
- electrokinetic barrier could be tested in synergy with the PRB in order to add at the barrier performance also the electroosmosis and electromigration contributions, having in this way two security levels;
- different percentages of reactive material could be tested in the PRB tests and mixtures of different reactive materials (e.g., granular MgO and TRM) could be experienced in the same PRB;
- the system should be tested using other pollutants such as arsenic, zinc or lead so as to find out if similar results could be achieved;
- the system could be tested using real samples of contaminated groundwater.

References

Acar Y.B., Gale R.J., Putnam G.A, Hamed J., Wong R.L., Electrochemical processing of soils: Theory of pH gradient development by diffusion, migration, and linear convection, J. Envir. Sci. Health, A25 (1990) 687-714.

Acar Y.B., Alshawabkeh A.N., Principles of electrokinetic remediation, Environ. Sci. Technol. 27 (1993) 2638-2647.

Acar Y.B., Gale R.J., Alshawabkeh A.N., Marks R.E., Puppala S., Bricka M., Parker R., Electrokinetic remediation: Basics and technology status, J. Hazard. Mater. 40 (1995) 117-137.

Alloway B.J., Heavy Metals in Soils, New York: John Wiley & Sons, second edition (1995).

Alshawabkeh A.N., Acar Y.B., Removal of contaminants from soils by electrokinetics: a theoretical treatise, J. Environ. Sci. Health, A27 (1992) 1835-1861.

Alshawabkeh A.N., Basics and applications of electrokinetic remediation, handouts prepared for a short course, Federal University of Rio de Janeiro (2001).

Altin A., Degirmenci M., Lead (II) removal from natural soils by enhanced electrokinetic remediation, Sci. Total Environ. 337 (2005) 1-10.

Altundogan H.S., Altundogan S., Tumen F., Bildik M., Arsenic adsorption from aqueous solutions by activated red mud, Waste Manag. 22 (2002) 357–363.

Altundogan H.S., Tumen F., Removal of phosphates from aqueous solutions by using bauxite II: The activation study, J. Chem. Technol. Biot. 78 (2003) 824–833.

Amrate S., Akretche D.E., Innocent C., Seta P., Removal of Pb from a calcareous soil during EDTA-enhanced electrokinetic extraction, Sci. Total Environ. 349 (2005) 56-66.

Apak R., Guclu K., Tugut M.H., Modelling of copper(II), cadmium(II) and lead(II) adsorption on red mud, J. Coll. Interface Sci. 203 (1998) 122–130.

Apak R., Tutem E., Hugul M., Hizal J., Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Water Res. 32(2) (1998) 430–440.

APAT, Agenzia per la protezione dell’ambiente e per i servizi tecnici, Annuario dei dati ambientali, 2005-2006.

Athmer C.J., Cost estimates for electrokinetic remediation, in: Reddy K.R. and Cameselle C. (Eds.), Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater; The Minerals, Metals and Materials Soc., John Wiley, New York (2009) 583-587.

ATSDR (Agency for Toxic Substances and Disease Registry), Toxicological profile for copper, Atlanta, GA (1990).

Baek K., Kim D.H., Park S.W, Ryu B.G., Electrolyte conditioning-enhanced electrokinetic remediation of arsenic-contaminated mine tailing, J. Hazard. Mater. 161 (2009) 457-462.

Balasoiu C.F., Zagury G.J., Deschênes L., Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition, Sci Total Environ. 280 (2001) 239-255.

Bertocchi A.F., Ghiani M., Peretti R., Zucca A., Red mud and fly ash for remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn, J. Hazard. Mater. B134 (2006) 112–119.

Brown R., Bio-char production technology, Bio-char Environmental Management Science and Technology, Eds J. Lehmann and S. Joseph, Earthscan, London (2009)

Buchireddy P.R., Bricka R.M., Gent D.B., Electrokinetic remediation of wood preservative contaminated soil containing copper, chromium and arsenic, J. Hazard. Mater. 162 (2009) 490-497.

Cang L., Zhou D.M., Alshawabkeh A.N., Chen H.F., Effects of sodium hypochlorite and high buffer solution in electrokinetic soil treatment on soil chromium removal and the functional diversity of soil microbial community, J. Hazard. Mater. 142 (2007) 111-117.

