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**Títol**

**Modelization of hazardous leached cation sorption on  
Hydrous Ferric Oxides (HFO) in multiple scenarios**

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“el fum s’esvaeix  
el temps torna a seguir  
torna a seguir el seu curs”

鞍馬

## Abstract

In this Final Degree Project it has been purposed the study of the effects on the surrounding lands the leaching (in aqueous medium) of a series of materials that have been recycled and which are formed by elements or compounds highly harmful or hazardous for human health. The study is also extended to modelize the minimization of environmental threat due to mining spillovers and leaching landfills.

This work is presented within an investigation about those phenomena that cause leaching of material components (harmful and harmless). This study involves physical phenomena and chemical phenomena (thus, physical-chemical phenomena are studied, with special attention to the sorption phenomenon as a solution for leaching).

Given some laboratory results on leaching experiments obtained by Material Division from the Construction Engineering from UPC and other ar data found in scientifi al articles it is analysed the effect on the environment by comparison with tolerated levels by law. The results on the hazardous leached metal cations are then run through an empirical model to retain them on HFO. The results are again analysed.

Some heavy metal cation intake effects on human health are described as well as techniques to detect and quantify this cations are described.

Finally, from all the work whics is put together, some global conclusions arise, as well as the lines of future work that are important to study further to get more and new knowledge about the topic.

Keywords: Leaching, Ground Water, Heavy Metal, Cation Pollutants, Material Recycling.

## Resum

En aquesta Tesina Final de Carrera ens hem proposat estudiar els efectes que poden tenir sobre el medi circumdant la lixiviació en medi aquós d'una sèrie de materials que s'han reciclat i que estan formats per elements o compostos altament nocius i/o peril·losos per a la salut humana. L'estudi també s'exten a la modelització per minimitzar l'amenaça ambiental degut a fuites mineres i lixiviació d'abocadors.

Es presenta el treball amb una investigació sobre els fenòmens que provoquen la lixiviació dels components dels materials (nocius i no-nocius). L'estudi és a nivell de fenòmens tan físics com químics (i, per tant, físico-químics, fent especial ènfasi al procés de sorció (o adsorció) com a solució a la lixiviació).

Donats uns resultats de laboratori existents d'assaigs de lixiviació duts a terme per la Secció de Materials del Departament d'Enginyeria de la Construcció de la UPC i altres dades d'articles científics, es planteja analitzar l'efecte en el medi per comparació amb els nivells tolerats per la llei. Els resultats d'aquesta lixiviació de cations peril·losos són doncs introduïts en un model empíric de retenció (adsorció o sorció) en HFO (Oxo-Hidròxids de Ferro (III)). Els resultats són altre vegada interpretats i analitzats.

Alguns efectes de la ingesta de cations de metalls pesants són descrits així com també les tècniques per detectar i quantificar aquests cations.

Per últim, se'n deriven unes conclusions globals del treball realitzat i unes línies d'investigació futures per complementar i aprofundir en l'estudi del tema.

Paraules o termes clau: Lixiviació, Aigua Subterrània, Metalls Pesants, Cations Contaminants, Reciclatge de Materials.



## Resumen

En esta Tesina Final de Carrera se nos ha propuesto estudiar los efectos que pueden tener sobre el medio circundante la lixiviación en medio acuoso de una serie de materiales que se han reciclado i que estan formados por elementos o compuestos altamente nocivos i/o peligrosos para la salud humana. El estudio también se extiende a la modelización hacia la reducción de las fugas mineras y lixiviación en vertederos.

Se presenta el trabajo con una investigación sobre los fenómenos que provocan la lixiviación de los componentes de los materiales (nocivos y no-nocivos). El estudio es a nivel de fenómenos tanto físicos como químicos (y, por tanto, químico-físicos, con especial atención al proceso de sorción (adsorción) como solución a la lixiviación).

Dados unos resultados de laboratorio existentes de ensayos de lixiviación llevados a cabo por la *Secció de Materials* del *Departament d'Enginyeria de la Construcció* de la UPC y otros datos de artículos científicos, se plantea analizar el efecto en el medio por comparación con los niveles tolerados por la ley. El resultado de esta lixiviación de cationes peligrosos se introduce en un modelo empírico de retención (adsorción o sorción) en HFO (Oxo-Hidróxidos de Hierro (III)). Los resultados son interpretados y analizados otra vez.

Algunos efectos de la ingesta de cations de metales pesados se describen así como también las técnicas para detectar y cuantificar estos cationes.

Por último, se derivan unas conclusiones globales del trabajo realizado y unas líneas de investigación futuras para complementar y profundizar en el estudio del tema.

Palabras o términos clave: Lixiviación, Agua Subterránea, Metales Pesados, Cationes Contaminantes, Reciclado de Materiales.

## Abbreviations and Symbols

HFO;Hydrous Ferric Oxide

EU;European Union

ARC;Agència de Residus de Catalunya

WFD;Waste Framework Directive

EAF;Electric Arc Furnace

MTZ;MassTransferZone

EDTA;Ethylen Diamin Tetraacetic Acid

TEM;Transmission Electron Microscopy

GFH;Granular Ferric Hydroxide

ICP-MS;Inductively Coupled Plasma-Mass Spectrometry

AAS;Athomic Absorbance Spectrometry

BSS;Black Steel Slag

WSS;White Steel Slag

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## **Chapter 1**

### **Introduction**

## 1.-Introduction

### 1.1-Recycling and reusing industrial waste into new raw material:

In general terms, within the last decades several reasons have led to the reutilization and recycling of industrial waste. New perspectives in the use of raw material have changed. The material life cycle scene is trying hard to use the “green” or “eco” labels by becoming more “sustainable” and “environmentally-friendly”.

Some reasons for this recycling phenomenon:

- Economical Reasons:

It is an extra cost for an industry the disposal of the waste by-products that can not be commercialized. If it is found a potential use for this waste material, then the by-product is no longer waste.

One of the main problems for certain industries is logistics. Transporting raw material from its origin to the industries or building scenarios is crucial. This is the reason why reusing waste materials is a real option for companies to cut off transportation costs in several circumstances.

- Social Reasons:

Less emissions of greenhouse effect gases is achieved by reduction of the journey for the transportation of raw material. This emission shortcuts is also obtained by avoiding the exploitation of natural resources if it is not needed by usage of reused waste by-products.

The relief of disposal loads on landfills due to the impossibility to find a further use for waste by-products can be achieved by reusing materials.[1]

As a clear example of this fact with the recycling idea behind is that it exists a waste exchange stock run by the Catalan Waste Agency (ARC) in where industries producing certain valuable by-products offer them to other industries which can use them as raw material. The principal goal of ARC is to link the demand with the supply so as to reduce to zero the by-product stock. [2]

#### 1.1.1-An example of industrial waste. Steel slag.

Because of the economical and environmental importance of this by-product and the focus of interest, steel slag is studied.

All over Europe steel is produced. Euroslag (European association representing the metallurgical slag producers and processors) states that in Europe in 2008 over 24 million tonnes of slag were reused in the cement industry. Euroslag estimates that such quantity of slag saved up to 22 million tonnes of CO<sub>2</sub>-emissions [3]. Apart from concrete applications steel slag uses may vary from road aggregate to fertilizers.

However, the line which defines waste and recyclable / reusable by-product (meaning that is no longer waste) is not clear [4,5]. Even in the EU the status of slag in terms of product usage availability depends on each state member's legislation [3].

Fortunately, thanks to the revision of the WFD (2008/98/EC), now steel slag is regarded as a by-product which mean that this is the end of a waste [3,6]. In spite of the European legislation, it may happen that in the same country (Spanish State situation) from region to region the possible uses for steel slag are not the same [7,8].

### 1.2-Overview of the typical run-off material phenomenon. Leaching:

When the solid materials come into contact with a liquid (usually this liquid is water) some constituents will dissolve to a greater or lesser extent. The degree of dissolution of individual constituents in the contacting liquid leads to a leachate or extract composition that is of interest for different purposes. Leaching of materials can occur in the field by exposure of materials to natural infiltration or precipitation or in the laboratory during column tests, batch leaching/extraction tests. Leaching/extraction tests are often designed to reflect a field exposure situation. There are a number of factors that can influence the rate at which constituents are dissolved from the material matrix that will be thoroughly studied further on.

**Leaching** is, therefore, the change of the solid particle compounds into the aqueous medium. It causes a very serious problem because if it is not studied, can severely modify the composition in water flow slowly and dangerously.

Given the extreme importance of leaching it is understandable that the recycled/reused materials must pass a test over leaching behaviour in front of certain water conditions. Governments usually establish certain values according to environmental legislations [7,8]. Countries traditionally engaged with environmental issues (i.e: The Netherlands and Scandinavian Family) have developed recommendations for testing granular waste materials in order to have a proper characterization for their further application [9].

The leaching phenomenon is now an important and relatively new field of study. Many authors have started developing since the last decades theories on leaching mechanisms and influent factors under different conditions [10].

In the same page, Leach XS is a virtual library in where to find the potential leaching species depending on the material used and on a determined scenario. It is a database in continuous growing and expansion. [11]

To give the reader a visual impression on the leaching potential hazardousness the following figure is showed.

