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## **Electrodialytic processes in solid matrices. New insights into batteries recycling. A review.**

*Short title:* New insights into Lithium-Ion batteries recycling.

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### **Abstract**

Electrodialytic Remediation has been widely applied to the recovery of different contaminants from numerous solid matrices solving emerging issues of environmental concern. Results and conclusions reported in studies about real contaminated matrices are summarized in this work. The influence of the pH value on the treatment effectiveness has been widely proved highlighting the phenomenon “water splitting” in the membrane surface. This dissociation of water molecules is related to the “limiting current” which is desirable to be exceeded at the Anion Exchange Membrane in order to produce the entering of protons toward solid matrix. Other important parameters for the optimization of the technique, such as the current density and the liquid to solid ratio, are also discussed through the revision of studies using real solid matrices.

This work also focusses on the pioneer proposal of electrokinetic technologies for the recycling of lithium ion batteries considering the relevance of waste properties in the design and optimization of the technique. From a thorough literature revision, it could be concluded that further experimental results are needed to allow an optimal

application of the technique to the rising problem of residues from batteries. The main aim of this work is to take the first steps in the recovery of valuable metals from spent batteries, such as Li and Co, incorporating principles of green chemistry.

### **Keywords:**

Environmental Remediation; Waste treatment and Waste Minimization; Membranes; Electrochemistry

### **Introduction**

Electrodialysis (ED) is one of the most relevant membrane methods to separate ionic species from an aqueous solution or other uncharged matrices.<sup>1</sup> The term “electrodialysis” appeared for the first time in the patent developed by Schollmeyer in 1900. The aim of that work was to purify sugar syrup using ozonation and iron or soluble zinc anode.<sup>2</sup> However, the principle of the process was previously studied in 1889 by Maigrot and Sabates.<sup>3</sup> In 1890, Ostwald studied the properties of membranes, discovering that a membrane is impermeable for any electrolyte when it is impermeable for its cations or anions.<sup>4</sup> By then, the relevant term “membrane potential” was also postulated, referring to the potential at the boundary between the solution and the membrane as a result of the concentration gradient.<sup>5</sup> In 1940, Meyer and Strauss suggested a multiple compartments ED cell, denoted as membrane stack, using many pairs of alternating anion-selective and cation-selective membranes between two electrodes.<sup>6</sup> That kind of setup design allows the simultaneous treatment of solutions in many parallel compartments with only a pair of electrodes.

The variety of electrodialysis applications led to the development of membranes with different properties. The desalination of brackish water and seawater, the main application of electrodialysis in the United States and Europe, requires membranes with

high selectivity and low electro-osmotic permeability. It entails the development of membranes based on heterogeneous structures by the dispersion of a fine ion-exchange resin powder within the solution of a matrix polymer and by the evaporation of the solvent.<sup>7</sup> Other important use of electrodialysis is the concentration of sodium chloride from seawater to produce table salt. This application involves the development of homogeneous membranes with very low electrical resistance. Although this kind of membrane was first proposed by Ionics Inc. in 1951-1953, it was not used at industrial scale until 1975 by the Japanese company Asahi Chemicals.<sup>8</sup>

Besides the desalination of saline solutions, currently the most relevant use at industrial scale of ED, other applications are being developed. Some examples are: purification, modification and concentration of food,<sup>1</sup> production of organic acids,<sup>9</sup> desalination of coal-mine brine,<sup>10</sup> treatment of industrial effluents,<sup>11</sup> demineralization of whey,<sup>12,13</sup> production of ultrapure water<sup>14</sup> and recovery of lithium from brine<sup>15</sup>. The Electrodealytic Remediation (EDR) is a technique that allows the removal of contaminants from soils and solid waste products combining the electrokinetic remediation (EKR) method with electrodialysis.

This work presents the idea of battery recycling via electrodealytic methods. With this aim, the application of EDR is thoroughly discussed paying special attention to the most relevant operating parameters. From the revision of EDR application to different solid matrices together with the analysis of waste properties of spent batteries, the applicability of the technology is evaluated.

## Electrochemical technologies

### Fundamentals of Electrokinetic Remediation

EKR consists of the application of an electric current between a pair of electrodes to mobilize and extract contaminants, such as toxic metals or organic compounds, from soils and other porous solid matrices.<sup>16-18</sup> The electric field prompts the transport of species through the porous media by electromigration, electroosmosis and electrophoresis transport mechanisms.<sup>16,19,20</sup> EKR is recommended for the *in situ* treatment of low water-permeability solid matrices. A schematic of the EKR process is presented in Figure 1.

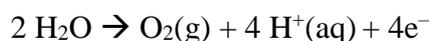
Diffusion is the movement of ionic and molecular constituent form of the contaminants due to the gradient of chemical potential. The electromigration transport mechanism, also known as ionic migration, refers to the movement of ionic charged species in the pore fluid towards the electrode of opposite charge. These two strongly coupled transport mechanisms are known as electro-diffusion, and typically defined by the Nernst-Planck transport equation.<sup>21</sup> Under common conditions for EKR treatments, the electromigration is some orders of magnitude greater than the diffusion.<sup>19</sup>

Another phenomenon that takes places in porous media as a consequence of the application of an electric gradient is the electroosmotic transport.<sup>22</sup> Most soils have negatively-charged surface, which produces a positively-charged diffuse layer of electrolyte at the solid-electrolyte interface region. Similar to the ionic migration transport, the positively-charged diffused layer flows towards the cathode under applied electric fields, sweeping along the aqueous phase and the dissolved species. Under certain circumstances, such as when the electrolyte concentration is high and the pH value of the pore fluid is very low, it is possible to reverse the polarity of the surface charge and the electroosmotic can flow from cathode to anode. This phenomenon is

known as “reverse electroosmosis”. Electrophoresis is the movement of charged particles of colloidal size due to the application of an electric potential. This movement can often be neglected when the solid phase is stationary as, for instance, in soils with low permeability. However, if the electric current is applied to slurry, this phenomenon may play an important role.<sup>23</sup>

In addition to these transport processes, the application of the electric field is inherently related to electrolysis reactions at the electrodes:<sup>16</sup>

Oxidation (at the anode):



Reduction (at the cathode):



Water electrolysis produces an acidic medium at the anode and an alkaline medium at the cathode.<sup>16</sup> The ionic migration of electrolysis products has relevance on the chemistry of the solid matrix.<sup>19</sup> The protons generated at the anode migrate towards the cathode and the hydroxide ions produced at the cathode migrate towards the anode. The progress of these acidic and alkaline fronts plays an important role on the transport and the transformations processes that affect the contaminants’ migration and removal during the EKR treatment. A schematic electrochemical remediation system is presented in Figure 2.

