
Convocatoria de Becas para Mujeres en la Ciencia L’Oreal – UNESCO - AMC

Propuesta de Investigación: Estudio de la Viabilidad Técnica para el Tratamiento Electroquímico de Desechos Radioactivos.

Responsable del Proyecto: Dra. Erika Bustos Bustos.

Monto Máximo: \$ 100,000.00 (Cien mil pesos 00/100 M.N.).

Duración de la Investigación: 1 año.

1. ESTATUS Y CONTRIBUCIÓN AL AVANCE DE LA INVESTIGACIÓN.

El proyecto del estudio de la viabilidad técnica del tratamiento electroquímico de suelo contaminado con compuestos radiactivos se sigue desarrollando con el fin de concretar una patente entre el Instituto de Investigaciones Nucleares bajo la responsabilidad de la Dra. Fabiola Monroy Guzmán, y el Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S. C. bajo la responsabilidad de la Dra. Erika Bustos Bustos.

2. RESULTADOS.

Con el apoyo de la beca L'Oreal – UNESCO – AMC se lograron los siguientes resultados (se anexan comprobantes de los productos finales, *):

1. ***“Tratamiento Electroquímico de Suelo Contaminado con Compuestos Radiactivos en Confinamiento”***. V. Valdovinos, F. Monroy – Guzmán y E. Bustos (Patente en elaboración).
2. ***“Electrochemical Treatment of Polluted Soil by Radionuclide Pollutants using Organic Solvents”***. V. Valdovinos, F. Monroy – Guzmán y E. Bustos (Artículo en elaboración).
3. ***“Treatment Methods for Radionuclides Wastes and its Electrochemical Applications”***. V. Valdovinos, F. Monroy – Guzmán and E. Bustos. InTech, 2013 (En prensa). *
4. ***“Optical Fibers to Detect Heavy Metals in Environment Generalities and Case Studies”***. Capítulo del libro “Soil Pollution”. J. A. García, D. Monzón, A. Martínez, S. Pamukcu, R. García and E. Bustos. InTech, 2014 (En prensa). *
5. ***“Characterization and Remediation of Soils and Sediments Polluted with Mercury: Occurrence, Transformations, Environmental Considerations and San Joaquin’s Sierra Gorda Case”***. Capítulo de libro “Soil Pollution”. I. Robles, J. Lakatos, P. Scharek, Z. Planck, G. Hernández, S. Solís and E. Bustos. InTech, 2014 (En prensa).

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6. **“Electrochemical Detection of Mercury Removal from Polluted Bentonite and Quartz using Different Removing Agents.”** I. Robles, Luis A. Godínez, J. Manríquez, F. Rodríguez, A. Rodríguez and E. Bustos. In Tech, 2014 (En prensa). *
7. **“Evaluación de Condiciones Electroquímicas para el Tratamiento de Líquidos Orgánicos Radiactivos Adsorbidos en Suelo”.** V. Valdovinos, F. Monroy - Guzmán y E. Bustos. XXIII Congreso Técnico Científico ININ - SUTIN. El Instituto Nacional de Investigaciones Nucleares y el Sindicato Único de Trabajadores de la Industria Nuclear en Toluca, Edo. De Méx., del 4 al 6 de diciembre del 2013 (Poster). *
8. **“Estudio de la Viabilidad Técnica para el Tratamiento Electroquímico de Desechos Radiactivos”.** Tesis para obtener el grado de Maestra en Ingeniería Ambiental, por parte de la Ing. Quím. Viridiana Valdovinos García. De noviembre 2012 a septiembre 2014. *

3. APLICACIÓN DE LA BECA.

Con el apoyo de la beca L’Oreal – UNESCO – AMC se pagaron inscripciones a actividades académicas, se adquirió material para continuar con nuestras actividades científicas en este proyecto, así como se pagaron viáticos para viajar de CIDETEQ al ININ y efectuar el proyecto:

CONCEPTO	MONTO
Cuotas de inscripción.	\$ 14,441.28
Materiales de consumo.	\$ 16,035.18
Viáticos.	\$ 69,523.54
TOTAL	\$ 100,000.00

Treatment Methods for Radionuclides Wastes and Its Electrochemical Applications

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1. INTRODUCTION.

There are many uses of radioactive materials which improve or facilitate human activities or quality of life of people. These uses are given in different fields of technology, ranging from power generation to supply entire cities or areas, to medical and industrial uses, even the smoke detectors in buildings. All these applications generate radioactive waste that may represent risks to the environment or to human beings, but it is necessary to have special attention to the management of radioactive waste.

In this chapter there are information about the generalities of radioactive wastes, such as its definition, origin, classification and stages of radioactive waste management. In addition, there are information about the current state of research and technologies which have been proposed for the treatment of radioactive waste, with their advantages and disadvantages, in special case of the electrochemical techniques to treat radioactive waste with theoretical considerations and cases of study. At the end of this chapter, there is information about the risk assessment and development of future strategies.

2. RADIOACTIVE WASTE.

2.1. ORIGIN OF RADIOACTIVE WASTE.

Radioactive waste are created from all activities that radioactive materials are used, either as part of the process or the use of such materials as a constituent of equipment or instruments that allow the realization of a practice. Due to large differences in the characteristics of the waste generated in the different areas and to a better understanding of these origins, is convenient to differentiate the activities coming from nuclear fuel cycle of applications coming from medical, research activities and industrial uses (Radiation Safety General Regulations, 1988; Méndez de Vigo, 2000).

2.2. CLASSIFICATION OF RADIOACTIVE WASTES.

Classification of radioactive waste is in order of any stage from its origin just to their collection, segregation, treatment, conditioning, storage, transportation and final disposal. In this case, in the Figure 1 is the physical classification of radioactive waste (IAEA, 1970 and 1994).

ACTIVITY	HALF-LIVE	SOURCES	FORM		
LOW LEVEL WASTE	VERY SHORT LIVE < 100 days	SEALED SOURCES	SOLID <table border="1"> <tr><td>COMPACTIBLE</td></tr> <tr><td>NON-COMPACTIBLE</td></tr> </table>	COMPACTIBLE	NON-COMPACTIBLE
COMPACTIBLE					
NON-COMPACTIBLE					
INTERMEDIATE LEVEL WASTE	SHORT LIVE < 30 years	OPEN SOURCES	LIQUID <table border="1"> <tr><td>AQUEOUS</td></tr> <tr><td>ORGANIC</td></tr> </table>	AQUEOUS	ORGANIC
AQUEOUS					
ORGANIC					
HIGH LEVEL WASTE	LONG LIVE >30 years	BIOLOGICAL			

Figure 1. Classification of radioactive waste (own creation).

Quantitative values of allowable activity content for each significant radionuclide will be specified on the basis of safety assessments for individual disposal sites, and the radiological classification of radioactive waste is (IAEA, 2009):

- **Exempt waste (EW):** Waste that meets the criteria for clearance, exemption or exclusion from regulatory control for radiation protection purposes (IAEA, 2004).
- **Very short lived waste (VSLW):** waste that can be stored for decay over a limited period of up to a few years and subsequently cleared from regulatory control according to arrangements approved by the regulatory body, for uncontrolled disposal, use or discharge. This class includes waste containing primary radionuclides with very short half-lives often used for research and medical purposes.
- **Very low level waste (VLLW):** Waste that does not necessary meet the criteria of EW, but that does not need a high level of containment and isolation and, therefore, is suitable for disposal in near surface landfill type facilities with limited regulatory control. Such landfill type facilities may also contain other hazardous waste. Typical waste in this class includes soil and rubble with low levels of activity concentration. Concentrations of longer lived radionuclides in VLLW are generally very limited.
- **Low level waste (LLW):** Waste that is above clearance levels, but with limited amounts of long lived radionuclides. Such waste requires robust isolation and containment for periods of up to a few hundred years and is suitable for disposal in engineered near surface facilities. This class covers a very broad range of waste. LLW may include short lived radionuclides at higher levels of activity concentration, and also long lived radionuclides, but only at relatively low levels of activity concentration.
- **Intermediate level waste (ILW):** Waste that because of its content, particularly of long lived radionuclides, requires a greater degree of containment and isolation that provided by near surface disposal. However, ILW needs no provision, or only limited provision, for heat dissipation during its storage and disposal. ILW may contain long lived radionuclides, in particular, alpha emitting radionuclides that will not decay to a level of activity concentration acceptable for near surface disposal during the time for which institutional controls can be relied upon. Therefore, waste in this class requires disposal at greater depths, of the order of tens of meters to a few hundred meters.
- **High level waste (HLW):** Waste with levels of activity concentration high enough to generate significant quantities of heat by the radioactive decay process or waste with large amounts of long lived radionuclides that need to be considered in the design of a disposal facility for such waste. Disposal in deep, stable geological formations usually several hundred meters or more below the surface is generally recognized option for disposal of HLW.

2.3. MANAGEMENT OF RADIOACTIVE WASTE.

The ultimate goal of waste management lies in its restraint and seclusion of the human environment, for a period of time and under conditions such that any release of radionuclides does not pose unacceptable radiological risk to people or the environment. Management should ensure that all charges are minimal for future generations.

A responsible management of radioactive waste requires the implementation of measures aimed at protecting human health and the environment. The basic steps for effective management of radioactive waste are part of a global system, ranging from waste generation to final disposal are: minimization of radioactive waste, pretreatment, characterization, treatment, conditioning, transport, storage and disposal (IAEA, 1970; Figure 2).

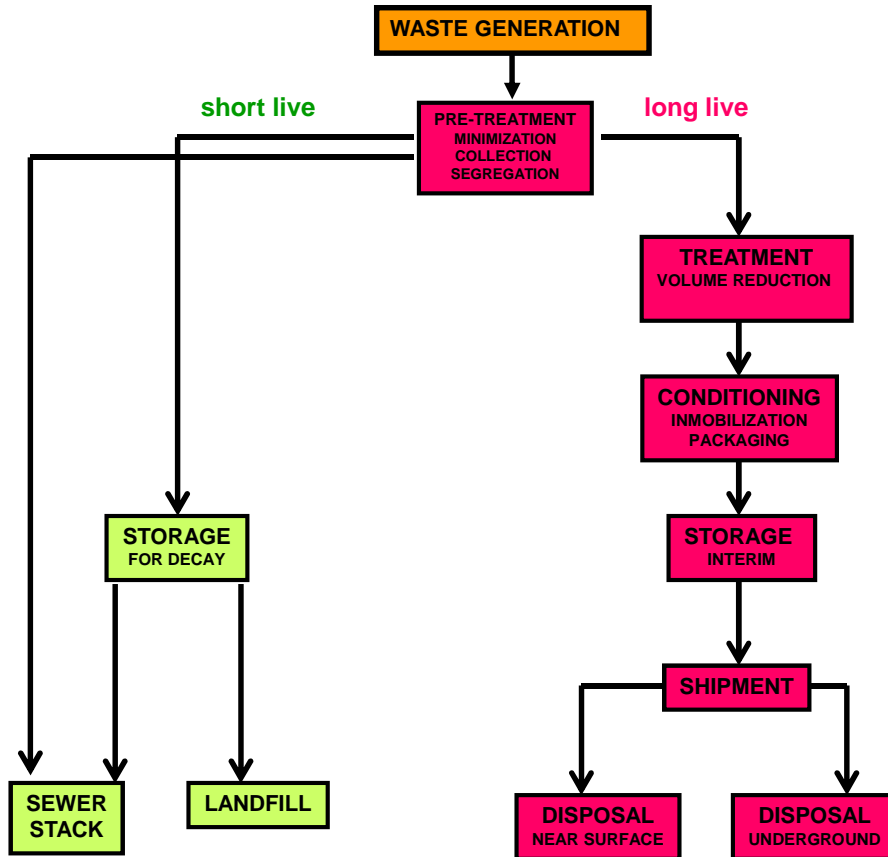


Figure 2. Steps for managing radioactive wastes (IAEA, 2001).

A management system should be applied in all steps of radioactive waste management, in order to ensure that activities, facilities, equipment and waste products in meeting the overall safety, health, environmental, security, quality and economic requirements, with safety and environmental protection being of primary importance (IAEA-2008, IAEA 2006a, 2006b).

Management system has to contain a description of the processes and supporting information that explain how work is to be prepared, reviewed, carried out, recorded, assessed and improved. In the design of work processes, a detailed sequence of steps in the activities for pretreatment, treatment, conditioning and disposal wastes should be considered, such as: (i) characterization of waste at each step in the overall waste management program, (ii) analytical methods such as sampling protocols for waste characterization or process control; (iii) monitoring of discharges; (iv) monitoring for clearance purposes; (v) non-destructive examination and testing; (vi) heat treatment, (vii) use of special handling tools and techniques, protective clothing or facilities for radiation protection, etc.

Identification of items should be established and documented on the basis of the importance to safety and environmental protection or waste isolation. Records shall specify: (a) the origin of the waste and the processes that generated it; (b) pretreatment of the waste; (c) clearance of the waste; (d) discharge of the waste; (e) characterization of the waste; (f) treatment of the waste; (g) design of the containers and/or packages and of equipment, structures, systems and components for the pretreatment, treatment of the waste.

Additionally, assessments must perform on work processes used in the waste management. Inspections and measurements have to be performed and the associated records maintained. Consequently, controls to activities, facilities, equipment and waste products will have to be designed, considering factors such as: (a) the quantities and potential hazards (radiological and non-radiological, for example chemical) of the waste, and the necessary degree of isolation; (b) the dispersibility and mobility of the waste forms involved and the necessary degree of containment; (c) the interval before disposal; (d) experience with, and maturity of, the technology and the potential for future advances; (e) the reliability of equipment and its function in relation to safety and environmental protection; (f) the complexity and degree of standardization of the activities; (g) the novelty and maturity of the activities; (h) ease of operation, maintenance of equipment and eventual decommissioning of the facility, etc.

Quality assurance requirements should be established for all phases of the waste management process to ensure that each waste is correctly processed and the final waste form has the required properties. This requires quality assurance parameters to be specified. Performance data must be documented for each parameter in order to demonstrate compliance. The quality assurance program should cover the following aspects: (1) waste characterization, (2) waste management process specification, (3) processing conditions, (4) product specification and (5) storage or disposal (HSEEA 2007; IAEA 2008, IAEA 2006).

2.4 SAFETY GUIDE.

Safety is a top priority in radioactive waste management, because of this, the purpose of this section is to present a brief guideline of recommended procedures for working with radioactive wastes. The safety aspects and environmental protection which need to be considered in the handling and processing of radioactive wastes are mainly associated with: flammability, toxicity, explosion and radioactivity.

Some of the most important aspects to consider regarding safety and environmental protection in the radioactive waste management are (IAEA 2008, IAEA 2006a,2006b):

- (1) The handling, processing and storage radioactive wastes require a permit which is authorized by a local regulatory agency.
- (2) The wastes must be adequately characterized; chemically, physically, and radiological as a precursor to waste management. The composition of waste should be known with sufficient accuracy that nuclear and conventional safety and environmental protection are not compromised. Toxic or hazardous constituents should be characterized by analytical means or from knowledge of the processes, so that hazards associated with treatment methods of waste can be identified. The reachability of radionuclides, toxic materials and the generation rates for volatile organic compounds or powders and other hazardous gases should be determined. It is important to know the chemical stability of radioactive waste: flammability, corrosively, reactivity, pyrophoricity, rapid oxidation promotion, biodegradability and the chemically incompatible waste forms should be carefully controlled. The amount of mobilizing agents such as chelating compounds, particularly stable ones, should be kept to a minimum. Waste containing hazardous constituents that are mobile in the environment, or constituents that enhance the mobility of radionuclides should avoid.
- (3) Several possible process options have to be identified for treating radioactive wastes and before selecting it should include a safety analyses. To prefer processes the cheapest and simplest to procure and operate. The best practical environmental options should be selected, with radiation doses and discharges as low as reasonably achievable (ALARA).
- (4) Radioactive liquid and gaseous discharges should be as low as reasonably achievable (ALARA) and meet regulatory and environmental restrictions.
- (5) It is suggested that cheap simple structures will be adequate for installation.
- (6) Personnel protection should be used in installation: protective clothing, rubber gloves, face mask, visors and personal dosimeters.
- (7) It is necessary to assess the radiation exposure of the operators on the site and to estimate the frequency and consequences of possible accidents related to the facility and the materials which it handles;
- (8) The waste processing area must to have suitable fire protection systems, adequate ventilation, and for the waste contains liquids a collection sump.
- (9) To ensure that radiation exposure to the workforce is as low as reasonably achievable (ALARA).
- (10) It is recommended having a central waste management facility.
- (11) Details of the safety methodology will be given in a planned technical document.

3. TREATMENT OF RADIOACTIVE WASTE.

The aim of the radioactive waste treatment is to minimize the volume of waste requiring management. Treatment process selection for waste depends upon its radiological and physicochemical properties and the quantity (IAEA, 2001; Adenot et al, 2005; Chang, 2001). The objective of this section is to provide a brief overview of usually techniques applied for the treatment of radioactive waste as Figure 3 shows.

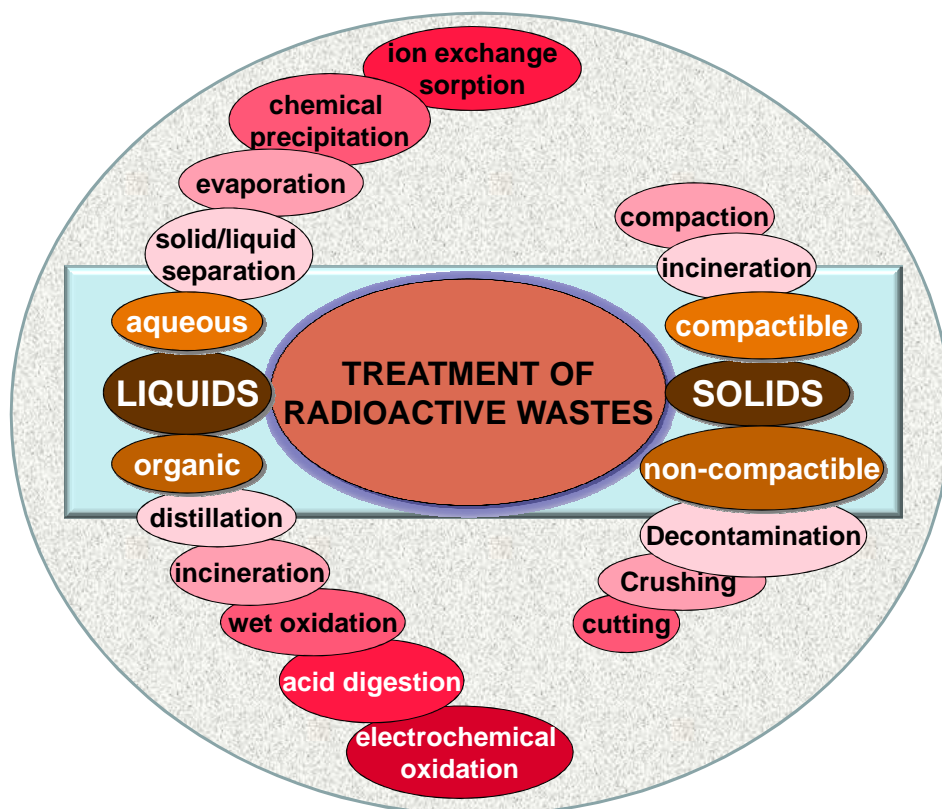


Figure 3. Classification of the treatment process applied to radioactive wastes (authors own creation).

3.1. TREATMENT OF AQUEOUS WASTE.

The processes available for treating aqueous radioactive waste are mainly: ion exchange/sorption, chemical precipitation, evaporation or ultrafiltration/reverse osmosis. However, liquid containing suspended matter must be treated to remove the particulates before primary treatment or after it. Sedimentation, decantation, filtration or centrifugation are treatments used commonly to clear the effluent wastes or to remove miscellaneous debris or insoluble particles (IAEA, 2001; Adenot et al, 2005; Abdel et al, 2011).

3.1.1. CHEMICAL PRECIPITATION.

Chemical precipitation processes are regularly used for removing radioactivity from low and intermediate level aqueous wastes at fuel reprocessing facilities, research laboratories and power stations. Precipitation processes are greatly versatile, relatively low investment and operational costs; and may treat from large volumes of liquid effluents containing relatively low concentrations of active species to those containing large amounts of particulates or high concentrations of inactive salts. However, in some cases, a pretreatment stage,

such as oxidization of organic contaminants, decomposition of complexed species, pH adjustment, change of the valency state or adjust the ionic species, should be applied prior to the formation of precipitate in order to improve the process. Radionuclides can be removed by precipitation, co-precipitation with a carrier or sorption on to particulates present in the waste (IAEA, 2001; Adenot et al, 2005).

3.1.2. ION EXCHANGE/SORPTION.

Ion exchange methods have extensive applications to remove soluble radionuclides from liquid waste produced in nuclear fuel cycle operations, radioisotope production and research facilities. It is very effective at transferring the radioactive content of a large volume of liquid into a small volume of solid.

Ion exchange process involves the replacement of cations or anions between an insoluble solid matrix containing ionizable polar groups and a liquid solution. When the ionic groups are negatives the exchange will involve cations and when they are positively charged they involve anions. The process is selective, stoichiometric and, as a rule, reversible; therefore ion exchangers can be "regenerated" and radioactive liquid waste recovered with high activity content or if the exchangers become "exhausted" they are removed and treated as radioactive wastes.

A wide range of materials is available for the ion exchange treatment of radioactive liquids: a) natural ion exchangers (clays, zeolites, cellulose, charcoals, collagen) and b) synthetic materials such as zeolites, hydrous oxide gels of metals or organic resins formed by highly polymerized cross-linked hydrocarbons containing ionic groups (sulfonic acid, carboxylic acid, amino groups, etc.).

Ion exchange processes can be operated in batch or continuous modes and if the wastes contain high concentrations of salts, suspended solids, organic contaminants or the radionuclide ionic form not suitable, the liquid wastes will have to be pre-treated before exchange process (IAEA, 2001 and 2002; Adenot et al, 2005).

3.1.3. EVAPORATION.

Evaporation process is effective for concentrating or removing salts, heavy metals and a variety of hazardous materials from waste effluent, reducing large volumes of liquid wastes with high factor decontaminations. The process is commonly used for the treatment of high, intermediate and low level waste effluents; in particular for the treatment of small volumes of highly active effluents and may be carried out through the use of commercially available evaporation equipment. However, evaporation has some important limitations: unsuitable for waste effluents containing large concentrations of inactive salts, expensive because its large energy requirement and the presence of some organic compounds can produce explosions during evaporation (IAEA, 2001; Adenot et al, 2005).

3.2. TREATMENT OF RADIOACTIVE ORGANIC LIQUID.

Liquid scintillation, solvents, oils and diverse biological fluids, generated in nuclear research centers, medical centers or industries are considered as radioactive organic liquid wastes. These wastes may present radioactive and chemical or biochemical hazards requiring treatments to remove or destroy chemically or biochemically hazardous components. The objective is to reduce the volume of radioactive waste which requires storage, transport, conditioning and land disposal, eliminating the organic components to enhance compatibility of the treated waste with secondary conditioning processes.

Processes such as incineration, wet oxidation, acid digestion, electrochemical oxidation and distillation, can be applied for treating radioactive organic liquid (IAEA, 1992 and 2001).

3.2.1. INCINERATION.

Incineration is used for reduction of solid and liquid radioactive waste volume, downscaling land requirements for disposal. Incineration combusts or oxidizes wastes at high temperatures, generating as end products of the complete incineration: CO₂, H₂O, SO₂, NO, and HCl gases. Emission control equipments for particulates, SO₂, NO_x and products of incomplete oxidation are needed to control emissions of regulated air pollutants.

The disadvantages of radioactive waste treatment with incineration are: off-gas filtering system are required to control radioactive discharges, thickening and dewatering wastes pretreatment may be required, is not economical for small solid waste plants and secondary waste volumes may be large (Chang, 2001; IAEA, 1992, 2001 and 2006; NEA, 1999).

3.2.2. WET OXIDATION.

The organic components of radioactive wastes such as ion exchange resins, foams, cellulosic waste and liquid scintillation can be transformed, degraded, or immobilized using wet oxidation.

Wet oxidation remedial process involves injecting an oxidizing agent, such as hydrogen peroxide, activated sodium persulfate, ozone, Fenton's Reagent (hydrogen peroxide with an iron catalyst) or other oxidant into the subsurface to destroy organic compounds.

The complete mineralization of carbon-based compound wastes by most chemical oxidizers produces carbon dioxide, water, and oxygen as well as minor concentrations of nontoxic ions, salts, and acids. Wet oxidation is thus a process analogous to incineration, with the advantage of using low temperatures (Twissel and Holt, 1996; IAEA, 1992; Chang, 2001).

3.2.3. ACID DIGESTION.

Acid digestion is an oxidative destruction technology for some liquid organic wastes (hexane, TBP) and organic constituents of mixed waste such as cellulose (paper), polyethylene, latex rubber, Tyvek™, neoprene, polyvinylchloride, polystyrene ion exchange resins, filters, plastics, and/or chlorinated cutting oils organic, that may reduce the waste volume of 20 to 100 times. Acid digestion process uses a mixed of nitric acid in a phosphoric acid carrier solution at temperatures below 200°C and at atmospheric or moderate pressures (< 20 psig). The principal organic portion of the waste is broken down and mineralized by the acid solution producing: inorganic constituents in solution, which can be immobilized easily in a glass or ceramic, and gases (CO₂, CO, O₂ and NO_x) that can be treated in an off-gas scrubbing system, to convert NO_x to reusable nitric acid (Report OST, 1999; IAEA, 1992 and 2001; Adenot et al, 2005).

3.2.4. DISTILLATION.

Distillation is a radioactive waste volume reduction technique used for pretreating liquid scintillation and miscellaneous solvent waste in conventional equipment. The process is simple, known, and cost effective if the valuable solvent is recycled or reused. The active residue could be either immobilized or destroyed by incineration (IAEA, 2001).

3.3. TREATMENT OF SOLID WASTE.

Solid wastes are produced by all applications and uses of radioactive materials, in normal operations and maintenance activities. Solid, low and intermediate level wastes are generally segregated into combustible, compactible and non-compactible forms.

Treatments for solid waste are used to reduce the waste volume and/or convert the waste into a form suitable for handling, storage and disposal (IAEA, 2001 and 2002; Chang, 2001; Adenot et al, 2005; NEA, 1999).

3.3.1. DECONTAMINATION.

Decontamination is defined as the removal of contamination from areas or surfaces of facilities or equipment by washing, heating, chemical or electrochemical action, mechanical cleaning or by other means. The decontamination objectives are mainly: to reduce the volume of equipment and materials requiring storage and disposal in licensed disposal facilities, to remove contamination from components or systems, to reduce dose levels in the installations and to restore sites and facilities to an unconditional-use condition. Decontamination processes may divide into chemical, electrochemical and mechanical processes:

- **Chemical decontamination.** In the chemical decontamination are used concentrated or dilute chemical reagents in contact with the contaminated item, to dissolve the contamination layer, covering the base metal and eventually a part of the base metal.
- **Decontamination by melting** presents the particular advantage of homogenising a number of radionuclides in the ingots and concentrating other radionuclides in the slag and filter dust resulting from the melting process, thus decontaminating the primary material. The problem with inaccessible surfaces or complex geometries is eliminated and the remaining radioactivity content is homogenised over the total mass of the ingot.
- **Mechanical and manual decontamination** included wet or dry abrasive blasting, grinding of surfaces and removal of concrete by spalling or scarifying, washing, swabbing, foaming agents, and latex-peelable coatings. These techniques are most applicable to the decontamination of structural surfaces which may be cleaned by sweeping, wiping, scrubbing or removed by grit blasting, scarifying, drilling and spalling.

A wet abrasive-blasting system uses a combination of water, abrasive media and compressed air, and is normally applied in a self-contained, leaktight, stainless steel enclosure. The dry abrasive-blasting technique, commonly called sandblasting or abrasive jetting, uses abrasive materials suspended in a medium that is projected onto the surface being treated, resulting in a uniform removal of surface contamination. The scarification process removes the top layers of a contaminated surface down to the depth of the sound, uncontaminated surface.

There are two basic disadvantages with the mechanical methods: the surface of the workpiece has to be accessible and many methods may produce airborne dust (IAEA, 2001 and 2002; Chang, 2001; Adenot et al, 2005; NEA, 1999).

3.3.2. COMPACTION.

Compaction is performed in order to reduce the waste volume and concentrates the radionuclides. Plastics, paper, absorbent material, and cloth are compatible in conventional compactors. Metal pipe, valves, conduit, wood, and other like items are compatible in super compactors. Compactors can range from low-force compaction systems (~5 tons or more) through to presses with a compaction force over 1000 tons (super compactors). Volume reduction factors are typically between 3 and 10, depending on the waste material being treated (IAEA, 2001 and 2002).

3.3.3. CUTTING.

Cutting and sawing operations are carried out mainly on large items which consist usually of metals or plastics. This waste has to be reduced in size to make it fit into packaging containers or to submit it to treatment such as incineration. The cutting is carried out either in the dry state in cells, using remote control when necessary and with conventional tools, or underwater. The cutting may also be done with plasma-jets, laser torches, or explosive fuses.

3.3.4. CRUSHING.

Crushing techniques may be used for size reduction of friable solids (glass, concrete, ceramics). In principle, all types of mill, grinder, and crushing machines of conventional technology can be used.

3.3.5. SHREDDING.

Shredding reduces void space and is particularly effective when plastics are compacted. Air, which is trapped between the folds of bulk plastic and in plastic bags and sleeving, takes up storage space. When the plastic is shredded, better use is made of the waste container space.

3.3.6. INCINERATION.

The size reduction, mixing and blending of the solid wastes is necessary for successful combustion operation.

4. ELECTROCHEMICAL TREATMENT OF RADIOACTIVE WASTE.

4.1. ELECTROREMEDIATION.

The electrochemical treatment, electroremediation, also known as electrokinetic remediation (EKR) process is classified as a physicochemical technology by the electrochemical transformation or destruction of organic and inorganic wastes, which offers many advantages such as the capacity to remove organic and inorganic pollutants by applying direct electric current into the soil. The EKR is easy to operate and involves the installation of electrodes into the organic or inorganic waste and the application of a low voltage gradient or direct current through them (Vazquez et al, 2007). This process is capable of mineralizing the organics into carbon dioxide and water completely, without emission of any toxic materials like dioxins. Several metal oxidizing agents like Ag(II)/Ag(I), Ce(IV)/Ce(III), Co(III)/Co(II), etc., have been tested with this process in pilot and commercial scale systems (Adenot et al, 2005; Chang, 2001; Prabhakaran et al, 2009; Farmer et al, 1991).

This technology requires having humid waste into which electrodes are inserted, the electrodes' terminals are connected to a power supply, and an electric current or potential gradient is applied to generate an electrical field. During this process, electrode reactions take place on its surface, generating protons (H^+) and hydroxyl (OH^-) at the anode and the cathode, respectively. The concentration of these ions near the electrodes creates an acid front that moves from anode to cathode and a basic front that moves from cathode to anode. These species interact with the soil to carry pollutants out into the pore solution. Some transport phenomena occur in the liquid phase of soil when direct current or voltage gradient is passed through the electrodes, such as ion migration (electromigration), electroosmosis and electrophoresis (Murillo – Rivera et al, 2009; Alcántara et al, 2008), inducing complex and coupled electrochemical and properties of matrix. In this case, the transport phenomenon depends on the chemistry of the pollutant (Pamuku and White, 1992; Reddy and Chinthamreddy, 2003; Braud et al, 1998).

If the pollutant is inorganic, as metals, these can be removed by electromigration, because the compounds are dissociated in ions. If the ions have negative charge (anions) they will move toward the anode, and if they have positive charge (cations) they will move toward the cathode, an important characteristic which can determine where the metal, in ionic form, can be recovered (Virikutya et al, 2002; Figure 4). Non-polar pollutants or organic pollutants can be removed by electroosmosis, attributed to the excess charges on the soil surface. There occurs the net ionic migration that represents the bulk movement along pore fluid through the electrical double layer of charge at the solid–liquid interface (Al-Shahrani and Roberts, 2005). And finally, electrophoresis is the movement of charged solid particles, including clay particles and bacterial cells with size less than 20 μm , in response to the electrostatic potential gradient. As in electromigration, positively charged particles migrate towards the cathode, and negatively charged particles migrate towards the anode, or they both simply move by a mechanical transport (Hamed et al, 1991; Méndez et al, 2012).

On other hand, many different soil remediation technologies are available to clean polluted waste, and most of them remove pollutants from the soil–water complex for further treatment or disposal in a more concentrated form. However, when the pollutants are persistent, toxic or simply have low solubility and a strong adsorption to soil surfaces and organic matter, the traditional remediation technologies are used, such as washing, and land-farming, amongst others. In these cases, electroremediation, also known as electrokinetic remediation (EKR) process is classified as a physicochemical technology, which offers many advantages such as the capacity to remove organic and inorganic pollutants by applying direct electric current into the soil, even in clays (Virikutytea et al, 2002). The EKR is easy to operate and involves the installation of electrodes into the soil or waste and the application of a low voltage gradient or direct current through them. This technology has the capacity to removed heavy metals (Pb^0 , Hg^0 , Cd^0 , Ni^0 , Cu^0 , Zn^0 , Cr^0); toxic anions (NO_3^- , SO_4^{2-}); mixtures of organic and ionic pollutants; cyanide; explosive compounds; hydrocarbons (gasoline, diesel, oil, BTEX: benzene, toluene, ethyl benzene and xylene); polychlorinated biphenyls (PCBs) and radioactive species (^{137}Cs , ^{90}Sr , ^{60}Co , ^{238}Ur); from both saturated and unsaturated soils, sludges and sediments (Virikutytea et al, 2002; Hamed et al, 1991).

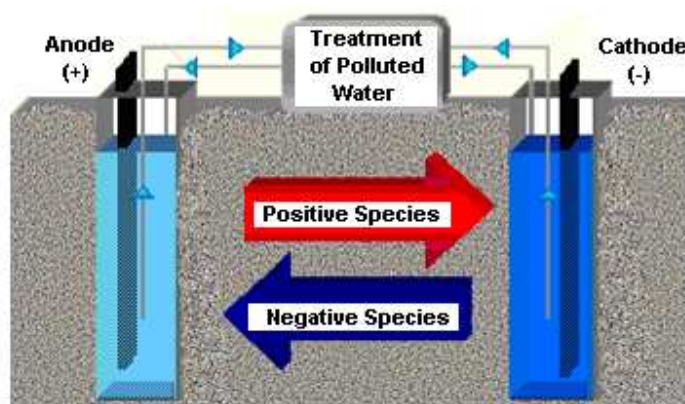


Figure 4. Electromigration of ions in an electrochemical arrangement to remove pollutant from the matrix (authors own creation).

Some researchers have published (Pamuku et al, 1990 and 1992; Reddy et al, 2003; Hamed and Bhadra, 1997; Reed et al, 1999; Khan and Alam, 1994) that the EKR application was better in clayed soils that had low concentration of heavy metal than even expensive regular mining procedures. However, a disadvantage was the time required to achieve over 90 % metal removal.

In order to improve the EKR process and diminish the removal time, some efforts have been focused on changing some operational parameters. For example, some researcher have modified the pH and the current density, introducing chemical compounds on electrolyte chambers (Yeung et al, 1996; Cox et al, 1996), or have added complexing and chelating agents to desorb the pollutant from soils (Cundy and Hopkinson, 2005; Ruiz et al, 2011; Colleta et al, 1997), or have modified the system, placing reactive barriers into the soil matrix (Ribeiro et al, 2005; Gómez et al, 2009) or simply they have tested different electrode material.

Thus, the efficiency of pollutant removal using EKR depends of many factors. However, it is important to select a good electrode material, especially when electrochemical technologies are used. Their selection can be according the thermodynamic and kinetic reactions carried out on their surfaces or by their mechanical, thermal and corrosion resistance.