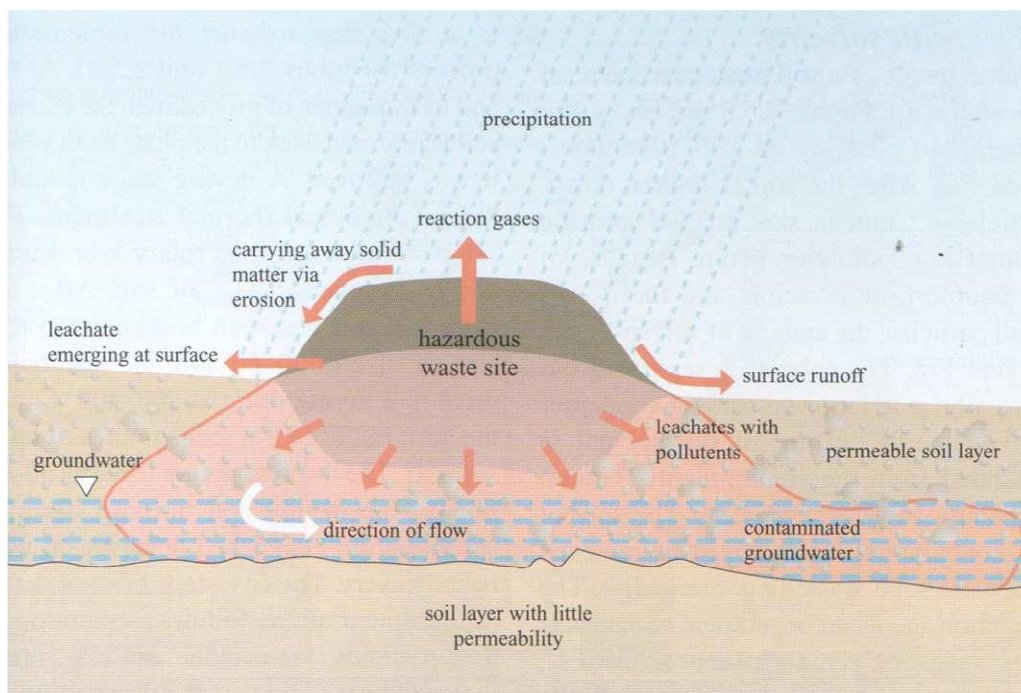


Figure 1.- Emission pathways from a hazardous waste site[12].

In this figure the reader can realize of how easy is for a leached pollutant to spread out from the initial deposition site. In this given example, the water rain penetrates into the soil and leaches part of hazardous compounds of the reused material (coloured in dark brown). This “new” polluted water stream can reach any groundwater flow and spread along it.

### 1.3-A potential solution for leaching problems. Sorption on HFO:

In this line, this study focuses on the preservation of the environment by presenting a solution to reduce the potential impact that reusing steel slag as a construction material might produce. In addition, the study also focuses on the reduction of leached hazardous heavy metal cations in landfills [13,14] and because of mining spillovers [15,16].

Bioremediation is seen as a possible solution for the treatment of contaminated soil. Bioremediation, in general refers to the application of “soft” technology based on the ability of microorganisms and plants to remove pollutants from the soil. Phytoextraction uses the ability of plants to remove the heavy metals from a contaminated area (soil) by absorbing on their biological structures [17, 18].

Some authors point out that soils have the property to retain heavy metals because of the complexation facilities that some substances which are present in soils have. Those are the humic substances [19].

In combination with humic substances, other authors investigated on HFO which have the property of retaining several heavy metals by complexation and sorption on the surface of minerals rich in iron with certain structures [20].

This study pretends to investigate the interaction between HFO and heavy metal cations in order to determine the degree of heavy metal retention due to leaching phenomenon.

## **Chapter 2**

### **Objectives**

## 2.-Objectives

In general terms, the objectives of the study are the following ones:

- Explain the need to study waste materials to control the leaching effects for pollutant spread-out while recycling or reusing them.
- Study the leaching causes and the Physical-Chemical principles that govern this phenomenon.
- Concern the reader for the potential hazard of soil/water pollutants, with special attention to inorganic cations – present by leaching.

More specifically for the content developed in this project:

- Propose an already studied methodology (modelisation) to prevent pollutant runaway once the leaching process has taken place.
- Compare the results of this methodology with the current law standards so as to check the effectiveness of the heavy metal cation sorption process and comment the difficulties that came out.

## **Chapter 3**

### **State of the Art**



### 3.-State of the Art

#### 3.1.-Introduction: The need for recycling and reusing waste materials.

Recycling is to introduce a material once again in the cycle of its own production. The etymology shows the meaning as “cycle again”. Reusing is to give a material a chance to be used again whether it is used for the same intention or for other intentions/uses. It is important to disambiguate the two terms because the meanings are not the same and – of course – involve different processes.

As it was pointed out in the introductory chapter, the reutilization of materials avoids the need to over exploit the natural resources and it enhances the logistics effectivity in terms of suppression of overcosts for transporting materials when close-by industries can supply the substitution materials to be used as raw material for other companies. In a whole, this is translated as less CO<sub>2</sub> emissions to the atmosphere and it is also regarded as an environmentally and socially beneficial activity among industries.

#### 3.2.-Steel slag.

Steel slag is the name that the by-product obtained from steel production is given. The process throughout steel is produced determines the type of the final steel slag obtained. The appearance steel slag may have is such like the following figure.



Figure 2.- Gravel-size steel slag with a lime pocket (photograph taken at Mittal Steel, Indiana Harbor West Steel Plant) [21].

Steel slag may have the appearance of a stone but its size and other properties may also depend on the manufacturing procedure, the stage of production and the scrap metal used in the steel production.

##### 3.2.1-Steel slag as waste.

It was not until the implementation of directive 2008/98/EC [6] that in all over the EU steel slag was still regarded as waste and thus, its further applications as a reusable product, limited. When this new directive appeared, it meant the possibility of preventing steel slag disposal to increase the applications as new construction material. The directive 2008/98/EC is comprehended in the Waste Framework Directive and it was intended to enhance and put up-to-date previous directives such as 2006/12, 75/439/EEC and 91/689/EEC also in response to steel producing industries petition to evolve the treatment of waste for the potential uses as new material.

However, steel slag as former waste and now regarded as a by-product thanks to 2008/98/EC has to be controlled when intended to be used in further applications. A clear example is given in autonomous legislations of Euskadi and Catalunya [7,8].

### 3.2.2-Different types of steel slag.

Modern steel procedures include the Electric Arc Furnace (EAF) in substitution of former furnace systems. In the Spanish State, the 80% of steel production was carried out via EAF [22]. This EAF production consists mainly of two steps, The first one is the casting stage (after which the black steel slag is withdrawn) and the second one is the secondary metallurgy or refining step (after which the white steel slag is withdrawn).

#### 3.2.2.1-Black steel slag.

Black steel slag is produced as a by-product after the first casting stage of steel-making process. In this first stage scrap iron is casted, then a liquid steel is obtained. At this moment oxygen is inserted in order to oxidize some iron (forming FeO) which now is liquid. After the oxidation, iron oxide can react with carbon (C) which is present in steel to form carbon monoxide (CO). The formation of this gas enables a bubbling stream upwards the cast iron which drags the slag to the top of the system. Then, by simply separating the slag on top (because of the CO it has a lower density, then floats on top) steel slag is withdrawn.

This obtained slag is then the waste of non-metallic substances that were present in the scrap iron. The slag obtained is called the oxidizing slag because it is formed when blowing oxygen in the cast iron. Because it is also formed in the first step of steel production it can also be called EAF slag. This slag is also called black steel slag because of its dark colour as shows.



Figure 3.- Appearance of black steel slag [23].

#### 3.2.2.2-White steel slag.

The white steel slag is obtained through the second main stage of steel production. As in this stage the liquefied steel is highly oxidated, it is added on top of it a reducing slag composed by calcium fluoride ( $\text{CaF}_2$ ), lime ( $\text{CaO}$ ) and graphite/coke ( $\text{C}$ ). Then, an Argon stream ( $\text{Ar}$ , inert gas) is used to blend slag and liquefied steel. Reduction reactions take place when remaining iron oxide ( $\text{FeO}$ ) is reduced to iron ( $\text{Fe}$ ) and carbon is oxidized to carbon monoxide ( $\text{CO}$ ). Again, the gas flow (both  $\text{CO}$  and  $\text{Ar}$ ) helps in mixing up the two phases. Now it is important that the gas stream enables a good contact between the reducing slag and steel because this way all the impurities present in steel will migrate to the slag. Finally, the  $\text{CO} + \text{Argon}$  gas stream will separate steel from slag by different density.

The remaining slag on top of the furnace is called reducing slag as it is formed in the reducing step. Because of its appearance it is also called the white steel slag, as shown.



Figure 4.- Appearance of white steel slag with iron impurities and black steel slag [12].

### 3.2.3-Steel slag as a profitable by-product.Its reuse.

Some of the potential uses for steel slag are the following [3]:

*For the black slag:*

Railway ballast

Drain filling

Landfill top-covering layer material

Gabions cages, environment restoration [5].

Structural layer: being able to absorb the traffic weight and distribute load along the pavement beneath.

Non-structural layer: Layer for reinforcement, as well as retention walls



Figure 5.- Urban integration of gabion cages in Malmö, Sweden.

*For the white slag:*

Steel production (reused as reducing slag)

Forest paths

Cement and concrete production

Unbond granular layers [4].

These different possibilities for steel slag are due to the physical and mechanical properties that materials ensure. As example, steel slag has as an average density of  $3600\text{kg/m}^3$  (reinforced concrete density is around  $2500\text{kg/m}^3$ ); and a compressive strength of  $200\text{MPa}$  (reinforced concrete compressive strength is around  $30\text{-}50\text{MPa}$ ) [3].

### 3.2.3.1-Need for the leaching tests to ensure the suitability for new uses.

Still all these applications mentioned above are susceptible of change from country to country, depending on the environmental requirements that regional or national governments decide that potential reusable by-products may fulfil.

Again, since the update of directive 2008/98/EC steel slag was not even considered as by-product, now the door is open to new applications such the stated before but always regarding the environmental disposition to meet with law. Law requirements usually explicit the leaching tests to ensure enough “goodness” of the material in relation to the environment. In the following chapter it is explained the leaching phenomenon from a physical-chemical focus because it is accepted that slag show good mechanical properties but its physical-chemical stability must be tested by special procedures.

## 3.3.-Leaching.

### 3.3.1-The leaching phenomena and factors affecting leaching.

Leaching is the migration of the solid phase of a matrix to the liquid phase of a fluid. This is release of the solid particle (usually from a solid matrix of a certain material) into the (usually) aqueous medium of a leaching fluid that passes by the solid matrix due to several factors and that follows some mechanisms.

*Most important physical factors (among others) influencing leaching [10]:*

- Particle size leaching is in part related to the surface exposed to leaching

The smaller size the particle is, the more exposed area the material will expose to the leaching fluid. In terms of specific area, the grain size is determinant because of the more contact area in which the interaction of the solid phase takes place with the liquid phase of the leaching fluid.