According to Acar et al., protons are the predominant current carrier in electrochemical systems. The ionic mobility of protons under electrical field is about two times the hydroxide ion mobility.<sup>24</sup> In unenhanced electrokinetic remediation, the acid and the alkaline fronts meet at approximately 2/3 of the normalized distance from the anode, and produce a zone with a low electrical-conductivity that hinders the movement of contaminants. Therefore, it is widely accepted that, in order to success with the selective

removal of contaminants, the application of EKR requires some enhancement to control either the protons or the hydroxide ions fronts, or both.<sup>25-30</sup> Enhancement techniques are typically based on the addition of reagent,<sup>29-31</sup> the use of semipermeable membranes<sup>32</sup> or the combination of EKR with other remediation techniques<sup>33</sup>.

For example, an acid-enhanced EKR system has the electrode compartments separated from the central compartment holding the solid matrix with passive membranes. The separators prevent from mixing of soil and electrolytes solutions. The alkaline front generated at the cathode is neutralized by means of the addition of acid, as, for example, acetic, citric or nitric acid.<sup>30</sup> Thus, the dissolution of the heavy-metal containing minerals is promoted.

The enhancement technique based on the use of semipermeable membranes, the basic of Electrodialytic Remediation, is presented in the follow section.

### **Fundamentals of Electrodialytic Remediation**

EDR was proposed at the Technical University of Denmark as an optimization of EKR (PCT/DK95/00209). The use of ion-exchange membranes in the process aims to:<sup>34-36</sup>

- 1) Reduce the amount of energy “wasted” on the transport of highly mobile ions between electrodes different than the target contaminant, such as  $H^+$  or  $OH^-$ ;
- 2) Prevent the reentering of contaminants from the electrolyte solutions into solid matrix as a consequence of changes of the ion charges, for example due to the formation of complexes compounds.

A schematic diagram of the experimental lab-scale setup for the EDR cell is presented in Figure 3. In the three-compartment cell, the solid matrix is placed in the central compartment, which is separated from the cathode compartment by a cation-exchange membrane (CEM) that allows only the transport of cations, and from the anode

compartment by an anion-exchange membrane (AEM) that allows only the entering of anions. The ion exchange membranes (IEMs) are a key in electro dialysis remediation, and their behavior is based on the concept of permselectivity which was first studied by Donnan.<sup>37</sup> The electric potential at the membrane-solution surface, known as Donnan potential, causes the exclusion of co-ions from the membrane matrix and it can be used as a measure of the permselectivity.<sup>36,38,39</sup>

A CEM allows the passage of cations and hinders the passage of anions, while the behavior of AEM does the opposite. That is, the membrane is charged with the same sign as co-ions. Therefore, the co-ions are excluded from the membrane phase and the counter-ions can pass through the membrane. Regarding to the types of IEMs, according to the charge and distribution of fixed ionic groups, it could be distinguished between monopolar (both CEMs and AEMs) and bipolar membranes (which has one exposed surface acting as a CEM and the other exposed surface as an AEM). For EDR, the monopolar membranes are the most widely used.<sup>40-43</sup> The IEM membranes prevent the high mobile protons and hydroxide ions to enter the central compartment promoting, therefore, more charge to be carried by the target contaminants in the matrix.

Similar to EKR, the transport phenomena occurring during EDR are: diffusion, electromigration, electroosmosis and electrophoresis. Hypothetically, a complete remediation of a solid matrix, taking into account that ions from the solid matrix are transported towards the electrode compartments but the ions from the electrode compartments are not entering the solid, would cause a solid volume without ions. This situation produces “water splitting”, *i.e.*, the dissociation of water molecules in the central compartment producing  $H^+$  and  $OH^-$  to carry the electric current.

Despite the AEM placed between the soil and the anode compartment hinders the transport of cations, the acidification of the central compartment has been observed

during EDR treatments.<sup>44,45</sup> This process is associated with the permselectivity of the membranes and with the water splitting due to a decrease of the conductivity in the regions near the surface of the membrane. Although theoretically the current cannot be higher than the limiting current, overlimiting current densities has been obtained experimentally.<sup>46,47</sup> As a consequence of operating at those conditions, the dissociation of water causes pH changes around the membrane. This situation is not desirable; not only because of the deterioration of membrane but also due to the reduction of the current efficiency. The optimum situation for EDR efficiency is the application of an electric current that causes the limiting current only exceeds at the AEM. Thus, water dissociation occurs at AEM causing the entering of protons through the solid towards the cathode while no production of  $\text{OH}^-$  occurs at the CEM.<sup>45</sup> This situation has been concluded to be the most common in EDR applications. In this respect, Krol et al. have studied that the change in pH was evident in AEM being almost negligible for CEM.<sup>47</sup> Some studies have related the water splitting with a thin layer at the surface of AEM caused by the protonation of groups such as tertiary amines present in the membrane.<sup>44,46</sup> De Lara et al. studied the transport of ions across IEMs under working conditions in EDR. A small fraction of  $\text{H}^+$  passing from the anode into the solid was detected even when the current was zero. Also, it was observed that the CEM acts ideally avoiding the entering of  $\text{OH}^-$  present in the cathodic electrode to the solid. This phenomenon is also associated with the acidification of solid matrix during EDR experiments.<sup>48</sup>

### **Overview of the current status of EKR and ED: Applications.**

Electrokinetic remediation has been widely used to treat soils polluted with inorganic species and organic compounds. The inorganic pollutants can be divided into cationic toxic metals (e.g., lead and cadmium), anionic metals (e.g. arsenic and chromium) and

radionuclides (e.g. strontium and uranium). As mentioned before, the electromigration is the most relevant transport process, but it directly depends on the specific pollutant type and solid properties. The movement of metals in soil as a consequence of applying an electric field was first reported by Segall et al. in 1980.<sup>49</sup> Although their aim was to dewater a dredged material disposal site, conclusions from this work were an inspiration for the development of electrochemical remediation applied to soils.<sup>50,51</sup> The early laboratory research on EKR pursued to study the fundamentals of the technique.<sup>22,25,52,53</sup> Those works were mainly carried out using spiked kaolinite, as a first step toward the development of the technique for real soils. However, the limited variety of sorption sites for contaminants together with other shortcomings makes not possible to extrapolate the results obtained with spiked soils to industrially and aged polluted soils.<sup>54-56</sup> Regarding large-scale EKR, an early work dealing with this subject was published by Acar and Alshwabkeh.<sup>57</sup> The authors studied the transport of lead through a spiked soil under electric field at pilot scale without applying any enhancement method. From results, it was concluded that lead was transported toward the soil zone close to the cathode compartment where the metal precipitates as hydroxide. Although the energetic cost obtained was too high for the technique, the authors claimed that the use of enhancement techniques involved a decrease in the power consumption.