4.2. ELECTRODES DURING THE ELECTROKINETIC REMEDIATION OF WASTES.

In that sense, some materials, as the case of titanium (Vázquez et al, 2004), platinum, gold, silver, stainless steel, among others used in EKR, suffer a kind of passivation, generating an oxide film on their surfaces which cover the active sites. This behavior occurs during the experimental conditions, which increases the electrical

resistances in the system. For that reason, it is necessary to pre-treat or pre-activate the material before using, to increase roughness or surface active sites. Also, carbon electrodes have been used in EKR processes because of their low cost and accessibility (Saichek and Reddy, 2003; Hu et al, 2002) and because they are inert. However, these kinds of materials commonly form bonds with the species in solution or form oxide film. As well, they can adsorb some species on their surface.

In order to increase the active sites, eliminate the passivation phenomenon, increase electrode life and improve the oxidant activity, it is necessary to modify electrode surfaces to obtain high overpotentials. Consequently, some electrode materials have been modified with metallic oxide, forming a thin layer on a base metal (usually titanium), i.e. $Ti|SnO_2-Sb_2O_3$, $Ti|IrO_2-Ta_2O_5$, $Ti|IrO_2$, $Ti|RuO_2$, and carbon| TiO_2 , among others (Hu et al, 2002; Méndez et al, 2012). These kinds of electrodes can be used as anodes in order to promote electrochemical oxidation. For that reason, the name "Dimensionally Stable Anodes" (DSA) was proposed by Comninellis and Pulgarin (Comninellis and Pulgarin, 1991) who demonstrated the high reactive surface of iridium DSA. These are able to degrade organic compounds by the presence of hydroxyl radicals on their surface, while being mechanically resistant to this reactive species and to pH changes (Comninellis, 1994).

4.3. CONFIGURATION OF ELECTRODES DURING AN ELECTROKINETIC REMEDIATION OF WASTES.

Furthermore, most conventional *in situ* methods have trouble managing the remediation of fine-grained soils with one or more of the following conditions: high water content, high organic matter content, high metal concentration; whereas electroremediation is suitable for wastes (Saichek and Reddy, 2005). Although, there are some aspects of electroremediation that require attention before the technology can be successfully implemented in the field, such as: soil characterization, type and concentration of pollutant and electrode material, as well as electrode array configuration and spacing.

In the last three decades, different research groups have been working in the electrokinetic treatment at different levels: laboratory, pilot system and directly in the site pursuing to remove organic pollutants (Gilbon, 2001), inorganic pollutants and radioactive wastes, among others (Hamed et al, 1991). Also, there are reports about the successful implementation of electrokinetic treatment *in situ*; one example is reported by Monsanto, DuPont and General Electric, who used the Lasagna™ remediation treatment *in situ* to remove trichloroethylene with 98% of efficiency (USEPA, 1997). Another practical example was developed by Sandia National Laboratories, who removed chromium *in situ* using Iridium/Titanium electrodes protected with a porous ceramic coating (Fernández, 2012).

Previous research has been focused on maximize electrokinetic extraction efficiency. Most laboratory or pilot electroremediation studies have been carried out in one dimension (1D) array, having only one anode (+) and one cathode (-), separated by the polluted soil. For field applications, the system must be effective and efficient; therefore it is required an appropriate electrode configuration, in order to accomplish this goal EKR treatment should be implemented in a bidimensional system (2D), this means that electrode array must be set up in respect to the x-y axis; however, there are few reports evaluating the performance of electrode configurations in the x-y plane, and there is no experimental data about performance of electrokinetic treatment with different electrode arrays (Méndez et al, 2012; Pérez – Corona et al, 2013; Reddy et al, 2001).

In addition, several flushing solutions have been investigated, such as water, acids, bases, chelating agents, alcohol, and other additives (Chaiyaraksa and Sriwiriyanuphap, 2004). In practice, acid washing and chelator soil washing are the two most prevalent removal methods (Giannis et al, 2007; Rampley and Ogden, 1988). Also, most of the electrokinetic equipment has been manufactured as a horizontal type. Laboratory-scale electrokinetic remediation has performed for TRIGA soil during the past 5 years, but in this time, a study related to pilot-scale electrokinetic remediation was performed (Kim et al, 2002 and 2003).

4.4. DESTRUCTION OF RADIOACTIVE ORGANIC WASTES.

The process developed for the removal of organic contaminants from bulk water using graphite based adsorbents with electrochemical regeneration at the University of Manchester (Brown and Roberts, 2007), was adjusted for the destruction of radioactive organic wastes, specifically oils contaminated with alpha radioactivity produced at Magnox Ltd nuclear decommissioning site in UK (Wickenden, 2001). This approach comprises four stages:

1. *Emulsification*: the oils contaminated are emulsified in water using CLAX 200S as organic emulsifying agent to give a stable emulsion.
2. *Adsorption*: the emulsion is vigorous mixing with the graphitic adsorbent (Nyex™ 1000 supplied by Arvia Technology Ltd) by fluidizing the adsorbent using air sparging. A quick adsorption is produced by the non-porous nature of the Nyex™.
3. *Sedimentation*: when the fluidising air is turned off, Nyex™ particles precipitate to form a bed in the anode compartment of the electrochemical cell.
4. *Electrochemical destruction*: two electrodes are placed either side of the bed and a direct electric current is passed through the bed which destroys the pollutant through anodic oxidation of the organic matter. Oxidation of the organic matter may produce soluble breakdown products or off-gases (CO, CO₂) and small amounts of H₂ and Cl₂ at the electrodes. After electrochemical treatment, the regenerated adsorbent is ready for immediate reuse and the whole cycle is repeated (Brown et al, 2013).

The treatment of radioactive oils by adsorption and electrochemical regeneration systems has been achieved at pilot scale 200 L. The latter consisted of three bipolar stacks of six electrochemical cells of each with an electrode area of 2 500 cm². Graphite plate bipolar electrodes were used and a micro-porous polyethylene membrane (Daramic, Grace GMBH) separated the adsorbent bed from the cathode. The catholyte solution, 0.3 wt % NaCl solution acidified to a pH of less than 2, was stored in a small tank and pumped through the cathode compartments of the six cells. The distribution of the radioactivity after the process was examined in the samples of the adsorbent and electrolyte after each regeneration cycle or after each destruction cycle for 1.5 L of contaminated oil using high-resolution gamma spectrometry for ²⁴¹Am, ¹⁵⁴Eu, ¹⁵⁵Eu, ¹³⁷Cs and ⁶⁰Co, liquid beta scintillation counting for ³H, ¹⁴C, ⁵⁵Fe, ⁶³Ni, ⁹⁰Sr, ²⁴¹Pu and ³⁶Cl, and alpha spectrometry for plutonium isotopes (^{239/240}Pu, Pu) and ²⁴¹Am (Brown et al, 2013).

The process was achieved with a specific treatment rate of 0.63 μL cm⁻² h⁻¹ using a current density of 10 mA cm⁻². Regeneration was carried out at a current of 1 A (20 mA cm⁻²) for 25 h L⁻¹ of oil with a regeneration energy of 48 kWh L⁻¹ of oil. And the oil loading on the adsorbent was less than 25 wt % on the adsorbent to avoid excessive cell voltage.

The process of adsorption coupled with electrochemical regeneration can remove and destroy around 95 % radioactive oils in the first cycle, and over 99% of the emulsified oil. Around 80 – 90 % of the majority of the radioactive species are transferred to the aqueous phase with a negligible discharge of tritium gas; hence no off-gas treatment before direct discharge to atmosphere is necessary (Brown et al, 2013).

Electrochemical oxidation using a boron-doped diamond (BDD) anode coupled with sonication is a promising method to oxidise (Low Level Waste) LLW or Intermediate Level Wastes (ILW) oils to carbon dioxide and water. The boron-doped diamond (BDD) electrodes contain non-aggressive and non-corrosive chemicals, are easy to dispose of and allow simple electrochemical cell configuration. Electro-oxidation tests were performed in an electrochemical cell which comprised a 250 mL beaker fitted with a rubber bung that held a BDD (DIAFILM PE™) anode and a stainless steel cathode applied 0.1 A, a cell potential of 5 – 15 Volts and sonication. The electrolyte contained oil, sodium sulphate and sodium hydroxide added at the start of the test to maintain an alkaline pH in order to trap the carbon dioxide as carbonate. The method was effective for unused hydraulic oil, vacuum pump oil and a waste used machine tool oil (Taylor et al, 2009).

Mediated Electrochemical Oxidation (MEO) process has been used by destroying the organic components of combustible mixed wastes and for dissolving radioactive materials, such as transuranic oxides (PuO₂). The radioactive components of the wastes dissolved in the electrolyte, can be recovered or immobilized for disposal (Chiba et al, 1995). The destroying organic process is accomplished via a mediator (oxidizing agent).

Several metal oxidizing agents like Ag(II)/Ag(I), Ce(IV)/Ce(III), Co(III)/Co(II), Fe(IV)/Fe(III) etc., in nitric or sulfuric acids have been tested (Chiba et al, 1995; Farmer et al, 1995). In particular, the Ag(II)/Ag(I) based MEO system is capable of destroying cutting oil, cellulose (paper and cloth), rubber (latex), plastics (Tyvek, polyethylene and polyvinyl chloride), biomass (bacteria) and ion exchange resins, attaining high destruction efficiencies at reasonable coulombic efficiencies (Chiba et al, 1995).

Ag(II) in a nitric acid solution produces highly reactive OH and NO₃ radicals which attack organic compounds converting most of them to CO₂, water, and inorganic ions. The resulting Ag(I) is recycled to Ag(II) at the anode of an electrochemical cell to maintain a supply of oxidant and minimize consumption of Ag. The Ag(II) migrates

back into the bulk electrolyte to continue the oxidation process. A microporous membrane is usually placed between the electrodes to prevent the oxidizer produced at the anode from being reduced at the cathode. Ag(II) is a very effective oxidizing agent for the destruction of nonhalogenated organic compounds. Unfortunately, halide ions liberated during the destruction of halogenated organics react with Ag(II) to form insoluble precipitates. Therefore systems tolerant to halide anions such as Ce(IV)/Ce(III), Co(III)/Co(II) and Fe(IV)/Fe(III) have been tested. Tests at Pacific Northwest Laboratory with the Cerium/HNO₃ system has shown that cerium provides the same or better oxidation rates for cutting oils that silver system (Schwinkendorf and Hart, 1995).

4.5. EXAMPLES OF ELECTROCHEMICAL TREATMENTS OF RADIOACTIVE WASTE.

4.5.1. CS-137 AND CS-134 REMOVAL FROM RADIOACTIVE ASH.

Combustible waste contaminated with ¹³⁷Cs and ¹³⁴Cs, generated by the tsunami within Fukushima, was incinerated, producing a large quantity of radioactive ash. A washing–electrokinetic decontamination method was developed by Kim and collaborators to decontaminate these radioactive ashes (Kim et al, 2002 y 2003). The process consists in a washing of contaminated ash with HNO₃ in three cycles using pH of 0 and ash (1g) – nitric acid (1 mL) mixture; the waste solution generated is precipitated with CaO and reused only those produced in the third washing. If the residual radioactivity of the washed ash is higher than the clearance concentration level, the washed ash is treated by electrokinetic equipment for decontamination. The removal efficiency of ¹³⁷Cs from radioactive ash is inversely proportional to an increase in the mixing ratio of ash weight (g)/solution volume (mL) and directly proportional to the increase in the concentration of HNO₃.

A pilot-sized washing–electrokinetic equipment was manufactured to remove cesium from lots of radioactive ash. The equipment consisted of 200 L washing equipment, 50 L electrokinetic equipment, and 150 L precipitation equipment. The electrokinetic equipment consisted of a couple of anode rooms, electrokinetic ash cells, cathode rooms and metal oxide separators. Cesium from radioactive ashes moves to the cathode room through electro-migration and electro-osmosis. 87 – 89 % of ¹³⁴Cs and ¹³⁷Cs in the radioactive ashes were removed in three washings and around 98 – 100 % from the waste solution after precipitation with CaO. If the radioactive ashes contain more than 30 – 40 Bq g⁻¹ of ¹³⁴Cs and ¹³⁷Cs the electrokinetic process requires between 8 – 10 days after three washings to reach below 2.0 Bq g⁻¹ (Kim et al, 2013).

4.5.2. SODIUM RECOVERY FROM ALKALINE NUCLEAR WASTE.

An electrochemical salt-splitting process has been developed to recover and recycle NaOH from radioactive wastes containing large amounts of sodium salts. Sodium separation process can save costs by reducing the disposal volume of wastes and by producing NaOH for recycle into waste treatment processes such as sludge leaching, regenerating ion exchange resins, inhibiting corrosion in carbon-steel tanks, or retrieving tank wastes (Fountain et al, 2009). The process is based on a two-compartment cell separated by a cation selective membrane. The waste enters into the anolyte electrodes, sodium ions migrate across membrane into the catholyte, under the influence of an applied electrical potential. Hydroxides form at the cathode by the reduction of water producing thus a sodium hydroxide solution (Kurath et al, 1997; Hobbs, 1999; Ambashta and Sillanpää, 2012; Fountain et al, 2009).

Platinized titanium (Pt/Ti) anodes and cathodes, and a Ceramtec® NASD membrane were tested by Hobb, applying a current density of 300 A m⁻² and a voltage of 5-5.6 V during a run time of 70 - 104 h. This approach allows retain anionic species such as nitrate, aluminate or sulfate in the compartment anolyte of the electrochemical cell, and can produce caustic from radioactive wastes with low levels of gamma radioactivity, which could be released for off-site use without further treatment (Hobbs, 1999).

Pacific Northwest National Laboratory (PNNL) and Ceramtec Inc. tested a NaSelect® (sodium super ionic conductor) ceramic membrane to separate sodium from Low Activity Waste (LAW) streams at Hanford site (Fountain et al, 2009; Pendleton et al, 2011). A pilot scale system was designed, built and operated to process 7 L h⁻¹ of LAW. The process selectively removed up to 80 % of sodium hydroxide from LAW and produced up to 50 % concentrated caustic for reuse in removal aluminum during sludge washing as a pretreatment step in the vitrification of radioactive waste; reducing about 39 % the waste volume. NaSelect® ceramic membrane

prevents migration of mono valent and multi valent elements and other radionuclides to the sodium hydroxide stream (Pendleton et al, 2011; Figure 5).

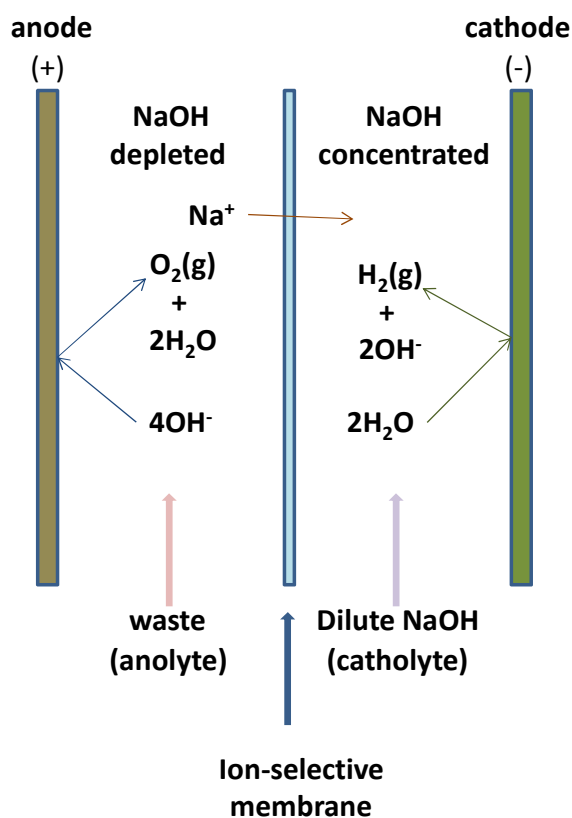


Figure 5. Electrochemical cell for the recovery of sodium hydroxide from alkaline salt solutions (Hobbs, 1999).

Electrolytic decontamination is accomplished by applying a low dc voltage through an electrolyte to induce a chemical reaction. Contamination is removed at the anode the working electrode and goes into solution. The cathode (counter electrode) can be constructed from stainless steel. Electrolyte solutions such as phosphoric or sulfuric acid, used normally in electropolished, have to be changed after a few articles decontaminated, resulting in large quantities of radioactive toxic waste that must be treated and/or disposed. Due to this, electrolytes with a very low toxicity from which the radioactive materials can be easily separated and recycled, are investigated and applied. Sodium nitrate has been chosen as electrolyte to decontaminate metals contained Pu and Am (Wedman et al, 1996). In this medium, both actinides can be precipitated or entrained in the ferric hydroxide formed as surface metal is removed, resulting a clean surface, free of contamination, and the separation of the radioactive waste from the solution. Thus, the electrolyte solution can be recycled, greatly reducing waste.

For this process, the appropriate current densities appear to be in the range of 0.1 to 0.2 A cm^{-2} . Higher current densities result in higher metal removal rates, but adversely affect the surface morphology by causing roughening, pitting, or burning. Optimum situation for the electrolytic decontamination process is the treatment of metal surfaces that have been electropolished before contamination (Wedman et al, 1996).

NaOH solutions have been used as electrolytes to decontaminate metal surface contaminated by tritium. In this approach, the metal to be decontaminated is submerge in the electrolyte, connected to the negative pole, and the anode (polytetrafluoroethylene wax-impregnated graphite), to positive pole; applying a current densities in the range of $10 - 50 \text{ mA cm}^{-2}$. The tritium adsorbed on the cathode surface is replaced by the hydrogen and ejected to the electrolytic solution. This process is proper to small metallic parts of complex

geometry or large pieces with simple geometry; and does not modify the surface metal, thus the object can be reused (Bellanger, 1992).

Other decontamination process for contaminated stainless steel equipment is accomplished by dissolution of the metal surface that is being decontaminated when it is in contact with a solution composed by an inorganic reduction-oxidation systems such as Ce(IV)/Ce(III), Cr(VI)-Cr(III), Ag(II)-Ag(I) or Co(III)-Co(II) in nitric acid. This solution is subsequently reoxidized by electrolysis (Lerch et al, 1980).

4.5.3. REMOVAL OF ¹³⁷Cs FROM SOIL.

The thick-target PIXE analysis was successfully applied at least to the analysis of the electrokinetic behavior of cesium mixed with the soil as CsBr. By using cesium as a test pollutant, we could clearly observe the effect of the electrolysis without taking into account complicated interactions between the contaminant and the soil, such as dissolution of soil particles and adsorption phenomena.

The water supply to the anode well was effective to enhance the removal rate. From the observed fast migration of the pore water, as well as from the result of a simple calculation on the electrophoretic flow velocity, it was concluded that the migration of cesium observed was due mainly to the electroosmotic flow. Remediation performance by increasing the electric conductivity of the soil by mixing NaCl was possible. This result was consistent with the reduction of the electroosmotic flow velocity due to the elevated ionic strength. It was found that the addition of NaCl makes no sense also from the viewpoint of the potential hazard due to toxic gas emission as well as the cost of electricity. Owing to the interference by major metallic elements in the soil, the detection sensitivity of the present method based on the simple LX-ray measurement was not enough to investigate behavior of the trace level Cs contaminants. In order to attenuate only Ti-K α but to allow high transmission of Cs-L α radiation, a thin foil of a single element having an absorption edge at an appropriate energy.

4.5.4. REMOVAL OF ⁶⁰Co AND ¹³⁷Cs FROM SOIL.

The pilot-scale electrokinetic remediation equipment suitable for the geological characteristics of a South Korean nuclear facility site was developed for the remediation of radioactive soil. The optimal experimental conditions were obtained with 50 L electrokinetic remediation equipment and the results are as follows: the removal efficiencies Co²⁺ and Cs⁺ from the artificially contaminated soil after 15 days were 98.4 % and 94.9 % respectively, and the generated effluent volume was 3.4 mL g⁻¹. The removal efficiencies of ⁶⁰Co and ¹³⁷Cs by nitric acid were increased by 3.1 % and 2.0 % more than those by acetic acid. The removal efficiencies of ⁶⁰Co and ¹³⁷Cs from the soil of high concentrations (1 320 Bq kg⁻¹ and 1 720 Bq kg⁻¹) were increased by 14.4 % and 3.8 % more than those from the soil of low concentrations (110 Bq kg⁻¹ and 120 Bq kg⁻¹).

The removal efficiency of ¹³⁷Cs from the soil of average 1.4 mm particle size was increased by about 2.3 % more than that from the soil of an average 0.7 mm particle size. The removal efficiencies of ⁶⁰Co and ¹³⁷Cs by the application of an electric current of 15 mA cm⁻² were increased by 1.4 % and 4.4 % more than those by the application of 10 mA cm⁻². A total removal efficiency of ⁶⁰Co and ¹³⁷Cs from the radioactive soil of about 2000 Bq kg⁻¹ was 95.8 % during electrokinetic remediation by the application of an electric current of 15 mA cm⁻² for 55 days (Gye – Nam et al, 2013).

On other hand, a soil washing system with a hydro-cyclone was very effective for decontaminating the radionuclides in the TRIGA (Training, Research, Isotope, General Atomic) soil in Korea. The size of the contaminated TRIGA soil ranged from very fine to more than 1.0 mm. The volume of soil particles larger than 1.0 mm was 28 - 52 %, and the volume of soil particles smaller than 0.06 mm was less than 4 - 10.5 %, but the volume of medium-sized soil particle was 43 - 61 %. The radioactive concentration was strongest in the soil particle smaller than 0.063 mm, as predicted. Oxalic acid was the best chemical agent for washing, especially for cobalt. A scrubbing time of 4 h was the optimum time to obtain a removal efficiency of more than 75 % for ¹³⁷Cs and ⁶⁰Co. A mixing ratio of the soil weight to the volume of the oxalic acid solution of 1:10 was the best for washing; two scrubbing cycles with 1.0 M oxalic acid avoided the generation of a considerable amount of waste solution. The removal efficiency with a hydro-cyclone was 30 % higher than that without. Vertical plates and alum had important roles in reducing the sedimentation time. The waste solution could be reused up to five times after passage through a column of a strong acid resin (Gye – Nam et al, 2007).

4.5.5. REMOTION OF ²³⁸U, ¹³⁷CS AND ⁸⁵SR FROM SOIL.

Experimental study seems to demonstrate that the feasibility of electrokinetic soil remediation for the removal of radionuclide contaminants from soils. The experimental results indicate that the technique is effective in radionuclide contaminants from soils with a relatively small amount of energy. Uranium and strontium were efficiently removed from kaolinite by electrokinetic remediation. In the case of cesium, the removal rate may be significantly slower than those of uranium and strontium. This is due to the lower ionic mobility and the affinity of cesium onto kaolinite. Acetic acid was effective as enhancing agent for buffering hydroxide ions produced by the cathode reaction, and prevented the precipitation of uranium ions in the cathode region.

Accordingly, the acetic acid increased the removal efficiency and decreased energy consumption. The use of citric acid was not efficient in removing uranium from kaolinite, because the direction of electromigration was opposite to that of electroosmosis. Since most metal-citrate chelates were negatively charged, they were transported toward the anode by electromigration while electroosmosis flowed toward the cathode. Therefore, removal efficiency significantly decreased. This result indicates that the selection of enhancement agent should be considered with respect to contaminant type and site characteristics. The electrokinetic removal of uranium from the soil weathered from uraniferous black shale was not efficient. This was due to the low proportion of the mobile fraction, since most uranium exists as residual fractions derived from enriched uraniferous parent rocks (Kyeong-Hee et al, 2003).

5. RISK ASSESSMENT AND DEVELOPMENT OF FUTURE STRATEGIES.

Nuclear site operations and successful site restoration depend on the availability of suitable waste management routes and facilities. Effective management of both radioactive and non-radioactive waste is essential to the delivery is a significant part of the process.

Strategic decisions about waste management are informed by the following key principles: risk reduction is a priority, centralised and multi-site approaches should be considered where it may be advantageous, waste should be minimised and the waste hierarchy should be used as a framework for waste management decision making and enables an effective balance of priorities including value for money, affordability, technical maturity and the protection of health, safety, security and the environment.

For Low Level Waste, disposal will be in fit for purpose facilities that reflect the nature of the wastes to be managed. Within this overall framework our priority is to achieve risk reduction by dealing with waste in ageing storage facilities and placing it into safer modern storage conditions. Diverse radioactive waste management and disposal solutions will be pursued where these offer benefits over previous arrangements. New waste management approaches will often require different transport arrangements and will be a matter of great interest to planning authorities and people living close to the sites involved.

Some general ideas about the underpinning strategies are showed in Figure 2, the basic steps for effective management of radioactive waste are part of a global system, ranging from waste generation to final disposal are: minimization of radioactive waste, pretreatment, characterization, treatment, conditioning, transport, storage and disposal (IAEA, 1970). All of these ideas with the intention to reduce the volume of radioactive wastes.

6. CONCLUSIONS.

Radioactive materials are extensively used in industrial and research activities into medical, agricultural and environmental applications, and in various other areas. During the production and use of these materials, radioactive waste will inevitably arise; this must be managed with particular care owing to its inherent radiological, biological, chemical and physical hazards.

Producers and users of radioactive materials must be sure that a waste management strategy exists prior to the start of waste generation. A well-developed waste management strategy should consider the entire

sequence of waste management operations, from the waste's production until its final disposal, including the various regulatory, sociopolitical and economic issues. The identified goal of radioactive waste management can be met with reasonable cost and resource use by implementing a carefully planned waste management strategy using appropriate technologies.

Waste containing long lived radionuclides must be treated, conditioned, stored and disposed of at a repository specifically designed for this purpose. Ample storage capacity is needed for the decay of short lived radionuclides and for storing long lived waste prior to, and after, the treatment and conditioning steps. Decay is the only natural way of reducing radioactivity (the process of transmutation of some long lived radionuclides is not considered viable at this time).

Since radionuclides have decay rates ranging from days to thousands of years, proper segregation of wastes depending on their half-lives, and separate treatment and conditioning of these wastes, is an important factor in the overall scheme of radioactive waste management. Treatment of waste involves operations intended to benefit safety and/or economy by changing the characteristics of the waste. There are different procedures to the treatment of radioactive waste, like:

1. *Treatment of aqueous waste*: ion exchange/sorption, chemical precipitation, evaporation, ultrafiltration / reverse osmosis (UF/RO), incineration, solid / liquid separation (sedimentation, filtration), centrifugation, hydrocyclone techniques, chemical precipitation (co-precipitation or isomorphous precipitation with the carrier, adsorption on to the floc or on added absorbers, flocculation, sedimentation, pH adjustment, chemical oxidation and reduction, ion exchange / sorption, evaporation and reverse osmosis.
2. *Treatment of radioactive organic liquid*: incineration, wet oxidation, electrochemical oxidation, acid digestion, distillation, phase separation by adduct formation and biological digestion.
3. *Treatment of solid waste*: decontamination, compaction, incineration and electroremediation.

In the case of electroremediation treatment of radioactive wastes offers many advantages such as the capacity to remove organic and inorganic pollutants by applying direct electric current into the soil, even in clays, it is easy to operate and involves the installation of electrodes into the soil or waste and the application of a low voltage gradient or direct current through them. In consequence, the EKR is a very good technological alternative to remove radioactive species as ^{22}Na , ^{137}Cs , ^{134}Cs , ^{89}Sr , ^{90}Sr , ^{60}Co and ^{238}U from both saturated and unsaturated radioactive soils, sludges, ash and sediments, with less time and high efficiencies of removal in comparison of the other alternatives to remove radioactive wastes.

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7. REFERENCES.

- Abdel, R. O., Rahman, H. A., Hung, Y. –T. (2011). Liquid Radioactive Wastes Treatment: A Review. *Water*, 3, 551-565.
- Adenot, F., Advocat, T., Bisel, I., Broudic, J. C., Brun, P., Cau-Dit-Coumes, C., Delage, F., Dussossoy, J. L., Faure, S., Fournel, B., Girol, C., Grandjean, A., Hollebecque, J. Fl., Lacombe, J., Ladirat, C., Lemort, F., Peugeot, S., Pinet, O., Poitou, S., Rouppert, F., Vistoli, P. P. (2005). Le traitement et le conditionnement des déchets. Rapport technique DTCD/SCD/2005/001, CEA, France.
- Alcántara, M. T., Gómez, J., Pazos, M., Sanromán, M. A. (2008). Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant – electrochemical degradation. *Chemosphere*, 70, 1438 - 1444.
- Al-Shahrani, S. S., Roberts, E. P. L. (2005). Electrokinetic removal of caesium from kaolin, *Journal of Hazardous Materials*, B122, 91 - 101.
- Ambashta, R. D., Sillanpää, M. E. T. (2012). Membrane purification in radioactive waste management: a short review. *Journal of Environmental Radioactivity*, 105, 76 – 84.

- Bellanger, G. (1992). Process for decontaminating the surface of a metallic component contaminated by tritium, and device for using said process, European Patent EP0274329.
- Braud, F., Tellier, S., Astruc, M. (1998). Modelling of decontamination rate in an electrokinetic soil processing, *International Journal of Environmental Analytical Chemistry*, 68, 105 – 121.
- Brown, N. W., Roberts, E. P. L. (2007). Electrochemical pre-treatment of effluents containing chlorinated compounds using an adsorbent. *Journal of Applied Electrochemistry*, 37, 1329 – 1335.
- Brown, N. W., Campen, A. K., Wickenden, D. A., Roberts, E. P. L. (2013). On-site destruction of radioactive oily wastes using adsorption coupled with electrochemical regeneration. *Chemical Engineering Research and Design*, 91 (4), 713 – 721.
- Colleta, T. F., Bruell, C. J., Ryan, D. K., Inyang, H. I. (1997). Cation-Enhanced Removal of Lead from Kaolinite by Electrokinetics. *Journal of Environment Engineering*, 123 (12), 1227 - 1233.
- Cominellis, Ch. (1994). Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. *Electrochimica Acta*, 39, 1857 - 1862.
- Cominellis, Ch., Pulgarin, C. (1991). Anodic oxidation of phenol for wastewater treatment. *Journal of Applied Electrochemistry*, 21 (8), 703 - 708.
- Cox, C. D., Shoesmith, M. A., Ghosh, M. M. (1996). Electrokinetic remediation of mercurycontaminated soil. *Environmental Science and Technology*, 30 (6), 1933 - 1039.
- Cundy, A. B., Hopkinson, L. (2005). Electrokinetic and land remediation and soil engineering, *Applied Geochemistry*, 20, 841 - 848.
- Chaiyaraksa, C., Sriwiriyanuphap, N. (2004). Batch washing of cadmium from soil and sludge by a mixture of Na₂S₂O₅ and Na₂EDTA. *Chemosphere*, 56 (11), 1129 – 1135.
- Chang, H. O. (2001). Hazardous and Radioactive Waste Treatment Technologies Handbook. CRP Press, USA.
- Chiba, Z., Schumacher, B., Lewis, P., Murguia, L. (1995). Mediated electrochemical oxidation as an alternative to incineration for mixed wastes, UCRL-JC-119133, Lawrence Livermore National Laboratory, USA.
- Farmer, J. C., Hickman, R. G., Wang, F. T., Lewis, P. R., Summers, L. J. (1991). Initial study of the complete mediated electrochemical oxidation of ethylene glycol, Report No. UCRL-LR-106479, Lawrence Livermore National Laboratory, Livermore, CA.
- Farmer, J. C., Wang, F. T., Hawley - Fedder, R., Lewis, P. R., Leslie, J. (1995). Summers, and Linda Foiles. Initial Study of Halide-Tolerant Mediators for the Electrochemical Treatment of Mixed and Hazardous Wastes. Lawrence Livermore National Laboratory, USA.
- Fernández, C. D. (2012). Descontaminación de Suelos. Department of Pedology, University of Granada, Granada, Spain.
- Fountain, M. S., Kurath, D. E., Sevigny, G. J., Poloski, A. P., Pendleton, J., Balagopal, S., Quist, M., Clay, D. (2009). Caustic recycle from handford tank waste using NaSICON ceramic membrane salt splitting process. PNNL-18216. Pacific Northwest National Laboratory, USA.
- Giannis, A., Gidakos, E., Skouta, A. (2007). Application of sodium dodecyl sulfate and humic acid as surfactants on electrokinetic remediation of cadmium-contaminated soil. *Desalination*, 211, 249 - 260.
- Gilbón, A. J. M. (2001). Electroremediación de Suelos Contaminados Con Hidrocarburos. Universidad Autónoma Metropolitana, Mexico City, Mexico.
- Gómez, J., Alcántara, M. T., Pazos, M., Sanromán, M. A. (2009). A two – stage process using electrokinetic remediation and electrochemical degradation for treating benzo[a]pyrene spiked kaolin. *Chemosphere*, 74 (11), 1516 - 1521.
- Gye-Nam, K., Wang-Kyu, Ch., Chong-Hun, J., Jei-Kwon, M. (2007). Development of a Washing System for Soil Contaminated with Radionuclides Around TRIGA Reactors. *Journal of Industrial and Engineering Chemistry*, 13 (3), 406 - 413.
- Gye-Nam, K., Seung-soo, K., Hye-Min, P., Wan-Suk, K., Uk-Ryang, P., Jei-Kwon M. (2013). Cs-137 and Cs-134 removal from radioactive ash using washing–electrokinetic equipment. *Annals of Nuclear Energy*, 57, 311 – 317.
- Hamed, J., Acar, Y. B., Gale, R. J. (1991). Pb(II) Removal from Kaolinite by Electrokinetics, *Journal of Geotechnical Engenning*. ASCE, 117 (2), 241 - 271.
- Hamed, J. T., Bhadra, A. (1997). Influence of current density and pH on Electrokinetics, *Journal of Hazardous Materials*, 55, 279 - 294.
- Hobbs, D. T. (1999). Caustic recovery from alkaline nuclear waste by an electrochemical separation process. *Separation and Purification Technology*, 15, 239 - 253.

- HSEEA (2007) Fundamentals of the management of radioactive waste. Health and Safety Executive, the Environment Agency and the Scottish Environment Protection Agency. December 2007.
- Hu, J. M., Meng, H. M., Zhang, J. Q., Cao, C. N. (2002). Degradation mechanism of long service life Ti/IrO₂-Ta₂O₅ oxide anodes in sulphuric acid, *Corrosion Science* 44 (8), 1655 - 1668.
- IAEA (1970). Standardization of Radioactive Waste Categories, Technical Reports Series No. 101, International Atomic Energy Agency (IAEA), Vienna.
- IAEA (1992). Treatment and conditioning of radioactive organic liquids. IAEA-TECDOC-656 International Atomic Energy Agency (IAEA), Vienna.
- IAEA (1994). Classification of Radioactive Waste, Safety Series No. 111-G-1.1, International Atomic Energy Agency (IAEA), Vienna.
- IAEA (2001). Handling and Processing of Radiactive Waste from Nuclear Applications. Technical Reports Series No. 402. International Atomic Energy Agency (IAEA), Vienna.
- IAEA (2001). Decontamination and Decommissioning of Nuclear Facilities. Technical Reports Series No. 401, International Atomic Energy Agency (IAEA), Vienna.
- IAEA (2002). Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchanger. Technical Reports Series No. 408. International Atomic Energy Agency (IAEA), Vienna.
- IAEA (2004). Application of the Concepts of Exclusions, Exemption and Clearance, IAEA Safety standards Series No. RS-G-1.7, International Atomic Energy Agency (IAEA), Vienna.
- IAEA (2006). Application of Thermal Technologies for Processing of Radioactive Waste, IAEA-TECDOC-1527, International Atomic Energy Agency (IAEA), Vienna.
- IAEA(2006) Fundamental Safety Principales. IAEA SAFETY STANDARDS SERIES. SF-1, IAEA, Vienna.
- IAEA (2006b) The Management System for Facilities and Activities. Safety Requirements No. GS-R-3. IAEA 2006.
- IAEA(2008) The Management system for the processing, handling and storage of radioactive waste. Safety Guide. No. GS-G-3.3, International Atomic Energy Agency (IAEA), Vienna.
- IAEA (2009). Classification of Radioactive Waste, Safety standards Series No. GSG-1, International Atomic Energy Agency (IAEA), Vienna.
- Khan, L. I., Alam, S. (1994). Heavy metal removal from soil by coupled electro-hydraulic gradient. *Journal of Environment Engineering* 120 (6), 1524 - 1543.
- Kim, S. O., Kim, K. W., Stüben, D. (2002). Evaluation of electrokinetic removal of heavy metals from tailing soils, *Journal of Environment Engineering*, 128, 705 - 715.
- Kim, G. N., Oh, W. Z., Won, H. J., Choi, W. K. (2003). Removal of cesium and cobalt from soil around TRIGA reactor using electrokinetic method, *Journal of Industrial and Engineering Chemistry*, 9 (3), 306 - 313.
- Kim, G. -N., Kim, S., Park, H. -M., Kim, W. -S, Park, U. -R, Moon, J. -K. (2013). Cs-137 and Cs-134 removal from radioactive ash using washing – electrokinetic equipment. *Annals of Nuclear Energy*, 57, 311 – 317.
- Kurath, D. E., Brooks, K. P., Hollenberg, G. W., Sutija, D. P., Landro, T., Balagopal, S. (1997). Caustic recycle from high-salt nuclear wastes using a ceramic-membrane saltsplitting process. *Separation and Purification Technology*, 11, 185 - 198.
- Kyeong-Hee, K., Kim, K., Soon-Oh, L., Chang-Woo, L., Myung-Ho, K., Kyoung-Woong, (2003). Electrokinetic processing for the removal of radionuclides in soils. *Separation Science and Technology*. 38 (10), 2137 – 2163.
- Lerch, R. E., Kennewick, J. A., Partridge, R. (1980). Decontamination of metals using chemical etching. US Patent Aug. 12, 4,217,192.
- Méndez de Vigo, G. E. (2000). Origin and Radioactive Waste Management, Official College of Physicians Illustrious. The 3rd. Edition, 105, 188.
- Méndez, E., Pérez, M., Romero, O., Beltrán, E. D., Castro, S., Corona, J. L., Corona, A., Cuevas, M. C., Bustos, E. (2012). Effects of electrode material on the efficiency of hydrocarbon removal by an electrokinetic remediation process, *Electrochimica Acta*, 86, 148 – 156.