- The time frame of interest

The leaching process does not occur instantly. Given a certain mass of liquid, the time in which liquid and solid phases are in contact determines the total amount of leached species.

- Flow rate of the leachant

The flow rate is related to the weathering of the solid matrix. Higher flow rate can impact with more energy on the solid matrix and erode the particles on the

surface. Then, the more erosionated the surface becomes, the more specific contact area is created.

- The temperature during leaching

All processes involving the migration of chemical species from a phase to another are enhanced by increasing temperature. Then, it is obvious to think that higher temperatures will lead to higher amounts of leached species.

- The porosity of the solid matrix

More porosity is often translated into more speed of the fluid in contact to the solid matrix. Hence, it is the same factor as the dependence on the flow rate of leachant.

- Hydrogeological conditions

It is a combination of both porosity, contribution of the components already dissolved in the leaching fluid and its flow rate.

*Most important chemical factors (among others) influencing leaching [10]:*

- Potential leachability of constituents

A solid matrix rich in organic or inorganic species in contact to a liquid (water) have a certain potential (at a given temperature) to be dissolved. This phenomenon is explained by the polarity affinity of solvents to dissolve the chemical compounds or chemical species. If certain polar species are in contact with a polar solvent (water) the presence of dipole-dipole interactions and hydrogen-bond interaction lead to the polar species (considered as belonging to a solid matrix in a solid state or phase) to be attracted by the electrostatic interactions of the solvent and then dissolve into it. This dissolution is favourable in terms of entropy because of the surrounding of the polar species by the molecules of the polar solvent, that allows the water molecules and the former solid species to be more stable. The other way round, apolar substances or species are properly dissolved in apolar solvents (usually organic solvents). Thermodynamically, this potential is known as the chemical potential and it is expressed through the thermodynamical equilibrium constants that are proper for each substance in relation to a certain solvent at a certain temperature and pressure [23].

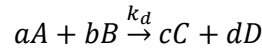
- Equilibrium or kinetic control of release

Leaching is usually carried out on undersaturated conditions. This means that the thermodynamical equilibrium forces the solid matrix to dissolve to fulfill saturation requirements of the liquid at a certain temperature. If the flow is so slow that the liquid



and the solid matrix have time to be in equilibrium, no more leaching is produced. Unfortunately equilibrium conditions require time and then kinetic control of release is the main factor from the two of them. To the limit, equilibrium is reached when two reversible process have equal rates [23].

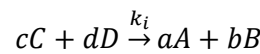
Let a process be:



Considering the process to follow a simple kinetics, the rate of the process can be described as:

$$r_d = k_d \cdot [A]^a \cdot [B]^b$$

And let its reverse pathway be:



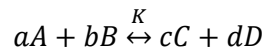
Again, considering the process to follow a simple kinetics, the reverse rate of the process can be described as:

$$r_i = k_i \cdot [C]^c \cdot [D]^d$$

In the equilibrium, both rates must be equal, then:

$$K = \frac{C^c \cdot D^d}{A^a \cdot B^b} = \frac{k_d}{k_i}$$

Equilibrium is represented by a double arrow and the thermodynamic constant, K:



To achieve this equilibrium a certain time must be elapsed. This is the reason for kinetics be dominant on equilibrium in leaching processes. In addition, the reverse processes are never favored because of the wash-off from the surface. Reactions can not turn back.

- The influence of pH on controlling solubility of specific chemical phases

pH is a measure of the concentration of protons ( $H^+$ ). A lot of chemical species have a structure dependent on pH. This is because of the capability of some atoms to pick protons from the medium. When species are deprotonated (still can attach protons on them) these substances have electric charge. The electrostatic effect has already been demonstrated as the main cause for leaching species because of the chemical potential for dissolution. On the other hand, electrostatic effects can lead to precipitation of species. Then, high values of the pH (deprotonated substances) may create high electrostatic interaction because of electrical charge. Then, the strong electric field created attracts opposite charge species forming agglomerations which tend to precipitate on surfaces. Important examples are sulphurs and phosphates.

It is also important to have an idea on the ionic character and covalent character of chemical species (inorganic salts). The more at the extremes of the periodic table that cation and anion are, the more soluble that these tend to be (they will have extremely ionic behaviour). Viceversa, it happens that the more close to each other species are in the periodic table, the less soluble that substances tend to be [24].

### 3.3.2-Leaching mechanisms.

*Most important physical mechanisms influencing leaching [10]:*

- Advection

Advection is a physical mechanism for leaching concerning the transportation of the species in the liquid phase. It may be explained as the movement of the liquid flow [25]. Advection is considered a leaching mechanism because of the particle removal from the surface by advection, then the chemical potential to dissolve more of the solid matrix is enhanced. Again, dissolution will take place and again, advection will remove the dissolved species from the surface. Leaching advances this way.

Control by advection can be described as the situation in which advection is the principal cause for the transportation of species.

The flow through a porous medium can be assimilated to the flow inside a real tubular reactor following a certain piston-flow.



Figure 6.-Representation of the advection transportation in a tubular reactor [26].

- Diffusion

Diffusion is a physical mechanism for leaching concerning the transportation of the species in a liquid phase. Diffusion is explained as the propagation of dissolved species in an aqueous medium because of the thermodynamical effect on Fick's law. This law expresses the flow of certain species towards the volumes of liquid in which the species is less concentrated. This is to say that migration tends to compensate the absence of dissolved species in all the volume.

Diffusion properties may vary from species to species. Ions should have more mobility in water than neutral species [23].



Control by diffusion is described as the situation in which no advection is present and then, species in the solution move by concentration gradient.

Table1.- Values of diffusion coefficientsof selected cations [27]

Diffusion Coefficients	$10^{-5} \text{ cm}^2/\text{s}$
$\text{Pb}^{2+}$	1,89
$\text{Zn}^{2+}$	1,41
$\text{Cd}^{2+}$	1,44
$\text{Hg}^{2+}$	1,83
$\text{Cu}^{2+}$	1,43
$\text{Ni}^{2+}$	1,32
$\text{Cr}^{3+}$	1,79
$\text{Ba}^{2+}$	1,69
$\text{H}^{+}$	9,31

The previous table shows that cations present similar values for diffusion movement except for the proton ( $\text{H}^{+}$ ) which shows higher values because of the polarizing power due to the extremely little size.

- Dispersion

It is a combination of both advection and diffusion. When none of advection and diffusion prevails, dispersion is the main mechanism. Dispersion is the base of several hydrogeological groundwater models for transport of contaminants.

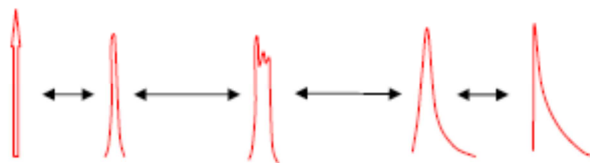


Figure 7.- Representation of the advection-diffusion transitions (dispersion models for transportation) in a tubular reactor [26].

In the previous figure, there is a transition from pure advection (on the left-side) to combination of advection and diffusion (dispersion) for the flow model of a real tubular reactor in a piston-flow reactor. The thinner the curve is the more advection is present in the movement. Diffusion is meant to be the conversion of the straight line to a curved figure.

- Erosion

Erosion is the mechanical impact on the surface of the solid matrix of the liquid particles. This constant impact can destroy the surface of the solid matrix reaching surface fragmentation and then the disappearance from the surface from the weathered particles. This mechanism enhances leaching because a more irregular surface has been shaped and then more contact area is faced to the liquid.

- Wash-off

This mechanism appearing in literature is also explainable through advection. Wash-off is the disappearance of the already dissolved species that are being carried away by advection. Then, as the particle is no longer over the surface, the chemical potential favors the new dissolution of that species because there is no practical equilibrium to deal with. The wash-off is the distancing movement of leached species away from the surface.

*Most important chemical mechanisms influencing leaching [10]:*

- Dissolution/Precipitation

Dissolution is the chemical process through which equilibrium is reached when in a solution there are undersaturation conditions. Precipitation is the process through equilibrium in which oversaturated solutions in certain species tend to precipitate such species to reach the equilibrium at a certain temperature. Similar chemical potential explanations are valid as stated before.

- Sorption processes

Sorption or adsorption is a very much important mechanism to study when dealing with leaching studies. In general, sorption is the process through which a particle or a species constituting part of a solution can be retained in a solid matrix (commonly these solid matrix are porous matrix). When the liquid penetrates in the porous, the dissolved species are stuck in the porous cavity and can not be released. The retention is due to electrostatic attractions and because of surface phenomena. The thinner porous are, the more effective the retention is. Sorption is differentiate from absorption because sorption is a surface phenomenon.

As it is showed on the following figure, particles approach the porous cavity from the bulk liquid into a thin layer (film) in which the concentration of species decrease because of the further adsorption in the porous. This effect attracts more particles (species of a constituent) from the bulk liquid (solution) to the layer (diffusion). The process is then iterative. This is the reason why the materials with adsorption capacity are able to retain such big portions of components from bulk solution.

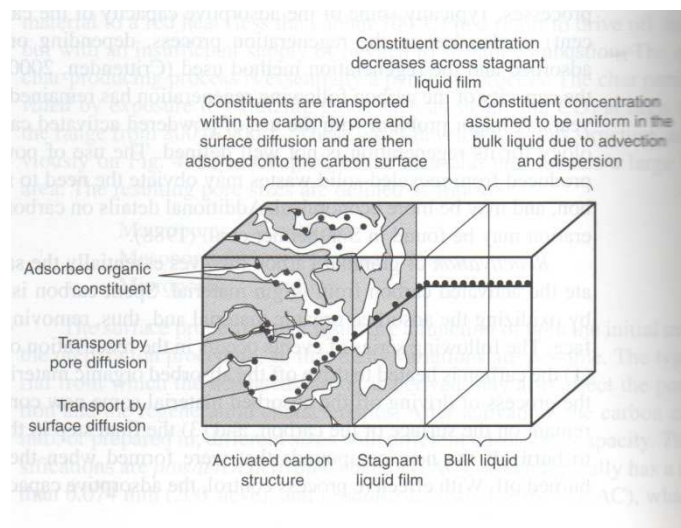


Figure 8.-Definition sketch for the adsorption of a certain species with activated carbon [28].