The first field-scale application of electrochemical remediation for soils was pioneered commercially by Reinout Lageman, Wiebe Pool and Geert Seffinga of Geokinetics during late 1980s.<sup>17</sup> They patented the use of circulating electrolytes and ion permeable wells to hold the anolyte and catholyte.<sup>58</sup> The developed technology, applied to some field soils contaminated with metals such as copper, zinc, cadmium, lead and nickel, consisted of a simple configuration with vertically or horizontally installed electrodes in the solid matrix together with drilling wells around the contaminated zone.

The technology was based on the electrokinetic transport phenomena without the addition of enhanced solutions. Simultaneously, the pollutant transport due to the movement of water through the electrical double layer was studied at MIT<sup>59</sup> and at Louisiana State.<sup>60</sup> A field demonstration of electrokinetic remediation with amendments by addition of other chemicals was conducted at the Naval Air Weapons Station (California) in 2000. The developed system included the addition of citric acid to control the pH in the treatment area.<sup>61</sup> The well-known remediation technology, Lasagna<sup>TM</sup> technology, was developed to recover soils polluted with organic compounds. The process consists in the application of an electric current to transport contaminants into the “treatment zones” where the enhancing solutions are added. The process was called “Lasagna” due to its layered configuration of treatment zones between the electrodes.<sup>62</sup> The Lasagna technology entailed many advantages that include the possibility of recycling the cathode effluent, which would favour the neutralization of the pH and the simplification water management; highly flexible treatment configuration and degradation methods and potential cost-effectiveness.<sup>63</sup>

Regarding EDR, patented in 1995, the majority of studies reported in literature are performed at lab scale until now. This technique was applied to polluted soils as an *in-situ* treatment in pioneer studies.<sup>34,35,64,65</sup> In 1994, Jensen et al. studied the influence of pH value on the removal of Zn and Cu from a polluted soil, observing that higher pH values promoted Cu removal. From the EDR experiments, it was also concluded that removal of Ca and Mg was hindering the removal of the target metals. These results emphasized the importance of solid composition when EDR is applied. Ottosen et al. studied the remediation of a Cu-polluted loamy sand from a former wood preservation plant aiming at the identification of relevant parameters to the remediation process. An important influence of the pH value on the removal of Cu was observed, finding a zone

of accumulation of metal in a soil zone where the pH had increased. It was also observed that, when the current was doubled, the rate of Cu removal increased by a factor of approximately 2.<sup>34</sup> Along the same lines, Hansen et al. evaluated the importance of key parameters for the optimization of the process, highlighting the importance of the pH, the current density and the addition of complexing agents. It was concluded that: 1) the pH value plays an important role on the mobility, speciation and sorption/desorption of toxic metals; 2) the addition of reagent, such as complexing agents, is needed in some situations in order to selectively remove contaminants from soils; and 3) keeping the current density below the limiting current density for the interface CEM-soil to avoid “water splitting” is crucial.<sup>35,64</sup>

Ribeiro et al. applied EDR to treated timber waste containing Cu, Cr and As using oxalic acid as assisting agent. The removal of Cu, Cr and As was: 93%, 95% and 99%, respectively. That study was pioneer in the application of EDR to solid matrix different than polluted soils.<sup>66</sup> Hansen et al. studied the influence of pretreating the solid matrix, copper mine tailing, on the efficiency of EDR. The study concluded that the acidification of the mine tailing with sulfuric acid entailed speeding up the remediation process. By comparing sulfuric and citric acids for the same solid matrix, the authors concluded that the energy consumption at field scale would be lowest adding the organic acid, explained with the formation of the stable complex:  $\text{Cu}(\text{C}_6\text{H}_7\text{O}_7)^+$  which together with acidic conditions promotes Cu dissolution minerals in the solid matrix.<sup>67,68</sup>

In 2005, a pioneer study evaluated the feasibility of the electro-dialytic remediation method at a pilot-scale containing up to 2 m<sup>3</sup> of solid matrix. This research was not only focused on the scaling-up of the technique but also on the optimization of experimental conditions. In this study, Pedersen et al. evaluated the removal of Cr, As and Cu from

treated wood obtained promising results: arsenic was almost completely removed from the solid matrix, and the concentration of Cr and Cu was drastically reduced.<sup>69</sup>

In spite of the promising results obtained in previously discussed research works, several factors, such as risk of exposure of adsorbed contaminants through ground water, high costs, long treatments times, difficult soil conditions, and the need for acidification to induce contaminant desorption, have limited the field implementation of EDR for some specific cases. In order to overcome these limitations, the application of electro-dialytic method to suspended solid, as an *on-site* process, was developed for fine grained materials, such as: fly ashes<sup>70</sup>, harbor sediments<sup>71</sup> and polluted soils<sup>72</sup>.

The typical cell for the application of electro-dialytic technique to solids in suspension is shown in Figure 4. The main difference from the experimental setup for treating a stationary matrix (Figure 3) is found in the central compartment. As can be observed, it consists of a stirrer to maintain the matrix suspended instead of the stationary solid matrix. Ottosen et al. compared the two options for application of EDR previously described: 1) to remediate a wet matrix (*in-situ* or *on-site*) and 2) to remediate a solid in suspension (*on-site*). With this aim, experiments were carried out with soils polluted with Cu and Pb. They observed a larger toxic metal mobilization in suspended soils due to faster acidification. Those results were congruent with a more efficient effect of the “water splitting” at the AEM for stirred soils, as the stirring reduced the gradients of potential nearby the membrane region. Additionally, transient and nonlinear changes occurring under the application of an electric current are overcome by the mixing for the stirred system. Nevertheless, it should be highlighted that the best option (between EDR applied to stationary soil or to stirred suspension of soil) depends on the specific case studied. In cases in which fast remediation is required, the more suitable option is the *on-site* treatment. On the other hand, for cases in which the fast remediation is not

required, the electrode units could be placed directly in soils becoming the best option for economic reasons.<sup>72,73</sup>

Regarding to the key parameters for EDR applied to suspended solids, the pH is the one which influence more the remediation results. The acidification of suspended soils is due to: 1) the exchange of  $H^+$  from the catholyte with cations from the solid suspension caused by the inter-diffusion over the CEM and 2) the water splitting at AEM. Jensen et al. studied the influence of current density and the liquid to solid ratio (L/S) on the water splitting concluding that higher values of these parameters could cause that the limiting current at the CEM would be exceeded. That would involve water splitting at CEM and, consequently,  $OH^-$  entering the solid and hindering the remediation processes.<sup>74</sup> In this line, Sun et al. compared the removal of Cu and As from different soil fractions using different liquid to solid ratios and current intensities. They concluded that the removal efficiency for both metals in soil fines is higher than in the original soil. In that work, it was also highlighted the importance of optimizing the L/S ratio and the remediation current for ED, finding that  $L/S > 7$  leads to very fast acidification processes hindering the transport of Cu and As<sup>75</sup>.

Recently, a new electro-dialytic setup, schematically presented at Figure 5, has been developed and patented at DTU (PCT/EP2014/068956). The new design for EDR consist of two compartments separated by a cation exchange membrane. The polluted material in suspension is directly placed in the stirred anode compartment.