Cang L., Zhou D.M., Wu D.Y., Alshawabkeh A.M., Coupling Electrokinetics with Permeable Reactive Barriers of Zero-Valent Iron for Treating a Chromium Contaminated Soil**,** Sep. Sci. Technol. 44 (2009) 2188-2202.

Cengeloglu Y., Kir E., Ersoz M., Removal of fluoride from aqueous solution by using red mud, Sep. Purif. Technol. 28 (2002) 81-86.

Chappell B.A., Brass P.S., Mewett J.R., Hall S.T., Electrokinetic remediation of arsenic contaminated soils and sediments, in: Naidu R., Smith E., Owens G., Bhattacharya P., Nadebaum P. (Eds.), Managing Arsenic in the Environment From Soil to Human Health (2006) 455-465.

Chen X.J., Shen Z.M., Yuan T., Zheng S.S., Ju B.X., Wang W.H., Enhancing electrokinetic remediation of cadmium-contaminated soils with stepwise moving anode method, J. Environ. Sci Heal A 41 (2006) 2517-2530.

Chimenos J.M., Fernandez A.I., Segarra M., Fernandez M.A., Espiell F., Utilizacion de magnesia para la estabilizacion de tierras contaminadas, Revista Tecnica Residuos 55 (2000) 69-72 (in Spanish).

Chung H.I., Kang B.H., Lead removal from contaminated marine clay by electrokinetic soil decontamination, Eng. Geol. 53 (1999) 139-150.

Chung H.I., Lee M., A new method for remedial treatment of contaminated clayey soils by electrokinetics coupled with permeable reactive barriers, Electrochim. Acta 52 (2007) 3427–3431.

Chung H.I., Kamon M., Ultrasonically enhanced electrokinetic remediation for removal of Pb and phenanthrene in contaminated soils, Eng. Geol. 77 (2005) 233-242.

Cooling D.J., Glenister D.J., Practical aspects of dry residue disposal Light Metals, Proceedings of the 121st TMS Annual Meeting, San Diego, CA, USA (1992) 25-31. Published by Minerals, Metals & Materials Soc (TMS).

Cortina J.L., Lagreca I., De Pablo J., Passive in situ remediation of metal-polluted water with caustic magnesia: evidence from column experiments, Environ. Sci. Technol. 37 (2003) 1971-1977.

Cundy A.B., Hopkinson L., Electrokinetic iron pan generation in unconsolidated sediments: implications for contaminated land remediation and soil engineering, Appl. Geochem. 20 (2005) 841-848.

Curkovic L., Cerjan-Stefanovic S., Filipan T., Metal ion exchange by natural and modified zeolites, Water Research 31 (1997) 1379-1382.

D'Aprile L., Romano E., Contaminated sites management and environmental liability in Italy: regulatory and technical aspects, ICCL Helsinki (2009).

Day S.R., O'Hannesin S.F., Marsden L., Geotechnical techniques for the construction of the reactive barriers, J. Hazard. Mater. 67 (1999) 285-297.

Decreto Legislativo (D.L.) 152/06, Part V, Annex 5 (Italian legislation on contaminated sites).

Erdem M., Altundogan H. S., Tümen F.**,** Removal of hexavalent chromium by using heat-activated bauxite, Miner. Eng. 17 (2004) 1045-1052.

European Commission. Reference document on best available techniques for management of tailings and waste-rock in mining activities, Directorate General JRC Joint Research Centre Institute for Prospective Technological Studies Sustainability in Industry, Energy and Transport, European IPPC Bureau (2004).

Faulkner D.W.S., Hopkinson L., Cundy A.B., Electrokinetic generation of reactive iron-rich barriers in wet sediments: implications for contaminated land management, Mineral. Mag. 69 (2005) 749-757.

Ferguson C.C., Assessing risks from contaminated sites: policy and practice in 16 European Countries, Land Contam. Recl. 7 (1999) 87-108.

Frau F., Ardau C., Mineralogical controls on arsenic mobility in the Baccu Locci stream catchment (Sardinia, Italy) affected by past mining. Mineral. Mag. 68 (2004) 15-30.

Frau F., Ardau C., Fanfani L., Environmental geochemistry and mineralogy of lead at the old mine area of Baccu Locci (south-east Sardinia, Italy), J. Geochem. Explor. 100 (2009) 105-115.

Garcia-Sanchez A., Alvarez-Ayuso E., Rodriguez-Martin F., Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils, Clay Miner. 37 (2002) 187–194.