- Murillo-Rivera, B., Labastida, I., Barrón, J., Oropeza - Guzman, M. T., González, I., Teutli - Leon, M. M. M. (2009). Influence of anolyte and catholyte composition on TPHs removal from low permeability soil by electrokinetic reclamation, *Electrochimica Acta*, 54 (7), 2119 – 2124.
- NEA (1999). Decontamination techniques used in decommissioning activities. A Report Nuclear Energy Agency (NEA), Task Group on Decontamination.
- Pamucku, S., Khan, L. I., Fang, H. –Y. (1990). Zinc detoxification of soils by electro- osmosis. Transportation Research record 1288, *Geotechnical Engineering*, 41 - 51.
- Pamucku, S., White J. K. (1992). Electrokinetic removal of selected heavy metals from soil, *Environmental Progress* 11 (3), 241 – 250.
- Pamucku, S., Wittle, J. K. (1992). Electrokinetic Removal of Selected Heavy Metals from. *Soil, Environmental Progress*. 11 (3) (1992) 241 - 250.
- Pendleton, J., Dayton, T., Duffey, K., Bhavaraju, S., Balagopal, Sh. (2011). Pilot-scale system for recycling caustic from LLW simulant. WM2011 Conference, Phoenix, AZ
- Pérez – Corona, M., Ochoa, B., Cárdenas, J., Hernández, G., Solís, S., Fernández, R., Teutli, M., Bustos, E. (2013). Comparison of different arrangements of electrodes during the electrokinetic treatment of polluted soil with hydrocarbons and its final application *in situ*. Recent Research Development in Electrochemistry, Transworld Research Network, 37/661 (2), Kerala, India, 59 - 80.
- Prabhakaran, D., Kannadasan, T., Basha, C. A. (2009). Mediated electrochemical oxidation process for destruction of TOC in a batch recirculation reactor, *International Journal of Chemical Technology Research*, 1 (4), 962 – 969.
- Radiation Safety General Regulations (1988). Official Journal of the Federation, November 22.
- Rampley, C. G., Ogden, K. L. (1988). Removal of Lead from Surrogate and Real Soils Using a. Water Soluble Chelator, Adsorption and Batch Extraction, *Environ. Sci. Technol.* 32 (7), 987 - 995.
- Reed, B. E., Berg, T. E., Thompson, J. C., Hatfield, J. H. (1995). Chemical conditioning of electrode reservoir during electrokinetic soil flushing of Pb-contaminated silt loam, *Journal of Environment Engineering*, 121, 805 - 815.
- Reddy, K. R., Donahue, M., Saichek, R. E., Sasaoka, R. (1999). Preliminary Assessment of Electrokinetic Remediation of Soil and Sludge Contaminated with Mixed Waste. *Journal of the Air & Waste Management Association*. 49 (7), 823 - 830.
- Reddy, K. R., Xu, C. Y., Chinthamreddy, S. (2001). Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis. *Journal of Hazardous Materials*. B84 (2 – 3), 279 - 296.
- Reddy, K. R., Chinthamreddy, S. (2003). Volumetric strains of clean sands subject to cyclic loads, *Journal of Geotechnical and. Geoenvironmental Engineering*, 263 – 272.
- Reddy, K. R., Chaparro, C., Saichek, R. E. (2003). Removal of Mercury from Clayey Soils Using Electrokinetics, *Journal of Environmental Science and Health, Part A – Toxic / Hazardous Substances & Environmental Engineering*, A38 (2), 307 - 338.
- Reddy, K. R., Chaparro, C., Saichek, R. E. (2003). Iodide – Enhanced Electrokinetic Remediation of Mercury – Contaminated Soils, *Journal of Environmental Engineering*, ASCE, 129 (12), 1137 – 1148.
- Report OST (1999). Acid digestion of organic waste. Mixed Waste Focus Area, Reference #1827, U.S. Department of Energy, USA.
- Ribeiro, A. B., Rodríguez - Maroto, J. M., Mateus, E. P., Gomes, H. (2005). Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine: Experimental and modeling, *Chemosphere*, 59 (9), 1229 - 1239.
- Ruiz, C., Anaya, J. M., Ramírez, V., Alba, G. I., García, M. G., Carrillo - Chávez, A, Teutli, M. M. M., Bustos, E. (2011). Soil arsenic removal by a permeable reactive barrier of iron coupled to an electrochemical process. *International Journal of the Electrochemical Science*, 6, 548 - 560.
- Saichek, R. E., Reddy, K. R. (2003). Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, *Chemosphere*, 51 (4), 273 - 287.
- Saichek, R. E., Reddy, K. R. (2005). Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: a review. *Critical Review of Environmental Science Technology*, 35, 115 - 192.
- Schwinkendorf, W. E., Hart. P. W. (1995). Low - temperature alternatives to incineration for doe mixed waste. WM'95 Conference Proceedings, Tucson, Az. USA, 1296 - 1303.
- Taylor, G. T., Newey, A. W. E., Bates, C. J., King, C. R., Dawes, K. (2009). Demonstration of electrochemical oxidation of oils using boron - doped diamond electrodes and its potential role in the disposal of radioactively contaminated waste lubricants. WM2009 Conference, March 1-5, Phoenix, USA.

- Twissel, M. A., Holt, N. S. (1996). Wet oxidation of organic radioactive waste. European Commission Nuclear Science and Technology. EUR 16776, Luxembourg. European Communities.
- USEPA, (1997). Resource guide for electrokinetics laboratory and field processes applicable to radioactive and hazardous mixed wastes in soil and groundwater from 1992 to 1997. US Environmental Protection Agency, Washington, DC.
- Vázquez, M. V., Hernández, F., Grandoso, D., Arbelo, C. D. (2004). Study of the electrical resistance of andisols subject of electro-remediation treatment, *Portugaliae Electrochimica Acta*, 22, 399 - 410.
- Vázquez, M. V., Hernández, F., Benjumea, D., Grandoso, D., Lemus, M., Arbelo, C. D. (2007). Electrokinetic determination of the buffer capacity of Andisols, *Science of the Total Environment*, 378 (1-2), 214 - 217.
- Virkutytea, J., Sillanpää, M., Latostenmaa, P. (2002). Electrokinetic soil remediation – critical overview. *Science of the Total Environment*, 289 (1-3), 97 - 121.
- Yeung, A. T., Hsu, Ch., Menon, R. M. (1996). EDTA-enhanced electrokinetic extraction of lead *Journal of Geotechnical and Geoenvironmental Engineering*, 122 (8), 666 - 673.
- Wedman, D. E., Martinez, H. E., Nelson, T. O. (1996). Electrolytic decontamination of conductive materials for hazardous waste management. LA-UR-96-3795, USA.
- Wickenden, D. (2011). Innovative treatment of radioactive oil waste – the Arvia® process. In: Proceedings of the 11th Tritium User Group Conference, Chapplecross, UK.

2 Optical Fibers to Detect Heavy Metals in Environment: 3 Generalities and Case Studies

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6 Additional information is available at the end of the chapter

8 1. Introduction

9 The fiber optic sensors can be used to create a truly distributed chemical sensing capability for
10 selectively detecting metal compounds by spatial and temporal acquisition over large distan-
11 ces in the subsurface. In addition the fiber optic sensors have several advantages such as small
12 size, light weight, immunity to electromagnetic interference (EMI), high temperature per-
13 formance, large bandwidth, high sensitivity, and environmental ruggedness (Krohn, 1988).
14 Most current technologies capable of detecting contaminants use strategically placed sensing
15 or monitoring devices. This works reasonably well if plausible event location is known, hence
16 settle recording vast amounts of benign data over time until the appearance of the suspected
17 event. This approach remains limited for application in large spatial scales in the geo-envi-
18 ronment and subsurface. A simple approach is to suppress all the benign data by triggered
19 transmittal of the signals only at the spatial and temporal vicinity of the event. This, in essence
20 the “truly distributed” sensing capable of delivering the event signal “*wherever*” and
21 “*whenever*” it might occur, as opposed to only at strategic places where the sensing devices are
22 pre-located. The revolutionary advances in flexible sensing and distributed data processing
23 permits us sensing in this truly distributed manner.

24 Sensors based on fiber optic cable functions make use of the following important features of
25 the cable to sense the environment: (1) optical loss: intrinsic and extrinsic energy loss proper-
26 ties, (2) refractive index: index profile in radial direction and the reduction of index fluctuation
27 along the axial direction; (3) shape: cross sectional shape and size, the surface finish and the
28 fluctuation of the size along axial direction. Present fiber optic sensors mostly use energy loss
29 principles (i.e., changes in optical power in linearly positioned wave-guides) for chemical

1 detection. These can be limited for distributed applications if energy depletes over a short
2 stretch of the fiber sensor, or frequent sensor points are needed at a prohibitively expensive
3 cost. Other sensors use the changes in refractive index and/or cross sectional size of the fiber
4 cable that change the light scattering property in optical fibers, known as Brillouin scattering
5 (Horiguchi et al, 1995; Kee et al, 2000). Fiber optic sensing based on Brillouin scattering has
6 been used successfully in civil infrastructure for health monitoring (Bao et al, 2001; Ohno et al,
7 2001). In this chapter a background on use of optical fibers for chemical sensing and new
8 developments and proposed advancements are discussed.

9 **2. Background**

10 **2.1. Overview of fiber optic sensors**

11 In an optical fiber sensor a physical, chemical or biological variable can interact with the light
12 and produce a change in one of their parameters. It is desirable to produce an optical signal
13 related uniquely to the parameter of interest. These sensors use the optical fiber either as the
14 sensing element (intrinsic sensors), or as a means of relaying signals from remote sensing area
15 to the signal processor (extrinsic sensor), or both. Optical fiber sensors take advantage of the
16 inherent fiber optic characteristics which include their lightweight, of very small size, passivity,
17 low-power requirement, resistance to electromagnetic interference, environmental impact
18 and corrosion, their bandwidth, and flexibility. They can be installed in areas normally
19 inaccessible by conventional sensors, they can be interfaced with data communication systems
20 and pose no risk of electric shock in live measurements. These attributes have allowed optical
21 fiber sensors to displace traditional sensors for measurement and monitoring of rotation,
22 acceleration, electric and magnetic field, temperature, pressure, acoustics, vibration, linear and
23 angular position, strain, humidity, viscosity, pH, gas and chemical content among many
24 others.

25 Use of Fiber Optic Sensors is a viable real-time data gathering approach by surface-adhering
26 or embedding the fiber to a specimen under evaluation. The concept of embedding fiber-optic
27 sensors into structures has generated a great deal of interests in aerospace engineering initially
28 and more recently in civil engineering. There are several types of chemical sensing techniques
29 based on optical waveguides (Ho et al, 2001). Among those are fiber Bragg gratings (FBG),
30 which is marking of a fiber with a laser to create a local narrow band pass filter sensitive to
31 environmental parameters (Guemes et al, 1998; Schulz et al., 1998). Optical time domain
32 reflectometry (OTDR) consists of sending a powerful light pulse and observe modification in
33 the reflected light due to local in homogenities along the fiber. The pulse losses correspond to
34 specific environmental interaction. The evanescent pulse technique is also based on OTDR, in
35 which the fiber cladding is modified to interact with the environment and the pulse travels
36 partially through the cladding. These sensors demand large optical power, due to the cumulative
37 energy loss at the points of contact with the chemicals.

1 Over the last decade, there has been rapid development in the area of smart sensor technologies, in particular using structurally integrated optical fiber to form the basis for smart structure
2 technology. A variety of configurations have been developed for measurement of strains and
3 deformations in structures, including localized-type such as fiber Bragg gratings and multi-
4 plexed long gauge interferometric sensors, and distributed sensing schemes including
5 Stimulated Brillouin Scattering (SBS) or Brillouin Optical Time Domain Analysis (BOTDA)
6 (Bao et al, 2001) and Brillouin Optical Time Domain Reflectometry (BOTDR) (Pamukcu et al,
7 2006; Anastasio et al, 2007).

9 Between different types of optical sensors reported, there are those based on sensitive coatings
10 onto the fiber surface, Fabry-Perot interferometers, long-period fiber gratings (LPFG), LPFG
11 with sensitive films, hetero-core devices, fiber Bragg gratings on doped fibers (i.e, Germanium
12 doped). Fiber gratings are structures consisting of a periodic perturbation of the optical
13 and/or geometrical properties of an optical fiber. Depending on the pitch of the perturbation,
14 fiber gratings fall into two distinct categories: short period gratings, known as fiber Bragg
15 gratings (FBGs) and, long period gratings (LPFGs). Stretching the fiber gratings causes a
16 change in grating period, hence the wavelength of the reflected light. This makes the FBGs
17 ideal for localized temperature and strain measurements. Unlike FBGs in which counter
18 directional coupling occurs in the core, co-directional coupling occur in LPFGs between the
19 core and cladding. This feature renders LPFGs sensitive not only to temperature and strain,
20 but also to bending causing a curvature, to hydrostatic pressure, to torsion and to ambient
21 refractive index changes. The closer the ambient refractive index to that of the cladding the
22 stronger the sensitivity to refractive index changes. It is this high sensitivity that has piqued
23 the interest in development of various types of refractive index-based LPFG sensors which
24 constitute most of the chemical sensing applications (Orellana and Haigh, 2008; Kasik et al,
25 2010).

26 Point detection fiber optic sensors have been developed successfully for measurement of liquid
27 levels, chemical species, drugs, environmental agents (such as pollutants and pesticides),
28 biochemical reactions, and to monitor a wide variety of chemical processes (Wolfbeis, 2000).
29 A fiber optic laser induced breakdown spectroscopy method was demonstrated in the field
30 using a push-cone device, which is a single point, single time measurement technique. The
31 most common configuration for optical pH sensors, and other environmental parameters,
32 employs a fluorescence indicator (Lee et al, 2000). Among the different types of optical fiber
33 devices used in pH sensing are, hetero-core fibers, U-bend fibers, fiber Bragg and long-period
34 gratings, fibers and fiber tips with active doped cladding, among others (Kocincova et al, 2007).
35 Some of the substances that can be detected or identified using optical fiber sensors are volatile
36 organic compounds (alcohols, formaldehydes, methane, ketones, CO_x, O₂, and H₂), some
37 metallic ions like Ca, Al, Cu, Zn, Hg, V and Pb (Jeronimo et al, 2007; Wolfbeis, 2008).

38 Wide application of advanced chemical sensing in the environment may suffer from scaling
39 issues. The real-world conditions often require self-referencing, spatially distributed, tempo-
40 rally continuous, and chemically selective sensors for monitoring regions spanning over long
41 lengths or wide areas. When large area monitoring for chemical agent intrusion is required,
42 use of currently available point sensors can be cost prohibitive. Other non-point, distributed

1 detection methods based on energy loss principles (Buerck et al, 2001) may also be inadequate
2 when scaled to wide area monitoring due to extensive energy input requirements.

3 One of the unique features of the optical fiber technology is the possibility to construct
4 distributed sensors, in which the measuring can be determined along a line of space with a
5 given spatial resolution (Galindez-Jamioy et al, 2012) by, for example, Brillouin optical time
6 domain analysis (BOTDA) (Cui et al., 2009, 2010 and 2011); an hetero-core LPFG sensors. In
7 here, we examine current and proposed application of these techniques to spatially distributed,
8 temporally continuous, and chemically selective sensing applications in soil and water
9 environment. The premise of Brillouin technique goes back to 1920 when physicist Leon
10 Brillouin first studied the diffusion of light by acoustic waves. The phenomenon he observed
11 was a frequency change of scattered light. The first major papers related to distributed fiber
12 optic sensor based on Brillouin were generated in mid-nineties (Bao, et al. 1995; Fellay et al,
13 1997). Current research on Brillouin sensing may be divided in three categories: photonics (the
14 physics of Brillouin); data processing and post processing to improve signal to noise ratios,
15 and applications of distributed sensing to civil infrastructure and environment.

16 **2.2. Fundamentals of optical techniques**

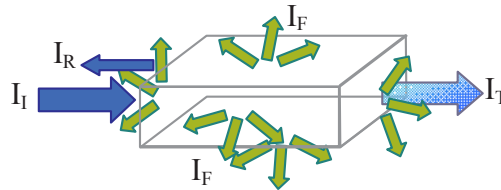
17 The interest on optical techniques to measure or detect chemical agents have been continuously
18 extending and growing over the last forty years. Special attention has been focused on the
19 development of optical sensor to detect heavy metals, due to the hazardous effects of these
20 ions on the health of human beings and ecosystems. Optical methods have the advantage of
21 being fast, simple, compact, portable, low-cost, with sensitivities and resolutions improved to
22 detect in the picomolar range.

23 Combined with other technologies, like microfluidics systems, optical waveguides, or MEMs,
24 optical methods are suitable for application where conventional electrodes cannot be used
25 because of their large size or because of the risk of electrode shock during in vivo measure-
26 ments. Due to their minute size; these optical microsystems are capable of gathering diverse
27 data with a small amount of analyte. The diversification of optical techniques have made
28 possible to construct novel sensing platforms to detect heavy metals in air, water or soil, food
29 and beverages, or biological samples.

30 Optical sensors to detect heavy metals employ an optical transduction technique, i. e. an
31 element that "translate" the chemical variable into an optical signal (intensity, wavelength,
32 polarization or phase), to yield analyte information (McDonagh et al, 2008, Grattan and
33 Meggitt, 1999). Optical chemical sensors can be categorized, according to the transduction
34 technique, in direct sensors and reagent-mediated sensing systems. In direct sensors the
35 element of interest is detected directly via an optical property of the sample such as scattering
36 or florescence, for example.

37 However, most heavy metals optical sensor uses an intermediate agent. Most of the optical
38 chemical techniques to detect heavy metals are based on optical absorption, fluorescence,
39 Raman spectroscopy, or surface plasmon resonance, whereby the perturbed signal is related
40 to the reaction of the intermediate agent under the presence of a specific heavy metal. In

1 general, all these techniques involves the interaction of an incident beam over an analyte or
 2 indicator element yielding transmitted, reflected or fluorescent signal. A schematic representa-
 3 tion of the spectroscopic principle, the working mechanism of an optical sensor is shown in
 4 Figure 1.



5

6 **Figure 1.** Representation of the optical signals in an optical chemical sensor. The incident beam I_i interacts with the
 7 heavy metal sensitive layer and depending on the optical properties of the sample one of the three signals (transmit-
 8 ted I_t , reflected I_r , and generated by fluorescence or scattering I_f) will be produced and will give information about the
 9 type and concentration of heavy metal present on the sample.

10 2.2.1. Absorbance-based techniques

11 Among the optical chemical techniques, the simplest to implement is that based on the
 12 measurement of light absorbed by a sensitive heavy metal layer. Absorption in a gas or liquid,
 13 where it is assumed that each single molecules equally contributes to the total light absorbed,
 14 may be characterized by a Beer-Lambert law, or simply the Beer law,

$$I_T = I_I 10^{-\epsilon C d} \quad (1)$$

15 where I_T and I_I represents the intensity of the transmitted and incident beam, ϵ is the molar
 16 absorptivity ($\text{Lmol}^{-1} \text{cm}$) and C is the concentration (mol L^{-1}) of the absorbing species and d is
 17 the absorption path length (cm). In the case of a solid, absorbing and homogeneous medium,
 18 the transmitted signal is calculated using the Lambert Bouguer law, expressed as $I_T = I_I e^{-\alpha x}$,
 19 where x is the thickness of the medium and α is the extinction coefficient. The Beer law can also
 20 be expressed in terms of the absorbance (or optical density) A :

$$A = \log_{10} \left(\frac{I_I}{I_T} \right) = \epsilon C d \quad (2)$$

21 There exists a linear relation between the absorbance and the concentration of the element to
 22 be measured. However, in order to observe the linear dependence of Absorbance on concentra-
 23 tion, the incident beam should be ideally monochromatic. In the case that a wide broadband
 24 light source is used, the contribution of all wavelengths must be considered, in such cases the
 25 equation (2) becomes:

$$\bar{A} = \log_{10} \left(\frac{\int I_T(\lambda) d\lambda}{\int I_I(\lambda) d\lambda} \right) \quad (3)$$

1 Also the presence of highly absorbing or highly scattering media should produce a deviation
 2 from perfect Beer law behavior. In the case that more than one absorbing material is present
 3 the absorbance contribution of each species must be considered. In most of the absorbance-
 4 based heavy metals sensors an intermediate agent, an optical film that changes its absorbance
 5 according to the concentration of a specific heavy metal, is used (Antico et al, 1999; Guo et al,
 6 2006).

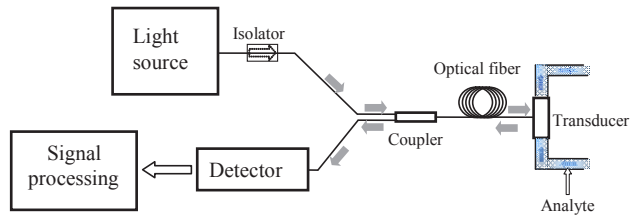
7 A special case of the absorption-based sensors are those schemes where materials that change
 8 their color under the presence of a specific heavy metal are used (Balaji et al, 2006; Prabhakaran
 9 et al, 2007). The reaction of the sensitive components to the concentration of a specific ion
 10 produces a photochromic reaction that can be observed with a naked eye. Such materials are
 11 often in solution, but for sensing the most attractive are those that can be deposited as thin
 12 films over a substrate. The instrumentation of absorption-based sensors is the simpler of the
 13 optical heavy metal techniques, since it can be implemented with a monochromatic light source
 14 and a photodetector. This also makes this technique very susceptible to be implemented in
 15 microscopic opto-fluidic configurations that could diversify the technique.

16 2.2.2. Reflectance-based techniques

17 It is well-known that chemical reactions could lead to changes in the complex refractive index
 18 of a substance; this fact has been impulse researchers to design and fabricate materials that
 19 react with heavy metals that can be used as transducers. When these materials, commonly in
 20 the form of a thin layer, are illuminated with an appropriated light the signal will be partially
 21 or totally reflected. However, this reflectance will change when the layer is in contact with a
 22 specific metal that it reacts with. If the refractive index of the layer is purely real, the changes
 23 in the reflected signal can be estimated by using the Fresnel formulae.

24 However, in most cases the optical response of these materials under the presence of heavy
 25 metals are more complex and involve a change in the real and imaginary parts of the refractive
 26 index, that produce changes in reflectivity and absorbance. Also, there is a contribution of
 27 scattered light. So, the reflected signal is composed of light from different sources, however,
 28 also in this complex response the signal reflected is used to deduce, directly or indirectly, the
 29 concentration C of the heavy metals.

30 The reflected-based techniques are specially used in optical fiber schemes since the set-up is
 31 very simple to implement (Yusof and Ahmad, 2003, Guillemain et al, 2009). The material
 32 sensitive to the heavy metals are directly deposited over the fiber tip or in a substrate that will
 33 be illuminated by an optical fiber. The reflected signal is usually collected by the same fiber,
 34 but frequently another fiber or fibers are used to collect it. The reflected signal propagates
 35 along the fiber to the detector, where it is analyzed in order to determine the heavy metal
 36 present and their concentration (Figure 2).



1

2 **Figure 2.** Diagram of a reflectance-based optical chemical sensor based on optical fibers.

3 2.2.3. Fluorescence-based techniques

4 Some materials have the property of being fluorescent when they are illuminated with a light
 5 source of appropriated wavelength. The fluorescence is the optical radiation generated when
 6 electrons of an atom or molecule return from the excited to the ground state after absorption
 7 of a photon from an excitation light source. In general the energy of the excited photon is lower
 8 than the absorbed one so the wavelength of the fluorescence signal is longer than that of the
 9 excitation.

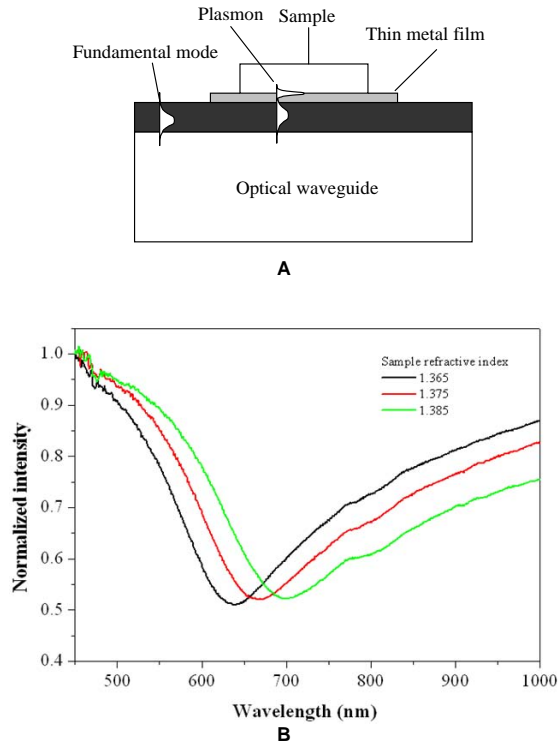
10 The intensity of the fluorescent signal (I_F) is proportional to the intensity of light absorbed by
 11 the sample ($I_T - I_R$), therefore it is possible to establish a direct relation between the intensity of
 12 the fluorescent signal and the concentration of an absorbing material. This feature is very
 13 important for sensing since intensity of the fluorescence increases as the concentration of the
 14 absorbing species augments. Although, we have just made reference to the fluorescence
 15 intensity, for sensing, the decay time of the fluorescence signal is more frequently used because
 16 this parameter is less sensitive to source fluctuations, interference from ambient light or drift
 17 due to aging of detector. It is possible to design and fabricate a fluorescent material sensitive
 18 to a specific heavy metal. Thus, the intensity, wavelength and life time of the fluorescent signal
 19 will change under the presence of this metal. Fluorescence-based techniques are the most used
 20 to detect the presence of heavy metals due to its extraordinary sensibility (Mayra et al.,
 21 2008; Achatz et al, 2011, Aksuner, 2011).

22 2.2.4. Surface plasmon resonance-based techniques

23 The most popular label-free refractometric technique is the Surface Plasmon Resonance (SPR),
 24 since it allows the direct observation of chemical reactions in real time without the use of
 25 markers or labels. SPR is a quantum optical-electrical phenomenon produced by the interaction
 26 of light with a metal surface. Actually, the surface plasmon is a charge density oscillation that
 27 exists at a metal-dielectric interface. The plasmon propagates in a direction parallel to the
 28 metal-dielectric interface in the boundary of the metal and the external medium (Figure 3).

29 These oscillations are very sensitive to any change in the optical refractive index of the material
 30 at the boundary. The optical excitation of plasmon can be achieved in a three-layer system
 31 consisting of a thin metal film sandwiched between two isolators of different dielectric constant

1 (Maier, 2007), where the phase-matching condition between the optical and plasmon wave
 2 vector is fulfilled. In the optical domain, the surface plasmon excitation will be observed as an
 3 intensity transmission loss at a specific wavelength. The wavelength of the dip depends on the
 4 refractive index of the two dielectrics and the thin metal film, and the propagation constant of
 5 the optical waveguide. There are three common method to excite surface plasmon, using a
 6 prism coupler and the attenuated total reflection, a periodic grating, and an optical waveguide
 7 planar (Figure 3A) or cylindrical. The prism coupler technique is the most popular since
 8 exhibits a good sensitivity, stability, and reproducibility for the measurement of heavy metals
 9 (Forzani et al, 2007; Lin et al, 2009; Abdi et al, 2011; Fen et al, 2012 and 2013; Fen and Yunus,
 10 2013). For heavy metal detection a sensitive thin film layer is deposited over the thin metal
 11 film, so when the target heavy metal interacts with the layer a refractive index change is
 12 produced. The surface plasmon conditions changes and the peak wavelength shifts as can be
 13 seen in Figure 3B. SPR is the most sensitive refractometric method, with a theoretical resolution
 14 of 1×10^{-7} , so it is possible to detect very small traces of heavy metals.



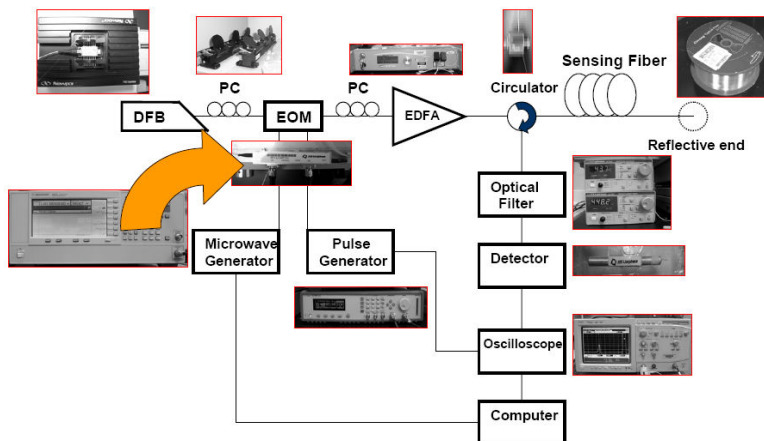
15

16 **Figure 3.** (A) A schematic representation of the surface plasmon excitation in a dielectric planar waveguide coupler
 17 configuration. (B) Optical transmission spectra of an hetero-core optical fiber coated with a 20 nm thin gold film when
 18 the fiber is immersed in a liquid with a refractive index of 1.365, 1.375, and 1.385, black, red and green line respective-
 19 ly.

2.3. Fundamentals of BOTDA and LPFG based sensing

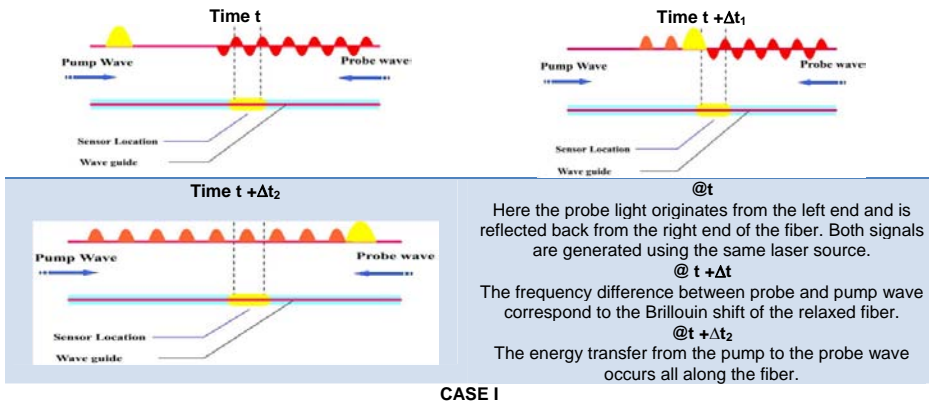
Figure 4, 5 and 6 show the stimulated Brillouin scattering based BOTDA photonics configuration and the principle of measurement used at Lehigh University Geo-sensing laboratory, respectively (Texier et al, 2005; Pamukcu et al, 2006; Turel and Pamukcu, 2006; Anastasio et al, 2007). Brillouin is a nonlinear effect, in which light is scattered at well-defined points along the fiber where the acoustic properties of the fiber are locally modified by the environment. The stimulated Brillouin scattering (SBS) is an acoustic – optical process which is useful for distributed measurements of a probe beam by the SBS interaction with a counter-propagating nanosecond pump pulse. In the SBS technique, as in a null detector, the pump and probe are initially de-tuned by a (frequency) that is slightly greater than the Brillouin frequency. Therefore, in unstressed fiber, the base line remains flat resulting in a self-referenced sensor eliminating the need for duplication with another reference fiber.

The Brillouin line being intrinsically narrow (~20-50MHz), the initial de-tuning can be quite small so that the amount of strain required to generate a signal is also quite small (0.001%), allowing for higher resolution and sensitivity of the sensor compared to other fiber-based measurement techniques. When SBS based sensors are used for environmental sensing the fiber is hitched or bonded with selective polymer transducers that are mass detectors in direct contact with the surrounding medium. The polymer reacts to the surrounding (i.e. moisture, pH, target chemical) by selectively absorbing the target compound and it swells. Localized swelling of the bonded or hitched polymer produces tangential, axial or radial stresses on the fiber depending on the physical coupling. These stresses result in axial straining of the fiber and a measurable change in its local acoustic properties, hence a Brillouin scatter of the transmitted light. The location of the generated signal is determined by time domain reflectometry.

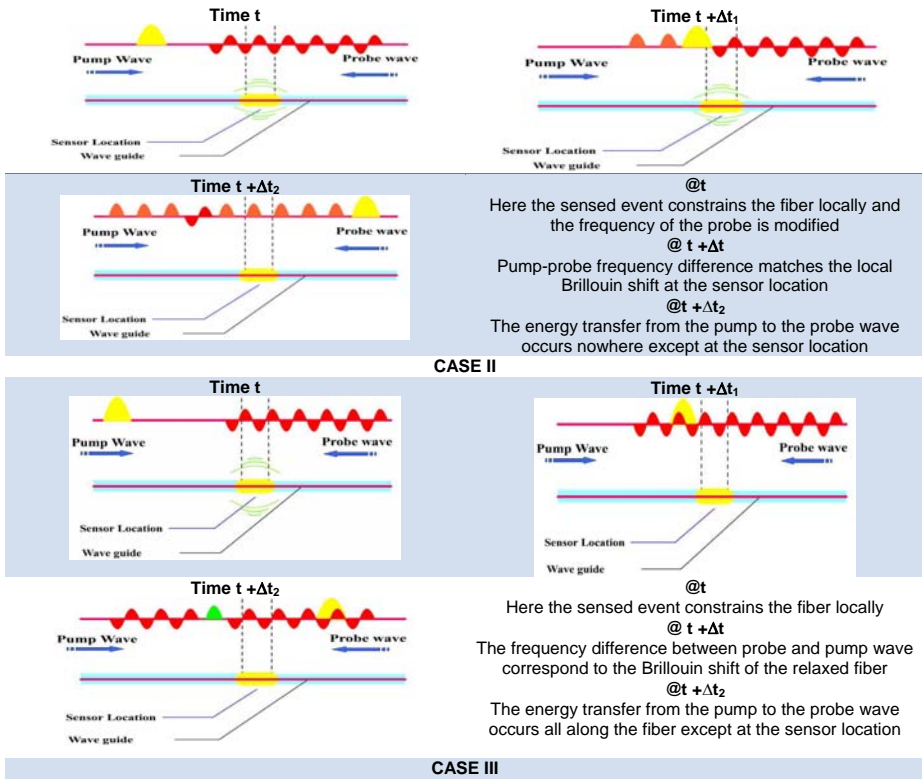


25

26 **Figure 4.** SBS based BOTDR photonics set up at Lehigh Geo-Sensing Laboratory.