The 2-Cell EDR design has been proven to reduce the acidification time since the supply of protons from electrolysis takes place directly in the suspended solid compartment.<sup>76</sup> Several studies has applied EDR to different solid matrices using two-compartment cell.<sup>42,77-82</sup> Regarding EDR applications, it has been widely applied to different matrices as can be concluded from numerous research works previously

discussed. Table 3 summarizes relevant information about important studies dealing with EDR applied to different matrices.

Table 1. Application of EDR to different solid matrices. (\*options for application: a) to treat the solid as stationary or b) to treat the solid as suspension)

Description	Cell *	Solid matrix	Electrolytes	Target species	Ref.
Remediation of heavy metal polluted soil	3-C <sup>a</sup>	Polluted soil	0.01 M NaNO <sub>3</sub> (pH adjusted to 3 using HNO <sub>3</sub> )	Toxic metals (Cu, Cr, Hg, Pb and Zn)	Hansen et al (1997) <sup>35</sup>
Remediation of soil polluted with Cu from Wood Preservation Industry	3-C <sup>a</sup>	Polluted soil Enhancement: ammonia addition to the soil.	0.01 M NaNO <sub>3</sub> (pH adjusted to 3 using HNO <sub>3</sub> )	Toxic metals (Cu, As)	Ottosen et al. (1997) <sup>34</sup>
Removal of Cu, Cr and As from Treated Timber Waste	3-C <sup>a</sup>	Treated timber waste	0.01 M NaNO <sub>3</sub> (pH adjusted to 2-3 using HNO <sub>3</sub> )	Toxic metals (Cu, Cr, As)	Ribeiro et al. (2000) <sup>66</sup> Velizarova et al. (2002) <sup>83</sup>
Removal of Cu from a real soil sampled at a wood preservation site in presence of different types of construction refuse in the soil on ED.	3-C <sup>a</sup>	Soil from a wood preservation site (Some experiments: adding a construction refuse placed in the soil).	0.01 M NaNO <sub>3</sub> (pH adjusted to 2 using HNO <sub>3</sub> )	Toxic metals (Cu)	Ottosen et al. (2002) <sup>84</sup>
Removal of toxic metals from different fly ashes	3-C <sup>a</sup>	Municipal Solid Waste incinerator (MSWI) fly ashes and wood combustion fly ashes. Enhancement: addition of an ammonium citrate and NH <sub>3</sub> mixture to the ash.	0.01 M NaNO <sub>3</sub> (pH < 2 using HNO <sub>3</sub> ) 0.25-0.5 M ammonium citrate/1.25-2.5% NH <sub>3</sub>	Toxic metals (Cd, Pb, Zn and Cu)	Pedersen et al. (2003) <sup>70</sup>
Removal of toxic metals from straw combustion fly ash	3-C <sup>a</sup>	Straw combustion fly ash	0.01 M NaNO <sub>3</sub> (pH adjusted to 2 using HNO <sub>3</sub> )	Toxic metals (Cd)	Hansen et al. (2004) <sup>85</sup>
Removal of toxic metals from wastewater sludge	3-C <sup>a</sup>	Wastewater sludge	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> )	Toxic metals (Cd)	Jakobsen et al (2004) <sup>86</sup>
Remediation of Copper mine tailings	3-C <sup>a</sup>	Mine tailing Enhancement: addition of citric or sulphuric acid to the solid.	Distilled water (pH below 4 using H <sub>2</sub> SO <sub>4</sub> at the catholyte)	Toxic metals (Cu)	Rojo and Hansen (2005) <sup>68</sup> Hansen et al (2005) <sup>67</sup>
Remediation of harbor sediments	3-C <sup>b</sup>	Harbor sediments	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> )	Toxic metals (Cu, Zn, Pb and Cd)	Nystroem et al. (2005) <sup>44</sup>
Remediation of treated waste wood in pilot scale	3-C <sup>a</sup>	Treated waste wood Enhancement: addition of 5 % oxalic acid solution or a mixture of water/Na benzoate. Pretreatment: Soaking step: 5% oxalic acid, 0.5 M H <sub>3</sub> PO <sub>4</sub>	NaNO <sub>3</sub> or oxalic acid	Toxic metals (Cu, Cr and As)	Pedersen et al. (2005) <sup>69</sup> Ribeiro et al. (2007) <sup>87</sup>
Remediation of MSWI fly ash	3-C <sup>b</sup>	MSWI fly ash	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cu, Pb) and Cl	Ottosen et al. (2006) <sup>88</sup>
Remediation of polluted soil (spiked kaolinite spiked soil and industrial polluted soil)	3-C <sup>a</sup>	Polluted soil	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cu)	Ottosen et al. (2006) <sup>54</sup>
Remediation of polluted soil	3-C <sup>b</sup>	Soil fines	0.01 M NaNO <sub>3</sub> (pH between	Toxic metals (Pb)	Jensen et al. (2006) <sup>89</sup>

<b>Description</b>	<b>Cell *</b>	<b>Solid matrix</b>	<b>Electrolytes</b>	<b>Target species</b>	<b>Ref.</b>
			1-2 using HNO <sub>3</sub> at catholyte and NaOH at anolyte)		
Recovery of toxic metals from sewage sludge ash from fluidized bed combustion	3-C <sup>b</sup>	Sewage sludge ash from fluidized bed combustion	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cd, Cr, Cu, Pb, Ni and Zn)	Pazos et al. (2010) <sup>90</sup>
Removal of Cd from biomass combustion fly ash suspensions	3-C <sup>b</sup>	Biomass combustion fly ash	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cd)	Kirkelund et al. (2013) <sup>91</sup>
Separation of Phosphorus and toxic metals from sewage sludge ash	3-C <sup>(1,2)b</sup> 2-C <sup>(3)b</sup>	Sewage sludge ash Dissolution of H <sub>2</sub> SO <sub>4</sub>	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	P and toxic metals (such as: Cu, Zn, Ni, Pb, Al, Fe, Cd, Cr)	Ottosen et al. (2014) <sup>92 (1)</sup> Guedes et al. (2014) <sup>93 (2)</sup> Ottosen et al. (2016) <sup>78 (3)</sup>
Remediation of polychlorinated biphenyls (PCB) contaminated soil with iron nanoparticles and surfactants	2-C <sup>b</sup>	Soil with organic pollutants Enhancements: Use of saponin and Tween 80 as surfactant.	0.01 M NaCl (pH control with HCl)	Organic contaminants (polychlorinated biphenyls)	Gomes et al. (2014) <sup>41</sup>
Simultaneous removal of organic pollutants and toxic metals from sediments	3-C <sup>b</sup>	Sediments	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Organic contaminants (PAH, PCD, TBT) and toxic metals (Cu, Pb and Zn)	Pedersen et al. (2017) <sup>94,95</sup>

## **A new challenge for EDR: Li-Ion batteries recycling**

From the previous discussion, it can be concluded that EDR has a great potential in the recovery of toxic metals from solid matrices (for example: soil, wood chips, fly ashes, sediments and mine tailing). This section addresses the potential application of EDR to residues from secondary batteries such as lithium ion batteries (henceforth LIBs), as well as it provides new insights into a problem of public concern. To that end, it is discussed the current situation of LIB recycling processes and the most relevant characteristic of the solid waste for the application of EDR.