Genç H., Tjell J.C., McConchie D., Schuiling O., Adsorption of arsenate from water using neutralized red mud, J. Coll. Interface Sci. 264 (2003) 327–334.

Genc-Fuhrmann H., Tjell J.C., McConchie D., Adsorption of arsenic from water using activated neutralized red mud, Environ. Sci. Technol. 38 (8) (2004) 2428 -2434.

Genc A., Chase G., Foos A., Electrokinetic removal of manganese from river sediment, Water Air Soil Poll. 197 (2009) 131–141.

Gent D.B., Bricka R.M., Alshawabkeh A.N., Larson S.L., Fabian G., Granade S., Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics, J. Hazard. Mater. 110 (2004) 53–62.

Gupta V.K., Gupta M., Sharma S., Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste, Water Res. 35 (2001) 1125–1134.

Hanahan C., McConchie D., Pohl J., Creelman R., Clark M., Stocksiek C., Chemistry of Seawater Neutralization of Bauxite Residues (Red Mud), Environ. Eng. Sci. 21(2) (2004) 125–138.

Hansen H.K., Rojo A., Testing pulsed electric fields in electroremediation of copper mine tailings, Electrochim. Acta 52 (2007) 3399-3405.

Hansen H.K., Rojo A., Ottosen L.M., Electrokinetic remediation of copper mine tailings – Implementation of bipolar electrodes, Electrochim. Acta 52 (2007) 3355-3359.

Kim C.L., Ong Y.S.K., Factors affecting EDTA extraction of lead from lead-contaminated soils, Chemosphere 51 (2003) 845-853

Kim S.O., Kim W.S., Kim K.W., Evaluation of electrokinetic remediation of arsenic-contaminated soils, Env. Geochem. Health 27 (2005) 443-453.

Ko I.W., Ahn J.S., Park Y.S., Kim K.W., Arsenic contamination of soils and sediments from tailings in the vicinity of Myungbong Au mine, Korea, Chem. Spec. Bioav. 15 (2003) 67-74.

Kumar S., Kumar R., Bandopadhyay A., Innovative methodologies for the utilisation of wastes from metallurgical and allied industries, Resour. Conserv. Recycl. 48 (2006) 301–314.

Lageman R., Wieberen P., Seffinga G., Electroreclamation: theory and practice, Chem. Ind. London 9 (1989) 585-590.

Lapointe F., Fytas K., McConchie D., Efficiency of Bauxsol™ in Permeable Reactive Barriers to Treat Acid Rock Drainage, Mine Water Environ. 25(1) (2006) 37-44.

Le Hecho I., Tellier S., Astruc M., Industrial site soils contaminated with arsenic or chromium: evaluation of the electrokinetic method, Environ. Tech. 19 (1998) 1095-1102.

Ledden C., A solar powered fence to keep out pollutants in groundwater, Fourth year under graduate project, University of Cambridge (2008).

Li Z., Yu J.W., Neretnieks I., Removal of Pb(II), Cd(II) and Cr(III) from sand by electromigration, J. Hazard. Mater. 55 (1997) 295-304.

Liu C.J., Li Y.Z., Luan Z.K., Chen Z.Y., Zhang Z.G., Jia Z.P., Adsorption removal of phosphate from aqueous solution by active red mud, J. Environ. Sci. 19 (2007) 1166–1170.

Lo I.M.C., Yang X.Y., EDTA extraction of heavy metals from different soil fractions and synthetic soils, Water, Air, Soil Pollut. 109 (1999) 219-236.

Lo Mastro R., A solar powered electrokinetic fence for keeping out heavy metal pollution, M.Phil. Thesis, University of Cagliari (2009).

Lynch R., Muntoni A., Ruggeri R. Winfield K., Preliminary tests of an electrokinetic barrier to prevent heavy metal pollution of soils, Electrochim. Acta 52 (2007) 3432–3440.

Maini G., Sharman A.K., Knowles C.J., Sunderland G., Jackman S.A., Electrokinetic remediation of metals and organics from historically contaminated soil, J. Chem. Techn. Biotechn. 75 (2000) 657-664.

Mariani M., Bemporad E., Berardi S., Marino A., Paglietti F., Methods for the analysis and remediation of contaminated sites, ISPESL - Prevention Today 4 (2008) 59-72.

Martin T.A., Ruby M.V., In situ remediation of arsenic in contaminated soils, Remediation Journal, 14 (2003) 21–32.