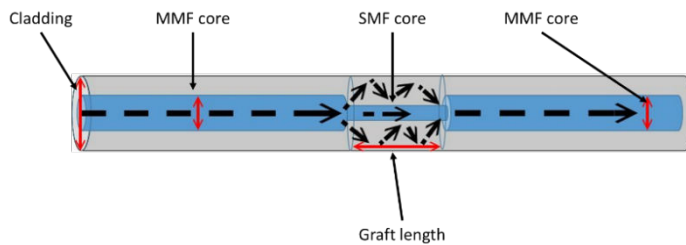
1
2 **Figure 5.** Measurement principles of SBS based sensing: case I.



3
4 **Figure 6.** Measurement principles of SBS based sensing: case II and III.

1 In the case of LPFG's the environmental changes produce a spectral shifts, that required a
 2 sophisticate or a complicate equipment. These devices are very sensitive to temperature
 3 changes so to measure another different parameter it is necessary to make the corresponding
 4 compensation. One alternative to avoid these difficulties are hetero-core fibers. These devices
 5 are constructed by changing the diameter of the core in a small length (mm) in a transmission
 6 line (Figure 5 and 6), which causes the optical wave to expand within the cladding in the single-
 7 mode region of the hetero-core, thus the evanescent field can easily interact with the external
 8 medium.

9 Owing to the core diameter mismatch, some of the light is guided by the cladding of the SM
 10 fiber (Figure 7). This makes the transmission of the device dependent on the refractive index
 11 of the external medium. The sensor exhibits maximum transmission changes when the index
 12 of the sample medium approaches that of the SM fiber cladding. The device can operate at
 13 different wavelengths as well as when coated with thick films made of variable index materials.
 14 Moreover, standard emitters, fibers, detectors, etc., are needed to fabricate the sensor, which
 15 makes it attractive for diverse applications (Villatoro and Monzon-Hernandez, 2006).



16

17 **Figure 7.** Schematic representation of the hetero-core fiber structure. A piece of single-mode fiber (SMF) of length L is
 18 inserted between two multimode fibers (MMF). Cladding diameter of both fibers is $125\ \mu\text{m}$ but the core diameters are
 19 different.

20 3. Investigation

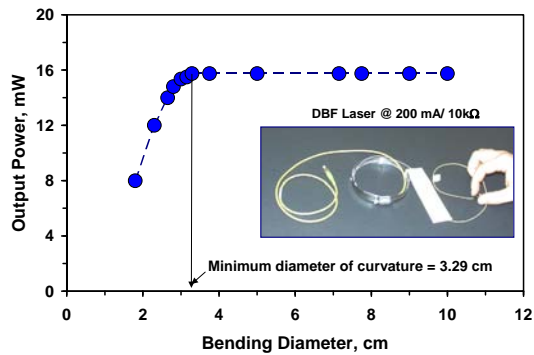
21 3.1. BOTDA/BOTDR applications and proposed sensor configurations

22 The usefulness of SBS for sensing is general: any change in external conditions, that affects the
 23 acoustic properties of the optical fiber, can in principle be detected. This is true of direct
 24 temperature and pressure changes, but can also be true of changes in chemical environment
 25 that can be made to result in temperature and pressure changes. An SBS based BOTDR sensing
 26 system was used to detect water content changes in soil. Water transducers (hydrophilic
 27 polymers) were tested to correlate Brillouin strain response to the water content of the
 28 surrounding soil environment. In these experiments, the optical fiber was wound and secured
 29 about discretely placed discs (2 cm length \times 5cm diameter) of AEP60 hydrophilic polymer
 30 (Figure 8A), strung along 100-m fiber continuous optical fiber. The diameter of the polymer

1 disc was selected to accommodate the minimum curvature of bending of the fiber, as shown
 2 in Figure 8B.



A



B

3

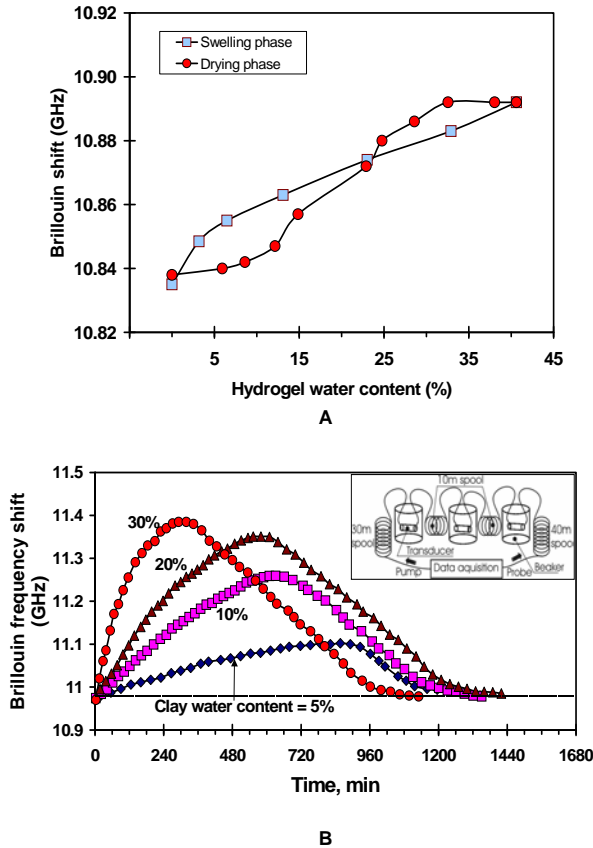
4 **Figure 8.** A photograph of the AEP60 hydrogel polymer discs used in sensor (A); assembly and test results for mini-
 5 mum fiber bending radius assessment (B).

6 The optical fibre at the inlet and outlet of the string of four transducers were spliced to spools
 7 of fibre on each end, and connected to the photonic set-up. Each water transducer was then
 8 embedded in a wet clay sample of predetermined water content (5, 10, 20 and 30% by dry
 9 weight of clay), as shown in the inset sketch of Figure 9B.

10 The clay samples were packed in equal volume, watertight, cylindrical cells of 14-cm diameter
 11 and 28-cm height. The experiments were conducted in a temperature-controlled environment,
 12 at 25°C so that Brillouin scattering measurements were not influenced by thermal expansion
 13 or contraction of the fibre. The Brillouin shift was measured with 5 to 20 minute intervals up
 14 to the maximum observable swelling. When no significant change in Brillouin shift was
 15 recorded for three consecutive measurements, the transducers were removed from the soil
 16 chambers and left for open air-drying.

17 The Brillouin shift measurements were recorded with 5 to 20 minute intervals until the drying
 18 phase was completed. Since Brillouin readings could be recorded for strains as low as 10, very
 19 small volume change due to water absorption could be detected in a few minutes. Figure 9B

- 1 shows the time rate of Brillouin signal changes during the hydrogel swelling and drying cycles
 2 of the 4-different water content clay hosts.

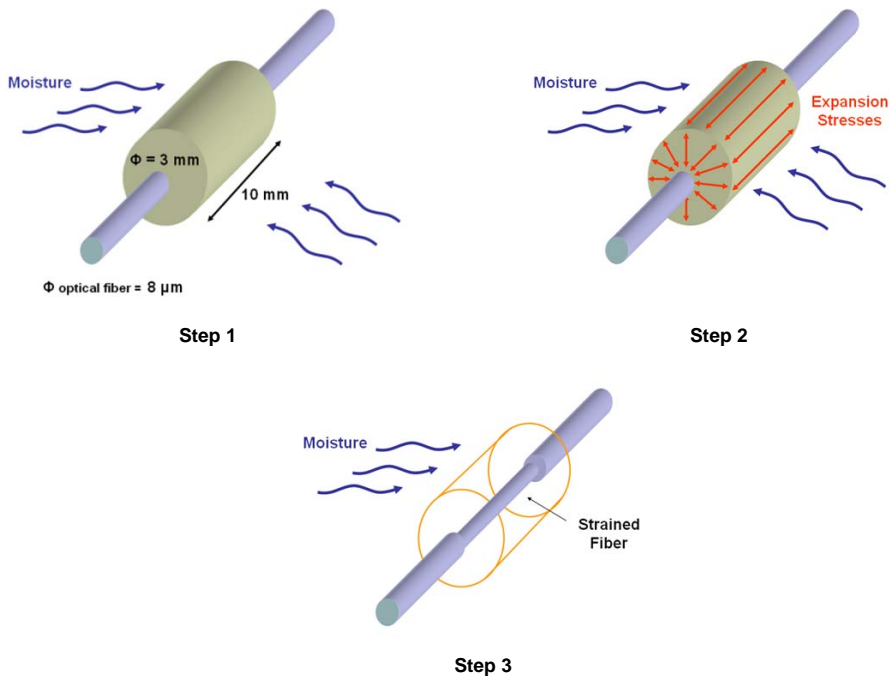


3

4 **Figure 9.** (A) Calibration of Brillouin Shift of fiber versus the water content by dry weight of the hydrogel disc. (B) Brillouin signal shift as a function of swelling/shrinkage time and clay water content (*Inset* – sketch of experimental set up).

7 In the experiments described above, the AEP60 polymer used would typically expand from
 8 38% to 400% over dry volume when exposed to water. They are non-toxic and are manufactured
 9 in medical grades, approved for use in human wound care applications. This group of
 10 polymers does not swell in hydrocarbons and chlorinated solvents and has high thermal
 11 resistance. They are cross-linked to give them mechanical stability and accurate expansion
 12 characteristics. The water absorption and expansion factor can be accurately pre-defined at the
 13 formulation stage. Full expansion is reproducible over many wetting and drying cycles and is
 14 consistent over a wide range of pH and dissolved solid concentrations. A different integration
 15 of optical fiber and polymer transducer was used to improve the polymer response kinetics as

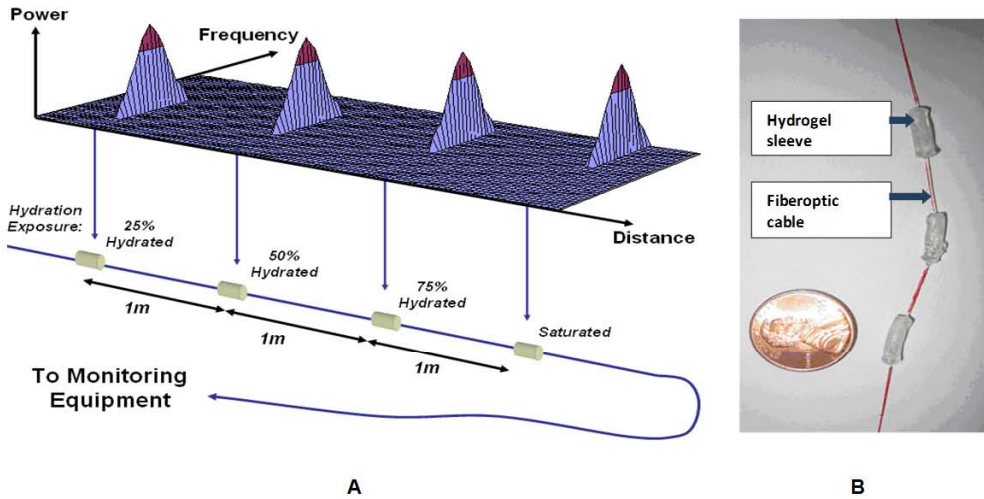
1 shown in Figure 10. In this design, the polymer was reduced to smaller size discrete sleeves
 2 (1cm length x 0.3 cm diameter) that were bonded over the optical fiber. The bonding adhesive
 3 used was Locktite 414, a super bonding, quick drying adhesive containing cyanoacrylate and
 4 is intended for plastics and vinyl. The Locktite 414 was applied to each end of the polymer
 5 sleeve also.



6

7 **Figure 10.** The working principle of the integrated sensor. Step 1 - Solution sorbed by the chemical selective polymer
 8 sleeve bonded onto the fiberoptic cable. Step 2 - The selective polymer swell upon encountering the target compound
 9 or ion in the solution. Step 3 - The swelling of the bonded polymer sleeve induces a "tangential pull" or "axial strain"
 10 on to the fiber locally.

11 The reduced size was anticipated to improve the swelling kinetics and alleviate the hysteresis
 12 affects observed in the previous configuration. The working principle of the integrated sensor
 13 is also depicted in Figure 10, where first the influx of the target substance (e.g. water) into the
 14 polymer transducer causes swelling of the bonded polymer. The swelling causes the bonding
 15 interface to strain and cause the fiber elongate in tangential pull. The fiber strain can then be
 16 recorded with location and amplitude, as shown in Figure 11, indicating where along the fiber
 17 line the influx of the target substance had occurred, and also the calibrated quantity of the
 18 substance based on the degree of swelling of the polymer, respectively.



32

A

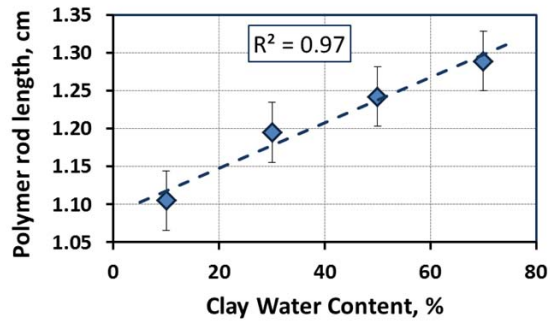
B

33 **Figure 11.** The operation schematic and the photograph of a spent water sensor: (A) Conceptual schematic of the
 34 integrated sensor assembly and its working principle as a distributed water sensor. (B) A laboratory prototype of the
 35 integrated water sensor.

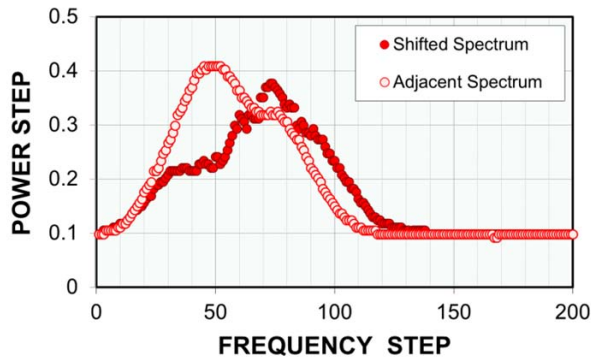
1 Repeated swelling and shrinkage tests of the polymer sleeve component of the integrated
 2 water sensor showed hysteresis of length and diameter change. Both the length and diameter
 3 of the of the polymer sleeve expanded by 35% (~0.35 cm and ~0.1 cm, respectively) after being
 4 soaked in water for three days. The majority of this expansion occurred during the first 12
 5 hours of soaking. Increasing with every cycle, the final dry length of the polymer was greater
 6 than the original by ~0.025 cm (~2.5%). As more cycles were completed, the diameter increased
 7 to its maximum faster, but the value of this maximum decreased. The final diameter of the
 8 polymer sleeve was fairly constant for each cycle, slightly less than the original by ~0.0005 cm
 9 (~0.2%).

10 The magnitude and rate of swelling correlated directly with the initial water content when the
 11 polymer sleeves were embedded in test clay specimens of different water contents. Once again
 12 the full swelling occurred between 8 to 12 h when the sleeves were embedded in wet clay.
 13 Figure 12A shows that the polymer linear extension and clay water content relation was fairly
 14 linear. The linear relation is desirable for robust calibration. Figure 12B shows the dimension-
 15 less frequency shift response of the integrated water sensor to clay water content increase. The
 16 figure plots two spectrums, the shift spectrum at the location of the expanded polymer and a
 17 spectrum near the polymer location that does not undergo the swelling stress.

21 The actual Brillouin frequency shift was measured 0.0432 GHz corresponding to axial strain of
 22 0.098% for the fiber. The actual elongation of the polymer rod was 3 mm, which fully trans-
 23 ferred to the fiber would have corresponded to an average strain of 0.14% for the fiber over
 24 the 12.6 ns pulse. This meant that about 70 percent of the axial tug generated by the swelling
 25 of polymer was transferred to the fiber. The other 30 percent can be attributed to slippage



A



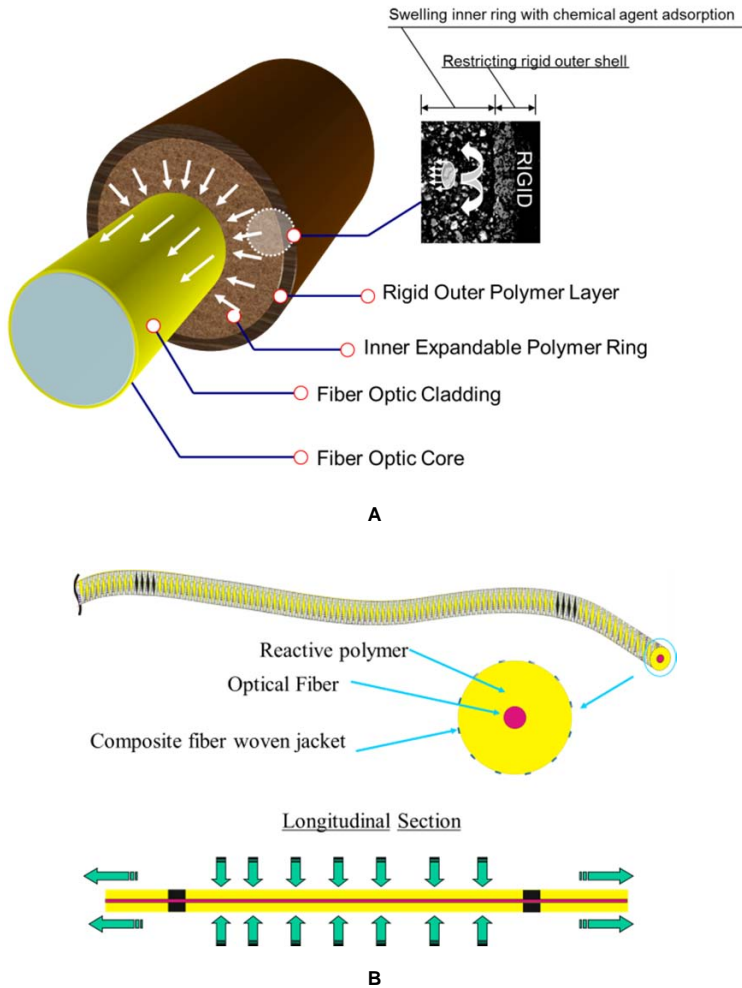
B

18

19 **Figure 12.** (A) Variation of embedded AEP60 polymer sleeve length vs clay w/c in swelling behavior. (B) Shifted frequency spectra for integrated sensor under swelling stresses with increased water.
20

1 across the length of the bond between the fiber and the polymer sleeve or other process related
2 inefficiencies.

3 These test results demonstrated the viability of integration of optical fiber with reactive
4 polymer as a BOTDR based sensor. Yet, the slow kinetics of the response (~12 hrs for full
5 swelling in case of water) rendered the prototype assembly limited for quick detection and
6 measurement purposes. Hence a new polymer and fiber-optic cable configuration is proposed
7 where a thin layer (e.g. on the order of few hundred μm) of the reactive polymer is brushed
8 and bonded onto the fiber-optic cable. Figure 13 presents variations of the conceptual sensor
9 where the reactive polymer coat is continuous. The working principle of this new configuration
10 is similar to the previous ones described, all based on BOTDR, with the exception that the
11 continuous coating of a thin layer reactive polymer is anticipated to provide a truly distributed
12 and fast detection mechanism.



13

14 **Figure 13.** Advanced integrated chemical sensors based on BOTDR/BOTDA: (A) Cross-section of integrated sensor
 15 with core/shell polymer layers; (B) Working principal of an integrated sensor with polymer/jacket combination.

1 3.2. Reactive polymers principles used as sensors

2 Point detection fiber optic sensors have been developed for measurement of liquid levels,
 3 chemical species (inorganic and organic), drugs, environmental agents (such as pollutants and
 4 pesticides), biochemical reactions, and to monitor a wide variety of various chemical processes
 5 (Wolfbeis, 2000). One of the major components of a sensor system is the sensing or recognition
 6 element. Polymers have often been utilized as a chemical sensing material. The interaction of
 7 an analyte with the polymer coating is of prime importance. A signal needs to be generated
 8 once this interaction occurs, and much work has been carried out to understand the interaction

1 of the polymer coating with the analyte molecules, especially in terms of the diffusion behavior
2 of the analyte through the polymer coating to the actual sensor itself and its subsequent
3 enrichment within the polymeric coating layer (Philips, et al, 2003).

4 The integrated chemical sensor based on BOTDR discussed in here is a single SBS (Stimulated
5 Brillouin Scattering) sensing optical fiber bonded with such a polymer, which swells selectively
6 in the presence of a target chemical. The polymer coat is cross-linked to swell in a preferential
7 direction. During swelling, the bonded polymer coat exerts a radial or tangential force at the
8 polymer-fiber interface, hence an axial strain on the fiber. The SBS signals are generated along
9 the fiber at the discrete points of chemical contact triggered by polymer swelling, hence the
10 local axial strains in the fiber. Consequently, the location of the target chemical can be detected
11 simply by linear positioning of the SBS signals over the entire length of the cable. Because the
12 detection is based on local physical changes in the fiber and not on loss of transmitted light,
13 widely distributed sensing is possible without high power requirements. The specific detection
14 and measurement components of the integrated sensor described above include, a core/shell
15 type (multi-layer) polymer coating, and an inner fiber optic cable core, or a rigid woven jacket
16 conceptualized in Figure 13.

17 In this conceptual design, the outer cross-linked polymer coating (shell) serves as a rigid, high
18 permeability filter and confinement to the inner polymer (core). The core is a flexible, chemi-
19 cally selective polymer, preferably with rapid mass sorption kinetics. While the highly
20 networked rigid polymer shell confines and directs the cores welling toward the fiber optic
21 cable, the selective detection of chemicals is based on the thermodynamics and kinetics of
22 chemical sorption and swelling of the core polymer layer. A volume change or "swelling"
23 occurs in the inner flexible polymer layer as a result of mass sorption of the surrounding
24 analyte. Solute/solvent sorption interrupts the intermolecular forces between individual
25 chains of a lightly cross-linked or a linear polymer adjacent to the glass fiber, resulting in
26 swelling forces. The outer, permeable but rigid polymer layer comprised of highly networked
27 cross-linked chains help confine the volume change tendency and direct part of the swelling
28 forces inward (radially and/or longitudinally) thus creating a hoop or a tangential stress on
29 the fiber at the polymer interface. This "pinch" or tug" of the fiber cause changes in the elastic
30 and refractive properties of the fiber locally, generating a shift in its original Brillouin frequency
31 at that local. Comparing the new frequency to the original, it is then possible to quantify the
32 change in terms of the swelling forces and the quantity of the absorbed substance.

33 A multi-chemical sensor can be developed by bundling polymer-coated fibers of different
34 functions and sensitivities. The entire sensor assembly can be several tens of kilometers of
35 optical fiber hosting several 100 measurement locations on the same line, each at a minimum
36 spatial resolution of 1-meter. The photonics assembly connected to one end of the fiber allows
37 fast detection of discrete sensing locations rendering the entire assembly a multiplexed
38 network of many point sensors on the same transmittal line. Hence, the fiber line coupled with
39 the stringed transducers can be embedded linearly or laced into a host medium (i.e. water
40 pipeline, paved surfaces, porous media such as soil or concrete) to detect target chemical(s)
41 online over large distances, areas or spaces by linear positioning of the fiber.

1 3.2.1. Reactive polymers

2 The molecularly imprinted polymers are often used to improve selectivity (Wolfbeis, 2000;
 3 Philips et al, 2003). The incorporation of desired functional monomers into the polymer
 4 structure further enhances the selectivity to a given analyte. These polymers are cross-linked
 5 and prepared by free radical polymerization processes such as solution or dispersion poly-
 6 merization with acrylic or vinyl monomers. Polyelectrolyte gels are charged cross-linked three-
 7 dimensional networks of monomers that possess high swelling capability due to solvent
 8 sorption. The amount of swelling is known to be a string function of pressure, temperature,
 9 ion concentrations and pH changes (Siegel, 1993; Siegel et al, 1998; Matsuo and Tanaka, 1988).
 10 Their swelling and kinetics depend on parameters such as the degree of cross-linking (Skouri
 11 et al, 1995), external salt molarity (Yin et. al, 1992), and the degree of gel ionization rule
 12 (Katchalsky and Michaeli, 1995; Yin et al, 1992).

13 An emulsion or miniemulsion polymerization approach can be utilized to prepare film-
 14 forming polymer latexes with desired functional moieties to be used to coat optical fibers. The
 15 base latex polymer may be based on acrylic (e.g., *n*-butyl acrylate, *n*-butyl methacrylate) or
 16 styrene/acrylic film-forming compositions (i.e., with glass transition temperatures (T_g) of room
 17 temperature or lower). These latexes are prepared by conventional emulsion polymerization
 18 or by a miniemulsion polymerization process in the case where monomers with very low water
 19 solubility are used. In the miniemulsion polymerization process, the monomer would be
 20 emulsified in the presence of an aqueous surfactant (such as sodium lauryl sulfate) / costabil-
 21 izer (e.g., hexadecane dissolved in the (co)monomer mixture) combination using a high shear
 22 device to form miniemulsion droplets which could then be polymerized in the presence of a
 23 free radical such as potassium persulfate.

24 The polymer would also be crosslinked to varying extents using crosslinking monomers such
 25 as ethylene glycol dimethacrylate, divinylbenzene, or bisacrylamide. In addition, functional
 26 monomers can be copolymerized along with the base acrylic or styrene/acrylic monomers. One
 27 type of monomer is a carboxylic acid such as methacrylic acid (MAA), which copolymerizes
 28 well with the base monomers. At high concentrations, this latex could function as an alkali-
 29 swellable latex whereby the latex particle size, and coating swellability, would increase
 30 dramatically upon neutralization in aqueous solutions of high pH (e.g. > 10) which would
 31 trigger a sensor response. N-methylol acrylamide (NMA) may also be incorporated into the
 32 base copolymer composition to obtain a crosslinked polymer, which can also act as a hydrogel,
 33 which could also swell when exposed to water. In addition, the monomer, N-(isopropylacry-
 34 lamide) (NIPAM) will also be utilized for forming hydrogel particles which can swell when
 35 exposed to water. Incorporating NIPAM into a polymer composition would also lead to the
 36 formation of a thermosensitive polymer coating since poly(NIPAM) exhibits a strong phase
 37 transition above 32°C. It is also possible to copolymerize a alkoxy silane-containing monomer
 38 with the acrylic or styrene-acrylic monomers via miniemulsion polymerization to enhance the
 39 compatibility of the polymer coating with the glass optical fiber.

1 3.2.2. Bonding/lamination

2 The extent of bonding of the polymer coating to the glass optical fibers is critical. The optical
3 fibers can either be coated with the manufacturer's cladding removed or in place. Preliminary
4 experiments have shown that it is difficult to coat the uncoated glass fibers. These fibers are
5 brittle without the manufacturer's cladding in place; the composition of which is unknown.
6 The fiber can be passed through a coagulant bath prior to its immersion in the latex bath.
7 Similar to dip coating, which has been utilized in preliminary coating experiments, the latex
8 will coagulate onto the glass fiber. The surface of the fiber needs to be made hydrophilic for
9 this process. This can be achieved by either physical adsorption of nonionic water-soluble
10 polymer such as poly(vinyl alcohol) (PVOH) or by corona treatment of the fiber surface. In
11 addition, the polymer processing techniques used in wire coating applications can also be
12 applied to the case of the optical fibers. Important coating parameters would include the solids
13 content of the latex (a high solids content is needed to control the rheology of the dispersion
14 to be coated; a reasonable viscosity is needed for effective coating). Latexes can also be made
15 self-thickening by the incorporation of carboxyl groups into the latex particles. A thickener can
16 also be added to a latex composition to adjust the coating viscosity.

17 In addition, the surface tension of the latex would need to be controlled to give good wetting
18 onto the glass fiber. Contact angle measurements on glass substrates can be used to determine
19 the optimum wetting behavior before moving on to the glass fiber itself. The thickness of the
20 polymer coating would also need to be varied to determine the necessary thickness needed to
21 give a good, measurable response when exposed to solvent or water containing the heavy
22 metal ions. If the coating is not thick enough, the response to the analyte may be too weak. If
23 the coating is not uniform on the fiber, there would be unexposed regions of the fiber which
24 would affect the detection limit and sensitivity. In addition, there needs to be good adhesion
25 of the coating to the fiber, otherwise delamination could occur. Silane adhesion promoters can
26 be explored to enhance adhesion of the polymer coating onto the glass fiber substrate. The
27 drying temperature and drying conditions (e.g., time and temperature that the latex-coated
28 fibers are dried in an oven to ensure good film integrity or the use of forced heated air flow
29 over the fibers) are also critical coating variables to be investigated.

30 3.2.3. Kinetics

31 The kinetics of swelling of the polymer coatings when exposed to aqueous or organic media
32 needs to be evaluated by monitoring the changes in the dimensions of the coating or the
33 gravimetric uptake of the media by the polymer. The time-dependent changes can be analyzed
34 to give an idea of the best polymer architecture to obtain an optimum sensor response when
35 exposed to a given chemical. The time constant for the sensor response needs to be determined
36 and correlated with the swelling kinetics of the polymer coating to achieve the best sensor
37 performance.

1 3.3. Development of a prototype pH sensor with reactive polymer coating

2 The development of an optical fiber pH sensor based on hetero-core fiber structure coated with
3 an acrylic polymer doped with Prussian blue is discussed here. In this design, the pH changes
4 of the surrounding medium affects the Prussian blue present in the layer and produce a change
5 in the refractive index of the layer. The pH changes are then observed as an increment in the
6 hetero-core transmission signal.

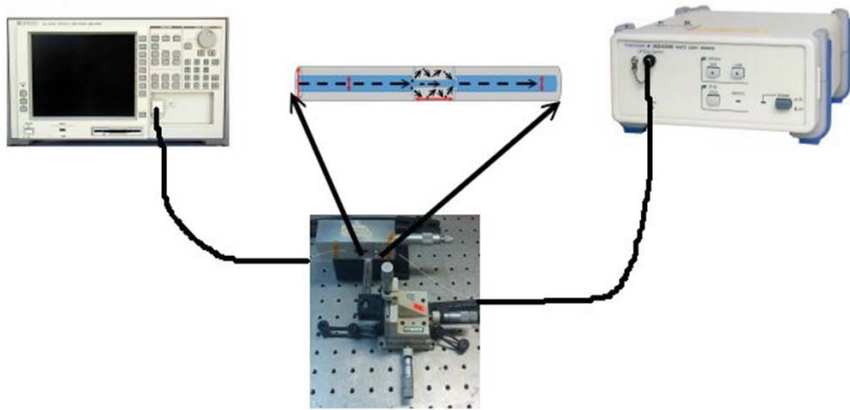
7 3.3.1. Building of hetero-core optical fibers with reactive layer

8 The hetero-core fibers were constructed using two different length and two different types of
9 optical fiber. In this case two types of single-mode fibers (SMA and SMB) and two of multimode
10 fibers (MMA and MMB) were used. First, two pieces of MM fiber, stripped of its coating
11 polymer (3 cm section) were spliced to a stripped SM fiber on each side. The hetero-core fibers
12 were treated with Prussian Blue 0.1 mM (PB), polyvinyl alcohol (PVOH) at 4%, acrylic polymer
13 emulsion (APE) at 50% plus and their combinations, like PVOH + PB and APE + PB to develop
14 a reactive coat over the stripped surfaces. A small U-shape container made of a glass capillary
15 was fixed to a mechanical mount and was filled with the mixture of polymer support and
16 Prussian blue sensitive material. Then the single-mode section of the hetero-core fiber was
17 immersed for 5 minutes into the solution after which the fiber was removed and dried at room
18 temperature. In this manner the sensitive material was adhered to the single-mode section of
19 the hetero-core fiber.

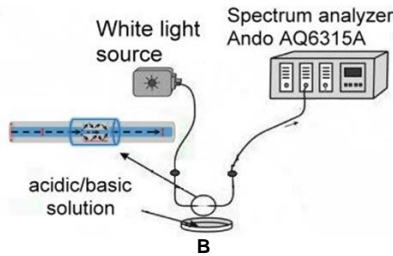
20 One end of the hetero-core fiber was connected to a white light source Yokogawa AQ4305 and
21 the other to the spectrum analyzer Ando AQ6315A (Figure 14A). The set-up was used to
22 measure the transmission light during the modification process of the fiber and later to
23 measure the response of the modified fiber to pH changes. In order to test the sensitivity of
24 the device to changes in pH, a test was designed which consisted of immersing the optical fiber
25 section modified with PVOH/AP or APE/AP, in a Petri dish where the pH was varied by adding
26 NaOH 0.1 M or 0.1 M HCl, recording each transmission spectrum changes in the wavelength
27 range from 350 nm to 1700 nm (Figure 14B).

28 The transmission spectra of two hetero-core fibers with PVOH/A (5mm and 10mm sections)
29 were measured in different pH solutions are shown in Figure 14A and 14B, respectively. As
30 seen in figure 15 the device has good sensitivity (-1.5 dB and -2 dB approximately), however
31 the signal is erratic and not repeatable for different pH changes. This was attributed to
32 solubility of PVOH in acidic conditions, and checked visually and with the transmission
33 spectrum analysis. A new polymer, acrylic polymers emulsion (APE) was selected to replace
34 PVOH. This polymer has similar characteristics as PVOH. It is water soluble, inexpensive, and
35 colorless when dried, and has been reported as a good support in manufacturing of modified
36 electrodes for pH determination.

40 The transmission spectra of two hetero-core fibers with APE/A (5mm and 10mm sections) were
41 measured in different pH solutions are shown in Figure 16A and 16B, respectively. As seen in
42 Figure 16A, the device showed very obvious changes when subjected to acidic and basic
43 conditions. The presence of three peaks in visible region, 400, 500 and 700 nm wavelengths



A



B

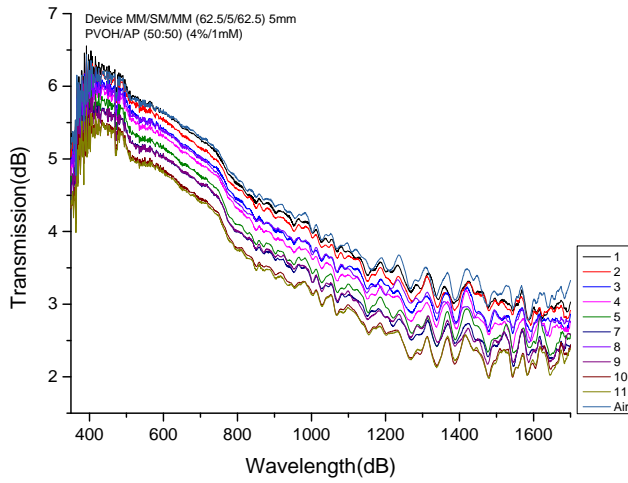
60

61 **Figure 14.** Set up to test prototype hetero-core fibers for chemical detection: (A) Diagram of the set-up to measure
 62 the transmission signal of the hetero-core fibers; (B) Diagram of the test system to determine the sensitivity of hetero-
 63 core fiber to pH changes.

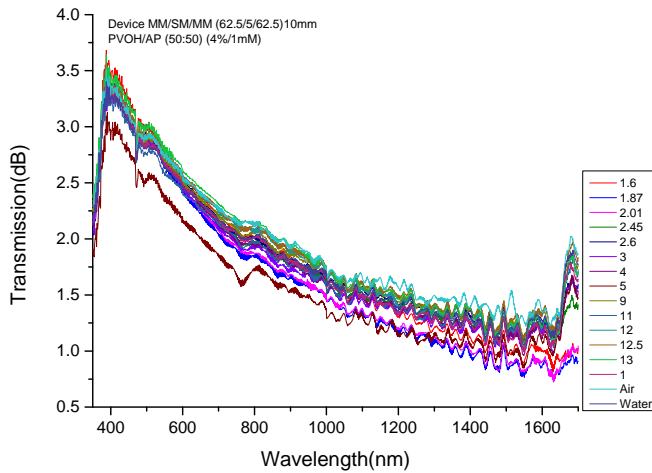
1 were noted when optical fiber was in air. These signals were attributed to light absorption and
 2 loss of light by index refraction changes by the composite material. In acidic pH values the
 3 light losses were in the range of 1.5 to 3 dB while for basic pH levels transmission near to 0.5
 4 dB.