### **An overview of current situation of LIBs recycling processes**

Lithium-ion batteries are the main energy storage device used in modern electronics, widely used nowadays in most portable electronic devices. Other applications that are increasing the demand of LIB are the hybrid and electric vehicles and the storage for energy from renewable sources and self-production. The wide range of applications of this kind of batteries is motivated by their characteristics: high energy density, long cycle lives, high roundtrip efficiency, wide range of operating temperature, high reliability, safety, chemistry with eco-friendly materials, fast recharge and low self-discharge rate.<sup>96,97</sup>

The use of LIBs in these sectors promotes the development of technologies with lower carbon emissions. For example, the US Energy Information has predicted that sales of electric vehicles will reach 6.9 million units <sup>98</sup> by 2035. The demand for LIBs in these emerging sectors entails an increase in the attention paid to the recycling of spent batteries.<sup>99-101</sup> It is estimated that the percentage of lithium used to manufacture batteries will increase to 66% of the current global production by 2025. Regarding

lithium recovery, a UNEP status report states that less than 1% of lithium is being recycled.<sup>15</sup> Furthermore, currently ~ 95% of LIBs are landfilled.<sup>102</sup>

Despite lithium itself is considered an environmentally-friendly material, the disposal of waste from this kind of batteries entails a risk for the environment as some of the components of the cells have high degree of toxicity. According to the European Union, some of the elements used in LIBs, such as cobalt and natural graphite, have a high economic importance and a high supply-risk, being classified as “Critical Raw Materials”.<sup>103</sup> Indeed, cobalt is considered a bottleneck in the LIB industry, which can only be addressed by battery recovery and recycling. Other relevant elements for the Li-ion battery sector are Al, Fe, Ti, P, Mn, Ni and Cu. Current trends will also place lithium in the list of critical materials by 2030.<sup>96</sup> Furthermore, lithium resources, mainly extracted from brine lakes and salt pans, are located in a very limited number of regions, namely in Argentina, Chile, Bolivia, China, USA, Canada, Russia, Congo and Serbia.

It is clear that battery recycling processes are necessary to reach sustainable ways to reduce the negative impact on the environment and the reuse of natural resources, as well as to decrease the dependence of international suppliers.<sup>104</sup>

### **Chemical composition of LIBs waste**

LIBs consist of a couple of electrodes usually contained in a stainless-steel shell or in a pouch case. During the operation of a LIB (discharge) lithium ion migrate from anode to cathode, producing electric current.

The most frequent anodic material is graphite supported on a copper foil that acts as a current collector. The current gravimetric capacity (amount of lithium that can be stored per mass of anodic material) of graphite anodes is around 372 mAh g<sup>-1</sup>. New anode materials, such as lithium titanate (LiTi<sub>5</sub>O<sub>12</sub>), carbon nanotubes or Al, Sn and Si

compounds, are being studied to be used as alternative anodes.<sup>105–107</sup> The aforementioned materials would increase the value of the waste of LIBs involving a significant growth of the concern about recycling processes.

The cathode is generally built from transition metals oxides. The cathode, supported on an aluminum foil, is composed of: ~ 85% metal oxide, ~ 10% polyvinylidene fluoride and ~ 5% carbon.<sup>101,108</sup> The most commonly used oxides in commercial batteries are: lithium cobalt oxide (LCO or  $\text{LiCoO}_2$ ), lithium manganese oxide (LMO or  $\text{LiMn}_2\text{O}_4$ ), lithium nickel manganese cobalt oxide (NMC or  $\text{LiNiMnCoO}_2$ ) and lithium nickel cobalt aluminum oxide (NCA or  $\text{LiNiCoAlO}_2$ ). The LCO batteries has the higher recycling value among the different batteries chemistries due to the higher amount of Co and Li.<sup>104</sup>

The separator, placed between the anode and the cathode, is usually made of polypropylene or microporous polyethylene. The cells also contain as electrolyte a lithium salt ( $\text{LiPF}_6$ ,  $\text{LiBF}_4$  or  $\text{LiClO}_4$ ) in a non-aqueous solvent as, *e.g.*, a mixture of ethylene glycol carbonate, propylene carbonate and dimethyl carbonate.<sup>100,109</sup> The electrolyte role is allowing the movement of lithium ions during the cycling process.

The bulk compositions of LIB are shown in Table 4.

Table 2. Average composition of LIBs from literature.

	Concentration (wt %)		
	Wang et al. (2016) <sup>110</sup>	Jha et al. (2013) <sup>111</sup>	Dorella and Mansur (2017) <sup>112</sup>
Metals			
Aluminum	5.20	4.30	8.02
Cobalt	17.30	23.67	29.49
Copper	7.30	22.13	16.48
Iron / Steel	16.50	*	*
Nickel	1.20	0.26	0.02
Lithium	2.00	2.87	3.14
Others			
Binders	2.40	*	*
Carbon (no	6.00	*	*

graphite)			
Electrolyte + Organic solution	14.00	*	*
Graphite	23.10	*	*
Plastics	4.80	*	*
Other	Balance	Balance	Balance

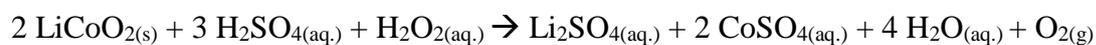
The composition and the mass of the different cells vary depending on the type of battery chemistry and the manufacturers.<sup>113</sup> Approximately 25 – 30% of the total mass of the battery corresponds to the cathode, where most of the toxic metals are found. The anode represents between 15 – 30% of the total mass of the battery.<sup>104</sup>

### **Current LIBs recycling solutions**

Swain presented a comprehensive review<sup>15</sup> on techniques for recovery and recycling LIBs, and classified the processes into: pyro-metallurgical, hydro-metallurgical, bio-hydrometallurgical and combined techniques. The pyro-metallurgical and hydro-metallurgical processes are the most used. Pyro-metallurgy is based on the application of thermal treatments to induce chemical changes in the residue while hydro-metallurgical processes take advantage of the chemical properties of metals in aqueous solutions for the recovery of the different components.<sup>15</sup> Currently, bio-metallurgical processes, based on the use of microorganisms (bacteria and fungi), are gaining importance with respect of hydro-metallurgical due to their higher efficiency, lower cost and fewer resources requirements.<sup>104</sup> In these processes, the formation of metabolic products, such as organic and inorganic acids, directly influences on the recovery efficiency of metals contained in the waste.<sup>114</sup> Some of the most important companies in the recycling of rechargeable batteries (Umicore, Toxco, Inmeco and Recupyl) develop their own processes based on pyrometallurgical, hydrometallurgical and combined techniques.<sup>15,109,115</sup>