Nevertheless, porous may be filled around. At that point, the efficiency for the sorption process is decreased in terms of uncapacity for the retention of the particles/species in the bulk liquid. Several models such as the the one studying the mass transfer zone (MTZ) explain this evolution through a non-stationary process.

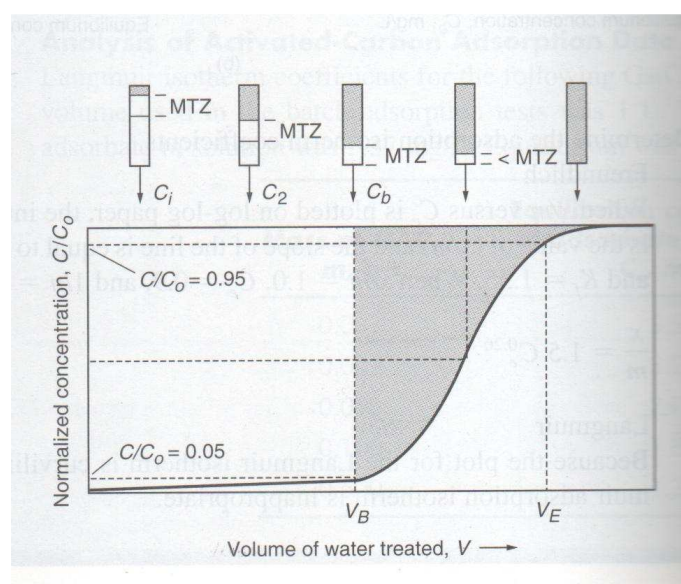


Figure 9.- Representation of the mass transfer zone in the sorption process [28].

The last figure represents the process for the end of life-cycle of a material for sorption (commonly activated carbon filters) in which the more volume of water treated, the more filled around the porous become. This model can also explain the leaching process via sorption-desorption mechanisms. The solid matrix may be a sorption material for inorganic/organic chemical species until the equilibrium is reached. Then, the reverse reactions can take place when equilibrium conditions are changed in order to reach a new equilibrium for new imposed thermodynamical conditions. The MTZ

model may represent the evolution for the so-called equilibrium process. In reality, when activated carbon filters are consumed, filters are replaced and restored.

- Complexation

Up to this point, the fluid causing leaching might be considered different from pure water. It might be a solution rich in chelating agents that may enhance dissolution further away from “normal” equilibrium. Chelating agents are specific substances (either organic or inorganic) which have a singular property for binding metal cations (typically of double or more valence – i.e.  $M^{+2}$ ,  $M^{+3}$ , etc.). These chelating species are able to create an incredibly stable reaction product by binding electron-rich zones with metal cations. These bound species in which the electrons are properly shared are more stable than their initial constituents. In practice, these complexing substances are called “sequestering agents” because the direct consequence for chelating-metal union is that metals are no longer reacting with any more species [29]. Some examples of chelating agents are carboxylic acids (EDTA) and other found in nature such as humic acids and fulvic acids [19].

- Redox

Redox (Reduction-Oxidation) reactions are, by far, the most common reactions in nature. Apart from the importance of their frequency, it is important to consider the Redox potential of an environment. (Usually, the redox potential is expressed as  $E$  or  $pE$ , in similar way as  $pH$  is defined). The study of Redox conditions is determinant to understand the development of a certain reactions and to know if whether a reactions is going to take place and in which direction. The  $pE$  scale is a measure of the oxidizing conditions or the reducing conditions of the atmosphere in where chemical species are found. When conditions are oxidizing (high  $pE$ ), chemical species tend to adopt the higher value of their valence this is to say that species may lose electrons. In reducing conditions (low  $pE$ ), happens the counter-effect, chemical species tend to have the minimum value they might have. This is to say that species tend to gain electrons from the environment.

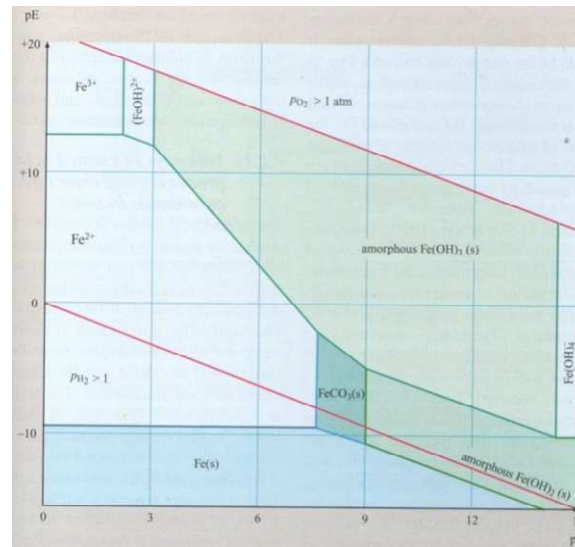


Figure 10.- Representation of the  $pH$ - $pE$  diagram for iron (Fe) species [12].

In the last figure it can be analyzed and interpreted the evolution of iron (Fe) species in accordance to the Redox conditions ( $pE$ ) and the acidity conditions,  $pH$ . When being in reducing conditions, iron tends to be metallic, whereas in oxidizing conditions, iron tends to be as Fe (III). If  $pH$  is acidic at that potential, iron species tend to be single-ions. In contrast, for high values of the  $pH$ , (at same oxidizing conditions) iron tends to be accompanied by hydroxides, as it can be read from the last figure.

So as it has been outline so far, there are a high variety of factors that may influence leaching and the mechanisms that govern the leaching process may be a huge number as well. This is the reason why, the leaching phenomenon is not an easy issue to deal with. In the following section, it is described the requirements to simplify and standardize the study of leaching in order to structure the hypothesis to work in relation to leaching and the further interpretation of results.

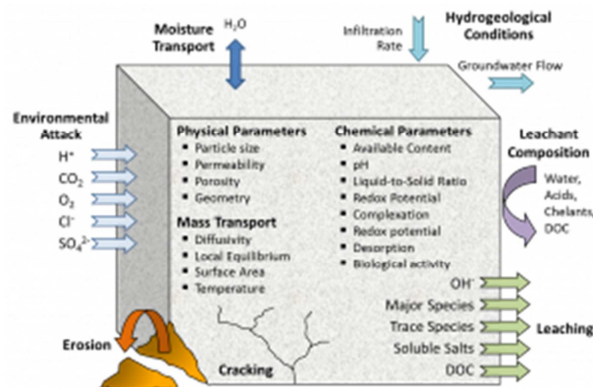


Figure 11.- Schematic representation of the factors and mechanisms influencing leaching [30].

### 3.3.3-The need for harmonization of leaching tests. Types of leaching tests.

As seen previously, such a big amount of factors affecting leaching must be under control or following certain rules so as the scientific community may be able to compare the results.

Scientists working or engaged with leaching tests have found difficulties on comparing the results of the leaching tests and to find the suitable leaching test for a series of materials which are normally analysed. That is why the Network for the Harmonization of leaching tests. Aims are such as [10]:

- Harmonize the existing tests already developed in scientific fields.
- Easy exchange of information
- Establishing the possibility to relate the behaviour of tested leaching materials to other fields and its interpretation. The creation of a common strategy to approach a valid interpretation assessed by experts that may help/validate data for analyses.
- Expansion of the Network of Harmonization of Leaching Tests.
- Formulation for approaches to solve general and specific issues/problems.

The main types of leaching tests proposed by the Network are:

#### 3.3.3.1-Monolithic leaching test.

Based on CEN TC 292 and NEN 7345, this leaching test consists of bathing a material (which represents the solid matrix) in a liquid (the leaching solution) to produce a leachate (the result of the leaching process) for a certain elapsing time. The results of this test pretend to give an idea of the solubility and diffusional processes implied with leaching. This is to say that several factors and parameters are of special importance when a material is in contact with a liquid that is under stagnation [31].

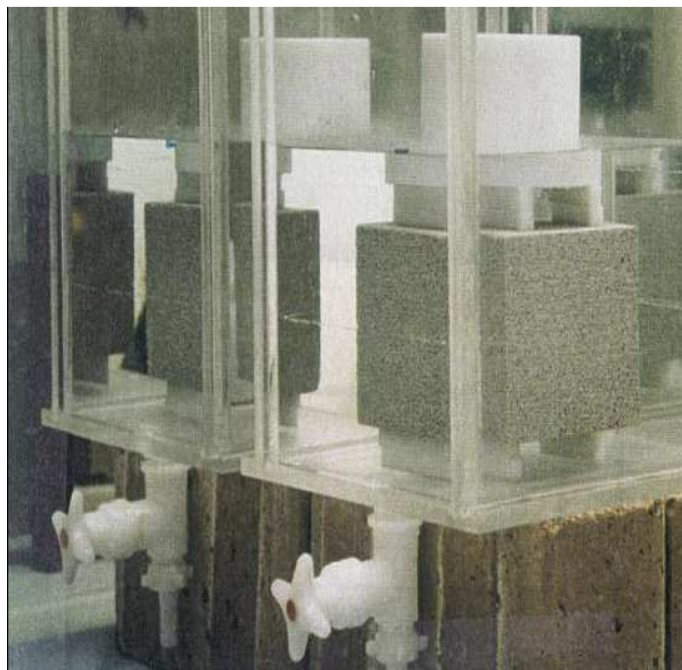




Figure 12.- Monolithic leaching test or Tank leaching test [32].

Therefore, in this test several parameters are clue to analyse results:

- **Type of liquid:** Depending on the liquid use for leaching, the results may vary. In relation to the type of liquid it can also be affecting the ionic strength of the solution contained in the liquid. Ionic strength is the measure of the electrostatical interactions of the electric field created by ionic species. Ionic strength is important to study whenever the concentrations of species is over  $10^{-4}$  M (mol/L).
- **Temperature:** Temperature is a key factor in the leaching mechanisms. At different temperatures, the thermodynamic factors change and so the potentials for releasing chemical species in to the leaching fluid. This test is normally carried out at room temperature.
- **Absence of stirring:** Is one of the special features of this test. As monolithic test consists of no stirring, advection processes do not affect the test. This is equivalent to study the diffusional processes once the solution of the chemical species has been produced. The only transportation phenomenon is diffusion.
- **Surface in contact with the liquid:** Liquid volume to area of material exposed is the definitive factor to study. This information can explain the results of the test by understanding the quantity of surface in contact with the leaching liquid. Thus, diffusion and solubility are for this test surface phenomena. Understanding the grade of roughness is a fundamental key. The common minimum thickness of the material is 4 cm. Wash-off effects can deeply be understood by surface in contact with water and by diffusional processes in terms that wash-off enhances leaching if advection is present.