Masschelyn P.H., Delaune R.D., Patrick W.H. Jr., Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil, Environ. Sci. Technol. 25 (1991) 1414-1418.

McConchie D., Saenger P., Fawkes R., An environmental assessment of the use of seawater to neutralise bauxite refinery wastes, in: V. Ramachandran and C.C. Nesbitt (Eds.), Proceedings of the 2nd International Symposium On Extraction and Processing for the Treatment and Minimisation of Wastes; The Minerals, Metals and Materials Soc., Scottsdale Arizona (1996) pp. 407– 416.

Mewett J.R., Electrokinetic remediation of arsenic contaminated soil, Degree of Master of Engineering Science, Australia (2005).

Ministry for the Environment, Land and Sea, Environmental challenges – Summary of the state of the environment in Italy, G8 Environment Ministers Meeting, Siracusa (2009).

Montini M., Recent Developments Environmental Legislation, (2008).

MPAF, Ministero delle Politiche Agrarie e Territoriali, “Metodi di analisi chimica del suolo”. D.M. 13/9/1999, Supplemento Ordinario n. 185 G.U. n. 248 21/10/1999.

Mulligan C.N., Yong R.N., Gibbs B.F., Remediation technologies for metal-contaminated soils and groundwater: an evaluation, Eng. Geol. 60 (2001) 193-207.

Mureddu M., Indagini di laboratorio sulla capacità del BAUXSOL^{TM} di migliorare la rimozione del cromo da acque contaminate, M.Phil. Thesis, University of Cagliari (2006).

Narasimhan B., Ranjan S.R., Electrokinetic barrier to prevent subsurface contaminant migration: theoretical model development and validation, J. Contam. Hydrol. 42 (2000) 1–17.

Ott N., Permeable reactive barriers for inorganics, Technology Innovation Office, USEPA, Washington DC (2000).

Ottosen L.M., Hansen H.K., Bech-Nielsen G., Villumsen A., Electrodialytic remediation of an arsenic and copper polluted soil – Continuous addition of ammonia during the process, Environ. Tech. 21 (2000) 1421-1428.

Ottosen L.M., Kristensen I.V., Pedersen A.J., Hansen H.K., Villumsen A., Ribeiro A.B., Electrodialytic removal of heavy metals from different solid waste products, Sep. Sci. Techn. 38 (2003) 1269-1289.

Ottosen L.M., Hansen H.K., Jensen P.E., Fawkes R., Electrokinetic removal of heavy metals, in: Reddy K.R. and Cameselle C. (Eds.), Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater; The Minerals, Metals and Materials Soc., John Wiley, New York (2009) 97-126.

Ouellet-Plamondon C., Innovative materials for soil mix technology permeable reactive barriers, First year PhD report, University of Cambridge (2009).

Page M.M., Page C.L., Electroremediation of contaminated soils, J. Environ. Eng. 128 (2002) 208-219.

Paradis M., Duchesne J., Lamontagne A., Isabel D., Long-term neutralisation potential of red mud bauxite with brine amendment for the neutralisation of acidic mine tailings, Appl. Geochem. 22 (2007) 2326-2333.

Pierce M.L., Moore C.M., Adsorption of arsenite and arsenate on amorphous iron hydroxide, Water Res. 16 (1982) 1247–1253.

Pomes V., Fernandez A., Costarramone N., Grano B., Houi D., Fluorine migration in a soil bed submitted to an electric field: influence of electric potential on fluorine removal, Colloid Surface A 159 (1999) 481-490.

Powell R.M., Puls R.W., Permeable Reactive Subsurface Barriers for the Interception and Remediation of Chlorinated Hydrocarbon and Chromium (VI) Plumes in Ground Water, U.S. EPA Remedial Technology Fact Sheet EPA/600/F-97/008 (1997).

Powell R.M., Puls R.W., Permeable Reactive Barrier technologies for Contaminant Remediation, U.S. EPA Remedial Technology Fact Sheet EPA/600/R-98/125 (1998).

Pradhan J., Das S.N., Thakur R.S., Adsorption of Hexavalent Chromium from Aqueous Solution by Using Activated Red Mud, J. Colloid Interf. Sci. 217 (1999) 137-141. **J**

Probstein R.F., Hicks R.E., Removal of contaminants from soils by electric fields, Science 260 (1993) 498-503.