Several studies deal with the extraction of metals (mainly Li and Co) from disposed LIBs, use different extractant agents, such as inorganic acids ( $\text{H}_2\text{SO}_4$ <sup>99,111,116</sup>,  $\text{HCl}$ <sup>117,118</sup>,  $\text{HNO}_3$ <sup>117,119</sup> or  $\text{H}_3\text{PO}_4$ <sup>120,121</sup>) and, as alternative with a lower negative impact on the environment, organic acids<sup>117</sup> (succinic acid<sup>122</sup>, maleic acid<sup>123,124</sup>, citric acid<sup>123,125</sup>, EDTA<sup>126</sup>, ascorbic acid<sup>127</sup>, tartaric acid<sup>117</sup> or acetic acid<sup>123,128</sup>).

The addition of reductants in acid leaching processes is widely accepted since  $\text{Co}^{3+}$  in LCO needs to be converted to  $\text{Co}^{2+}$ .  $\text{H}_2\text{O}_2$  is used as reductant because it do not add new ions into the solution.<sup>111,124</sup> It should be noted that the absence of reductant could be interesting to selective recovery Li. The dissolution of LCO in  $\text{H}_2\text{SO}_4$  has been widely demonstrated to be difficult due to the strong bond between cobalt and oxygen. For this reason, a reductant, as it was aforementioned, such as hydrogen peroxide is added to promote the dissolution.<sup>116</sup> The reactions taking place are:



Jha et al. studied the influence of several parameters in the hydrometallurgical process for the recovery of Li and Co from LIBs of mobile phone using sulfuric acid as lixivate. Their results showed an increase in the percentage of leaching of Co and Li with higher concentration of acid (in presence of  $\text{H}_2\text{O}_2$ ), temperature and time. On the industrial applications, it should be highlighted that  $\text{H}_2\text{SO}_4$  is the only used agent. The addition of other inorganic acid, such as  $\text{HCl}$ , have limitations such as the emission of gases ( $\text{Cl}_2$ ).<sup>111</sup>

Gao et al. analyzed the leaching efficiencies using different organic and inorganic acids, concentrations, S/L ratios, reductant agents and temperature. According to their results, it was concluded that the use of inorganic acids allowed higher leaching efficiency than

organic acids, as well as higher treatment capacity. This fact was associated with the higher concentration of  $H^+$ . Also, the authors observed that the higher initial pH value of the solution was, the lower leaching speeds of Li and Co was obtained. Regarding to the addition of organic acids, selective separating of other important metals presented in the LIBs waste, such as Al, is achieved. However, for organic acids, the low S/L ratio is one of the problems for applications at field scale. For this reason, they proposed to combine the use of organic and inorganic acids to improve the recovery of metals from solid.<sup>117</sup>

### **Proposal of a novel way for LIBs recycling.**

The application of EDR to residues from spent LIBs requires the development of a pretreatment process. First, the LIBs must be separated and sorted according to the cathode chemistry with the aim of making the process more efficient.<sup>110</sup> With this purpose, the so-called SORBAREC system was developed. This technology identifies LIB types using X-Ray transmission.<sup>129</sup> Before disassembling the batteries, it is important to carry out a discharge step in order to remove the excess capability. It is aiming at avoiding the risk of short-circuiting and self-ignition associated with the potential contact of anode and cathode.<sup>125</sup> The discharge could be performed by immersing the LIBs in liquid nitrogen or in sodium chloride solution.<sup>125,130</sup> After this, mechanical methods are applied to reduce scrap volume and to concentrate valuable metals. Sometimes, the use of thermal processes is carried out in order to effectively isolate the cathode materials obtaining scraps with a higher content of the target metals, Co and Li.<sup>131</sup> Before applying the recovery method, it is also required in order to characterize the LIBs waste in order to optimize the design of the EDR application.

So far, most of the research related to the use of electrodialysis for the recovery of lithium focus on improving the separation processes in brines.<sup>132,133</sup> The application of the EDR to LIBs residues could be performed according to the principles described in

this paper. It would require the optimization of the most relevant operating parameters, such as pH value, selection of enhancing agent, current density, type of membrane, L/S ratio. Iizuka et al. carried out the separation of Li and Co from a solution that reproduced the content of these metals in the waste coming from Li-Ion batteries.<sup>126</sup> In that research, promising results were obtained by making use, as an improvement agent, of EDTA.

Song and Zhao proposed a promising method of extracting lithium from lithium high-salt solution since conventional methods, such as evaporation and concentration, are time and energy consuming resulting in low recovery efficiencies. The method is based on the precipitation of Li to  $\text{Li}_3\text{PO}_4$  prior separation via ED. The experimental system consisted of an electrolytic cell with cation-exchange membranes, titanium cathode and graphite anode. By optimizing the solution pH, about 99% of impurity metals were effectively precipitated. After the precipitation of Li to  $\text{Li}_3\text{PO}_4$  by addition of sodium phosphate, the ED was applied obtaining a decreased of P/Li from 1.48 to 0.23.<sup>134</sup> These promising results showed that the proposed method has great potential as a recovery method of Li from spent secondary batteries. To the best of our knowledge, the literature reported regarding the application of ED to LIBs recycling is very scarce without any reference regarding ED applied to solid waste. Therefore, further research regarding the recovery not only of lithium but also of cobalt applying the electrodialysis to solid wastes is needed.

## **Conclusions**

This review allows a new insight into potential applications of EDR. The optimization of key parameters for EDR, such as pH value, selection of enhancing agent, current density, type of membrane, is discussed reporting relevant results found by different

authors. From literature, it could be concluded that, among other issues, further studies about membrane selection according to different solid matrices treated are needed.

This work also interrelated the EDR studies reported in literature and the knowledge of current recycling processes of LIBs to propose a new approach for an emerging public concern issue: the revalorization of metals from spent batteries. It has been widely demonstrated that the understanding of the metal behavior in presence of acidic solution results essential to optimize key parameters in EDR. The acidification processes taking place in EDR treatments is one of the most influential processes in the effectiveness of remediation technology. Further studies taking into account the characteristics of LIBs waste, as well as the potential use of combination of inorganic and organic acids as enhancing agents are needed to reach a successful application of EDR. For that, the issues discussed in this work, such as: the understanding of the principles of EDR applied to solid matrices and the relevance of solid characterization for the design and optimization of experimental conditions; establish the initial steps to the design and optimization of the technology.