Figure 13.- EAF slag cut into geometrical shape in order to determine surface area. One material prepared for the monolithic test [5].

- Time duration of the test: This is a parameter depending on the scope for the test. Obviously, for time extrapolation is a crucial parameter to take into account. It is clear that the effect of time is direct.
- Time in between refreshing the liquid: this parameter may be used to simulate the rain effect over the material surface. It may also give an idea of the behaviour of the material under intermittent conditions over time.

After the test, the leachate is analysed and therefore, the species present in the final solution are determined and quantified. In the monolithic leaching test, all the last parameters must be stated in order to report results and to be able to interpretate and make any possible extrapolation for the behaviour of the material in relation to leaching throughout time.

### 3.3.3.2-Percolation leaching test.

The percolation leaching test is an assay typically pointed out for those cases in where the material is granulated. This means that in real situations, the water or potential leaching liquid will penetrate in the granular matrix and will interact in a certain different way from the previous studied in the monolithic test case. Thus, for this method, the tests consist of artificial columns filled with the granular material to study (as the similarity of the tubular reactor with a granular solid bed inside). The test consists of making the leaching liquid flow through the granular bed which fills the



column. At his moment, leaching happens. In addition, this test is designed to study leaching at the pH of the granular material, according to EN 14405 [33].

In order to simplify the issue, it can be pointed out that the same parameters as in the monolithic test that must be reported are time duration, time in between the refreshing the liquid, temperature and type of liquid. In addition, there are two parameters that may change. At the granular material leaching test, as there exists a flow of liquid through the existing porous, there is also an advection phenomenon that, in combination with the always existing diffusions process, gives a result of a dispersion process. Dispersion enhances leaching (as stated previously) because of the wash-off effect from the surface and the increasing chemical potential for solution of the solid components.

Appart from this transportation phenomena, there is also a contact surface concern. When particles are granular, the specific surface is much more high than in monolithic materials. As a result, then, even more exposed area is in contact with the liquid and

Other comments: Granular-percolation leaching tests have normaly a series of determined values on each parameter to study. For temporal exposition to the liquid, a world-wide value of 24h is agreed, and room temperature is the most common temperature to perform tests.



Figure 14.- Several columns filled with material for the performance of the granular leaching test [30].

### 3.3.3.3-Availability leaching test.

Availability tests are less common assays usually carried out in the characterisation of materials towards environmental uses. These tests usually provide information about the total content of constituents that can be involved at a long term by the release from the solid matrix of the studied material [9,31].

Availability tests, thus, may consist of a total extraction of the leachable components in the solid matrix. This procedure may follow an extraction via use of chelating agents (EDTA) or even *aqua regia* (solution of concentrated  $\text{HNO}_3$  and  $\text{HCl}$  in relative composition in volume of 1:3, respectively) [15].

### 3.3.3.4-pH-dependence leaching test.

The pH dependence test are based on CEN/TS 14429 (CEN/TS, 2006) [16], defines the influence of pH via a titration process where it is observed a release of the species that partially constitute the solid matrix. It is a test that can give the behaviour of materials in case of pH variation and can also provide information of the material buffer capacity in front of pH variations.

### 3.3.3.5-Compliance tests.

In general, compliance tests are those tests to carry out to assess the behaviour of a certain material to be compared with the reference values of a law or a certain regulation. These tests can comprehend monolithic tests, percolation tests or others or even the combinations of several of them, always according to laws and regulations. As an example, throughout this study it has been mentioned the regulations in Euskadi and Catalunya, both establishing a percolation test to assess the materials for their further use [7,8].

### 3.3.3.6-Leaching Models.

The prediction for the release of leached compounds is the main goal for modeling scenarios. Through years of investigations, some authors have collected a huge amount of data in order to create a database for modeling predicting the future behavior of previously known materials under specific conditions. The management of the information acquired after years of research and testing different working hypothesis following the harmonized methodologies has led to the formulation for the suitability of materials for a certain use without stepping into the laboratory. A clear example of this will be to have a great library of information for leaching mechanisms and behavior of materials is the Leach XS leaching model [11].

### 3.3.4-Main test parameters.

Having seen the conditions influencing the leaching of different typologies of leaching tests and the parameters under which to carry out the tests, the most common and recommended parameters are:

#### *Temperature*

Room temperature is the most common temperature to carry out the leaching tests. In some cases, when it is relevant to induce a major leaching process, temperature is raised. Solubility is very sensitive to temperature, thus in this case, leaching compounds are overestimated.

#### *Leachant:*

Demirelaized water is the most common leachant used. However, as stated before in availability tests, EDTA or other chelating agents may be used to enhance the extraction of chemical species.

It is important, though, to understand, that is the behavior under natural conditions is studied, then, the more alike conditions are in the laboratory, the more reliable results from the tests might be. This does not mean that unexpected conditions should not also be taken into account.

*Practical L/S ratio values:*

The L/S ratio is the quantity of liquid (L) used in the leaching test per unit (kg) of solid material tested.

The most commonly used LS ratios are around 10. This is a practical consideration. It is easy to separate the chemical species from the solid matrix at higher L/S values but when performing the test this may be not very practical. In addition, the release of leachates may vary with time. The higher the L/S is, the more extreme conditions in reality may be performed in the test [9]. This is the reason why higher L/S are more used in availability tests and special screening tests. According to the environmental situation that is imitated in laboratory L/S should be also accommodated to.

*pH*

In many leaching tests the pH is not controlled and therefore is determined by the material subjected to testing. However, the pH of a leaching system can be affected in an uncontrolled manner when the system is exposed to the atmosphere. Due to uptake of carbon dioxide, which is even enhanced by stirring, the pH may change during a leaching experiment. Such changes are not very reproducible. Materials with little buffering capacity are most sensitive to pH changes [10].

**3.3.5-Other parameters.**

In addition, the study of leaching must keep special attention to parameters such as material properties: granulometry, drainage, porosity and structure, composition, sorption properties and cation exchange capacity. Other parameters are related to the environment or to the liquid phase in contact with the material, such as pH, redox potential, dissolved organic carbon and complexation capacity. Other general parameters which can be considered are the water regime, rainfall and evaporation and biological factors [10].

At the following page, the reader will be able to see an overview of the leaching process study and some general steps to take into consideration.

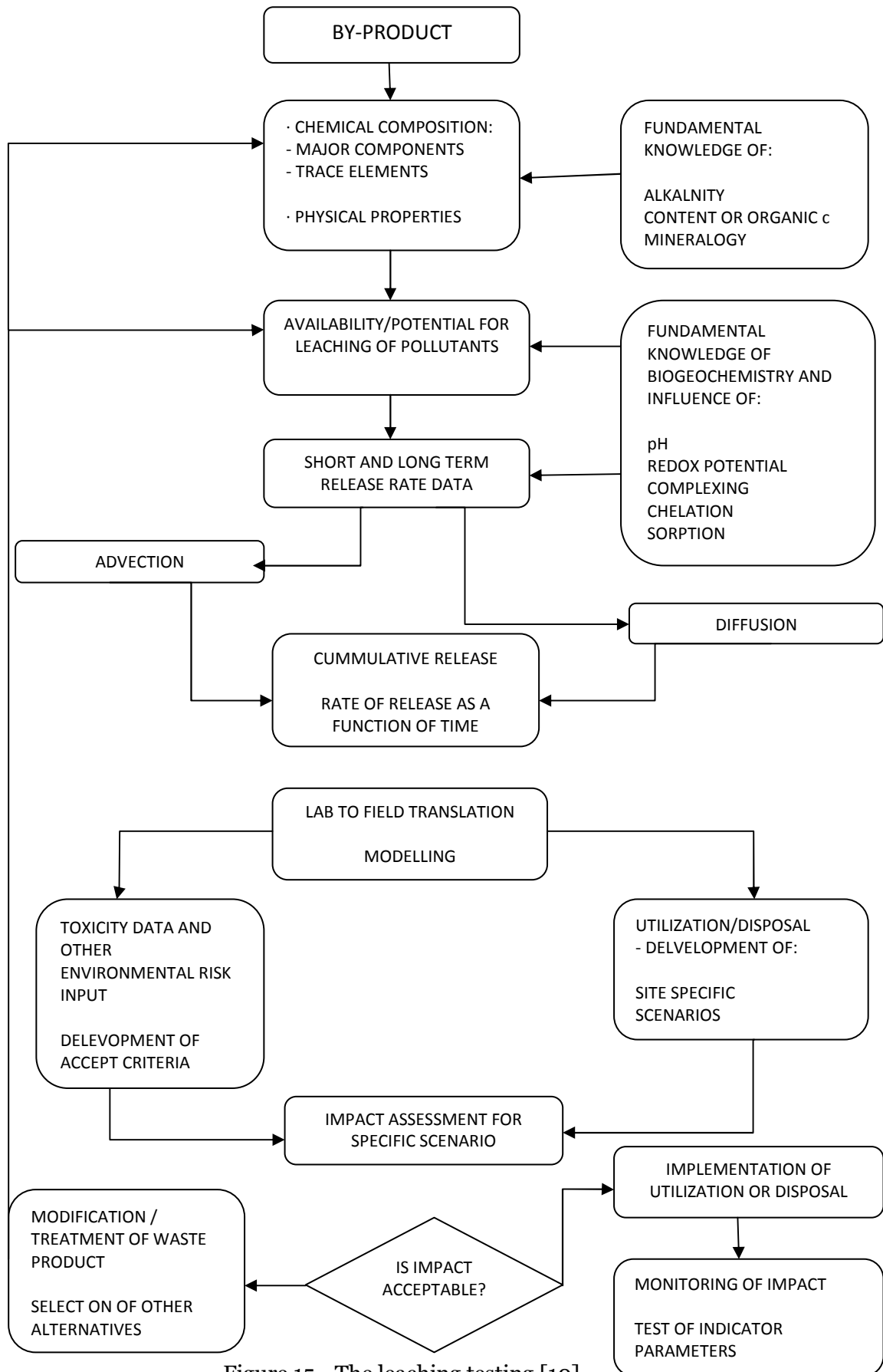


Figure 15.- The leaching testing [10].