Reddy K.R., Shirani A.B., Electrokinetic remediation of metal contaminated glacial tills, Geotech. Geol. Eng. J. 15 (1997) 3-29.

Reddy K.R., Parupudi U.S., Devulapalli S.N., Xu C.Y., Effects of soil composition on the removal of chromium by electrokinetics, J. Hazard. Mater. 55 (1997) 135-158.

Reddy K.R., Chinthamreddy S., Electrokinetic remediation of heavy metal-contaminated soils under reducing environments, Waste Manag. 19 (1999) 269-282.

Reddy K.R., Chinthamreddy S., Effects of initial form of chromium on electrokinetic remediation in clays, Adv. Environ. Res. 7 (2003) 353-365.

Reddy K.R., Chinthamreddy S., Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions, J. Environ. Eng. 130 (2004) 442-455.

Reddy K.R., Saichek R.E., Enhanced electrokinetic removal of phenanthrene from clay soil by periodic electric potential, J. Environ. Sci. Heal. A 39 (2004) 1189-1212.

Reddy K.R., Cameselle C., Overview of electrokemical remediation technologies, in: Reddy K.R. and Cameselle C. (Eds.), Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater; The Minerals, Metals and Materials Soc., John Wiley, New York (2009) 3-28.

Ribeiro A.B., Villumsem A., Bech-Nielsen G., Refega A., Vieira e Silva J., Electrodialytic remediation of a soil from a wood preservation industry polluted by CCA, Proceedings of the 4th International Symposium on Wood Preservation, paper no 50101:14 (1998).

Ricart M.T., Hansen H.K., Cameselle C., Lema J.M., Electrochemical treatment of a polluted sludge: different methods and conditions for manganese removal, Sep. Sci. Techn. 39 (2005) 3679-3689.

Rohrs J., Ludwig G., Rahner D., Electrochemically induced reactions in soils - A new approach to the in-situ remediation of contaminated soils - Part 2: remediation experiments with a natural soil containing highly chlorinated hydrocarbons, Electrochim. Acta 47 (2002) 1405-1414.

Ruggeri R., Applicazione dell'elettrocinesi, PhD Thesis, University of Cagliari (2005).

Sandoval-Gonzales A., Silva-martinez S., Blass-Amador G., Ultrasound leaching and electrochemical treatment combined for lead removal soil, J. New Mater. Electrochem. Syst. 10 (2007) 195-199.

Sanjay K., Arora A., Shekhar R., Das R.P., Electroremediation of Cr(VI) contaminated soils: kinetics and energy efficiency, Colloid Surface A 222 (2003) 253-259.

Sawada A., Mori K., Tanaka S., Fukushima M., Tatsumi K., Removal of Cr(VI) from contaminated soil by electrokinetic remediation, Waste Manag. 24 (2004) 483-490.

Schwartz D. T., Buehler M. F., Christiansen D. X., Davis E. J., In-situ monitoring of electrochemical transport processes in Hanford Grout Vault Soil, J. Hazard. Mater. 55 (1997) 23-37.

Selinus O., Essentials of medical geology: impacts of the natural environment on public health, (2005).

Sharma H.D., Reddy K.R. (Eds.), Geoenvironmental engineering: site remediation, waste containment and emerging waste management technologies, published by John Wiley, New York (2004).

Smith E., Naidu R., Alston A.M., Arsenic in the Soil Environment: A Review, Adv. Agron. 64 (1998) 149-195.

Striegel J., Sanders D.A., Veenstra J.N., Treatment of Contaminated Groundwater Using Permeable Reactive Barriers**,** Environ. Geosci. 8 (2001) 258-265.

Virkutyte J., Sillanpaa M., Latostenmaa P., Electrokinetic Soil Remediation - critical overview, Sci. Total Environ. 289 (2002) 97-121.

Wang S., Mulligan C.N.. Natural attenuation processes for remediation of arsenic contaminated soils and groundwater, J. Hazard. Mater. B138 (2006) 459-470.

Weng C.H., Lin Y., Chu S.H, Yuan C., Laboratory-scale evaluation of Cr(VI) removal from clay by electrokinetics incorporated with Fe(0) barrier, Practice periodical of hazardous, toxic and radioactive waste management 10 (2006) 171-178.

Weng C.H., Lin Y., Lin T.Y., Kao C.M., Enhancement of electrokinetic remediation of hyper-Cr(VI) contaminated clay by zero-valent iron, J. Hazard. Mater. 149 (2007) 292-302.