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Table 3. Application of EDR to different solid matrices. (\*options for application: a) to treat the solid as stationary or b) to treat the solid as suspension)

Description	Cell *	Solid matrix	Electrolytes	Target species	Ref.
Remediation of heavy metal polluted soil	3-C <sup>a</sup>	Polluted soil	0.01 M NaNO <sub>3</sub> (pH adjusted to 3 using HNO <sub>3</sub> )	Toxic metals (Cu, Cr, Hg, Pb and Zn)	Hansen et al (1997) <sup>35</sup>
Remediation of soil polluted with Cu from Wood Preservation Industry	3-C <sup>a</sup>	Polluted soil Enhancement: ammonia addition to the soil.	0.01 M NaNO <sub>3</sub> (pH adjusted to 3 using HNO <sub>3</sub> )	Toxic metals (Cu, As)	Ottosen et al. (1997) <sup>34</sup>
Removal of Cu, Cr and As from Treated Timber Waste	3-C <sup>a</sup>	Treated timber waste	0.01 M NaNO <sub>3</sub> (pH adjusted to 2-3 using HNO <sub>3</sub> )	Toxic metals (Cu, Cr, As)	Ribeiro et al. (2000) <sup>66</sup> Velizarova et al. (2002) <sup>83</sup>
Removal of Cu from a real soil sampled at a wood preservation site in presence of different types of construction refuse in the soil on ED.	3-C <sup>a</sup>	Soil from a wood preservation site (Some experiments: adding a construction refuse placed in the soil).	0.01 M NaNO <sub>3</sub> (pH adjusted to 2 using HNO <sub>3</sub> )	Toxic metals (Cu)	Ottosen et al. (2002) <sup>84</sup>
Removal of toxic metals from different fly ashes	3-C <sup>a</sup>	Municipal Solid Waste incinerator (MSWI) fly ashes and wood combustion fly ashes. Enhancement: addition of an ammonium citrate and NH <sub>3</sub> mixture to the ash.	0.01 M NaNO <sub>3</sub> (pH < 2 using HNO <sub>3</sub> ) 0.25-0.5 M ammonium citrate/1.25-2.5% NH <sub>3</sub>	Toxic metals (Cd, Pb, Zn and Cu)	Pedersen et al. (2003) <sup>70</sup>
Removal of toxic metals from straw combustion fly ash	3-C <sup>a</sup>	Straw combustion fly ash	0.01 M NaNO <sub>3</sub> (pH adjusted to 2 using HNO <sub>3</sub> )	Toxic metals (Cd)	Hansen et al. (2004) <sup>85</sup>
Removal of toxic metals from wastewater sludge	3-C <sup>a</sup>	Wastewater sludge	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> )	Toxic metals (Cd)	Jakobsen et al (2004) <sup>86</sup>
Remediation of Copper mine tailings	3-C <sup>a</sup>	Mine tailing Enhancement: addition of citric or sulphuric acid to the solid.	Distilled water (pH below 4 using H <sub>2</sub> SO <sub>4</sub> at the catholyte)	Toxic metals (Cu)	Rojo and Hansen (2005) <sup>68</sup> Hansen et al (2005) <sup>67</sup>
Remediation of harbor sediments	3-C <sup>b</sup>	Harbor sediments	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> )	Toxic metals (Cu, Zn, Pb and Cd)	Nystroem et al. (2005) <sup>44</sup>
Remediation of treated waste wood in pilot scale	3-C <sup>a</sup>	Treated waste wood Enhancement: addition of 5 % oxalic acid solution or a mixture of water/Na benzoate. Pretreatment: Soaking step: 5% oxalic acid, 0.5 M H <sub>3</sub> PO <sub>4</sub>	NaNO <sub>3</sub> or oxalic acid	Toxic metals (Cu, Cr and As)	Pedersen et al. (2005) <sup>69</sup> Ribeiro et al. (2007) <sup>87</sup>
Remediation of MSWI fly ash	3-C <sup>b</sup>	MSWI fly ash	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cu, Pb) and Cl	Ottosen et al. (2006) <sup>88</sup>
Remediation of polluted soil (spiked kaolinite spiked soil and industrial polluted soil)	3-C <sup>a</sup>	Polluted soil	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cu)	Ottosen et al. (2006) <sup>54</sup>

<b>Description</b>	<b>Cell *</b>	<b>Solid matrix</b>	<b>Electrolytes</b>	<b>Target species</b>	<b>Ref.</b>
Remediation of polluted soil	3-C <sup>b</sup>	Soil fines	0.01 M NaNO <sub>3</sub> (pH between 1-2 using HNO <sub>3</sub> at catholyte and NaOH at anolyte)	Toxic metals (Pb)	Jensen et al. (2006) <sup>89</sup>
Recovery of toxic metals from sewage sludge ash from fluidized bed combustion	3-C <sup>b</sup>	Sewage sludge ash from fluidized bed combustion	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cd, Cr, Cu, Pb, Ni and Zn)	Pazos et al. (2010) <sup>90</sup>
Removal of Cd from biomass combustion fly ash suspensions	3-C <sup>b</sup>	Biomass combustion fly ash	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Toxic metals (Cd)	Kirkelund et al. (2013) <sup>91</sup>
Separation of Phosphorus and toxic metals from sewage sludge ash	3-C <sup>(1,2)b</sup> 2-C <sup>(3)b</sup>	Sewage sludge ash Dissolution of H <sub>2</sub> SO <sub>4</sub>	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	P and toxic metals (such as: Cu, Zn, Ni, Pb, Al, Fe, Cd, Cr)	Ottosen et al. (2014) <sup>92(1)</sup> Guedes et al. (2014) <sup>93(2)</sup> Ottosen et al. (2016) <sup>78(3)</sup>
Remediation of polychlorinated biphenyls (PCB) contaminated soil with iron nanoparticles and surfactants	2-C <sup>b</sup>	Soil with organic pollutants Enhancements: Use of saponin and Tween 80 as surfactant.	0.01 M NaCl (pH control with HCl)	Organic contaminants (polychlorinated biphenyls)	Gomes et al. (2014) <sup>41</sup>
Simultaneous removal of organic pollutants and toxic metals from sediments	3-C <sup>b</sup>	Sediments	0.01 M NaNO <sub>3</sub> (pH below 2 using HNO <sub>3</sub> at catholyte)	Organic contaminants (PAH, PCD, TBT) and toxic metals (Cu, Pb and Zn)	Pedersen et al. (2017) <sup>94,95</sup>

Table 4. Average composition of LIBs from literature.