8 In order to identify the origin of signals found, the concentration of Prussian blue was increased
 9 to 2 mM. As we can see in Figure 16B, the intensity of transmission peaks at 400, 500 and 700
 10 nm was increased, suggesting that they are due to increased concentration of AP in the
 11 composite. It also shows that the device sensitivity increased from 1.5 to 3 dB with 1mM
 12 concentration of AP until 4 to 6 dB with 2mM concentration of AP for acidic pH solutions, but
 13 behaved same as previous in basic solutions. Finally there was a good return to initial
 14 conditions after each change of interface (Figure 17).

18 Subsequently we performed a sensitivity analysis for pH changes by taking the APE/AP
 19 modified fiber signal in air to use as a normalizing reference. As shown in Figure 18, there is
 20 good sensitivity to pH values lower than 7 with gains up to 6 dB at 400 nm (absorption or loss
 21 peak), whereas above pH 7 the peak is inverted, turning in a gains peak which may be due to



A

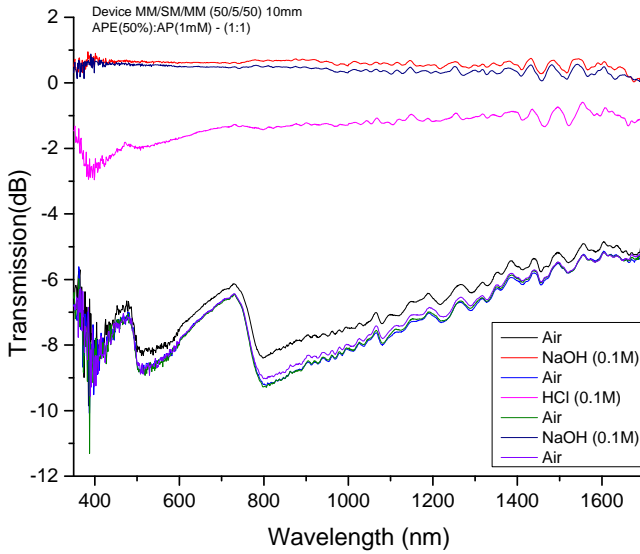


B

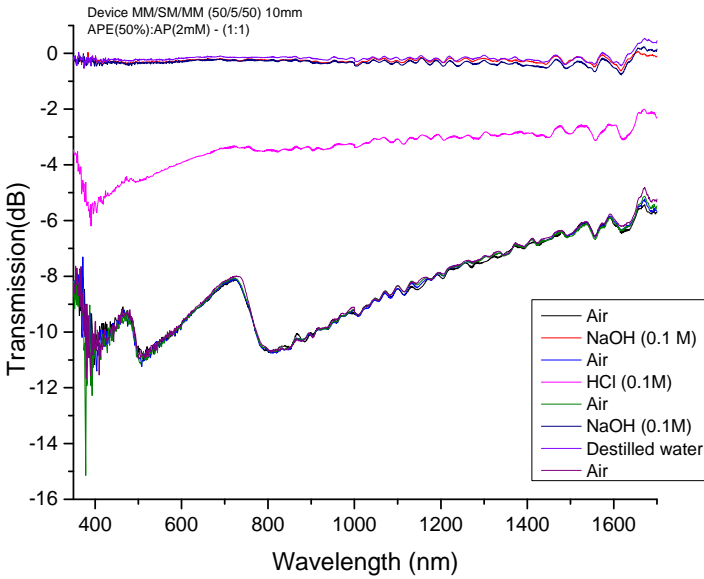
37

38 **Figure 15.** Transmission spectra of hetero-core fiber with PVOH/AP and its sensitivity to pH change with 5 mm (A) and
 39 10 mm (B) length.

1 the hydration process of the polymer and breaking of complex of AP by hydration. To identify
 2 the changes in transmission spectrums, the most characteristic signals (400, 700 and 800 nm)
 3 and the response to 1500 nm (common wavelength in telecommunication systems) were
 4 plotted independently.



A

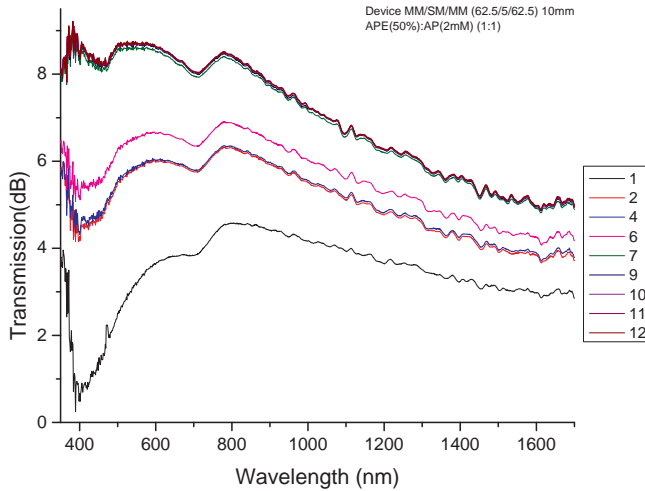


B

5

6
7

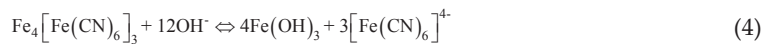
Figure 16. Transmission spectra of hetero-core fiber with APE/AP and its sensitivity to pH change with 1 mM (A) and 2 mM (B) AP.



15

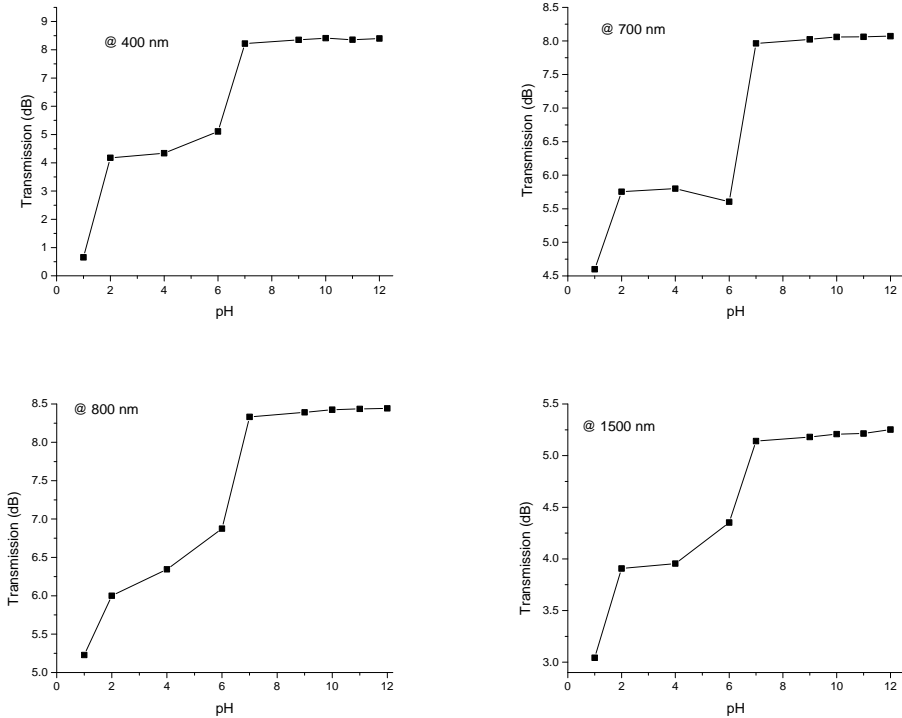
16 **Figure 17.** Transmission spectrum normalized to air of the modified hetero-core device with APE/AP (2mM) and its
 17 sensitivity to pH changes.

1 Analyzing the charts of Figure 18 shows that the transmission intervals are decreasing with
 2 increasing wavelength, which demonstrates good sensitivity of the device. As previously
 3 mentioned, the pH changes were more evident at pH values less than 7, due to that pH values
 4 higher than 7, it promotes the process of hydration of Prussian blue complex (Equation 4) and
 5 the signal grows weak on each pH change (García – Jareño et al, 1996).



6 Based on the results obtained so far, the 10 mm rather than the 5mm length hetero-core device
 7 is recommended since their sensitivity and the evanescent wave field is bigger than 5 mm
 8 length devices. Also the 10 mm length device provides a gain of about 2 dB at throughout the
 9 analysis spectrum.

10 Actually, all devices showed in this paper are preparing to their application in real scenarios,
 11 with the intention to quantify physicochemical properties directly to polluted soil without
 12 extraction from the field and pre-treatment of sample, which could reduce time and costs of
 13 analytical determination, increasing the sensibility, detection and quantification limits in
 14 comparison with spectroscopic and spectrometric techniques, to take the best professional
 15 decision to remediate in the better technical conditions the polluted soil.



5

6 **Figure 18.** Transmission spectrum of hetero-core device modified with APE/AP and its sensibility to pH changes at
 7 400, 700, 800 and 1500 nm wavelength.

1 4. Conclusion

2 For pollution detection and soil remediation purposes it is essential to have relevant and
 3 reliable information on the soil structure, the hydrogeological circumstances and accumulation
 4 zones of the detected pollutants. Combined application of geological, hydrogeological and
 5 geophysical investigations prior the placement of the optical fiber in the field may increase the
 6 efficiency of the monitoring technique.

7 Spatially resolved mapping of chemical constituents is an important need in a variety of
 8 environmental and geo-environmental applications. For example, spatially resolved analyte
 9 monitoring can simultaneously indicate and locate when an accepted level of exposure to toxic
 10 or explosive species has been exceeded, and can track its source.

11 The capability of long-range distributed sensing is unique to optical – fiber technology. A
 12 distributed fiber optic sensor returns a value of a target measurement as a function of the linear
 13 position along the fiber length. The only contact between the point to be measured and the
 14 observation area is the optical fiber.

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14 References

- 15 [1] Abdi, M. M., Abdullah, L. Ch., Sadrolhosseini, A. M., Yunus, W. M. M., Moxsin, M.
 16 M., Tahir, P. M. (2011). Surface plasmon resonance sensing detection of mercury and
 17 lead ions based on conducting polymer composite, *Plos One*, 6, e24578.
- 18 [2] Achatz, D. E., Ali, R., Wolfbeis, O. S. (2011). Luminescent chemical sensing, biosens-
 19 ing, and screening using upconverting nanoparticles, *Top Current Chemistry*, 300, 29 –
 20 50.
- 21 [3] Aksuner, N. (2011). Development of a new fluorescent sensor based on a triazolo-
 22 thiadiazin, derivative immobilized in polyvinyl chloride membrane for sensitive de-
 23 tection of lead (II) ions, *Sensors and Actuators B*, 157, 162 – 168.
- 24 [4] Anastasio, S., Pamukcu, S., Pervizpour, M. (2007). BOTDR Detection of Chemical &
 25 Liquid Content, Proc. of the 7th FMGM, GSP 175 Int. Sym. on Field Measurements in
 26 Geomechanics, ASCE, Boston, MA, 1 - 12.
- 27 [5] Anastasio, S., Pamukcu, S., Pervizpour, M. (2007). Chemical Selective BOTDR Sensing
 28 for Corrosion Detection on Structural Systems, Chang, ed., Proc. of the 7th Int. Work-
 29 shop on Structural Health Monitoring (IWSHM 2007), Stanford, CA, 1701 - 1708.

- 1 [6] Antico, E., Lerchi, M., Rusterholz, B., Achermann, N., Badertscher, M., Valiente, M.,
2 Pretsch, E. (1999). Monitoring Pb^{2+} with optical sensing films, *AnalyticalChimicaActa*,
3 388, 327 - 338.
- 4 [7] Balaji, T., Sasidharan, M., Matsunaga, H. (2006). Naked eye detection of cadmium us-
5 ing inorganic-organic hybrid mesoporous material, *Analytical Bioanalytical Chemis-*
6 *try*, 384, 488-494.
- 7 [8] Bao, X., DeMerchant, M., Brown, A., and Bremner, T. (2001). Tensile and compressive
8 strain measurement in the lab and field with the distributed Brillouin scattering sensor.
9 *Journal of Lightwave Technology*, 19, 1698.
- 10 [9] Bao, X., Dhliwayo, J., Heron, N., Webb, D. J., Jackson, D. A. (1995). Experimental and
11 theoretical studies on a distributed temperature sensor based on Brillouin scattering,
12 *Journal of Light Technology*, 13, 1340 - 1348.
- 13 [10] Buerck, J., Roth, S., Kraemer, K., Mathieu, H. (2001). OTDR distributed sensing of liq-
14 uid hydrocarbons using polymer-clad optical fibers, Proceedings of The Second In-
15 ternational Symposium and Workshop on Time Domain Reflectometry for
16 Innovative Geotechnical Applications, C. H. Dowding, ed. Academic, Evanston, IL,
17 496 - 509.
- 18 [11] Cui, Q., Pamukcu, S., Xiao, W., Guintrand, C., Toulouse, J., Pervizpour, M. (2009).
19 Distributed fiber sensor based on modulated pulse base reflection and Brillouin gain
20 spectrum analysis, *Applied Optics*, 48 (30), 5823 - 5828.
- 21 [12] Cui, Q., Pamukcu, S., Lin, A., Xiao, W., Toulouse, J. (2010). Performance of double
22 side band modulated probe wave in BOTDA distributed fiber sensor, *Microwave and*
23 *Optical Technology Letters*, 52, 2713 - 2717.
- 24 [13] Cui, Q., Pamukcu, S., Lin, A., Xiao, W., Herr, D., Toulouse, J., Pervizpour, M. (2011).
25 Distributed temperature sensing system based on Rayleigh scattering BOTDA, *IEEE*
26 *Sensors Journal*, 11(2), 399 - 403.
- 27 [14] Cui, Q., Pamukcu, S., Xiao, W., Pervizpour, M. (2011). Truly distributed fiber vibra-
28 tion sensor using pulse base BOTDA with wide dynamic range, *IEEE Photonics Tech-*
29 *nology Letters*, 3 (24), 1887 - 1889.
- 30 [15] Fellay, A., Thévenaz, L., Facchini, M., Niklès, M., Robert, P. (1997). Distributed sens-
31 ing using stimulated Brillouin scattering: towards ultimate resolution, *Optical Fiber*
32 *Sensors*, OSA Technical Digest Series, Optical Society of America, Washington, D.C.
33 16, 324 - 327.
- 34 [16] Fen, Y. W., Mahmood, W., Yunus, M., Yusof, N. A. (2012). Surface plasmon reso-
35 nance optical sensor for detection of Pb^{2+} based on immobilized p-tert-butylca-
36 lix[4]arene-tetrakis in chitosan thin film as an active layer, *Sensors and Actuators B*,
37 171 - 172, 287 - 293.

- 1 [17] Fen, Y. W., Yunus, W. M. M. (2013). Utilization of chitosan - based sensor thin films
2 for the detection of lead ion by surface plasmon resonance optical sensor, *IEEE Sen-
3 sors Journal*, 13, 1413 - 1418.
- 4 [18] Fen, Y. W., Yunus, W. M. M., Talib, Z. A. (2013). Analysis of Pb(II) ion sensing by
5 crosslinked chitosan thin film using surface plasmon resonance spectroscopy, *Optik*,
6 124, 126 - 133.
- 7 [19] Forzani, E. S., Foley, K., Westerhoff, P., Tao, N. (2007). Detection of arsenic in ground-
8 water using a surface plasmon resonance sensor, *Sensors and Actuators B*, 123, 82 - 88.
- 9 [20] García-Jareño, J. J., Navarro-Laboulais, J., Vicente, F. (1996). Electrochemical Study of
10 Nafion Membranes / Prussian Blue Films on ITO Electrodes. *Electrochimica Acta*, 41,
11 17, 2675 - 2682.
- 12 [21] Galindez-Jamioy, C. A., López-Higuera, J. M. (2012). Brillouin Distributed Fiber Sen-
13 sors: An Overview and Applications. *Journal of Sensors*, 204121, pp 17.
- 14 [22] Grattan, K. T. V., Meggitt, B. T. (1999). Optical Fiber Sensor Technology, Chemical
15 and Environmental Sensing, KlumerAcademinc Publishers, Vol. 4.
- 16 [23] Guillemain, H., Rajarajan, M., Sun, T., Grattan, K. T. V. (2009). A self-referenced re-
17 flectance sensor for the detection of lead and other heavy metal ions using optical fi-
18 bres, *Measurement Science Technology*, 20, 045207.
- 19 [24] Guo, L., Zhang, W., Xie, Z., Lin, X., Chen, G. (2006). An organically modified sol-gel
20 membrane for detection of mercury ions by using 5,10,15,20-tetraphenylporphyrin as
21 a fluorescence indicador, *Sensors & Actuators B*, 119, 209 - 214.
- 22 [25] Horiguchi, T., Shimizu, K., Kurashima, T., Tateda, M., Koyamada, Y. (1995). Devel-
23 opment of a distributed sensing technique using Brillouin scattering, *Journal of Light-
24 wave Technology*, 13, 1296 - 1302.
- 25 [26] Jerónimo, P., Araújo, A., Conceição, B. S. M., Montenegro, M. (2007). Optical sensors
26 and biosensors based on sol-gel films, *Talanta*, 72, 13 - 27.
- 27 [27] Kasik, I., Mrazek, J., Martan, T., Pospisilova, M., Podrazky, O., Matejec, V., Hoyerova,
28 K., Kaminek, M. (2010) Fiber-optic pH detection in small volumes of biosamples,
29 *Analytical and Bioanalytical Chemistry*, 398, 1883 - 1889.
- 30 [28] Katchalsky, A., Michaeli, I. (1995). Polyelectrolyte gels in salt solutions, *Journal of Pol-
31 ymer Science*, 15 (69).
- 32 [29] Kee, H. H., Lees, G. P., Newson, T. P. (2000). All-fiber system for simultaneous inter-
33 ro-rogation of distributed strain and temperature sensing by spontaneous Brillouin scat-
34 tering. *Optics Letters*, 25, 695.
- 35 [30] Kocincova, A., Borisov, S., Krause, C., Wolfbeis, O. (2007). Fiber-optic microsensors
36 for simultaneous sensing of oxygen and pH, and of oxygen and temperature. *Analyti-
37 cal chemistry*, 79, 8486 - 8493.

- 1 [31] Krohn, D. A. (1988). Fiber Optic sensors: Fundamental and applications, Instrument
2 Society of America.
- 3 [32] Lee, S. -H., Kumar, J., Tripathy, S. K. (2000). Thin film optical sensors employing pol-
4 yelectrolyte assembly. *Langmuir*, 16.
- 5 [33] Lin, T. -J., Chung, M. -F. (2009). Detection of cadmium by a fiber-optic biosensor
6 based on localized surface plasmon resonance, *Biosensors and Bioelectronics*, 24, 1213 -
7 1218.
- 8 [34] Maier, S. A. (2007). Plasmonics Fundamental and applications, Springer.
- 9 [35] Matsuo, E. S., Tanaka, T. (1988). Kinetics of discontinuous volume phase transition of
10 gels, *Journal of Chemical Physics*, 89 (3): 1695.
- 11 [36] Mayra, T., Klimant, I., Wolfbeis, O. S., Werner, T. (2008). Dual lifetime referenced op-
12 tical sensor membrane for the determination of copper (II) ions, *Analytical ChimicaAc-
13 ta*, 462, 1 - 10.
- 14 [37] McDonagh, C., Burke, C. S., MacCraith, B. D. (2008). Optical Chemical Sensors, *Chem-
15 ical Review*, 108, 400 - 422.
- 16 [38] Ohno, H., Naruse, H., Kihara, M., Shimada, A. (2001) Industrial applications of the
17 BOTDR optical fiber strain sensor, *Optical Fiber Technology*, 7, 45 - 64.
- 18 [39] Orellana, G., Haigh, D. (2008) New trends in fiber-optic chemical and biological sen-
19 sors. *Current Analytical Chemistry*, 4, 273 - 295.
- 20 [40] Pamukcu, S., Cetisli, F., Texier, S., Naito, C., Toulouse, J. (2006). Dynamic strains with
21 Brillouin scattering distributed fiber optic sensor, *GeoCongress 2006*, 187, ASCE pp.
22 31 - 36.
- 23 [41] Pamukcu, S., Texier, S., Toulouse, J. (2006). Advances in water content measurement
24 with distributed fiber optic sensor, *GeoCongress 2006a*, 187, ASCE, pp. 7 - 12.
- 25 [42] Phillips, C., Jakusch, M., Steiner, H., Mizaikoff, B., Fedorov, A. G. (2003). Model-based
26 optimal design of polymer-coated chemical sensors, *Analytical Chemistry*, 75, 1106 -
27 1115.
- 28 [43] Prabhakaran, D., Nanjo, H., Matsunaga, H. (2007). Naked eye sensor on polyvinyl
29 chloride platform of chromo-ionophore molecular assemblies: A smart way for the
30 colorimetric sensing of toxic metal ions, *Analytical ChimicaActa*, 601, 108 - 117.
- 31 [44] Siegel, R. A. (1993). Hydrophobic weak polyelectrolyte gels: studies of swelling equi-
32 libria and kinetics, *Advanced Polymer Science*, 109, 233.
- 33 [45] Siegel, R. A., Falamarzian, M., Firestone, B. A., Moxley, B. C. (1988). pH-controlled re-
34 lease from hydrophobic/polyelectrolyte copolymer hydrogels, *Journal of Controlled
35 Release*, 8, 179.

- 1 [46] Skouri, R., Schosseler, F., Munch, J. P., Candau, S. J. (1995). Swelling and elastic prop-
2 erties of polyelectrolyte gels, *Macromolecules*, 28, 197.
- 3 [47] Texier, S., Pamukcu, S., Toulouse, J. (2005). Advances in subsurface water-content
4 measurement with a distributed Brillouin scattering fibre-optic sensor, Proc.of SPIE
5 5855, 17th Int. Confer. On Optical Fibre Sensors, OFS-17, Bruggs, Belgium, pp. 555 -
6 558.
- 7 [48] Texier, S., Pamukcu, S., Toulouse, J., Ricles, J. (2005). Brillouin scattering fiber optic
8 strain sensor for distributed applications in civil infrastructure, Chang, ed., 5th Int.
9 Workshop on Structural Health Monitoring (IWSHM 2007), Stanford, CA, pp. 1395 -
10 1402.
- 11 [49] Turel, M., Pamukcu, S. (2006) Brillouin scattering fiber optic sensor for distributed
12 measurement of liquid content and geosynthetic strains in subsurface, Geoshanghai
13 GSP: Site and Geomaterial Characterization, ASCE, Shanghai, PRC, pp. 72 - 79.
- 14 [50] Villatoro, J., Monzón-Hernández, D. (2006). Low-cost optical fiber refractive-index
15 sensor based on core diameter mismatch. *Journal of Light-wave Technology*, 24, 1409 -
16 1413.
- 17 [51] Wolfbeis, O. (2008). Fiber-optic chemical sensors and biosensors. *Analytical chemistry*
18 80, 4269 – 4283.
- 19 [52] Wolfbeis, O. S. (2000). Fiber-Optic Chemical Sensors and Biosensors, *Analytical Chem-*
20 *istry*, 72, 81R.
- 21 [53] Yin, Y. L., Prud'homme, R. K., Stanley, F. (1992). Chapter 6: Relationship between
22 poly(acrylic acid) gel structure and synthesis. In A.J Harland and R.K. Prud'homme,
23 editors, *Polyelectrolyte Gels*. ACS Symp. Series 480, ACS Washington D.C.
- 24 [54] Yusof, N. A., Ahmad, M. (2003). A flow-through optical fibre reflectance sensor for
25 the detection of lead ion based on immobilized gallocynine, *Sensors and Actuators B*,
26 94, 201 – 209.

2 **Characterization and Remediation of Soils and** 3 **Sediments Polluted with Mercury: Occurrence,** 4 **Transformations, Environmental Considerations and** 5 **San Joaquin's Sierra Gorda Case**

6 I. Robles, J. Lakatos, P. Scharek, Z. Planck,
7 G. Hernández, S. Solís and E. Bustos

8 Additional information is available at the end of the chapter

10 **1. Introduction**

11 Soil as important part of the ecosystems which must be protected in the environment
12 context, and it is necessary be studied the possible overall impact of measures for protec-
13 tion, with a very special attention from mining activities. The soil resource occupies a
14 fundamental part of the ecosystems; when a soil is degraded, the others components of the
15 ecosystems are degraded too.

16 The fate of the heavy metal in soils depends upon many soil processes that are governed by
17 several soils properties of which soil pH and redox potential are known to be the most
18 important parameters. Thus, the solubility of trace elements is often shown as a function of
19 pH affected by amount and kind of organic matter. Trace elements are known to be accumu-
20 lated in surface soils as a result of contamination from point sources as mining activities. An
21 appreciable amount of the soils has been made unusable because of pollution. Highly conta-
22 minated soils belong to a high healthy risk to human being and their environmentally harmful
23 effects. That is why soil should be correctly understood and underestimated long range lethal
24 effects that can have irreversible consequences. The improvement of soils damaged and
25 contaminated by pollutants need of the particular soils, requires a full understanding of soil
26 properties and of the deteriorating factors.

27 Mercury is one of the most toxic elements to human health and ecosystem; because of all
28 mercury species are toxic. A wide variety of mercury species exist in the environment and its

1 various chemical forms can differ in bioavailability, transport, persistence, and toxicity. Still,
 2 every mercury species is toxic with methyl mercury being the most toxic species. The World
 3 Health Organization (WHO) recommends a maximum methyl mercury intake of 1.6 $\mu\text{g Kg}^{-1}$
 4 per week, while the Environmental Protection Agency (EPA) lists a maximum recommended
 5 intake of 0.1 $\mu\text{g Kg}^{-1}$ of body weight per day for adults. Due to high bioaccumulation, mercury
 6 is found on many levels of the food chain(Hinton and Veiga, 2001; Bengtsson, 2008).Any form
 7 of mercury in the environment may evolve into a more toxic species (methyl mercury) under
 8 biogeochemical transformation processes (Figure 1). Due to these processes and the high
 9 mobility of mercury species, a good understanding of how mercury species transform and
 10 accurate monitoring are essential for assessing the risk of mercury in the environment.

11 The impact of mercury depends strongly on its chemical species; understanding mercury
 12 transformations and the impact of its various chemical forms are vital to preventing harmful
 13 effects on humans and the environment. Nevertheless, the physicochemical characteristics of
 14 mercury are either useful or necessary for many industrial and agricultural applications, and
 15 mercury may be scattered over large area, depending on the source (Leopold et al, 2010).

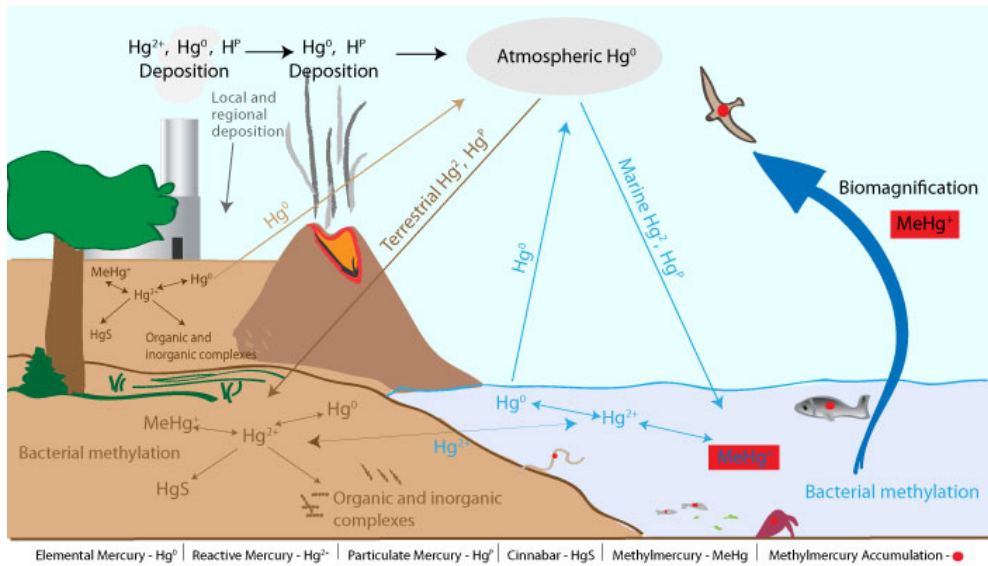


Figure 1. Biogeochemical transformation processes of mercury(Leopold et al, 2010).

18 Mercury concentrations in ground water indicate that the highest concentration of mercury in
 19 groundwater comes from the soil and from aquifers. While simulating mercury predictions
 20 can often be difficult, mercury can be estimated in experiments conducted in batch mode or
 21 in columns. The percentage of Hg that can potentially leach from the soil was previously
 22 estimated in batch experiments. Distribution analyses of species in leachate confirmed the

1 presence of inorganic species (Hg^{2+} and Hg^0) ranging from 90 – 100 % (Bollen, 2008; Harvey,
2 2002).

3 The most commonly used techniques for the remediation of mercury contaminated soils have
4 been classified as either excavation techniques or containment techniques, and are grouped as
5 follows (Hinton and Veiga, 2001): (a) *ex situ* treatments: physical separation, thermal treat-
6 ments, hydrometallurgical treatments; (b) *In situ* recuperation: vapor extraction coupled with
7 evaporation (soil), permeable reactive barriers; (c) *In situ* leaching and extraction: electrokinetic
8 separation, interceptor systems, phytoremediation, passive remediation; (d) *containment*:
9 pump and treat impermeable barriers, sealed surfaces and drainage, stabilization and solidi-
10 fication, sediment covering.

11 2. Physicochemical properties of mercury

12 Mercury (Hg) is a chemical element with an atomic number of 80. Mercury is a silver plated
13 heavy metal, liquid and odorless at normal conditions. It easily alloys with many other metals
14 like gold or silver producing amalgams, is insoluble in water and soluble in nitric acid. The
15 main source of Hg is cinnabar or mercury sulfide (HgS), a stable compound and insoluble
16 usually recovered as a byproduct of ore processing. Mercury in this form is found in the earth's
17 crust average concentrations of 0.5 ppm (Hinton and Veiga, 2001).

18 Mercury is one of the most toxic elements to human health and ecosystem. At temperatures
19 above 40 °C mercury produces toxic and corrosive fumes. It is harmful by inhalation, ingestion
20 and contact, is a very irritating to skin, eyes and respiratory tract, even to nervous system, its
21 gaseous form is absorbed by lung tissues (Hinton and Veiga, 2001, Bengtsson, 2008).

22 A wide variety of mercury species exist in the environment and its various chemical forms can
23 differ in bioavailability, transport, persistence, and toxicity. Still, every mercury species is toxic
24 with methyl mercury being the most toxic species. This element can exist in the environment
25 as elemental (Hg^0), oxidized inorganic (Hg^{2+} -mercuric, Hg_2^{2+} -mercurous) or oxidized organic
26 (methyl/ethyl mercury) forms. Mercuric and mercurous forms are more stable under oxidizing
27 conditions. In moderately reducing conditions, the organic or inorganic mercury can be
28 reduced to its elemental form and be converted to forms leased by biotic or abiotic processes:
29 these are the most toxic forms of mercury, as well as being soluble and volatile. Hg (II) forms
30 strong soluble complexes with a variety of organic and inorganic ligands oxidized in aqueous
31 systems. Hg sorption in soil, sediment and humic materials is an important mechanism for the
32 removal of mercury from solutions, another mechanism, a high pH is their co-precipitation
33 sulfide (HgS) (Leopold et al, 2010).

34 Any form of mercury in the environment may evolve into a more toxic species (methyl
35 mercury) under biogeochemical transformation processes. Due to these processes and the high
36 mobility of mercury species, a good understanding of how mercury species transform and
37 accurate monitoring are essential for assessing the risk of mercury in the environment. The
38 impact of mercury depends strongly on its chemical species; understanding mercury trans-

1 formations and the impact of its various chemical forms are vital to preventing harmful effects
 2 on humans and the environment. Nevertheless, physicochemical characteristics of mercury
 3 are either useful or necessary for many industrial and agricultural applications, and mercury
 4 may be scattered over large area, depending on the source (Leopold et al, 2010; Nick, 2012).

5 The metal mercury (Hg^0) is mainly used to produce chlorine gas and caustic soda, and is part
 6 of some types of alkaline batteries, fluorescent lamps, electrical contacts, and instruments such
 7 as pressure gauges and thermometers, among others. Hg salts are used in antiseptic ointments
 8 and creams and skin lightening. Among the activities that generate the most pollution by Hg,
 9 is the burning of coal and chlor-alkali plants: other important sources are mining and metal-
 10 lurgy and the burning of municipal solid waste, which may contain instruments such as
 11 pressure gauges, thermometers, alkaline batteries and fluorescent lamps. The mercury
 12 released into the air tends to settle and adhere to soil organic matter (Hinton and Veiga,
 13 2001; Nick, 2012).

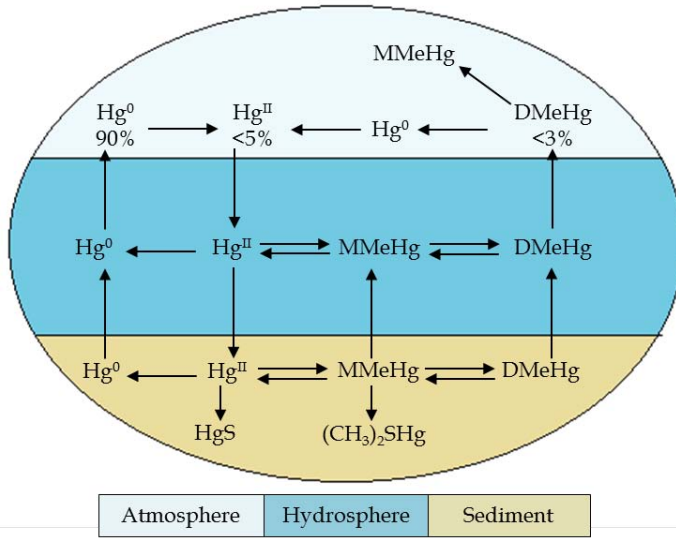
14 Natural and anthropogenic mercury emissions are mainly in the form of elemental mercury
 15 (Hg^0), which makes up about 99% of total atmospheric mercury. However, biogeochemical
 16 transformations can oxidize it, forming Hg^+ and Hg^{2+} . Most inorganic Hg compounds are water
 17 soluble in small doses, and can be found in soil and sediments. In contrast, the presence of
 18 inorganic forms of Hg^{2+} bonded to organic and/or inorganic species ($[\text{HgCl}_x]^{2-x}$; $[\text{Hg}^{\text{II}}\text{-DOC}]$;
 19 $[\text{HgS}]$) depends on the local chemical environment. The life time of these compounds in air is
 20 very short (on the scale of minutes) and they are rapidly removed by deposition processes
 21 because of high water solubility and surface activity. Figure 2 shows the main mercury species
 22 in the atmosphere, hydrosphere and sediment (Leopold et al, 2010; Nik, 2012; Slowey et al,
 23 2005; Wartel et al, 1999; Shi et al, 2005).

24 Over 90% of surface water mercury is from atmospheric deposition. Hg^{2+} usually undergoes
 25 a biomethylation process that forms methylmercury (MeHg , CH_3Hg^+) and dimethyl mercury
 26 (DMeHg , $(\text{CH}_3)_2\text{Hg}$), though these reactions can be reversed using microorganisms and/or
 27 photolytic decomposition. All these species are highly mobile.

28 Three main forms of mercury are found in natural waters: elemental mercury (Hg^0), inorganic
 29 Hg^{2+} (Hg^{2+} and its complexes) and organic mercury (MeHg , MeHg complexes and DMeHg).
 30 With solubility (at 25°C) of 0.08 mg L⁻¹, Hg^0 can be found at all depths. Inorganic mercury
 31 (Hg^{2+}) and MeHg forms complexes with other dissolved compounds in fresh water, but for the
 32 most part, only forms complexes with chlorine in sea water. DMeHg is found in the deep sea.
 33 (Wartel et al, 1999, Shi et al, 2005, Slowey et al, 2005).