Weng C.H., Coupled electrokinetic-permeable reactive barriers, in: Reddy K.R. and Cameselle C. (Eds.), Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater; The Minerals, Metals and Materials Soc., John Wiley, New York (2009) 483-503.

Wenzel W.W., Kirchbaumer N., Prohaska T., Stingeder G., Lombi E., Adriano D.C., Arsenic fractionation in soils using an improved sequential extraction procedure, Anal. Chim. Acta 436 (2001) 309-323.

West L.J., Stewart D.I., Effect of zeta potential on soil electrokinesis, in: Characterization, containment, remediation, and performance in environmental geotechnics, Geotechnical Special Publication 46, ASCE, New York (1995) 1535-1549.

Wieczorek S., Weigand H., Schmid M., Marb C., Electrokinetic remediation of an electroplating site: design and scale-up for an in-situ application in the unsaturated zone, Eng. Geology 77 (2005) 203-215.

Wong J.S., Hicks R.E., Probstein R.F., EDTA-enhanced electroremediation of metal contaminated soils, J. Hazard. Mater. Special edition on electrochemical decontamination of soil and water, 55 (1997).

Yeung A.T., Mitchell J.K., Coupled fluid, electrical and chemical flows in soil, Geotechnique 43 (1993) 121–134.

Yeung A.T., Hsu C., Menon R.M., EDTA-enhanced electrokinetic extraction of lead, J. Geotech. Eng. (ASCE), 122 (1996) 666-673.

Yeung A.T., Hsu C., Menon R.M., Physicochemical soil-contaminant interactions during electrokinetic extractions, J. Hazard. Mater. 55 (1997) 221-237.

Yuan C., Chiang T.S., The mechanism of arsenic removal from soil by electrokinetic process coupled with iron permeable reaction barrier, Chemosphere 67 (2007) 1533-1542.

Yuan C., Chiang T.S., Enhancement of electrokinetic remediation of arsenic spiked soil by chemical reagents, J. Hazard. Mater. 152 (2008) 309-315.

Yuan C., Hung C.H., Chen K.C., Electrokinetic remediation of arsenate spiked soil assisted by CNT-Co barrier - The effect of barrier position and processing fluid, J. Hazard. Mater. 171 (2009) 563-570.

USEPA (U.S. Environmental Protection Agency), Engineering Bulletin: In Situ Soil Flushing, EPA 540/2-91/021, Office of Research and Development, USEPA, Washington, DC (1991).

USEPA (U.S. Environmental Protection Agency), In Situ Remediation technology: Electrokinetics, EPA 542/K-94/007, Office of Research and Development, USEPA, Washington, DC (1995).

USEPA (U.S. Environmental Protection Agency), Innovative Site Remediation Design and Application, Volume 4: Stabilization/ Solidification, EPA 542-B-97-007, Office of Solid Waste and Emergency Response, USEPA, Washington, DC (1997).

USEPA (U.S. Environmental Protection Agency), Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA/600/R-98/125, Office of Research and Development, USEPA, Washington, DC (1998).

USEPA (U.S. Environmental Protection Agency), Arsenic treatment technologies for soil, waste and water, EPA-542-R-02-004, Office of Solid Waste and Emergency Response, USEPA, Washington, DC (2002).

USEPA (U.S. Environmental Protection Agency), Recent developments for in situ treatment of metal contaminated soils, EPA 542-R-97-004, Office of Solid Waste and Emergency Response, USEPA, Washington, DC (2002).

USEPA (U.S. Environmental Protection Agency), In situ treatment technologies for contaminated soil, EPA 542-F-06-013, Office of Solid Waste and Emergency Response, USEPA, Washington, DC (2006).

Zhang S., Liu C., Luan Z., Peng X., Ren H., Wang J., Arsenate removal from aqueous solutions using modified red mud, J. Hazard. Mater. 152 (2008) 486-492.

Zijlstra J.J.P., Dessì R., Peretti R., Zucca A., Treatment of percolate from metal sulfide mine tailings with a permeable reactive barrier of transformed red mud, Water Environ. Res. 82 (2010) 319-327.

Internet web sites:

www.redmud.org
www.virotec.com
www.minambiente.it
www.abandonedmines.gov
www.epa.gov
www.biochar.org
www.sciencedirect.com