### 3.4.-Solutions to leaching problems.

In this section, several remediation techniques for the leaching problem are commented with special attention on HFO, which is studied in depth.

#### 3.4.1-Bioremediation.

In the Soil Science, the “Bioremediation” term refers to the usage of the properties of biological systems to perform a natural remediation on the soil. This is the application of “soft” technology based on the ability of microorganisms and plants to remove pollutants from the soil. Phytoextraction is based on the ability of selected plants which can remove the heavy metals (or other anthropogenic pollutants) from a contaminated area (soil) by absorbing on their biological structures [17, 18].

Other authors have already studied bioremediation as a solution for removing pollutants from industrial effluents [34]. In this study case, authors studied an artificial solution spiked with several heavy metals such as iron ( $\text{Fe}^{2+}$ ), manganese ( $\text{Mn}^{2+}$ ), (belonging to a background solution, among other chemical species) and the study heavy metals cobalt ( $\text{Co}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ). Results showing the goodness of the heavy metal removal from the spiked solutions were studied via Langmuir’s and Freundlich’s isotherms. These isotherms show the curve for the sorption process which is performed by the macrophyte (plants) in contact with the aqueous solution. The authors discuss which is the metal that most affinity presents versus the retention by the macrophyte. The metal most adsorbed was copper followed by zinc. Cobalt and nickel show very little affinity for the macrophyte.

#### 3.4.2-Cation binding by humic substances [19].

Following the idea of sorption of heavy metal cations onto certain substances/species, it can be found that certain organic substances present in the soil (Humic acids and Fulvic acids) can also retain the hazardous cations onto their surface. This may be achieved by the chelating power of humic and fulvic acids because of the presence of carboxylic groups in the terminal chains. Carboxylic groups are organic acid functional groups that when deprotonated, hold a negative electrical charge among one carbon and two oxygens. This negative charge is shared between the two oxygens, stabilizing the functional group. In addition, humic and fulvic acids have a special structure in where a very huge chain holds a lot of organic functional groups and in the end of the chain there is oftenly a carboxylic group.

Humic and Fulvic acids are easily deprotonated (so the molecule behaves as a real acid-it releases protons) because by doing so there is an internal flow of electrons that give the molecule more stable conditions (this is called aromaticity).

Finally, as stated before, when some positive cations come around the molecule, the functional groups work as a chelating agent because of the further stability gained by filling the coordination sites of the organic chain of humic and fulvic acids. The coordination sites are, in this case, the extremes of the chain ending with carboxylic or carboxylated groups.

The idea behind this theory is that the own molecules of the soil are capable of retaining a certain quantity of metals. The total amount of retained metals will be determined by the concentration of the chelating substances.

### 3.4.3-HFO (Hydrous Ferric Oxides).

In the same way than with humic substances, other authors investigated on HFO, which have the property of retaining several heavy metals by complexation and sorption on the surface of minerals rich in iron with certain structures.

Goethite is a mineral in which HFO chemical species are found because of the own structure of the mineral. This is the reason why a large number of authors studying complexation and sorption phenomena of heavy metals on HFO decide to study Goethite as well.

The study of the sorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on Goethite mineral (HFO) [35] has been performed through models and laboratory work to validate the results obtained in the modelling step. In this study, the hypothesis for the model state that ion metals reach the diffusional-control layer area from the bulk solution and from this layer up to the surface of the mineral, where the HFO are. Then in this reaction, ion metals are bond and protons are released, so that the charge remains balanced.

The main apotation of this work is that the rate at which reactions take place is depending on pH and metal concentration, both at once. The authors point out that for small metal ion concentrations at a low pH, the rate determining step (the slowest process) is the diffusion of the metals in the surface of the HFO in Goethite. Once the metal reaches the surface, the complexation and sorption process takes place at higher speed, leadind to a stationary state.

On the other hand, for high ion metal concentration and high pH in the solution, the diffusional transport from the outer layer to the surface is fast. However, the rate determining process is the diffusion of the released protons in the surface reaction to the diffusional layer and from there to the bulk solution.

This last paper is also interesting in terms of formation of the Goethite mineral to carry out the study of pollutant sorption on HFO. The authors decide to create their own mineral particles by synthesis in the laboratory. From an iron source, the raw mineral is precipitated with NaOH under vigorous stirring to form a colloidal suspension that is stored and aged at 4°C. The colour of the suspension is initially red and turns yellow with time. By this time, the suspension is dialized until constant conductivity. The yellow suspension is kept under argon to avoid oxidation of the minerals and any other alterations of the crystals of HFO formed (Goethite).

Other authors that had studied HFO in the past, created a theory in which [20] determined a family of constats for the sorption on HFO because of the incredibly high affinity with cations that this oxo-hydroxide presents.

This family of sorption constants on HFO were determined under certain conditions and were found semi-empirically. In general terms, the model is based on the



generalizes idea of the two-layer model. It describes the sorption of dissolved species (solutes) at oxide surfaces as a chemical reaction with the specific surface sites. These surface reactions that happen include cation binding (which is the reaction of our interest) among others. The model based on this two-layer theory is expressed by equilibrium constants (such like the mass law). These constants are result of combination of two terms: an “intrinsic” term corresponding to the chemical free energy of binding to a specific surface site, and a variable “coulombic” term corresponding to the coulombic free energy of binding contributed by the electrostatic charge at the surface [20].

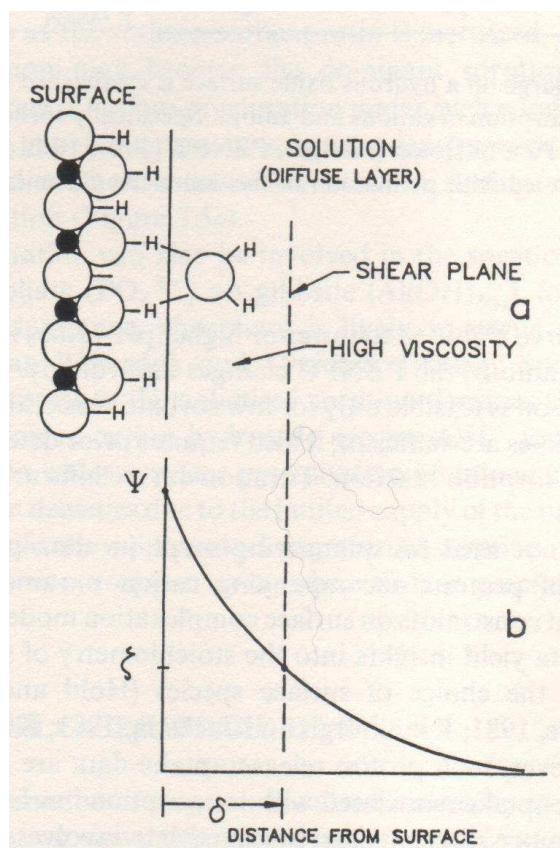


Figure 16.- Representation of the two-layer model description of the zone (dotted line) separating bulk solution and diffuse layer and also showing the sorption sites on HFO [20].

In this last figure it is represented the idea of the double-layer (two-layer) model. Reactions take place at the inner layer (diffusion layer), preferably at the surface (active sites) of the oxides.

The hypothesis under which the complexation-sorption constants were determined were the following [20]:

- Use of standard oxide preparation (to have HFO).
- Room temperature controlled from 20°C to 30°C.
- Absence of competing ions.

- Absence of CO<sub>2</sub>.
- Perform the experiments with the enough equilibrium time (so that reactions take place when analysis are carried out).
- Use a proper method for solid-liquid separation.

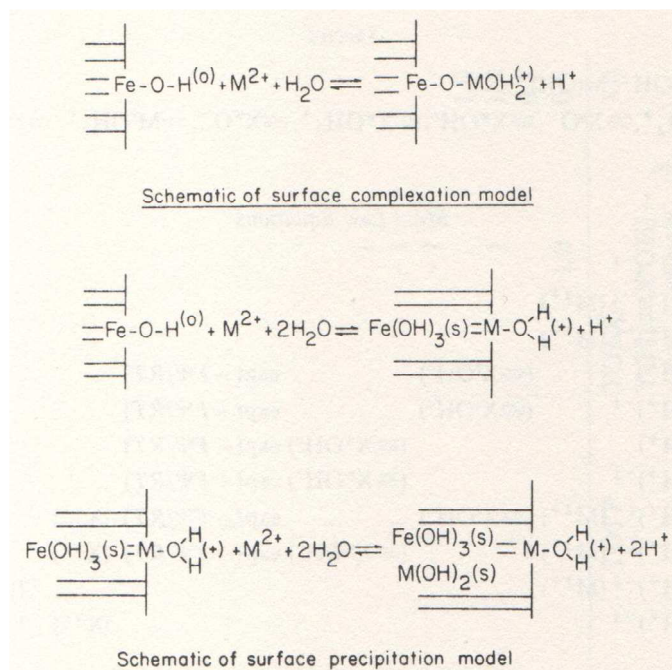


Figure 17.- Representation of the reactions in the two-layer model description of the HFO mechanism for retention of metals [20].

On the last figure it can be interpreted the mechanism of the reactions that follow the HFO sorption modelling. In the first stage, the iron oxide, water and the metal meet together. At a second stage, the oxygen captures the metal and at the same time, the metal binds the water molecule which releases a proton at once.

There may be a second interpretation for a precipitation model on the surface which is the union to the metal of two hydroxyl groups, but this may happen at higher pH values.