34 **3. Edaphology properties of soil related with mercury**

35 Soil is a collection of natural bodies on the Earth' surface, in places that most of them have been
 36 modified by man in its quality and containing living matter and supporting or capable of
 37 supporting plants. Soil grades at its lower margin to hard rock or to earthy materials virtually
 38 devoid of roots, animals or marks of other biologic activity.



69

70 **Figure 2.** Distribution of mercury species in atmosphere, hydrosphere and sediment (Leopold et al, 2010).

1 In general, physical, chemical and biological soil characteristics are highly correlated parameters that are necessary to understand. The specific elemental composition of each particular
 2 soil reflects, to a degree modified over time by weathering and the chemical composition of the
 3 parent material from which the soil is formed. For instance, the extractability of the different
 4 elements depends on the soil properties.
 5

6 Soil as important part of the ecosystems which must be protected in the environment context,
 7 and it is necessary be studied the possible overall impact of measures for protection, with a very
 8 special attention from mining activities. The soil resource occupies a fundamental part of the
 9 ecosystems; when a soil is degraded, the others components of the ecosystems are degraded too.

10 The fate of the heavy metal in soils depends upon many soil processes that are governed by
 11 several soils properties of which soil pH and redox potential are known to be the most
 12 important parameters. Thus, the solubility of trace elements is often shown as a function of
 13 pH affected by amount and kind of organic matter. Trace elements are known to be accumu-
 14 lated in surface soils as a result of contamination from point sources as mining activities.

15 An appreciable amount of the soils has been made unusable because of pollution. Highly
 16 contaminated soils belong to a high healthy risk to human being and their environmentally
 17 harmful effects. That is why soil should be correctly understood and underestimated long
 18 range lethal effects that can have irreversible consequences. The improvement of soils
 19 damaged and contaminated by pollutants need of the particular soils, requires a full under-
 20 standing of soil properties and of the deteriorating factors.

21 Mercury is a microelement: its Clark value in the Earth's crust is 56 µg Kg⁻¹ (Fügedi et al,
 22 2011). It is characterized by a dual geochemical behavior: it is liable to extreme concentration

1 and to dispersion, the latter resulting in an approximately entirely even concentration. It is
2 found either as a native metal (near to 80 % in hydrothermal and vapors) or in cinnabar,
3 corderoite, livingstonite and other minerals. Cinnabar (HgS) is the most common ore. Mercury
4 ores usually occur in very young orogenic belts where rock of high density on upper mantle
5 is forced to the crust of the Earth (Ozerova, 1996).

6 Given that mercury is enriched by an extremely wide variety of geological processes
7 (Fergusson, 1990) from the formation of hydrocarbon to hydrothermal mineral occurrences, it
8 can be regarded as an universal geochemical indicator of young geological effects; its disper-
9 sion halos are more extensive than that of any other element (Fügedi et al, 2011).

10 Historically there were two main registered Mercury mines: Almaden (Spain) and Idrija
11 (Slovenia) in Europe. Later new occurrences were found in California and worldwide. It was
12 used in gold separation. In Mexico we know mercury mines from the Pre-Hispanic era (Scharek
13 et al., 2010) and a usage in cultic fests (Figure 3). In 2005, China was the top producer of mercury
14 with almost two-thirds global share followed by Kyrgyzstan. Several other countries are
15 believed to have unrecorded production of mercury from copper electro winning processes
16 and by recovery from effluents.



17

18 **Figure 3.** Typical cinnabar occurrences in a limestone system (Formation Las Trancas, San Joaquin, Querétaro, Mexico,
19 photo by P. Scharek)

1 4. Mobilization and loadings the mobilized mercury

2 The mobilization of the different mercury forms can due to by evaporation and dissolution.
 3 Here we do not deal with the erosion which able to mobilize all form of mercury if it has
 4 attached to the solid particle, however in case of soils and fly as particles in the flue gas this
 5 particle associated mobilization mechanism can play important role in the mercury transport.

6 4.1. Evaporation

7 The evaporation governed by the vapor pressure depends on the volatility of the compound
 8 and the temperature. Concerning the volatility of the different mercury compounds evapora-
 9 tion at ambient temperature can be significant in case of elemental and the organic mercury
 10 cases, however the volatilization of the other mercury forms (the inorganic mercury com-
 11 pounds) can become considerable if the temperature reaches a couple hundred degree
 12 centigrade. All of the mercury compounds have relatively low boiling points (Table 1), some
 13 of them decompose before melting, others can sublimate. Based on these data it is obvious the
 14 vaporization can play important role of the mercury compound transport and mobilization.

Hg	Melting T, °C		Boiling T, °C	
	-38.9		356.5	
HgS (cinnabar, α)	580 sublimate			
HgS (metacinnabar, β)	446 sublimate			
Hg ₂ O	100 decompose			
HgO	500 decompose			
Hg SO ₄	450 decompose			
Hg ₂ Cl ₂	302		384	
HgCl ₂	277		304	
HgBr ₂	237		322	
HgI ₂	259		354	
CH ₃ HgCl	-		92	
(CH ₃) ₂ Hg	-43		94	

15 **Table 1.** Melting and boiling points of the mercury and mercury compounds

16 The partial pressure of the elemental mercury (Hg⁰) reach 1 Pa at 42 °C and enhances expo-
 17 nentially till the boiling point ($T_b = 356.5$ °C). At 20 °C the Hg vapor pressure is 0.18 Pa the Hg
 18 concentration in the air saturated with the mercury is $7.64 \cdot 10^{-8} \text{ mol dm}^{-3} = 15.3 \mu\text{g m}^{-3}$. Due to
 19 this high volatility the elemental mercury evaporate if stored and processed an open container.
 20 Elemental mercury can escape from solution if the oxidized mercury is able to reduce. The

1 analytical data will be inaccurate if the sample is not preserved agents the elemental mercury
2 formation.

3 Concerning the Global mercury contamination till the middle of the past century evapora-
4 tion of elemental mercury used to extract silver and gold was the main source of the
5 mercury emission, (Nriahu, 1994). All the once produced and recently available elemental
6 mercury stock (in the past five century one million tons was produced from cinnabar and
7 from other ores) if in used either evaporation or after transformation can contribute to the
8 mercury contamination worldwide, (Hylander and Meili, 2003). This is the reason why the
9 elemental mercury use is banned. Recently one of the most significant sources of mercury
10 emission by evaporation is the coal firing. During the coal burning the mercury associated
11 with pyrite and be organically bonded to the coal minerals are released in the combus-
12 tion flame as elemental mercury, which is partially oxidized to Hg(II) in homogeneous and
13 heterogeneous catalytic reaction governed by the chlorine and the ash content of the
14 combustion gases (Sondreal et al, 2004).

15 Generally accepted view is that the evaporated oxidized forms of mercury contaminate the
16 environment locally, close to the emission source. However they can transform to elemental
17 mercury and depend on this transformation rate it can become part of the global mercury cycle.

18 The transformation of the oxidized to reduce the reduced to oxidized forms can happen both
19 in gas and aquatic environment according to the circumstances. There is similar transformation
20 between the inorganic and organic forms.

21 Different species of macro algae from the dissolved mercury can produce different methylated
22 mercury compounds in the ocean. Because of these methylated mercury compounds have high
23 volatility and at the dimethylated form has low solubility in ocean water they are easily emitted
24 into the atmosphere and can contribute significantly to the global atmospheric mercury
25 (Pongratz and Heuman, 1998). Beside this different bacteria (e.g. sulfate reducing) and in case
26 of abiotic route the tin- alkyls and the humic acids also can transform the dissolved mercury
27 (II) to methyl mercury form (Weber, 1993). A quite detailed set of possible transformation in
28 gas and aquatic media and the Henry constants which inform about the dissolved compound
29 volatility are collected by Shon et al, 2005.

30 During heating mercury compounds can transform directly or via oxides to elemental
31 mercury. Beside the elemental mercury only the halogenides and the sulfides since last have
32 a tendency to sublime can occur in evaporated forms. The sulfides at presence of oxygen at
33 600 °C transforms to Hg and SO₂, however in presence of Fe and CaO the HgS also will
34 decompose to Hg and Fe- or Ca- sulfides. Using the temperature programmed evaporation
35 technique based on the volatility difference of mercury compounds the compound forms can
36 be distinguished and can use for mercury speciation in solids (Lopez-Anton et al, 2010, 2011).

37 In a high temperature process since the mercury compounds decompose the original specia-
38 tion of mercury does not preserve a new speciation can formed which determined by the gas
39 composition. In the high temperature gases high portion of mercury exists in elemental and
40 just a small portion in oxidized form. This is the reason why these technologies such as coal
41 fired energy production, the cement kiln, the incineration has difficulty in the mercury capture.

1 Focusing to the soil, the heating comes from sunlight can mobilize only the weakly sorbed
2 elemental and organic mercury but the fire on the soil surface, for example the forest fire can
3 evaporate the less volatile mercury forms as well. This case the contamination level of the fired
4 soil decreases but, due to the transport, at other places the contamination becomes higher
5 (Caldwel et al, 2000).

6 The volatilization can be the cause of contamination but can use for decontamination as well.
7 Based on the volatilization of mercury compounds, mercury removal process was established
8 from coal cleaning by mild pyrolysis (Wang et al., 2000) and for the soil cleaning by thermal
9 treatment. In case of coals the speciation of mercury determines the maximum efficiency of
10 the mercury removal. The efficiency of the process generally remains below 100 %, (bituminous
11 coal case at 500 °C it was approx. 75 %). Since the efficiency remains below 100 % the rest of
12 mercury still remain in the process and pass to the flue gas after the coal burning. The speciation
13 of the mercury in the contaminated soil also has influence on the efficiency of the thermal
14 remediation, see more details later.

15 Concerning that the different mercury forms exhibit different volatility the actual distribution
16 of the mercury species in a medium the rate of the transformation process which able to modify
17 it together govern the mercury mobilization by evaporation.

18 It is well known, if elemental mercury forms in the water this elemental mercury can easily
19 escape to the gas phase. It is quite intensive if gas bubbling through the water or the water
20 surface is disturbed (Okouchi and Saaski, 1984).Sunlight induced H_2O_2 formation in alkaline
21 condition can result reduction of the oxidized mercury forms to elemental mercury. This can
22 explains that the Hg concentration above the lake water surface can be higher day time than
23 night. The fulvic and humic compounds are able to complex the mercury (II) ion in aquatic
24 media but these compounds can take part in the mercury alkylations, further at a suitable pH
25 can work as a reducing agent. (The redox potential at 0 pH for Hg (II) reduction is 0.85 V(Allard
26 and Arsenie, 1991).

27 This type of mercury transformation between oxidized and reduced forms together with the
28 alkylation will generate not only a modification between the concentrations of the mercury
29 species in the aquatic phase but will modify the mercury transport between the phases. The
30 mercury transformation processes are important in the technological processes used for the
31 mercury removal since can effect they efficiency (Somoano et al., 2007).

32 **4.2. Dissolution**

33 The mobilization by dissolution can arrange two groups: (a) dissolutions ways exist in the
34 nature (b) dissolution way can be applied in the laboratory and in the remediation technology
35 to determine the loading forms or remove the mercury from the contaminated media.

36 *4.2.1. Dissolutions ways exist in the nature*

37 The solubility of elemental mercury and the ore of mercury can find in the nature (cinnabar
38 etc.) are verylow in water. This low solubility result low mercury concentration level in aquatic

1 phase and restricts the transport between phases by dissolution. However the oxidation both
 2 cases enhances these mercury forms solubility. The elemental mercury can be oxidized by
 3 ozone, halogens, some components of acid rains, or by oxy-acids in laboratory (HNO₃ and the
 4 hot H₂SO₄) resulting a soluble form. The ozone in air if does not consumed by the other more
 5 reactive air contaminants can oxidize Hg to Hg(II) (Iverfeld and Linquist, 1986; Shonet et al, 2005).

6 In aquatic media oxidation can occur at acidic conditions if the sunlight produces oxidative
 7 radicals OH, or peroxides. This process can play role in the trap of the physically dissolved
 8 elemental mercury in water, and also can hinder the transformation of the oxidized mercury
 9 forms towards the reduced elemental mercury direction. The oxidative transformation of
 10 elemental mercury is essential in case of many mercury capture process since the oxidized
 11 forms of mercury has higher tendency to sorb and dissolve, therefore different oxidation
 12 procedures are available and applied in the demercuration technologies (Ko et al, 2008;
 13 Lakatos et al, 2009; Sondreal et al, 2004).

14 However the mercury in the natural minerals is in the oxidized forms these minerals luckily
 15 due to the very low solubility can be considered not a mobile occurrence of the mercury. The
 16 environmental risk improves if the natural processes can transform the minerals a more soluble
 17 form. One of the most significant ore transformations which effect the mercury mobilization
 18 is the sulfide ore oxidation in the air. The oxidations of sulfides to sulfate a considerable
 19 enhancement ensue in mercury solubility (Holley et al, 2007). This process, the oxidation of
 20 the tailings, can accused for the mercury contamination all around the abandoned mercury
 21 ore mines.

Compound	Solubility in Water c, ppm
Hg	0.049*
HgS (cinnabar, α)	0.01
HgS (metacinnabar, β)	-
HgSO ₄	-
Hg(NO ₃) ₂	soluble
Hg ₂ O	51
HgO	51
Hg ₂ Cl ₂	10
HgCl ₂	66000*
HgBr ₂	5100
HgI ₂	51
CH ₃ HgCl	5780
(CH ₃) ₂ Hg	-

22 *Solubility from paper of Ko et al, 2008.

23 **Table 2.** Solubility of different mercury compounds.

1 Among the mercury compounds (Table 2) the mercury-chloride and nitrates are those which
 2 have the highest solubility in water. The simple cationic form of Hg(II) is not the common form
 3 in the aquatic media, it exist only in acidic solutions, at less acidic condition the dissolved
 4 mercury appears as HgOH^+ , HgOHCl , $\text{Hg}(\text{OH})_2$ and HgCl_2 molecules and complex anions
 5 HgCl_4^{2-} at high chloride concentration. It means that the sea water contains the oxidized
 6 mercury mainly in this chlor- complex form. Beside the chlor- complex the mercury -fulvo and
 7 -humic complexes also exists in aquatic environment. The speciation in the solution, the
 8 molecular forms govern the mercury loadings and play important role at the way and
 9 efficiency of the removal.

10 4.2.2. Dissolution for leaching mercury from different medium

11 Beside the thermal way and the application of the species sensitive analytical methods for
 12 mercury analysis (XPS, EXAFS etc.) the sequential extraction is often applied technique to
 13 specify the mercury chemical form and associations in solids. The thermal methods and the
 14 species sensitive elemental analysis can distinguish the elemental Hg, the HgS forms and the
 15 organically bonded mercury forms which generally exist in the soil. However these techniques
 16 do not allow doing any estimation about mobility and bioavailability of mercury. To get the
 17 loading specific information in soil for mercury, beside the classical Tessier six step extraction
 18 used generally, different modified procedure are available for Hg which able to distinguish
 19 better the mercury forms than the Tessier method can do (Orecchio and Polizzotto, 2013; Han
 20 et al,2006).For example it can determine mercury bounded to amorphous iron oxides (by
 21 NH_4 oxalate-oxalic acid extraction), mercury bonded to crystalline iron oxides (by
 22 $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 25 % acetic acid extraction), non-cinnabar mercury (elemental mercury, organic
 23 bounded, humine bounded (by 4 M HNO_3 extraction), cinnabar mercury (by extracted with
 24 saturated Na_2S , Han et al, 2006).The advantage of this protocol is the ability of the separation
 25 of humic and sulfide bounded mercury which important in the soil case. Two set of sequential
 26 extraction regime can compared at Table 3 and 4.

29 Mobilization of mercury can occur through complex formation, ligand exchange reactions with
 30 chloride and sulfur-containing ligands which leading to enhanced Hg solubility in soil
 31 solutions. The sulfur containing ligands: tiosulfates ($\text{S}_2\text{O}_3^{2-}$), thiocyanites (SCN^-) can mobilize
 32 the mercury efficiently and could improve the phytoextraction efficiency (Moreno et al, 2004).

33 Removal mercury by phytoextraction from soils and others soil like materials eg. waste water
 34 plants biosolids often need additives which improve the solubility of the mercury. These
 35 mobilizations agents are used in accelerate phytoextraction. One type is the chelating agents:
 36 citrate, oxalate, malate, succinate, tartarate, salicilate, acetate, and amino-poly-carboxylic acids:
 37 EDTA (Lomonte et al, 2011). Since the EDTA is persistent compound, recently the biodegrad-
 38 able ethylendiamine-disuccinate (EDDS) or nitrilotriacetic acid (NTA) suggested as alternative
 39 chelator instead of EDTA (Evangelu et al, 2007).

40 Specific compounds used the mercury extraction from tissues: they can pay role in case of
 41 poisoning for detoxification : EDTA was tested for detoxification by Aposhian, (Aposhian et
 42 al,1995), 2,3- dimercapto- 1- propansulfonate was used to extract mercury from tissues of rats
 43 exposed to different mercury compounds (Buchet and Lauwerys, 1989). The EDTA was not

Mobilization Protocol	Determination of Association of Mercury to Soil Component
Loading form of mercury	Extraction procedure
Water soluble mercury	NH ₄ -acetate
Exchangable mercury	(1 M NH ₄ -acetate pH 7 set with NH ₄ OH;solid:liquid 1:25, 30 min 25 °C)
Carbonate bounded mercury	Hydroxylamine – HCl
Easily reducible oxides bounded mercury (Mn-oxides)	(0.1 M NH ₂ OH.HCl +0.01 M HCl;solid:liquid1:25, 30 min 25 °C)
Elemental and organic bounded mercury	H ₂ O ₂ (3 mL 0.1 M HNO ₃ +5 mL 30 % H ₂ O ₂ 80 °C 2 h;2mL H ₂ O ₂ 80 °C 1 h;50 mL1M NH ₄ - acetate)
Amorphous iron- oxide bounded mercury	NH ₄ -oxalate –oxalic acid (0.2 M oxalate buffer 1:1, pH 3.25;solid : liquid1:25)
Crystalline iron oxide bounded mercury	Hydroxilamine – HCl- acetic acid (hot) (0.04 M NH ₂ OH.HCl in 25 % acetic acid;97-100 °C 3 h;solid:liquid1:25)
Non cinnabar bounded mercury (Hg, organically bounded, humin bounded) TOT (non cinnabar mercury)	4 M HNO ₃ (4 M HNO ₃ 80 °C16 h solid:liquid1:25)
Cinnabar bounded mercury	Na ₂ S (4 mL saturated Na ₂ S 12 h repeated twice)

48 **Table 3.** Mobilization protocol for determination of association of mercury to soil component (Han et al, 2006).

Mobilization Protocol	Determination of Association of Mercury to Soil Component
Loading form of mercury	Extraction procedure
Water soluble mercury	H ₂ O100°C, 1h stirred, solid:liquid 1:8
Exchangable mercury	Na-acetate (1M Na-acetate, 1 h stirred, solid:liquid1:8)
Carbonate bounded mercury	Na-acetate –aceticacidpH 5 (1M Na-acetate –aceticacidpH 5, 4 h stirred, solid:liquid1:8)
Fe, Mn-oxide bounded mercury	Hydroxylamin HCl-acetic acid 0,04 M NH ₂ OH.HCl in 25 % Acetic acid, 96 C, 6 h, Solid:liquid (1) :8
Elemental and organic bounded mercury	Mineralisation by HNO ₃ -H ₂ O ₂ ((a)heated previously 180 °C - organic bounded -microwave digestion in cHNO ₃ -H ₂ O ₂ mixture; (b) no heat -elemental +organic bounded - microwave digestion in cHNO ₃ -H ₂ O ₂ mixture)
Sulfid bounded mercury	Aqua regia (HCl:HNO ₃ 3:1)

27 **Table 4.** Mobilization protocol for determination of association of mercury to soil component (Orecchioand
28 Polizzotto, 2013).

27 found the best for mercury removal in human application since does not the best chelator for
28 Hg and has side effects, however there are two other compounds which suggested to keep in
29 stock in any poison control center as mercury chelator DMPS (2,3-dimercapto-1-propane
30 sulfonic acid, (unithiol)) and DMSA (meso-2,3 dimercapto succinic acid, succimer, Guzziet al,
31 2010).

1 4.3. Loadings of mercury

2 The mercury contaminations are in the environment can exist different phases: as vapor in the
3 air (Hg, and compounds, particle associated), dissolved in aquatic media (Hg^{2+} , $\text{Hg}(\text{OH})_2$,
4 HgCl_2 , HgCl_4^{2-} , different complexes, particle associated) and solid as precipitates or minerals
5 and in associated forms bonded to different manner to the component of different solids (soil,
6 fly ash, waste water sludge etc). In the previous section it was demonstrated that how the
7 associations can be identified.

8 The loadings of mercury to solid can be considered as positive or negative phenomenon. It can
9 restrict the dispersion of the contamination one side it is positive, the negative this way it can
10 preserve the contamination. Since the loadings depends on the character of the collector and
11 the speciation of the mercury, difficult to establish general rules for this process. However it
12 can state that the elemental mercury has low sorption ability, the cationic sorbs better than the
13 anionic forms on clays, and negatively charged carbon surfaces (coals, activated carbons,
14 humic materials) the loading is more effective to that surfaces which have contain sulfides. It
15 was interesting findings after the cinnabar oxidation a part of liberated mercury could load to
16 the cinnabar surface this way it can be not just the source but the collector of mercury ions.
17 Unfortunately the most toxic forms (alkyls) have the highest ability for bioaccumulation.

18 The nature works against the mercury contamination. Except the alkylation it transforms the
19 mercury toward the most stable less soluble form. Near the chlor-alkali plant the total mercury
20 sometimes reach the four order of magnitude higher level, than the background concentration,
21 luckily it found a non-volatile and non-soluble associations since transforms to sulfides
22 (Bernaus et al, 2006).

23 The history of mercury contamination is recorded by loadings. The dept profile of mercury
24 concentration on peat can provide a clear picture how the mercury contamination changed
25 during the mankind history (Barraclough et al, 2002).

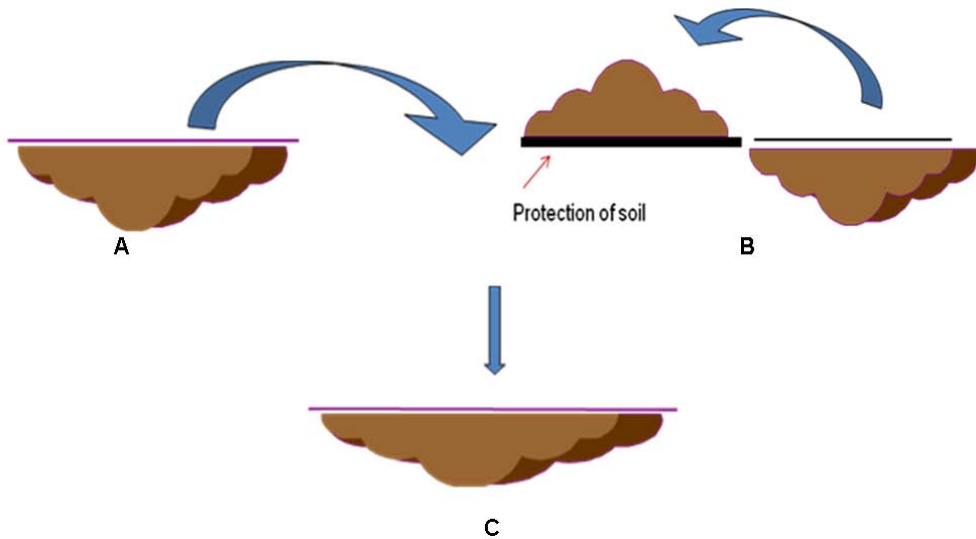
26 The loadings play important role in the environmental technologies used for decrease the
27 mercury emission or clean the contaminated medium. Sulfur and halogen containing carbons,
28 oxidative inorganic sorbents (Lakatos et al., 2009) were developed for elemental mercury
29 removal from flue gas. Beside a range of, classical, functionalized sorbents, sulphur containing
30 carbon nanotubes widen the collection one can chose among for eliminate the mercury
31 contamination in aquatic media (Pillay et al, 2013).

32 The coals especially the low rank and the oxidized coals are very good mercury ion collectors.
33 Due to this feature we must face that the coal-firing are the main source of the anthropogenic
34 mercury contamination nowadays. However this material offers us an application for cure a
35 slice of the mercury problem: remove the mercury from aquatic media. It can use in batch mode

1 or dynamic systems as the reactive barrier material, by the high mercury capture coal are able
2 to retard or remove the aquatic mercury contamination (Lakatos et al,1999).

3 5. Remediation of polluted soil with mercury

4 The most commonly used techniques for the remediation of mercury contaminated soils have
5 been classified as either excavation techniques or containment techniques, and are grouped as
6 follows (Hinton and Veiga,2001): excavation and *ex-situ* treatments, containment and *in situ*
7 chemical treatment (Figure 4).



8
9 **Figure 4.** Representation of the techniques for the remediation of mercury contaminated soils: (A) excavation and *ex-situ*
10 treatments, (B) containment and (C) *in situ* chemical treatment.

11 5.1. Excavation and *ex situ* treatments

12 They will be treated off-site soil contaminated when removing soil or contaminated soil-like
13 materials to a place outside the place in which they are located, for submission to authorized
14 treatment fixtures. The excavation and *ex situ* treatments considered in this classification are
15 (Hinton and Veiga, 2001):

- 16 1. *Physical separation.* Mercury has affinity for the smallest particles of soil.
- 17 2. *Thermal treatment.* The volatility of mercury increases with increasing temperature;
18 therefore, a heat treatment technique of excavated soil is a potentially effective technique
19 for the removal of mercury in soils.

- 1 3. *Hydrometallurgical treatment*. Chemical extraction of mercury in contaminated soils can be
2 induced by four mechanisms: desorption of adsorbed species, oxidation of metallic
3 mercury, use of strong complexing agents, and dissolution of Hg precipitate. The
4 efficiency and mechanism employed decrease with respect to time due to recomplexation,
5 readsorption and removal of the soluble fraction. Two of the two most promising
6 hydrometallurgical techniques are electrokinetics and electroleaching / methods of
7 leaching.
- 8 4. *In situ recuperation*. *In situ* techniques have not been studied as much as *ex situ* techniques
9 due to surface heterogeneity and longer treatment times. However, *in situ* techniques may
10 be promising due to better cost-effectiveness and practicality.
- 11 5. *Vapor extraction coupled with evaporation*. Vacuums are used in unsaturated zone to remove
12 volatile and semi-volatile contaminants.
- 13 6. *Permeable reactive barriers*. Dissolved compounds react with compounds found on the walls
14 and then precipitate out. This technique has been employed for the treatment of sites
15 contaminated with organic compounds and metals. These barriers are placed perpendic-
16 ularly to the flow of contaminants.
- 17 7. *In situ leaching and extraction*. Used together with pumps in treatment, this method uses
18 chemicals injections to improve the solubility of mercury in groundwater.
- 19 8. *Electrokinetic separation*. This process involves the generation of an electric field by
20 applying a potential difference or current into a soil matrix. Metals such as mercury
21 migrate towards electrodes placed in the soil where they accumulate and can be removed
22 at a lower cost by excavating the affected area.
- 23 9. *Interceptor systems*. Interceptor systems such as ditches and drains are simple and effective
24 for the recovery of mercury as free product, but these treatments are limited by site
25 topography and stratigraphy.
- 26 10. *Phytoremediation*. Some plants have the ability to assimilate and concentrate metals in soil.
27 The recovery of these metals occurs after collecting and incinerating the plants.
- 28 11. *Passive remediation of the wetlands*. Using wetlands to immobilize mercury is a controversial
29 topic as some wetlands contain microorganisms that can convert mercury into even more
30 toxic species.

31 5.2. Containment

32 In the containment treatment the soils are treated on one side of the contaminated site, where
33 the processing is performed on an area adjacent to the contaminated site or an area within the
34 contaminated site upon removal of soil or soil-like materials. In this classification are (Hinton
35 and Veiga, 2001):

- 1 1. *Pump and treat*. With certain contaminants or systems, pollution removal is not possible
2 and it is necessary to protect hydraulic content. When the contaminant mass remains in
3 the subsurface, pump and treat systems can prevent site contamination.
- 4 2. *Impermeable barriers (sealed surfaces and drainage)*. Mud barriers are slightly permeable
5 barriers made of bentonite or cement-bentonite mixtures. Generally, these barriers are
6 between 0.5 and 2 m thick and have a maximum depth of 50 m. There are other types of
7 barriers that are constructed by injection molding or by vibratory forces. On the other
8 hand, surface seals and drainage are used to controlling filtration and limit pollutant
9 movement towards groundwater.
- 10 3. *Stabilization and solidification*. Stabilization and solidification techniques use both *in situ* or
11 *ex situ* conditions by mixing impacted sites. Stabilization attaches contaminants to the soil
12 structure, which usually decreases soil permeability. Moreover, solidification improves
13 the physical characteristics of materials such as mud or sediments; they can be excavated
14 and transported more easily.
- 15 4. *Sediment covering*. *In situ* covering involves placing an insulating layer over the contami-
16 nated material.

17 5.3. *In situ* chemical treatment

18 Another option is the *in situ* chemical treatment option, which is the name of all treatments
19 that involve the injection of a chemical reagent into an aquifer source upstream of the conta-
20 minated site. This chemical agent reacts with the contaminant, transforming it into an innoc-
21 uous form; eventually, it can pump through a given volume of water which can later be
22 recycled for injection. The following actions must be considered:

- 23 1. Increase the output rate of the ground water through the contaminated zone by increasing
24 the hydraulic gradient through injection and extraction.
- 25 2. Transform the contaminant using chemical reaction within the aquifer.

26 5.4. Electroremediation of polluted soil with mercury

27 Electroremediation has been successfully applied in a variety of soil restoration studies, this
28 methodology having the advantage of exhibiting simultaneous chemical, hydraulic and
29 electrical gradients. Indeed, for efficient mercury removal from a saturated soil with electro-
30 remediation, application of either an electric field or direct current through two electrodes
31 (anode and cathode) is required. These are usually inserted in wells containing a supporting
32 electrolyte made from inert salts, leading to improved electric field conductive properties
33 (Rajeshwar et al, 1994; Huang et al, 2001; Acar and Alshawabkeh, 1993).

34 Furthermore, since electroremediation is a physicochemical technique based on ion transport,
35 it is an excellent tool for the removal of inorganic species, such as Hg^{+2} (Rajeshwar et al, 1994;

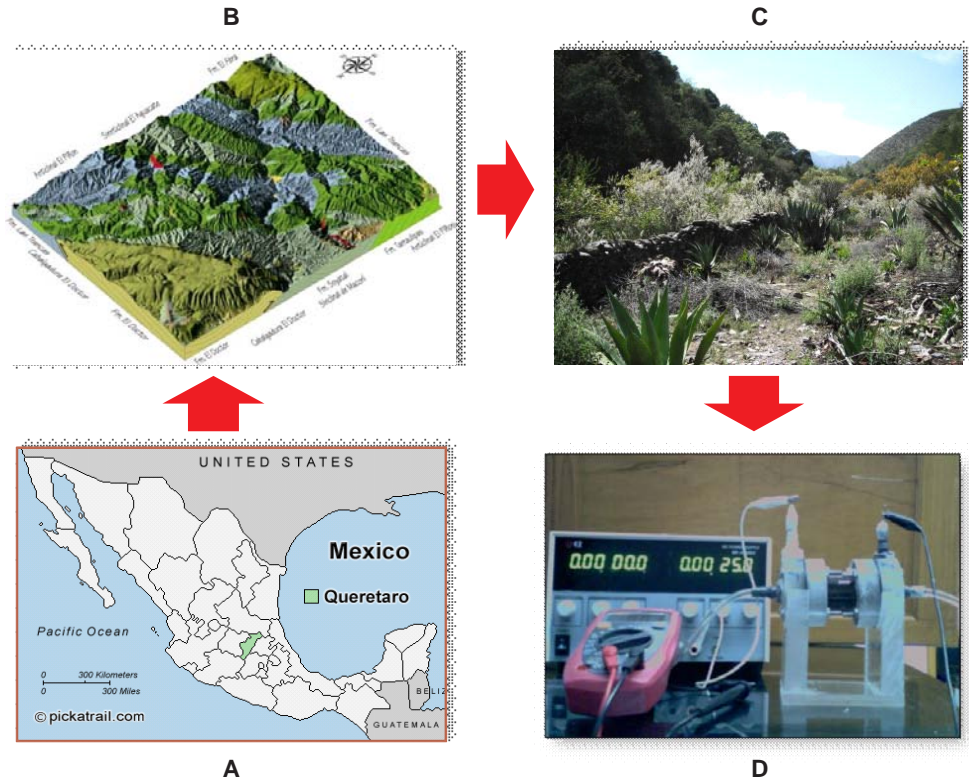
1 Bustos, 2013). The main advantages of electroremediation, as compared with other soil
2 treatment procedures, are (Huang et al, 2001; Acar and Alshawabkeh, 1993; Ibañez et al, 1998;
3 Segall and Bruell, 1992; Cabrera – Guzmán et al, 1990): (1) electroosmotic flow is not dependent
4 on either pore or particle size, (2) hydraulic gradient is enhanced by electromigration, (3)
5 treatment can be applied *in situ*, (4) it can be applied to low permeability soils, (5) there is
6 minimal disruption of normal activities at the site, (6) the required investment is usually lower
7 than that for other conventional treatments, and (7) it can be applied in conjunction with
8 techniques such as pumping, vacuum extraction or bioremediation.

9 The processes taking place during electroremediation can be classified into two main catego-
10 ries: (a) processes occurring as a consequence of the applied electric potential. These processes
11 include electromigration (ion transport), electroosmosis (mass transport), and electrophoresis
12 (charged particle transport); (b) processes occurring in the absence of an electric potential. This
13 includes concentration induced processes like diffusion, sorption, complexation, precipitation
14 and acid - base reactions (Reed et al, 1995; Bustos, 2013).

15 Specifically, for mercury polluted soil electroremediation, the use of complexing agents like
16 ethylenediaminetetraacetic acid (EDTA), KI, and NaCl under a constant potential gradient has
17 been reported (Reddy et al, 2003). Based on the above precedents, the electroremediation was
18 developed aided by extracting agents for mercury removal from San Joaquin's Sierra Gorda
19 soil samples (Figure 5, Robles et al, 2012).

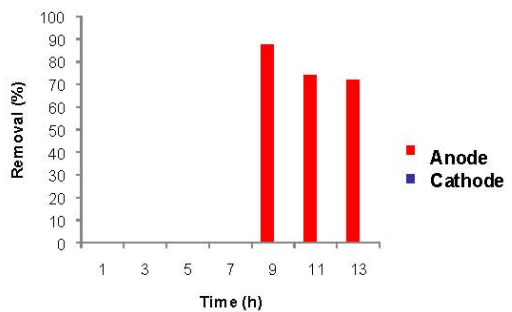
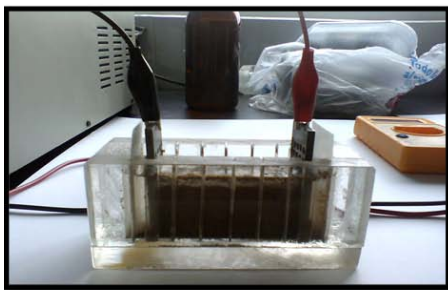
20 Electroremediation of mercury polluted soil, facilitated by the use of complexing agents,
21 proved to be an attractive alternative treatment for the removal of mercury from polluted soil
22 in mining areas located at Sierra Gorda in Queretaro, Mexico (Figure 5A and 5B). Implemen-
23 tation of this remediation protocol is expected to improve the living conditions and general
24 health of the population in the Mine "El Rincón" in San Joaquin (Figure 5C). Experimental
25 observations suggest that it is possible to remove up to 75 % of metal contaminants in mercury
26 polluted soil samples by wetting them with 0.1M EDTA, placing them in an experimental cell
27 equipped with Ti electrodes, and then applying a 5 V electric field for 6 hours (Figure 5D,
28 Robles et al, 2012). When we followed the electrochemical removal of mercury in a batch reactor
29 (Figure 6A), it was removed around 87% of Hg^{2+} in a time of 9 hours close to the anode side
30 by the presence of EDTA (Figure 6B). The pH remains nearly constant at 4 and conductivity
31 showed values close to 10 mS cm^{-1} by the ionic species.