	Concentration (wt %)		
	Wang et al. (2016) <sup>110</sup>	Jha et al. (2013) <sup>111</sup>	Dorella and Mansur (2017) <sup>112</sup>
<b>Metals</b>			
Aluminum	5.20	4.30	8.02
Cobalt	17.30	23.67	29.49
Copper	7.30	22.13	16.48
Iron / Steel	16.50	*	*
Nickel	1.20	0.26	0.02
Lithium	2.00	2.87	3.14
<b>Others</b>			
Binders	2.40	*	*
Carbon (no graphite)	6.00	*	*
Electrolyte + Organic solution	14.00	*	*
Graphite	23.10	*	*
Plastics	4.80	*	*
Other	Balance	Balance	Balance

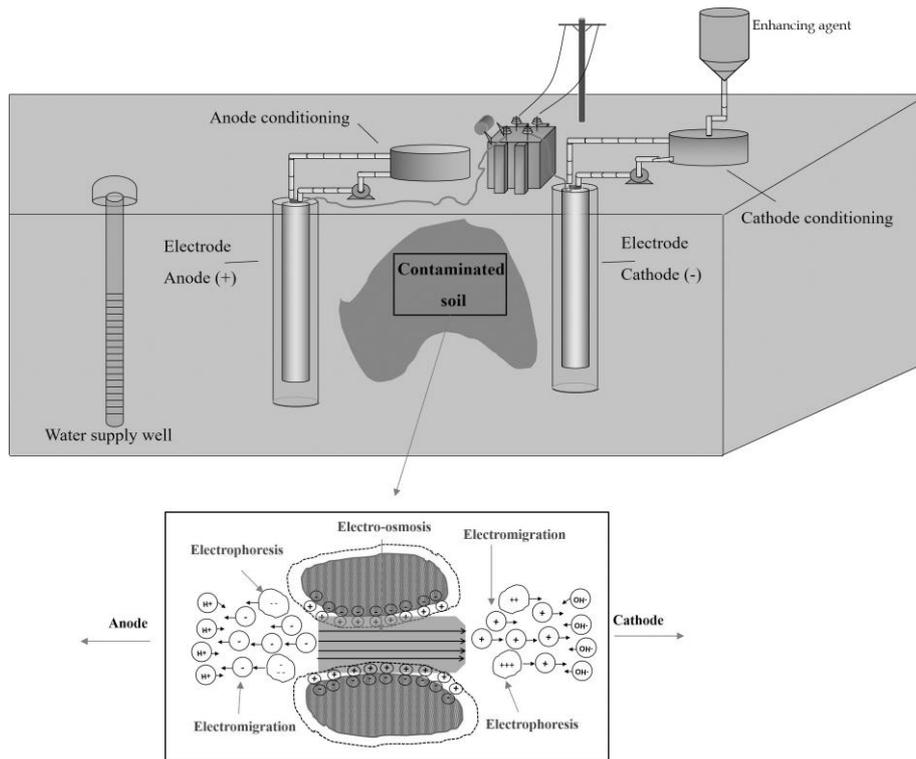


Figure 1. Electrokinetic remediation field setup. Electrochemical transport processes.

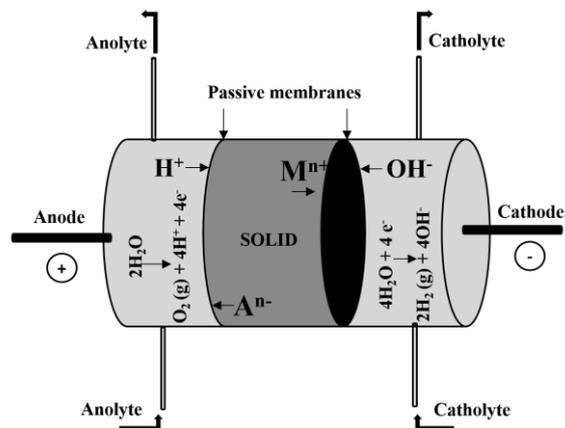


Figure 2. Schematic of the experimental cell for EKR experiments.

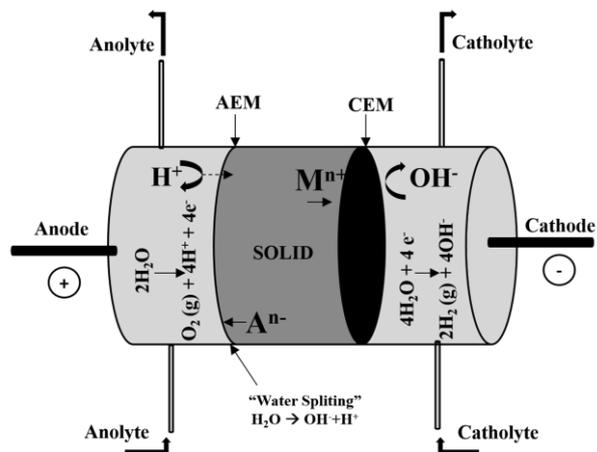


Figure 3. Schematic of the experimental cell for EDR experiments applied to a stationary, saturated solid matrix.

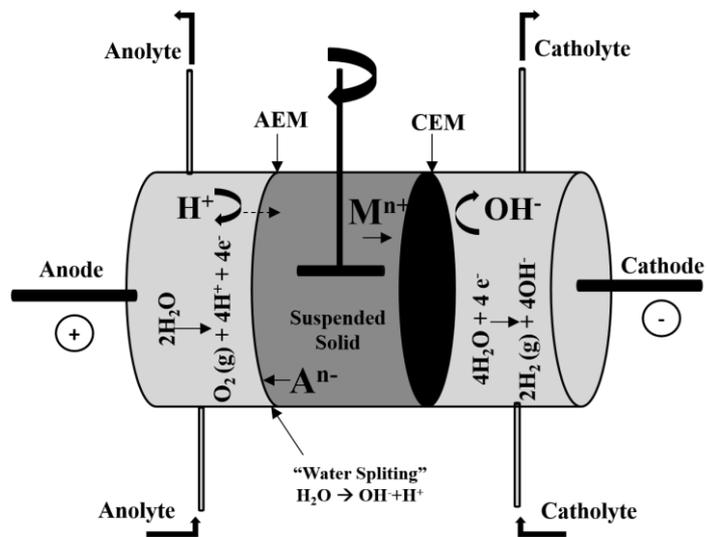


Figure 4. Schematic of the experimental 3-compartment cell for EDR experiments applied to a stirred suspension of solid.

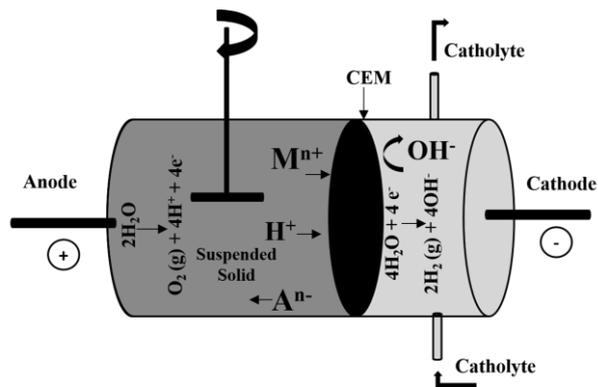


Figure 5. Schematic of the experimental 2-compartment cell for EDR experiments applied to a stirred suspension of solid.