The HFO sorption model may generate graphics such as the following:



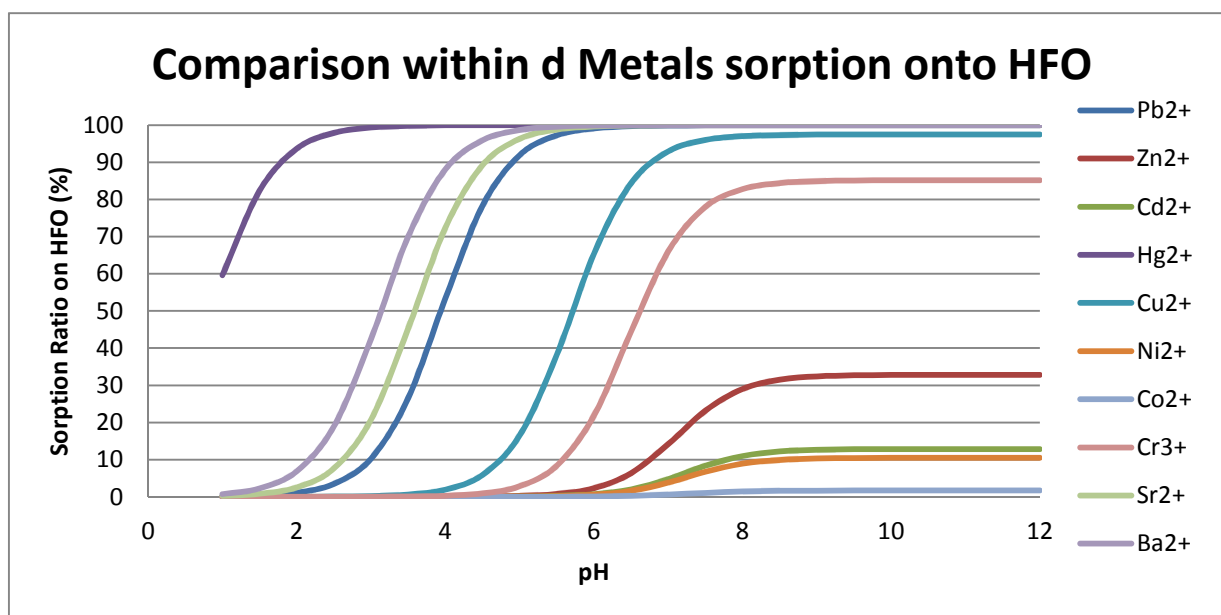


Figure 18.- Representation of the HFO retention model on the stated metals. Ionic Strength is  $10^{-2}\text{M}$ .

In general, in this example for an ionic strength of  $10^{-2}\text{M}$ , retention of metals obtain high yields for several represented species except for Nickel, Cobalt, Cadmium and Zinc. The other metals are successfully captured by HFO.

Finally it is remarkable to comment that HFO (granular HFO) have also been investigated in relation to the retention by sorption of arsenic [36].

#### 3.4.4-Further comments on literature.

When studying surface processes (such as sorption) it is considered important to understand the behaviour of the surface itself. Nowadays, there exist techniques through which the structure of the surface can be studied. The determination of the active sites on a surface is critical to understand the superficial yield this surface will provide on the superficial processes implied. For this purpose, TEM (Transmission Electron Microscopy) is an already existent technique that allows to determinate active sites. In addition, BET (Brunauer – Emmet - Teller) is an isotherm model that takes into account the reality of the surface and it is usually used after a TEM analysis to provide accurate information about the sorption in relation with the superficial yield [37].

Finally, it is interesting to comment that throughout the research period, there is a main tendency from authors to carry out the tests without following any harmonization recommendation. In addition, the most used leaching tests are the ones in relation to availability, which are preferred among scientist and not engineerings.

### 3.5.-Available data.

In this section, it is stated the numerical data and the background conditions found on literature that will be used in the HFO modelisation.

#### 3.5.1-Steel slag leaching tests results. Thresholds for the acceptance of materials.

As seen before, at the department of materials, UPC, two authors carried out research and test over steel slag. Among many tests results they found out that steel slag can sometimes fulfil the compliancy tests and sometimes not. Here there is a table which resumes part of their work and study:

*Table 2.- Values of compliancy leaching tests for steel slag (White and Black) adapted from [4,5]*

Compliance Leaching test results for Steel Slag (White and Black) (L/S = 10L/kg) (values in mg/kg)				
Species	Black Slag [4]	White Slag [4]	Black Slag [5]	Conformity [7]
Pb <sup>2+</sup>	0,17	0,03	0,0018483	0,5
Zn <sup>2+</sup>	5,17	0,17	0,030614	4
Cd <sup>2+</sup>	nd	nd	0,0000283	0,04
Hg <sup>2+</sup>	nd	nd	0,0002077	0,01
Cu <sup>2+</sup>	0,12	nd	0,0170373	2
Ni <sup>2+</sup>	nd	nd	0,0042123	0,4
Cr <sup>3+</sup>	0,33	nd	0,0423247	0,5
Ba <sup>2+</sup>	4,11	34,67	1,0031007	20

Obs: nd is “not detected”; the squared values are the ones over the regulation value.

The results on these compliancy tests will be used in the modelisation to provide clues for the improvement of the leaching release (independently on whether the leaching assay complies or not the regulations). Of course, for those values over the limit, then, the improvement of the capturement of the HFO metal-sorption can be translated into a relief in the leaching emissions and can provide new uses for the materials.

#### 3.5.2-Studies on Aznalcóllar spillover [15,16].

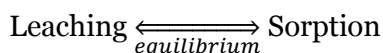
As a result of the natural disaster of Aznalcóllar (a mining-waste dam collapsed and all the valley – where 60km downstream there is Doñana National Park- was flooded with toxic heavy metal sludges.) several authors took part on the investigation for the remediation of the contaminated soils. On the research for the remediation of the heavy metal leaching and posterior run-off, several material (industrial waste) were tested to study the performance of toxic cation sorption on them. The proposed materials are sugar foam, wollastonite silicate (that can increase the pH if mixed up with soil) and

zeolitic materials (that have a very specific sorption capacity). Unfortunately, authors do not propose a model for this materials.

As main factors for the heavy metal cation mobility (in general terms, cation mobility) the authors consider that it depends on:

- a) The metal considered
- b) The type of interaction in the solid phase of soil
- c) Acidity (pH dependence)
- d) Oxidic or Anoxic conditions (Redox conditions)
- e) The presence of ligands that may form soluble complexes
- f) The ionic composition of the soil solution

Thus, it is interesting to focus this work on the idea of the equilibrium between leaching and sorption:



So, leaching is, thus, understandable as a desorption process, but is more than that, because (as seen previously) leaching is a sum of dissolution, re-dissolution, desorption, washing away, etc.

In the Aznalcóllar article, the authors consider important to carry out batch single extractions tests (availability tests) because this is the most common approach for estimating the mobility of metal cations (heavy metal cation mobility) in soils and sediments. In addition, the results of this test are suitable to determine the environmental impact and potential restoration actions.

The authors explain that their experiments took place with three different kind of extracting solutions to leach the metals prior to the quantification/determination analysis. The purpose of this triple experimentation is to see the effect of the ionic nature of the species in the solution that is in contact with the leachable cations.

These solutions are:

- a) Unbuffered solution ( $\text{MgCl}_2$  or  $\text{CaCl}_2$  solutions). The nature of these solutions is to reproduce the pH and the effect of the rain. When it rains, the fallen water can play the role of leaching agent. This solution does not stabilize the pH so, if protons are released to the solution, pH will decrease and vice versa.
- b) Buffered solution without chelating effect (buffer consisting of acetic acid-acetate). This solution can stabilize the pH value and simulate

- c) Buffered solutions with chelating effect (buffer consisting of EDTA). This solution can stabilize the pH and can provide a chelating effect which might stabilize divalent cations so, then, the leaching effect is more acute and the leaching process is enhanced.

Furthermore, authors carry out an extraction of all metal cations by an attack with aqua regia so all kind of organic matrix is destroyed, there is no sorption or precipitation process or phenomenon and then, all the heavy metal cations can be quantified and determined.

The results of this article are interesting in the direction that the authors see how pH-dependent leaching heavy metal cations are. The information of this article is used the other way round the authors of the article present it. This means that the authors of this article mind what is leached due to the hazardous effect on the environment if expanded by run-off. In this project it is important to see and quantify the effect on sorption once the materials have leached heavy metal cations. So all parameters favouring leaching from sludge or contaminated soil are interesting to prevent so as sorption remains as the main phenomenon.

As a result of the extraction of trace elements the authors find out that at a low pH, the leaching of trace elements (heavy metals) is higher than for neutral or basic pH (pH comprehended between 7 and 13). This is consistent with the idea that the number of sites for cation sorption decreases with pH. Then, at low pH values (acid values of pH) it exists a competition for the sorption sites between the cations and the protons ( $H^+$ ).

Some results on this study will be used later on this study project to test the efficiency of the HFO model chosen to retain the heavy metal pollutants. A modelisation on the Aznacóllar data will be performed and results commented.

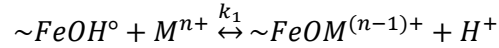
### 3.5.3-Studies on landfill leachates [14]. Removal of heavy metals by sorption on Iron Fines

Other authors studied the sorption interaction of activated carbon, bone meal and iron fines to eliminate heavy metal cations from landfill leachate.

Many authors have studied the good properties of activated carbon when eliminating solid, liquid or gas pollutants from a phase. The well known properties of activated carbon (specific area) make it a very good-retaining agent by sorption processes. This way, this is a good agent to eliminate pollutants. However, it is a costly material and not very intelligent to use if can not be regenerated.

Bone meal and iron fines are cheap as may be an industry byproduct. In this study attention will be paid to iron fines to develop the research. This process takes place when iron particles in contact with leached heavy metal cations interact and create some binding mechanism through which heavy metal sorption takes place. Authors propose a mechanism via  $Fe(O)$  oxidation into  $Fe(II)$  or  $Fe(III)$  and then, there is a

complexation reaction in where the polluting cations are sorbed onto Fe(III) and a proton is released.



However, the authors do not agree with this model they initially propose because the pH would enormously vary and that does not happen throughout the experimentation.