35 The efficient removal of mercury contaminants observed under these conditions is attributed
36 to electromigration of the coordination complexes that form between the terminal hydroxyl
37 groups in EDTA and divalent mercury (Hg^{+2}), which is probably strengthened by supramo-
38 lecular interactions between unshared electrons at EDTA's tertiary amino nitrogens and Hg
39 $^{+2}$. These interactions are particularly effective with the presence of potassium ions. This
40 observation is supported by molecular modeling of several possible interactions in the
41 proposed complex using the Density Functional Theory method (B3LYP LANL2DZ, Robles et
42 al, 2012, Figure 7).



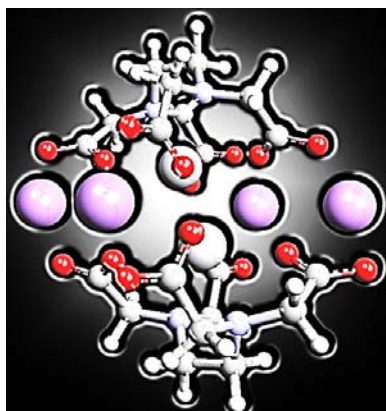
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Figure 5. Localization of Queretaro in Mexico (A) with satellite image from San Joaquin's Sierra Gorda, Queretaro (B) where there is the Mine "El Rincón" (C) with high concentration of Hg^{2+} , which was removed with electroremediation process in continues flow in presence of EDTA (D).



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Figure 6. Electroremediation process in batch reactor assisted by EDTA (A), and its corresponding removal percentage of Hg^{2+} followed during 13 h of treatment, close to anode and cathode.



32

1 **Figure 7.** Optimized conformation and molecular structure of the proposed $2 \text{Hg}^{2+} / 2 \text{EDTA} / 4 \text{Na}^{+}$ complexes (B3LYP
2 LANL2DZ, Robles et al, 2012).

3 **6. Conclusions**

4 Mercury is a non-essential metal that can bioaccumulated in living organisms, causing toxic
5 effects of various kinds. Therefore, it is vital to understand how this metal is transmitted
6 through the environment and the changes that occur due to contact with living organisms, or
7 environmental conditions such as high temperatures or strong winds. A study of the reactions
8 that form organic or inorganic compounds, which are even more toxic, is also necessary to
9 limit mercury toxicity. This research gives a brief overview of the techniques commonly used
10 for treatment of sediment and soil contaminated with mercury, mobilization and loadings the
11 mobilized mercury across different matrixes of environment, in specially electroremediation
12 of mercury polluted soil, facilitated by the use of complexing agents as EDTA, proved to be
13 an attractive alternative treatment for the removal of mercury from polluted soil in mining
14 areas.

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9 References

- 10 [1] Acar, Y. B., Alshawabkeh, A. N. (1993). Principles of Electrokinetic Remediation. *Environmental Science and Technology*, 27 (13), 2638 - 2647.
- 11
- 12 [2] Allard, B., Arsenie I. (1991). Abiortc reduction of mercury by humic substances in aquatic system- an important process for mercury cycle. *Water Soil Air Pollution*, 56, 457-464.
- 13
- 14
- 15 [3] Aposhian H. V., Maiorino R. M., Ramirez D. G., Charles M. Z., Xu Z., Hurlbut K. M., Munoz J.P., Dart. R. C. ,Aposhian M. M. (1995). Mobilisation of heavy metals by newer, therapeutically useful chelating agents. *Toxicology*, 97, 23-38.
- 16
- 17
- 18 [4] Barraclough, F. R., Givelet, N., Cortizas, A. M, Goodsite, M. E., Biester, H. Shoty, W. (2002). An analytical protocol for determination of total mercury concentrations in solid peat samples. *The Science of Total Energy*, 292, 129-139.
- 19
- 20
- 21 [5] Bengtsson, G. (2008). Mercury sorption to sediments: dependence on grain size, dissolved organic carbon, and suspended bacteria. *Chemosphere*, 73, 526-531.
- 22
- 23 [6] Bernaus A., Gaona X., Ree D., Valiente M. (2006) Determination of mercury in polluted soils surrounding a chlor-alkali plant. Direct speciation X-ray absorption spectroscopy techniques and preliminary geochemical characterisation of the area. *Analytica Chimica Acta*, 565, 73-80.
- 24
- 25
- 26
- 27 [7] Bollen, A. (2008). Mercury speciation analyses in HgCl₂-contaminated soils and groundwater-implications for risk assessment and remediation strategies. *Water Research*, 42, 91-100.
- 28
- 29
- 30 [8] Buchet J. P., Lauwerys R. R. (1989). Influence of 2,3 dimercaptopropane-1-sulfonate and dimercaptosuccinic acid on the mobilisation of mercury from tissues of rats pre-
- 31

- 1 treated with mercuric chlorid, phenylmercury acetate or mercury vapours. *Toxicology*, 54, 323-333.
2
- 3 [9] Bustos, E. (2013). Remediación Electro – Cinética de Suelos Contaminados con Hidro-
4 carburo. Chapter 5: Remediación de Suelos y Acuíferos Contaminados en México:
5 Bases Teóricas y Experiencias Reales. Luis G. Torres Bustillos y Erick R. Bandala
6 González. FUNDAP / CONCyTEQ / GTZ, México.
- 7 [10] Cabrera - Guzmán, D., Swartzbaugh, J. T., Weisman, A. W. (1990). The Use of Micro-
8 scale in Hazardous Waste Site Remediation. *Journal of Air and Waste Management As-*
9 *sociation*, 40, 1670 – 1676.
- 10 [11] Caldwell C. A., Canavan C. M., Blom N. S. (2000). Potential effect of forest fire and
11 storm flow on total mercury and methyl mercury in sediments of an arid-lands reser-
12 voir. *The Science of the Total Environmental*, 260, 125-133.
- 13 [12] Evangelu M.W.H., Ebel, M., Schaefer, A. (2007). Chelate assisted phytoextraction of
14 heavy metals from soil. Effect, mechanism, toxicity and fate of chelating agents. *Che-*
15 *mosphere*, 68, 889-1003.
- 16 [13] Fergusson, J. E. (1990). The Heavy Elements: Chemistry, Environmental Impact and
17 Health Effects, Pergamon Press
- 18 [14] Fügedi, U, J. Vatai and L. Kuti (2011). Mercury Content in the Superficial Geological
19 Formations of Hungary, *Central European Geology* Vol. 52 (3-4), 287-298
- 20 [15] Guzzi G., Minoia C., Pigatto P.: Fatal mercury poisoning and chelating agents. Letter
21 to the Editor. *Forensic Science Intern.* 202, (2010), 61.
- 22 [16] Han, F. X., Su, Y., Monts, D. L., Waggoner, C.A., Plodinec, M.J. (2006). Binding, distri-
23 bution and plant uptake of mercury in a soil Oak Ridge, Tennessee, USA. *Science of the*
24 *Total Environment*, 368, 753-768.
- 25 [17] Harvey, J. W. (2002). Interactions between surface water and ground water and ef-
26 fects on mercury transport in the north-central everglades. Reston Virginia: USGS,
27 Science for changing world.
- 28 [18] Hinton, J., Veiga, M. (2001). Mercury contaminated sites: a review of remedial solu-
29 tions. National Institute for Minamata Disease. In: Proceedings of the NIMD (Nation-
30 al. Institute for Minamata Disease)
- 31 [19] Holley, E.A, Mc. Quillan, A. J., Craw, D., Kim, J. P, Sander S. G. (2007). Mercury mobi-
32 lization by oxidative dissolution of cinnabar and metacinnabar. *Chemical Geology*, 240,
33 313-325.
- 34 [20] Hylander, L. D., Meili, M. (2003). 500 years of mercury production: global annual in-
35 ventory by region until 2000 and associated emissions. *The Science of Total Environ-*
36 *ment*, 304, 13-27.

- 1 [21] Huang, C. P., Cha, D., Chang, J. -H, Qiang, Z. (2001). Electrochemical Process for in-
2 situ Treatment of Contaminated Soils, Newark, Delaware.
- 3 [22] Ibanez, J. G.; Singh, M. M.; Szafran, Z.; Pike, R. M. (1998). Laboratory Experiments on
4 Electrochemical Remediation of the Environment. Part 3. Microscale Electrokinetic
5 Processing of Soils. *Journal of Chemical Education*, 75 (5), 634 - 635.
- 6 [23] Iverfeld, A., Lindquist, O. (1986). Atmospheric oxidation of elemental mercury by
7 ozone in the aqueous phase. *Atmospheric Energy*, 20, 1567-1573.
- 8 [24] Ko, K. B., Byun, Y., Cho, M., Namkung, W., Shim, D. N., Koh, D. J., Kim, K. T. (2008).
9 Influence of HCl on oxidation of gaseous elemental mercury by dielectric barrier dis-
10 charge process. *Chemosphere*, 71, 1674-1682.
- 11 [25] Lakatos, J., Brown, S. D., Snape, C. E. (1999). Influence of coal properties on mercury
12 uptake from aqueous solution. *Energy and Fuel*, 13, 1046-1050.
- 13 [26] Lakatos, J., Akcin, G., Brown, S. D., Snape, C.E. (1999). Application of coal and bio-
14 mass type sorbents for Hg(II) and Cr(VI) removal in the environmental protection
15 technology. Challenges of an interdisciplinary Science, *Academiai Kiado, Budapest*,
16 327-336.
- 17 [27] Lakatos, J., Cheng-gong, S. C., Perry, R., Kennedy, M., Snape, C. E. (2009). Ultra high
18 capacity co-precipitated manganese oxide sorbents for oxidative mercury capture.
19 237 th ACS meeting Spring, Salt Lake City.
- 20 [28] Leopold, K., Foulkes, M., Worsfold, P. (2010). Methods for the determination and
21 speciation of mercury in natural waters- a review. *Analytica Chimica Acta*, 663 (2),
22 127-138.
- 23 [29] Lomonte, C., Doronila, A., Gregory, A., Baker, A.J.M., Kolev, S.D. (2011). Chelate -as-
24 sisted phytoextraction of mercury in biosolids. *Science of Total Environment*, 409,
25 2685-2692.
- 26 [30] Lopez -Anton, M. A., Yuan, Y., Perry, R., Morato - Valer, M. (2010). Analysis of mer-
27 cury species present during coal combustion by thermal desorption. *Fuel* 89, 629-634.
- 28 [31] Lopez -Anton, M., Perry, R., Abad - Valle, P., Diaz - Somano, M., Martinez -Tarazo-
29 na, M. R., Morato-Valer, M. (2011). Speciation of mercury in fly ashes by temperature
30 programmed desorption. *Fuel Processing Technology*, 92, 707-711.
- 31 [32] Moreno, F. N., Anderson, C.W.N., Stewart, R.B., Robinson, B.H. (2004). Phytoreme-
32 diation of mercury contaminated mine tailings by induced plant-mercury accumula-
33 tion. *Environmental Practice*, 6, 165-175.
- 34 [33] Nik, M. G. (2012). The estudy of mercury pollution distribution aroun a chlor-alkali
35 petrochemical complex, Bandar Iman, southern Iran. *Environmental Earth Science*, 67
36 (5), 1485 - 1492.

- 1 [34] Nriahu J. O. (1994).Mercury pollution from the past mining of gold and silver in
2 Americas. *The Science of Total Environment*, 149, 167-181.
- 3 [35] Orecchio, S., Polizzotto (2013). Fractionation of mercury in sediments during drain-
4 ing of Augusta (Italy) coastal area by modified Tessier method. *Microchemical Journal*,
5 110, 452-457.
- 6 [36] Okouchi, S., Sasaki, S. (1984). Volatility in mercury in water. *Journal of Hazardous Ma-*
7 *terials*, 8, 341-348.
- 8 [37] Ozerova, N. A. (1996). Mercury in Geological Systems In: W. Baeyens, R. Ebinghaus
9 and O. Vasiliiev (eds) (1996). Global and Regional Mercury Cycles: Sources, Fluxes
10 and Mass Balances, NATO ASI Series 2. Environment Vol. 21 Kluwer Academic Pub-
11 lishers Dordrecht/Boston/London, 463-474
- 12 [38] Pongratz, R., Heumann, K. G. (1988).Production of methylated mercury and lead by
13 polar macroalgae. A significant natural source for atmospheric heavy metals in clean
14 room compartments. *Chemosphere*, 36, 1935-1946.
- 15 [39] Pillay, K., Cukrowska, E. M., Coville N.J. (2013).Improved uptake of mercury by sul-
16 phur-containing carbon nanotubes.*Microchemical Journal*, 108, 124-130.
- 17 [40] Rajeshwar, K., Ibanez, J. G., Swain, G. M. (1994). Electrochemistry and the environ-
18 ment, *Journal of Applied Electrochemistry*, 24,1077-1091.
- 19 [41] Reed, B. E., Berg, M. T., Thompson, J. C., Hatfield, J. H. (1995). Chemical conditioning
20 of electrode reservoirs during electrokinetic (EK) soil flushing of a Pb- contaminated
21 silt loam, *Journal of Environmental Engineering ASCE*, 121 (11)805 - 815.
- 22 [42] Reddy, K. R., Chaparro, C., Saichek, R. E. (2003). Removal of Mercury from Clayey
23 Soils Using Electrokinetics, *Journal of Environmental Science and Health, Part A – Tox-*
24 *ic / Hazardous Substances & Environmental Engineering*, A38 (2), 307 - 338.
- 25 [43] Reddy, K. R., Chaparro, C., Saichek, R. E. (2003). Iodide – Enhanced Electrokinetic
26 Remediation of Mercury – Contaminated Soils, *Journal of Environmental Engineering*,
27 ASCE, 129 (12),1137 – 1148.
- 28 [44] Robles, I., García, M. G., Solís, S., Hernández, G., Bandala, Y., Juaristi, E. and Bustos
29 E. (2012). Electroremediation of mercury polluted soil facilitated by complexing
30 agents, *International Journal of Electrochemistry Science*, 7, 2276 – 2287.
- 31 [45] Robles – Gutiérrez, I., Solís – Valdéz, S., Hernández – Silva, G., Bustos, E. (2012). Elec-
32 troremediation of Mercury Polluted Soil by Complexing Agents. Environmental In-
33 fluences of Mercury Ore Processing: Case Studies Selected at Slovenian, Mexican,
34 Hungarian Group Meeting in Idrija, Editors: Mateja Gosar, Tatjana Dizdarevič, Miloš
35 Miler, UNESCO, Slovenian National Committee of the International Geoscience Pro-
36 gramme, Idrija, Slovenia.

- 1 [46] Segall, B. A.; Bruell, C. J. (1992). Electroosmotic Contaminant Removal Processes,
2 *Journal of Environmental Engineering*, 118 (I), 84 - 100.
- 3 [47] Scharek, P. Hernández-Silva, G. Solorio-Munguia, G. Vassallo-Morales, L. Bartha,
4 A. Soliz-Valdez, S. Tullner, T. (2012). Total Mercury Content In Soils, Sediments and
5 Tailings in San Joaquin, Querétaro, Mexico Annual Report of the Geological Institute
6 of Hungary, 2010, 125-129
- 7 [48] Shi, J. B., Liang, L. N., Jiang, G. B., Jin, X. L. (2005). The speciation and bioavailability
8 of mercury in sediments of Haihe River, China. *Environment International*, 31, 357-
9 365.
- 10 [49] Shon Z. H., Kim K.H., Kim M.Y, Lee M. (2005). Modelling study of reactive gaseous
11 mercury in urban air. *Atmospheric Environment*, 39, 749-761.
- 12 [50] Slowey, A. J., Rytuba, J. J., Brown, J. G. E. (2005). Speciation of mercury and mode of
13 transprot from placer gold mine tailings. *Enviromental Science and Technology*, 39 (6),
14 1547-1554.
- 15 [51] Somoano M. D., Unterberger S., Hein K. R. G. (2007). Mercury emission control in
16 coal-fired plants: The role of wet scrubbers. *Fuel Processing Technology*, 88, 259-263.
- 17 [52] Sondreal, E.A., Benson, S.A., Pavlish, J.H., Ralston N.V.C. (2004). An overview of air
18 quality III. Mercury, trace element and particulate matter. *Fuel Processing Technology*,
19 85, 425-440.
- 20 [53] Wang M., Keener T. C., Khang S.J. (2000). The effect of coal volatility on mercury re-
21 moval from bituminous coal during mild pyrolysis. *Fuel Process Technology*,
22 67,147-161.
- 23 [54] Wartel, M., Mikac, N., Ouddane, B., Niessen, S. (1999). Speciation of mercury in sedi-
24 ments of the Seine estuary (France). *Applied Organometallic Chemistry*, 13 (10), 715 -
25 725.
- 26 [55] Weber J. H. (1993). Review of possible path for abiotic methylation of mercury(II) in
27 the aquatic environment. *Chemosphere*, 26, 2063-2077.

Electrochemical Detection of Mercury Removal from Polluted Bentonite and Quartz using Different Removing Agents

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1. INTRODUCTION.

Heavy metals (also known as the trace metals) are a large group of elements which are industrially and biologically important; in consequence they are defined as the group of elements with an atomic density greater than 6 g cm⁻³. Some of these heavy metals are toxic to living organisms in high concentrations. Heavy metals of greatest concern in terms of human health, agriculture and ecotoxicology are arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb), thallium (Tl), and uranium (U). However, some other heavy metals, such as cobalt (Co), chrome (Cr), manganese (Mn), and zinc (Zn), are necessary for the healthy growth of plants and / or animals but only in small concentrations. In addition, deficiencies of "essential" trace elements or heavy metals (often called "micronutrients") have limited agricultural productivity in many parts of the world, which include the lack of Zn, Cu and Mn in crops and Co, Mn, Cu and Zn in livestock (Alloway, 1990).

Mercury (Hg) has a high surface tension, meaning it easily forms small, compact, spherical drops. Although mercury droplets are stable compared to those of other metals, they can evaporate at high vapor pressures. High mercury concentration in the environment can be dangerous and increases as elemental mercury evaporates and enters the atmosphere. In addition, high concentrations of indoor mercury may pose an inhalation risk.

Mercury, which is commonly found in the earth's crust as salts such as mercuric sulfide, is released into the environment by volcanic eruptions. In addition to volcanic eruptions, erosion of rocks and soils can also release mercury. Anthropogenic sources of mercury include mercury produced as a by-product of the mining and refinement of others metals like copper, gold, lead and zinc. Mercury can also be released through recycling operations and is sometimes obtained from natural gas or other fossil fuels.

Approximately a third of the mercury circulating in the environment is produced naturally, while the remaining two-thirds are from industrial activity or other human activities. Due to the increase in industrial activity, the quantity of mercury circulating in the environment (atmosphere, soils, lakes, streams and oceans) has increased two to fourfold since the beginning of the industrial era. As a result, mercury levels in our environment are dangerously high.

Most of the mercury in the environment, released from both natural and anthropogenic sources, is elemental mercury (Hg⁰), including 99% of total atmospheric mercury. However, biogeochemical transformations of mercury can create Hg¹⁺ and Hg²⁺. Most inorganic mercury compounds (Hg¹⁺) are mildly water soluble and can be found in soils and sediments. In contrast, inorganic Hg²⁺ compounds vary depending on the local chemical atmosphere. Hg²⁺ has a short atmospheric lifetime (minutes) and is quickly removed through deposition due to its high surface activity and water solubility. Soil microorganisms oxidize mercury to its 2+ form (Leopold et al, 2010; Godarzi et al, 2012; Slowey et al, 2005; Mikac, 1999, Shi et al, 2005).

For the determination of metal in low concentrations a number of techniques can be applied (Table 1), in particular colorimetry and atomic absorption spectrometry. Colorimetric determinations do not need expensive instrumentation, but there are some disadvantages such as the need for destruction of the organic material and a separation step to avoid metallic interferences. Atomic absorption is very useful for the sensitive detection and quantitative determination of many metals, especially when using the flameless technique, but the instrumental requirements are rather expensive, another disadvantage of this techniques is that they require pretreatment of the sample differs often from metal to metal so that they do not lend themselves for systematic analyses in which it is not known which metal (s) may, or not be presented (Bodle et al, 1980; Bigham, 1990; Sarzaniniet al, 1994).

Techniques for total mercury determination include hydride generation atomic absorption (Chapple, 1990) and cold vapor atomic absorption (US-EPA Method 7471). For a general determination of mercury species, high-performance liquid chromatography with inductively coupled plasma mass spectrometry can be used (Fodör, 2000, 2005, 2007; Franke and Zeeuw, 1976). In consequence, there is a need for the relatively simple and

rapid analytical procedure capable to carry out systematic screening for heavy metals (Franke and Zeeuw, 1976). Some electrochemical techniques can determine all the different mercury species and oxidation states.

Table 1. Analytical techniques to determine mercury.

Technique	Hg / ng mL ⁻¹
X – rayFluorescence.	10
Neutron Activation.	2
Gold Film.	0.5
Differential Pulse Voltammetry.	0.04
Cold Vapour Atomic Absorption (CVAAS).	0.01
Cold Vapour Atomic Fluorescence (CVAFS).	0.0001
Inductively Coupled Plasma – Mass Spectrometry (ICP – MS).	0.001
Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP – AES).	50

Electrochemistry provides analytical techniques characterized by instrumental simplicity, moderate cost and portability. Some as stripping methods use a variety of electrochemical procedures which all share a characteristic initial stage. First, the analyte is deposited on an electrode, usually starting from a stirring solution. After an exact period of time, electrolysis is interrupted, stirring is stopped and the quantity of analyte deposited is measured using voltammetric procedures. During the second stage of the analysis, the analyte is redissolved or liberated from electrode (Woolever et al, 2001).

In Anodic Stripping Voltammetry (ASV, Figure 1), the electrode behaves as a cathode during deposition and as an anode during redissolution, where it is oxidized by the analyte again and returns to its original form (Skoog, 1997; Dogan-Topal et al, 2010; Pineda et al, 2009; Anguiano et al, 2012; Bustos, 2012). ASV has been used to detection of trace metals ions in solution at $\sim 10^{-11}$ M (or sub-ppb) concentrations have been reported (Hubert, 2001). This technique is advantageous to other analytical techniques is its simplicity of use, low cost of instrumentation, and being monodestructive (Woolever et al, 2001).

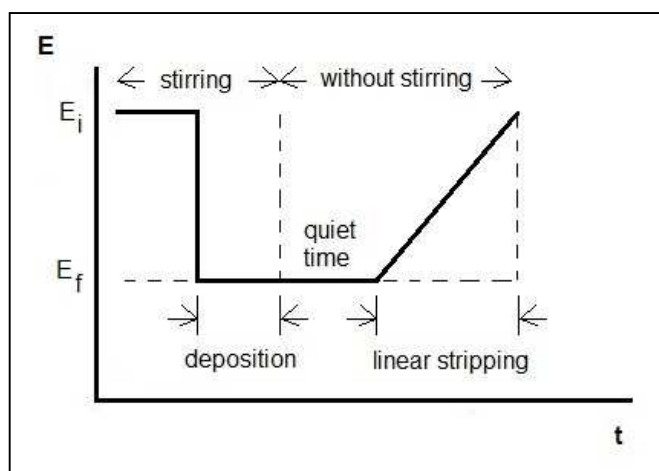


Figure 1. Potential sequence used as perturbation in an ASV experiment.

As shown in Figure 1, there are three sequential steps in a typical ASV experiment: deposition or preconcentration, quiet time and linear stripping. During the deposition step, the electroactive species are reduced up to their zero-valence form under stirred electrolytic solutions. In this sense, E_f must be a more negative potential than E_i . Later, the stirring is stopped during the quiet time in order to avoid convection transport of ions through the solutions. Finally, the species previously reduced are selectively oxidized during an anodic linear sweep and the current is recorded as function of the potential applied without stirring of the electrolytic solutions (Scholz, 2002).

Differential Pulse Stripping Voltammetry (DSPV, Figure 2A) is comparable to Normal Pulse Voltammetry (NPV, Figure 2B) in that the potential is also scanned with a series of pulses. However, it differs from NPV because each potential pulse is fixed, of small amplitude (10 to 100 mV), and is superimposed on a slowly changing base potential. Current is measured at two points for each pulse, first point just before the application of the pulse and second one at the end of the pulse (Ari et al, 1990; Brett and Oliveira, 1998). These sampling points are selected to allow for the decay of the nonfaradaic (charging) current. The difference between current measurements at these points for each pulse is determined and plotted against the base potential (Woolever et al, 2001; Franke and Zeeuw, 1976).

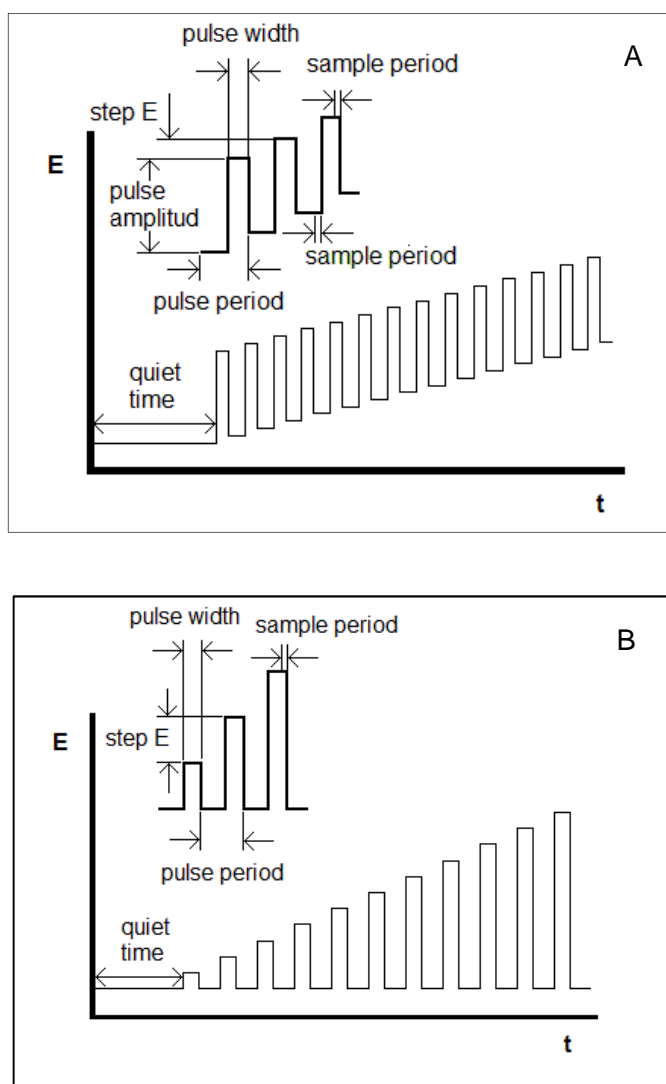


Figure 2. Potential wave form used as perturbation in a DSPV (A) and NPV (B) experiment.

Square Wave Voltammetric (SWV) technique is among the most sensitive means, for the direct evaluation of concentrations; it can be widely used for the trace analysis. The perturbation consists of a square wave having constant amplitude, superimposed at the same time upon a staircase wave form. The current is measured at the end of each forward half-cycle (I_f) and at end of each reverse half-cycle (I_r). The difference between both current values ($I_f - I_r$) is displayed as a function of the applied potential E as shown in Figure 3. Therefore, the effect of the charging current is notably decreased in SWV since any residual charging current is completely removed (Bard and Rubinstein, 1999; Ari et al, 1990; Scholz, 2002; Zbigniew et al, 1994; Brett and Oliveira, 1998).

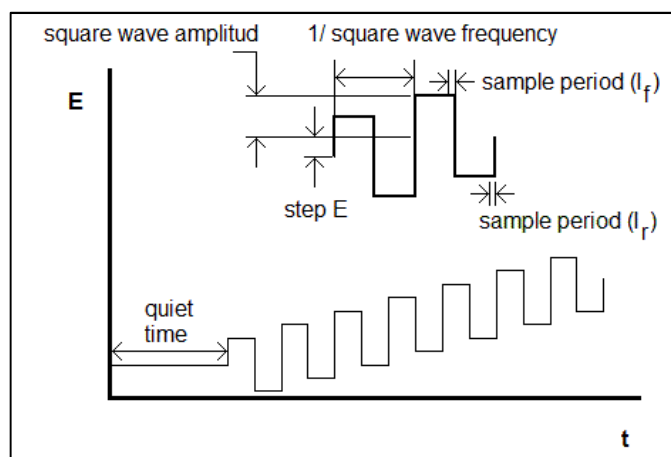


Figure 3. Potential wave form used as perturbation in a SWV experiment.

SWV has several advantages, has an excellent sensitivity and the rejection of background currents, this speed coupled with computer control and signal averaging allows for experiments to be performed repetitively and increases the signal-to-noise ratio. Applications of SWV include the study of electrode kinetics with regard to preceding, following, or catalytic homogeneous chemical reactions (Franke and Zeeuw, 1976; Dogan – Topal et al, 2010).

Using ASV, the concentration of mercury in liquid samples can be determined. For the determination of mercury in soil, ASV is used after an acid digestion which removes mercury from soil samples (Lamble and Hill, 1998). Some alternative methods for the removal of mercury in soil samples also exist, such as the use of removing agents as called in Table 2, in these studies removing agents were used to remove some heavy metals from different samples (Reddy and Camesselle, 2009; Reddy, 2005; Haheb, 2012; Tandy et al, 2004; Rhazi, 2002; Cox, 1996; Robles et al, 2012). In this paper, we compared the efficiency of eight removing agents showed in Table 2 in the ability to remove mercury from polluted bentonite and quartz comparing DSPV, SWV and ASV.

Table 2.Scientific publications about metal extractions facilitated by removing agents.

Removing agent	Concentration	Sample	Removed Metal	η / %
Ethylenediamine tetraacetic acid (EDTA)	0.2 M	Low permeability soil polluted with heavy metals	Hg	20
Diethylenetriamin pentaacetic acid (DTPA)	0.2 M			50
Potassium iodide (KI)	0.2 M			80
Hydroxypropyl- β -cyclodextrine (HPCD)	10%			15
Ethylenediaminetetraacetic acid + cysteine + sodium chloride (EDTA + Cys + NaCl)	275 mgL ⁻¹ , 1.25%, 0.5 % Respectively	Rawfish	Hg	90
Ethylenediamine tetraacetic acid (EDTA)	0.4 and 4 mM	Polluted soil	Cu, Pb	(Cu)- EDTA (84), NTA (66), EDDS (67)
Ethylenediamine disuccinic acid (EDDS)				(Pb)- EDTA (94), NTA (65), EDDS (67)
Iminodisuccinic acid (IDSA)				
Ácidometilglicíndi acetic (MGDA)				
Nitrilotriacetic acid (NTA)				
Chitosan	0.02 mMg ⁻¹ (Co ²⁺ and Ca ²⁺)	Polluted water	Co, Ca, Cr, Cu	Cu (53), Co (11)
	1.2 mMg ⁻¹ (Cr ³⁺)			
	2 mMg ⁻¹ (Cr ³⁺)			
Potassium iodide (KI)	0.1 M	Polluted soil	Hg	99
Potassium iodide (KI)	0.1 M	Polluted soil	Hg	62
Ethylenediamine tetraacetic acid (EDTA)	0.1 M			75

Table 2 contains references about different removing agents reported to remove different metals. These studies analyzed the removal of metals from different samples, obtaining the highest efficiencies using removing and complexing agents by exchanging charges of cations to remove mercury in the first case, or coordinating cations in the second case (Wypych, 2004; Montuenga, 1979; Přibil, 1982; Buffle, 1990; Spencer et. al. 2000; Malone, 1999).

2. EXPERIMENTAL PROCEDURE.

Stripping voltammetric measurements were carried out using the potentiostat/galvanostat Epsilon modular electrochemical analysis system. Three-electrode electrochemical cell (Figure 5) was used with glassy carbon electrode as working electrode, a platinum wire as auxiliary electrode and an Ag/AgCl as reference electrode (Pineda et al, 2009; Anguiano et al, 2012; Bustos, 2012). Glassy carbon electrode was polished in cloth with an alumina suspension of 1, 0.3 and 0.05 μm . Between each polish it was rinsed with deionized water, and then it was sonicated during 5 min in deionized water to eliminate any residual alumina.

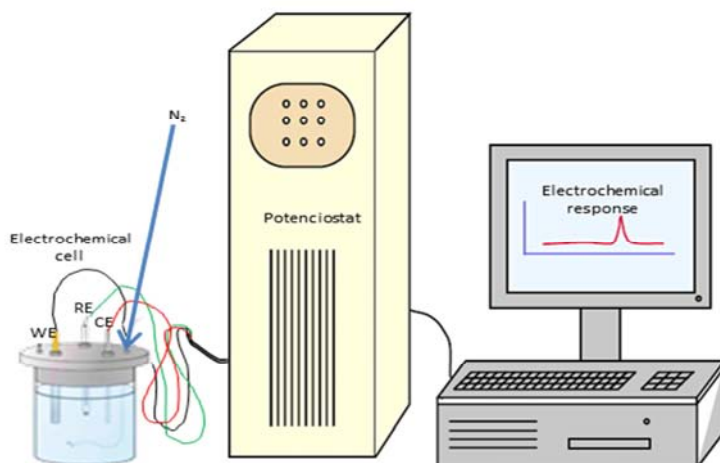


Figure 5. Scheme of a 3-electrode cell used in voltammetry techniques, where gas inlet is used for bubbling electrolyte solution with an inert gas and with controlled temperature.

2.1. REAGENTS AND SOLUTIONS.

Reagents used in this study were: Potassium chloride, potassium iodide, potassium hydroxide, sodium hydroxide, ethylenediaminetetraacetic acid, and hydrochloric acid obtained from J. T. Baker; sodium chloride from Sigma Ultra; chitosan from crab shells practical grade, β -cyclodextrin hydrate, L-cysteine were obtained from Aldrich. For mercury pollution were used mercury chloride (II) from Merck, and mercury oxide (II) obtained from Hach. Calcium bentonite from Lodibent Bentonite, and sand white quartz from Sigma Aldrich.

Removing agents tested were 0.1 M potassium iodide (KI), 0.1 M potassium chloride (KCl), 0.1 M potassium hydroxide (KOH), 0.1 M hydrochloric acid (HCl), 0.1 M ethylenediaminetetraacetic acid (EDTA), 10% hydroxypropyl- β -cyclodextrine (HPCD) in deionized water, 0.01 M chitosan and a mixture of 275 mgL^{-1} EDTA, 1.15% cysteine and 0.5% sodium chloride (NaCl). All of the agents, with the exception of chitosan, had previously been tested for the ability to remove metals in soil samples. Control experiments were carried out with water. Solutions were prepared using water type I, according to ASTM-D1193-99. Chitosan were dissolved in acetic acid. Samples of quartz and calcium bentonite were polluted with mercuric chloride (HgCl_2) and mercuric oxide (HgO) at concentrations of 10 and 25 mgL^{-1} . Eight removing agents were tested to find the most effective. The percentage of mercury removed was quantified by ASV after extracting the liquid from the bentonite/quartz samples.

2.2. TECHNIQUES AND PROCEDURES.

Electrochemical techniques as Anodic Stripping Voltammetry (ASV), Differential Stripping Pulse Voltammetry (DSPV) and Square Wave Stripping Voltammetry (SWSV) were tested to select adequate technique to quantify mercury removal efficiency. After select adequate technique, calibration curves were created for all different removing agents for the addition of both HgCl_2 and HgO .

Experimental conditions for ASV were as follows: pre-concentration potential -0.6 V vs. Ag/AgCl, deposition time 6 min, quiet time 30 s, scan rate 20 mV/s. An increase in signal due to increasing mercury was monitored and recorded along with the increment in current associated with the concentration addition. For SWSV were used an initial potential of -0.2 mV, a deposition potential of -0.6 V for a deposition time of 10 s; a quiet time of 5 s, a SW frequency of 50 Hz, a potential step of 0.005 V. For DSPV were used an initial potential of -0.2 mV, a deposition potential of -0.6 V for a deposition time of 10 s; a quiet time of 5 s, a potential step of 4 mV, a pulse width of 50 ms, a pulse period of 200 ms, pulse amplitude of 50 mV. All experiments were carried out at room temperature ($25\pm 1^\circ\text{C}$) (Anastasiadou et al, 2010). Calibration curves for mercuric quantification were done using electrochemical techniques to select the best.

3. RESULTS AND DISCUSSION.

3.1 Selection of detection technique

To select the technique to quantify mercury was realized calibration curves with both mercury compounds by ASV, DSPV and SWSV. Figure 6 shows the comparison of mercury detection using different electrochemical techniques. Mercury chloride was not showed but resembled same behavior. Table 3 shows comparison of electrochemical techniques of both mercury compounds, where it shows that any technique can be used to quantify mercury by its low detection and quantification limits, but the use of ASV shows the best fit with the lowest DL and QL. In consequence, ASV was selected to quantify mercury in solution, which was removed from polluted bentonite and quartz.

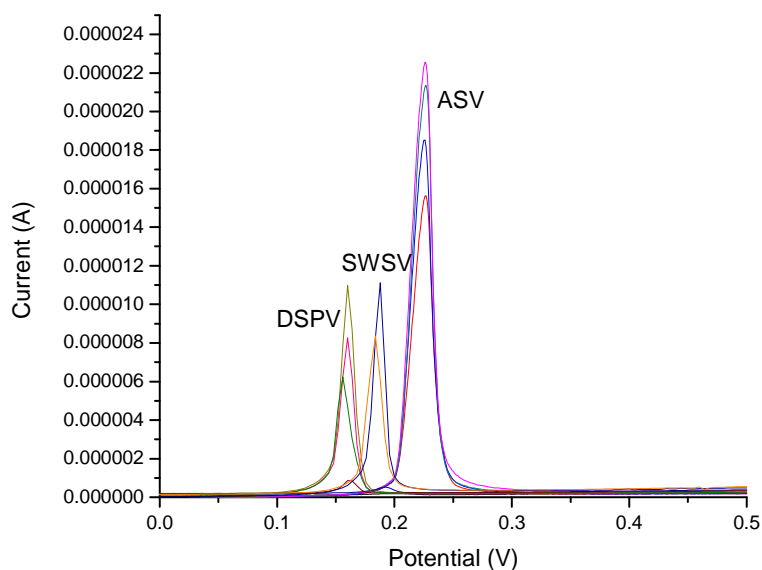


Figure 6.ASV-DSPV-SWSV comparison to select technique to quantify mercury removed.

Table 3. Parameters comparison of stripping voltammetry to quantify mercury. R^2 is the correlation coefficient, m represents the slope of linear regression; DL means Detection Limits, QL represents Quantification Limits.

Mercury Compound	Technique	Linear Equation	R^2	m ($\mu\text{A mM}^{-1}$)	DL (pM)	QL (nM)
HgCl ₂	ASV	2549.30x - 0.0355	0.993	2549.30	112.043	0.373
	DPSV	299.43x - 0.5035	0.978	299.43	422.226	1.407
	SWSV	467.50x - 1.3763	0.981	467.50	479.046	1.597
HgO	ASV	6793.30x - 5.4037	0.998	6793.30	42.046	14.015
	DPSV	1313.70x - 1.0952	0.968	1313.70	96.237	32.079
	SWSV	2347.90x - 1.6533	0.971	2347.90	95.385	31.795

3.2 Electrochemical responses of removing and complexing agents

After obtaining encouraging calibration results for mercury detection using ASV with sequential addition on removing agents proposed. Electrochemical answer of removing and complexing agents in the presence of mercury compounds was obtained (Figure 7).

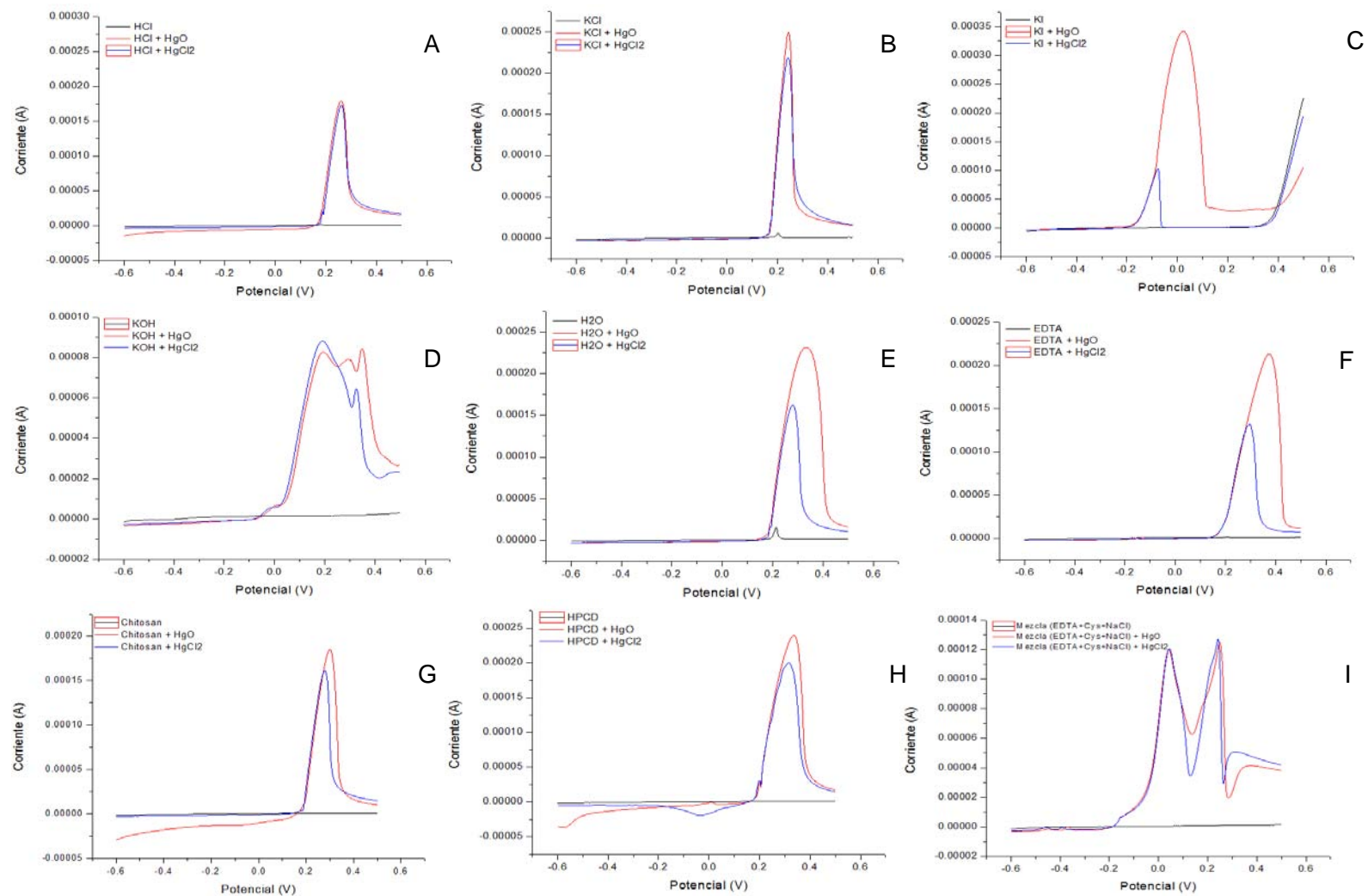


Figure 7. Electrochemical behavior of mercury compounds to removing agents: (A) HCl, (B) KCl, (C) KI, (D) KOH, (E) H₂O, (F) EDTA, (G) chitosan, (H) HPCD and (I) EDTA+Cys+NaCl.

White the ASV showed before, calibration curves of each of one mercury compounds added to removing agents was obtained as Figure 8 shows with the ASV response for chitosan.

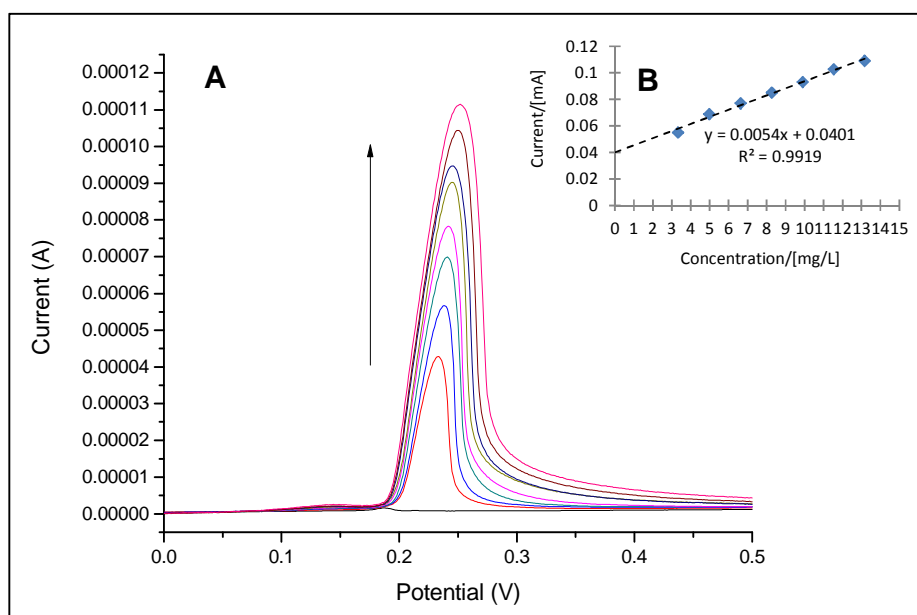


Figure 8.ASV detection of HgO addition to chitosan in 0.1 M HCl using vitreous carbon, platinum wire and Ag|AgCl as work, counter and reference electrode with a scan speed of 70 mV s^{-1} (A), and linear fit of HgO addition to chitosan (B).

Table 4 shows corresponding equations of different removing agents, including fitting (R^2), sensibility (obtained from the slope m), detection and quantification limits (DL and QL respectively) for both mercury compounds. DL and QL represent fundamental performance characteristics of measurement processes, where DL or Limit of Detection (LOD) is defined as an indicator of the minimum detectable analyte net signal, amount or concentration. His term is widely understood and quoted by most chemists as a measure of the inherent detection capability. In general, the LOD is taken as the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified, under the stated conditions of the test. In another hand, QL or Limit of Quantification (LOQ) is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions of test. The general equation to determine detection and quantification limit is:

$$\frac{LOD}{LOQ} = \frac{F(SD)}{b}$$

Where F is a factor of 33 and 10 for LOD and LOQ, respectively. SD represent the standard deviation of the ordinate intercept, or residual standard deviation of the linear regression; and b the slope of the regression line. For a linear calibration curve, it is assumed that the instrument response y is linearly related to the standard concentration x for a limited range of concentration. This model is used to compute the sensitivity b and the LOD and LOQ. Therefore, the LOD and LOQ can be expressed as

$$LOD = \frac{3S_a}{b} \quad ; \quad LOQ = \frac{10S_a}{b}$$

Where S_a is the standard deviation of the response and b is the slope of the calibration curve. The standard deviation of the response can be estimated by the standard deviation of either y-residuals, or y-intercepts, of regression lines. This method can be applied in all cases, and it is most applicable when the analysis method does not involve background noise. It uses a range of low values close to zero for calibration curve, and with a more homogeneous distribution will result in a more relevant assessment (Currie 1995, 1999; Guidance 2000).

Table 4. Calibration curves corresponding to each removing agents.

Removing Agent	HgO				
	Equation	R ²	m (mA mg ⁻¹)	DL (µg L ⁻¹)	QL (µg L ⁻¹)
HCl	y=0.0077x+0.0980	0.993	0.0077	0.2000	0.6680
KCl	y=0.0093x+0.0421	0.999	0.0093	0.0676	0.2250
KI	y=0.0141x+0.1194	0.982	0.014	0.0292	0.0974
KOH	y=0.0035x+0.0280	0.994	0.0035	0.2750	0.9160
EDTA	y=0.0039x+0.0369	0.988	0.0039	1.2400	4.1400
HPCD	y=0.0069x+0.0730	0.982	0.0069	0.1100	0.3660
Cys+EDTA+NaCl	y=0.0083x+0.0162	0.999	0.0083	0.0454	0.1510
Chitosan	y= 0.0054x+0.0401	0.992	0.0054	0.1480	0.4930
Complexing Agent	HgCl ₂				
HCl	y=0.009x+0.0576	0.995	0.009	0.1710	0.5710
KCl	y=0.0092x+0.0538	0.993	0.0092	0.0684	0.2280
KI	y=0.0106x+0.1018	0.980	0.0106	0.0386	0.1290
KOH	y=0.0005x+0.0484	0.970	0.0005	1.9200	6.4100
EDTA	y=0.0033x+0.0421	0.975	0.0033	1.4700	4.8900
HPCD	y=0.0056x+0.0487	0.995	0.0056	0.1350	0.4510
Cys+EDTA+NaCl	y=0.0163x-0.1353	0.987	0.0163	0.0231	0.0770
Chitosan	y=0.0046x+0.0406	0.986	0.0046	0.1740	0.5790

As can be seen in Table 4, we obtained a good QL and DL of mercury compounds in the presence of removing and complexing agents. So ASV is a good technique to determine mercury concentration in presence of removing agent too. In this way, removal efficiencies of mercury were analyzed in the next section.

3.3 Mercury removal efficiencies

Removal percentages were calculated in base of fitting equations for all the different removing agents, they are show in Figures 9 and 10. Due to structural differences in bentonite and quartz (Figure 11), mercury removal behaved differently for the two.

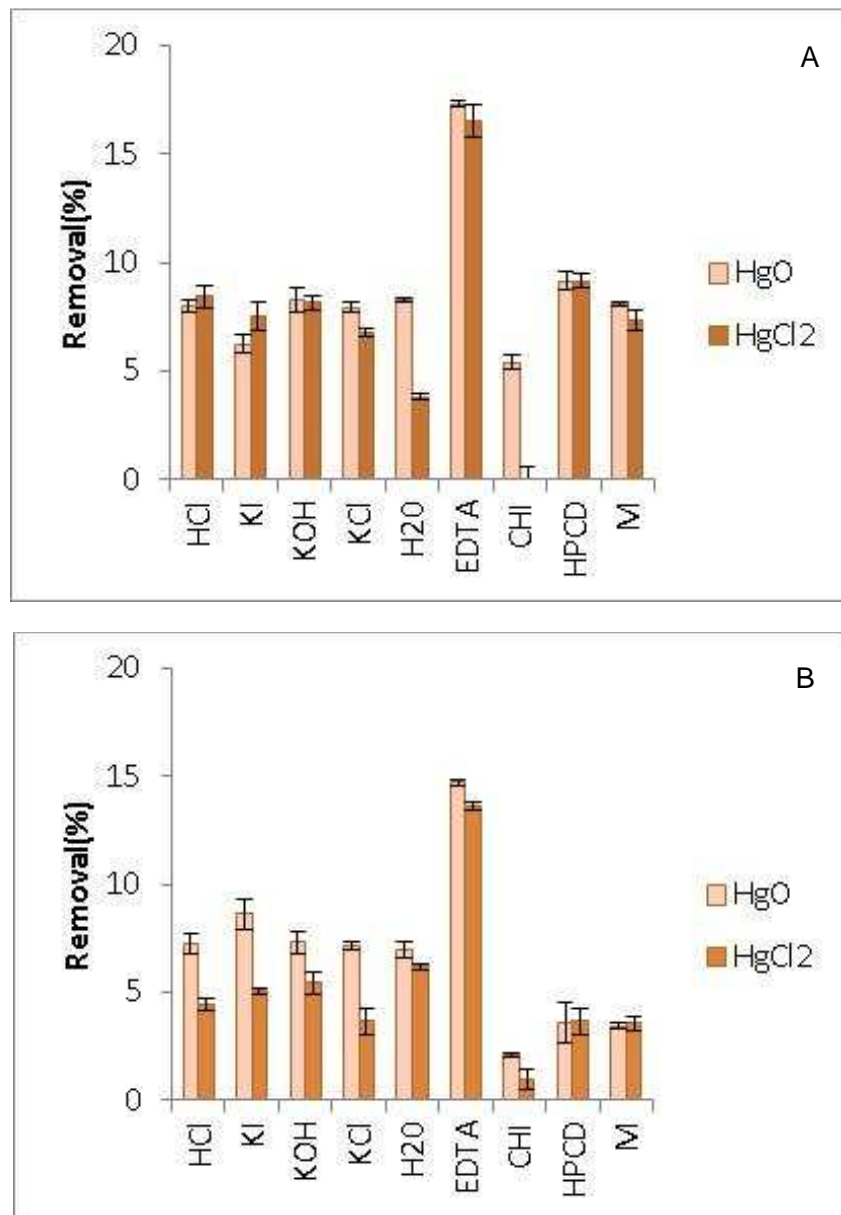


Figure 9. Removal percentages of mercury (HgCl₂ and HgO) in bentonite using different removing agents with 10 mg L⁻¹ (A) and 25 mg L⁻¹ (B) mercury concentration.

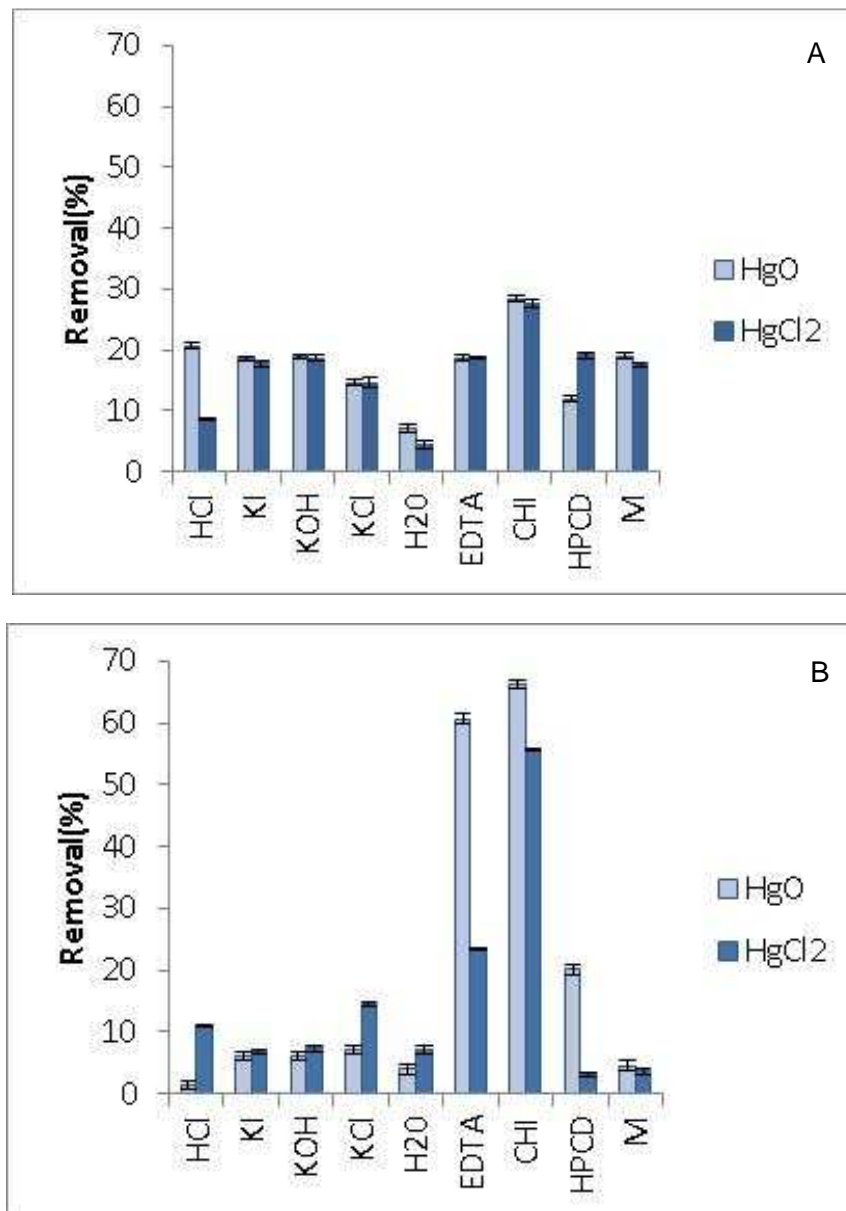


Figure 10. Removal percentages of mercury (HgCl₂ and HgO) in quartz using different removing agents with 10 mg L⁻¹ (A) and 25 mg L⁻¹ (B) mercury concentration.

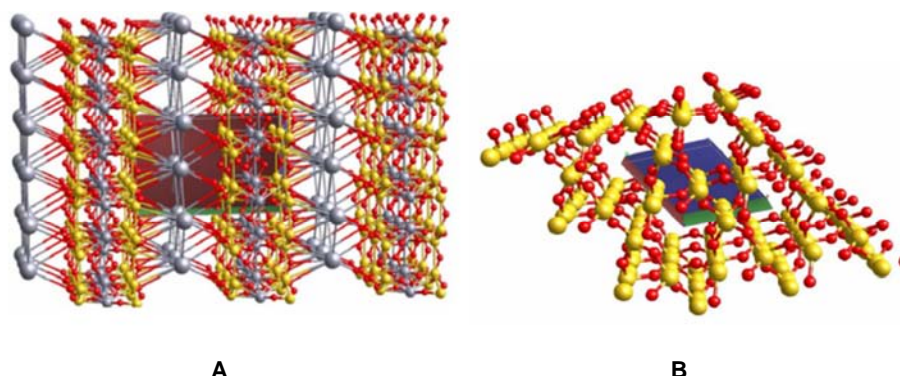


Figure 11. Representation of the structure of bentonite (A) and quartz (B) (Bruker AXS Advanced X-Ray Solutions Software).

Quartz is ordered as strong matrix of oxygen-silicon bonds, which prevent metal ions from penetrating its structure (Figure 11B). On the other hand, metal ions can easily slip into bentonite, which is formed of stacked layers, due to the gaps between the layers (Figure 11A). Because of the strong organized bonds in quartz, mercury is more easily removed from quartz than bentonite. Moreover, the particle size of bentonite is lower than quartz, and therefore has a bigger surface area and as a synthetic colloid, in addition, it has negative charges which attract positive ions. Once bentonite and quartz samples were contaminated with HgO or HgCl₂, removing agents were added. After 24 h the sample was collected and analyzed by ASV.

In order of the results obtained, bentonite adsorbed chitosan easily, swelling up dramatically which made it difficult to remove the supernatant. Therefore, the removal of mercury from bentonite using chitosan was inefficient (Figure 9, less than 5 %). This effect was consequence of the affinity of chitosan to the layers of bentonite and it was retained inside of this clay. In contrast, when the chitosan was used to remove Hg²⁺ from quartz (Figure 9), this got a removal close to 30 % when it was 10 mg L⁻¹, and the double of removal was when quartz had 25 mg L⁻¹ mercury; this increase was proportional to the concentration of mercury ions over quartz, where chitosan took off the pollutant from particle surface to the solution. Anyway, all the different extracting agents used to remove mercury remove metals by electrostatic forces, forming ionic bonds. Thus, magnitude depends on ionic charge.

On the other hand, complexing agents act differently with metallic ions. Metals tend to lose electrons during chemical reactions, creating metallic ions. The positive charge of these cations attracts negative ions to form complexes held together by covalent bonds. Donating species (ligands) needs to have a lone pair of electrons which can be donated to form a bond. Water, ammonia and halides are common inorganic ligands (Buffle, 1990; Malone, 1999; Montuenga, 1979).

Stronger compounds as EDTA and chitosan tend to remove more mercury contamination present in the bentonite and quartz samples, than 0.1 M KI, 0.1 M KCl, 0.1 M KOH, 0.1 M HCl, 0.1 M EDTA, 10 % HPCD, 0.01 M chitosan and a mixture of 275 mg L⁻¹ EDTA, 1.15% cysteine and 0.5 % NaCl by the different arrangement of mercury ions in these chemical solutions, with less than 10 % removal from bentonite (Figure 9), and less than 20 % from quartz (Figure 10) in both concentrations of Hg²⁺: 10 and 25 mg L⁻¹.

With ASV has been possible study the thermodynamic and kinetic of adsorption of Hg (II) on Ca-Bentonite, detecting the pollutant in solution to confirm that Ca-Bentonite has a good adsorption capacity of Hg²⁺ adjusting the results to Freundlich isotherm as a mathematical model, with a pseudo second order of reaction. Using the standard potential (E°) obtained after the ASV, we obtained different thermodynamic parameters as equilibrium constant (K_{eq}), free standard energy (ΔG°) and entropy (ΔS°) of Hg²⁺ – Ca-Bentonite. These results indicate us that the process of adsorption is spontaneous, endothermic and irreversible by a possible inclusion and interchange of Hg²⁺ with Ca²⁺ between the Bentonite slides.

In addition, we have used the ASV to evaluate the electroremediation of mercury polluted soil using complexing agents like EDTA removing up to 75 % of metal contaminants in mercury polluted soil samples by wetting them with 0.1M EDTA, placing them in an experimental cell equipped with Ti electrodes, and then applying a 5 V electric field for 6 hours in a batch reactor; Hg²⁺ was removed around 87% in a time of 9 hours close to the anode side by the presence this complexing agent (Robles et al, 2012).

4. CONCLUSIONS.

ASV was selected as an electrochemical technique to quantify the percentage of mercury removed in liquid samples, which were derived from bentonite and quartz samples previously polluted with two mercury compounds (HgO and HgCl₂). Eight removing agents were analyzed: 0.1 M KI, 0.1 M KCl, 0.1 M KOH, 0.1 M HCl, 0.1 M EDTA, 10 % HPCD, 0.01 M chitosan and a mixture of 275 mg L⁻¹ EDTA, 1.15% cysteine and 0.5 % NaCl, using both extracting (ionic bond complexes) and complexing agents (covalent bond complexes).

The best result of the removal of Hg²⁺ from bentonite and quartz were obtained with complexing agents: EDTA and chitosan. For bentonite, the most effective removing agent was EDTA which removed 17% of both Hg compounds. In the case of quartz, chitosan was the best removing agent, removing 62% of HgO and 53% of HgCl₂.

This is the first report of the use of chitosan to remove mercury ion from bentonite and quartz, which is a very good new alternative of complexing agent because it is biodegradable, cheap and easy to obtain (derived from shrimp exoskeleton), with potential application to quantify mercury in polluted soil during some remediation strategy to verify its cleaning without a pre-treatment of sample.

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6. REFERENCES.

- Alloway, B. J. (1990). Heavy metals in soils, John Wiley and Sons, Inc. New York.
- Anastasiadou, Z. D., Jannakoudakis, P. D., Girousi, S. T. (2010). Square wave anodic stripping voltammetry determination of eco-toxic metals in samples of biological and environmental importance. *Central European Journal of Chemistry*, 8 (5), 999 - 1008.
- Anguiano, D. I., García, M. G., Ruíz, C., Torres, J., Alonso – Lemus, I., Alvarez – Contreras, L., Verde – Gómez, Y., Bustos, E. (2012). Electrochemical Detection of Iron in a Lixiviant Solution of Polluted Soil Using a Modified Glassy Carbon Electrode. *International Journal of Electrochemistry*, 2090 - 3537.
- Ari, I., Andrzej, L., Rolf, S. (1990). Contemporary Electroanalytical Chemistry. Plenum Press. New York and London, 419 - 429.
- Bard, A. J., Rubinstein, I. (1999). Electroanalytical Chemistry: A Series of Advances. Marcel Dekker, Inc. USA, Vol. 14.
- Bigam, M. D. (1990). Field Detection and Implications of Mercury in Natural Gas, SPE Prod. Eng., 120 - 124.
- Bodle, W. W., Attari, A., Serauskas, R. (1980). Considerations for Mercury in LNG Operations", Inst. of Gas Tech., 6th. Int. Conference on LNG, Kyoto Japan, Paper 1.
- Brett, Ch. M. A., Oliveira, A. M. (1998). Electroanalysis. Oxford University Press Inc. New York.
- Buffle, J. (1990). Complexation Reactions in Aquatic systems, an Analytical Approach, Editorial Ellis Horwood, Great Britain.
- Bustos, E. (2012). Design, Construction and Characterization of an Electrochemical Sensor of Mercury in Soil. Environmental Influences of Mercury Ore Processing: Case Studies Selected at Slovenian, Mexican, Hungarian Group Meeting in Idrija, Editors: Mateja Gosar, Tatjana Dizdarevič, Miloš Miler, UNESCO, Slovenian National Committee of the International Geoscience Programme, Idrija, Slovenia.
- Chapple, G. (1990). The determination of arsenic, selenium and mercury levels in U.S. EPA quality control samples using the GBC HG3000 continuous-flow hydride generator, GBC AA Applications, N° 17, Australia.

- Cox, C. D. (1996). Electrokinetic remediation of mercury contaminated soils using iodide / iodine lixiviant, *Environmental Science and Technology*, 30, 1933 - 1938.
- Currie, L. A. (1999). Detection and quantification limits: origins and historical overview. *Analytica Chimica Acta* 391, 127 - 134.
- Currie, L. A. (1995). Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC recommendations). *Pure & Applied Chemistry*, 67 (10), 1699 - 1723.
- Fodör, P. (2000). Development of analytical systems for the simultaneous determination of the speciation of arsenic and selenium, *Analytical Chimica Acta*, 413, 13 – 23.
- Fodör, P. (2005). Arsenic speciation in farmed hungarian freshwater fish, *Journal of Agricultural and Food Chemistry*, 53, 9238 - 9243.
- Fodör, P. (2007). Selenium speciation studies in Se- enriched chives by HPLC-ICP-MS, *Food Chemistry* 101, 1398 – 1406.
- Franke, J. P., Zeeuw, R. A. (1976). Differential Pulse Anodic Stripping Voltammetry as a Rapid Screening Technique for Heavy Metal Intoxications, *Archives of Toxicology*, 37, 47 - 55.
- Godarzi, N. M., Shahbazi, B., Grigoryan, K. (2012). The study of mercury pollution distribution around a chlor-alkali petrochemical complex, Bandar Imam, southern Iran. *Environmental Earth Science*, 67, 1485 – 1492.
- Guidance for industry, Analytical Procedures and Methods Validation: Chemistry, Manufacturing, and Controls, Federal Register (2000) 65, 776 - 777.
- Haheb, P. (2012). Reduction of mercury from mackerel filled using combined solution of cysteine, EDTA, and sodium chloride, *Journal of Agricultural and Food Chemistry*, 60, 6069 - 6076.
- Hubert H. G. (2001). *Electrochimie Physique et Analytique*. Presses Polytechniques et Universitaires Romandes, 345.
- Lamble, K., J., Hill S. J. (1998). Microwave digestion procedures for environmental matrices, *Analyst*, 123, 103R – 133R.
- Leopold K., Foulkes, M., Worsfold, P. (2010). Methods for the determination and speciation of mercury in natural waters- a review, *Analytica Chimica Acta*, 663, 127 – 138.
- Malone, L. J. (1999) *Introducción a la química*, Segunda Edición, Editorial Limusa, México D. F.
- Mikac, N. (1999). Speciation of mercury in sediments of the Seine estuary (France). *Applied Organometallic Chemistry*, 13, 715 – 725.
- Montuenga, C. (1979). *Formación de complejos en química analítica*, editorial Alhambra, Madrid.
- Pineda, K. A., Bustos, E., García, M. G. (2009). Determination of Heavy Metals in Samples with Caolite of Guanajuato by Voltammetry with Anodic Redissolution. *ECS Transactions*, 20 (1), 21 – 29.
- Přibil R. (1982). *Applied complexometry*, Volume 5 of Pergamon series in analytical chemistry.
- Reddy K. (2005). Electrokinetic remediation of metal-contaminated field soil, *Separation Science and Technology*, 40, 1701-1720.
- Reddy, K., Camesselle C. (2009). *Electrochemical remediation technologies for polluted soils, sediments and groundwater*, Wiley, New Jersey.
- Rhazi, M. (2002). Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste, *European Polymer Journal*, 38, 1523 - 1530.
- Robles, I., García, M. G., Solís, S., Hernández, G., Bandala, Y., Juaristi, E. and Bustos E. (2012). Electroremediation of mercury polluted soil facilitated by complexing agents, *International Journal of Electrochemistry Science*, 7, 2276 – 2287.
- Sarzanini, C., Sacchero, G., Aceto, M., Abollino, O., Mestasti, E. (1994). Determination of mercury in naphtha. *Analytical Chimica Acta*, 284, 661 - 667.
- Scholz, F. (2002). *Electroanalytical Methods: Guide to Experiments and Applications*. Springer-Verlag, Berlin, Heidelberg, 191 - 208.

- Shi, J., Liang, L., Jiang, G., Jin, X. (2005). The speciation and bioavailability of mercury in sediments of Haihe River, China. *Environment International*, 31 (3), 357 – 365.
- Skoog, D. A. (1997). *Fundamentos de química analítica*, Editorial Reverté, Barcelona.
- Slowey, A. J., Rytuba, J. J., Brown, G. E. (2005). Speciation of mercury and mode of transport from placer gold mine tailings. *Environmental Science & Technology*, 39, 1547-1554.
- Spencer, J. N., et al (2000). *Química, Estructura y Dinámica*, Editorial CECSA, México.
- Tandy, S., Bossart, K.; Mueller, R.; Ritschel, J.; Hauser, L.; Schulin, R.; Nowack, B. (2004). Extraction of heavy metals from soils using biodegradable chelating agents, *Environmental Science and Technology*, 38, 937 - 944.
- US - EPA, Method 7471 (<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7471b.pdf>).
- Woolever, C. A., Starkey, D. E., Dewald, H. D. (2001). Differential pulse anodic stripping voltammetry of barium and lead in gunshot residues, *Forensic Science International*, 117, 185 - 190.
- Wypych, F. (2004). *Clay Surfaces: Fundamentals and Applications*, Elsevier Academic Press.
- Zbigniew, G., Chalmers, T. A., Bryce, W. A. J. (1994). *Fundamentals of Electrochemical Analysis*. 2nd edition. Polish Scientific Publishers, 136 – 140.

XXIII

**CONGRESO
Técnico Científico**

En memoria del ingeniero Marcos Mazari Menzies

4 al 6 de diciembre de 2013

El Instituto Nacional de Investigaciones Nucleares

y el

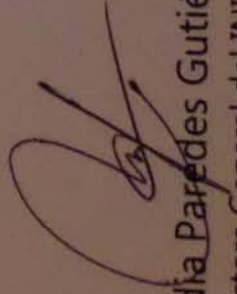
Sindicato Único de Trabajadores de la Industria Nuclear

Otorgan el presente

Reconocimiento

a *V. Valdovinos, F. Monroy-Guzman, E. Bustos*

Por su participación con el trabajo Evaluación de condiciones electroquímicas para el tratamiento de líquidos orgánicos radiactivos absorbidos en suelos en el XXIII Congreso Técnico Científico ININ-SUTIN, realizado en el Centro Nuclear de México, del 4 al 6 de diciembre de 2013.



Dra. Lydia Paredes Gutiérrez
Directora General del ININ



C. P. Sergio Gómez Aceves
Secretario General del SUTIN

Diciembre de 2013





Sanfandila, Pedro Escobedo, Qro., a 12 de diciembre de 2012
SP324/12

Dra. Erika Bustos Bustos
Investigador Titular
Subdirección de Investigación
CIDETEQ, S.C.
Presente

Me permito informarle que en su pasada reunión del día 5 de Diciembre del presente año, el Consejo de Posgrado asignó el Comité Tutorial de la alumna Viridiana Valdovinos García, quien desarrollará el proyecto: *"Estudio de Viabilidad Técnica para el Tratamiento Electroquímico de Desechos Radioactivos"*, bajo su dirección quedando integrado de la siguiente manera:

Dra. Erika Bustos Bustos
Dra. Fabiola Monroy Guzmán
M. en C. Jesús Cárdenas Mijangos

Sin más por el momento, agradezco su atención no sin antes reiterarle que me encuentro a sus órdenes, para cualquier duda o comentario al respecto.

Atentamente,

Dr. Juan Manríquez Rocha
Subdirector de Posgrado

C.c.p. Dra. Fabiola Monroy Guzmán.- Director de Tecnología – CIDETEQ, S.C.- De conocimiento
M. en C. Jesús Cárdenas Mijangos.- Investigador Titular – CIDETEQ, S.C.- De conocimiento