Then, they suggest that the mechanism goes through a primary oxidation of Fe(o) to Fe(II) or Fe(III) and then the complexation reaction (as stated above) combined with ion exchange and also combined with a co-precipitation with Fe minerals, which could be the most dominating mechanism. Of course there is an uncertainty with this last statement. Anyway, authors see that the partial oxidation of initial Fe(o) to Fe(II) or Fe(III) is needed to achieve a good yield in soption process.

Some results on this study will be used as well later on this study project to test the efficiency of the HFO model chosen to retain the heavy metal pollutant. A modelisation on this data will be performed and results commented.

## **Chapter 4**

### **Elements. Toxicology. Detection.**

## 4.-Elements.Toxicology. Detection [39,40].

Note: The pictures concerning the periodic table [38] used in this chapter follow an aesthetic objective. Their use is not meant to give any explanation about the content of this study.

### 4.1.-Brief Introduction:

Within this chapter some hazardous elements found in water sources are described. As it is the will of the author, there is also a brief description of the chemical instrumentation used to detect and quantify them.

### 4.2.-Elements. Toxicology:

#### 4.2.1.-Lead

,70	7,34	1,80	8,6
33	<b>82</b>	207,2	82
304	<b>Pb</b>	327,46	<b>E</b>
473		1749	
,85		11,35	
	PLOM		BI
+3		+2 +4	
6p <sup>1</sup>	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	[Xe]	
,04	7,42	2,33	7,2
34)	<b>114</b>	(289)	<b>11</b>
	□□		□

Lead is a highly toxic cation because of its biocummulative nature. It attacks the nervous system and the kidneys heart and reproductive failure. Provokes saturnism (accumulation of lead in the body) and cancer. It is currently being eliminated from gasoline (to avoid premature detonation) because of the release in the air.

#### 4.2.2.-Cadmium

1,90	9,39	1,60	6,4
582	<b>48</b>	112,411	4
1,78	<b>Cd</b>	321,07	<b>I</b>
,162		767	
0,50		8,65	
	CADMI		II
+1		+2	
	[Kr] 4d <sup>10</sup> 5s <sup>2</sup>	[K	
1,90	8,99	1,70	5,
566	<b>80</b>	200,59	<b>8</b>
...		...	

Cadmium is an ion which is present in a wide variety of fish, tobacco and fertilizers. It causes damage in the kidney, osteoporosis and other disorders related to the substitution of Calcium, Magnesium and Zinc with biological functions.

#### 4.2.3.-Mercury

,90	8,99	1,70	5,7
66	<b>80</b>	200,59	8
,18	<b>Hg</b>	-38,83	<b>1</b>
356		356,73	
9,3		13,55	
	MERCURI		TA
+3		+1 +2	
i <sup>1</sup>	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	[Xe]	
,54	10,43	2,00	6,1
72)	<b>112</b>	(285)	<b>1</b>
	□□		□

Mercury is found in thermometers, cosmetics and electric bulbs. Many fish contain Mercury. It can get inside the human body by normal breathing, skin touch and intake. Affects the kidney, lungs and brain. It can easily destroy the neurons by cathalitic effect. Causes lost of vision, muscular debility and neurological problems. It can be transmitted from the mother to the baby in the prenatal-stage.

## 4.2.4.-Chromium

9415	24	51,9961	25
1910	<b>Cr</b>	1907	<b>Mn</b>
3407		2671	
6,11		7,19	
	<b>CROM</b>		<b>Mn</b>
+4 +5	+2 +3 +6		
	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>		[Ar]
1,60	6,77	1,60	7,4
9064	42	95,94	43
2477	<b>Mo</b>	2623	<b>Tc</b>

Chromium is widely distributed in the Earth's crust. It can exist in valences of +2 to +6. In general, food appears to be the major source of intake. It can substitute other oligo-essential substances and can be dangerous because of the redox potential if it is ingested under Cr<sup>+6</sup>, which is extremely oxidant, damaging any biological system and destroying cellular membranes, etc. It is the cause of cancer.

## 4.2. 5.-Several mechanisms for toxicity for other cations.

In general, when soluble inorganic cations may be dangerous, this is because the interaction with the metabolism. This is to say that when the pollutant gets inside the human body, due to diffusion it reaches all parts of the body. If the size of the cation is similar to the size of an oligo-element (needed for biological functions) it may replace it, altering the structure of the protein which initially uses the oligoelement. At a long term, this protein may be destroyed for the unstable new structure. This protein destruction may be the cause for several diseases related to the intake of heavy metals. Another common mechanism for toxicity is the precipitation of phosphate in cells. When big heavy metal cations are bound to a phosphate, precipitation occurs, and then, the phosphate is no longer available for biological functions. This may lead to cellular disorders.

## 4.2.-Detection [29]:

Detection of inorganic cations may be carried out by ICP-MS or ASS:

ICP-MS:

(ICP-MS) is the technical acronym for *Inductively coupled plasma mass spectrometry*. It is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10<sup>12</sup> (part per trillion). This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.

Compared to atomic absorption techniques, ICP-MS has greater speed, precision, and sensitivity. However, analysis by ICP-MS is also more susceptible to trace contaminants from glassware and reagents. In addition, the presence of some ions can interfere with the detection of other ions.

The variety of applications exceeds that of ICP-OES and includes isotopic speciation

For coupling to mass spectrometry, the ions from the plasma are extracted through a series of cones into a mass spectrometer. The ions are separated on the basis of their



mass-to-charge ratio and a detector receives an ion signal proportional to the concentration.

The concentration of a sample can be determined through calibration with certified reference material such as single or multi-element reference standards. ICP-MS also lends itself to quantitative determinations through isotope dilution, a single point method based on an isotopically enriched standard.

AAS:

(AAS) is the technical acronym for Atomic Absorbance Spectrometry. This is a technique commonly used when determining several inorganic cations but this technique has sensitivity limits as its detection thresholds are quite higher in comparison with ICP-MS. Nevertheless is an existent technique.

Ibáñez, C. [41] discussed in depth which were the difficulties on her work dealing with Mercury contamination because of the incredibly easy-binding nature of Mercury. In consequence, Mercury is a “dirty” element, as it “sticks” everywhere it goes through. Special care and attention must be kept on this element determination and quantification.

## **Chapter 5**

### **Modeling. Hypothesis and Equations.**

## 5.-Modeling. Hypothesis and equations.

### 5.1.-Modeling. Hypothesis and equations:

In this section, the physical-chemical reactions involved in the study of pollutant retention will be studied in order to carry out a modelisation upon the results of the sorption on HFO materials [20] and following the considerations of some soil science literature [19]. These materials may perform a reduction in the release of hazardous chemical species because of leaching. Further on, in this section

The first part of the study involves the mass transfer reactions onto the soil surface particles. These reactions are mainly complexation reactions given by sorption phenomena and mainly controlled by the pH of the aqueous solution circulating within the soil.

Previous studies show that the relationship between the amount of sorbed pollutant concentration and the free initial concentration follow a sigmoid curve, as it was stated before. This is to say that the Freundlich or the Langmuir model is followed in the kinetics of the sorption process.

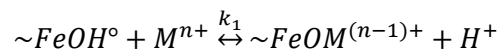
This cited studies of surface complexation modelling [20] establish that there is a typically- used mass law action that comes to unify a difficult situation within variables. The authors determined a series of constants under certain conditions stated previously. The implementation of these constants is used following the expression [19]:

$$\%ret = 100 \cdot \frac{[M^{n+}] \cdot 10^{K_{HFO}}}{1 + [M^{n+}] \cdot 10^{K_{HFO}} + \frac{[H^+]}{K_{ac}^{HFO}}}$$

Where %ret represents the retention of the metal over the HFO.  $[M^{n+}]$  is the initial concentration of the metal in the bulk solution (from the leaching test);  $K_{HFO}$  is the semi-empirical constant of the HFO-sorption-model theory,  $[H^+]$  is the concentration of protons and the  $K_{ac}^{HFO}$  is the acidity constant of the HFO (because HFO may release protons, behaves as an acid) which remains constant [20].

Given Equation:

In general, we can write down the following molar balance equation for the sorption process: (Note that an equilibrium process is described, as the arrows point both sides of the equation)



Considerations:

Note that the ~ character means that the compound is adsorbed on to the surface ( it is not a free compound belonging to the bulk solution). Actually, the formula for the  $\sim FeOH^\circ$  compound would not be stoichiometrically correct, as there would be two positive charges “above” the iron symbol, indicating that we are referring this text to Fe (III).

Before starting with the model, it is important to say that the expression for the equilibrium constant for the sorption process (complexation and precipitation on to the surface) is written by the mass action law. Then, we are able to express:

$$k_1 = \frac{[\sim FeOM^{(n-1)+}] \cdot [H^+]}{[\sim FeOH^\circ] \cdot [M^{n+}]}$$

Strictly talking, when the concentration is below  $10^{-4}$  the activity coefficient is negligible and then the concentration equals the activity.

To calculate the influential ionic strength (IS), it has been used a formulation by calculation via the conductivity parameter [42].

$$IS = 1.6 \cdot 10^{-5} \cdot [conductivity]$$

The HFO model is now applied to the leaching tests of the Materials department (UPC) [4,5], to some of the availability test results of the sludges in the Aznalcóllar spillover [15] and finally to the retention results of granular leaching test of iron fines [14].

Hypothesis:

From now on, it will be supposed:

- The soil under study has a minimum concentration of Ferrous or Ferric components which are sorbed – or at least are part of the soil matrix - so as to enable us to apply the theory of heavy metal sorption onto hydrous ferric oxide (HFO). This HFO compounds can be those present in the general and common clay soils typically found in most parts of Catalonia, due to – in part – to the degradation of the Feldspar rock in to clay minerals, for instance. ( Generally, this kind of soils can be found in the superficial areas exposed to moist or water sources and have a typically red-coloured clay texture).
- Although there is a pH-dependence existing within the model, it will be supposed that pH is given by the material and, may only change because of the release of the protons in sorption-complexation process.

- The initial concentrations for the heavy metal pollutant run-off is given by the leaching laboratory results carried out by the department via a leaching percolation test under conditions stated as follows:
- The initial concentration for the heavy metal pollutant run-off is considered to be in a steady-state.

## **Chapter 6**

### **Results and analysis of calculations**

## 6.- Results and analysis of calculations

### 6.1-Results on applicaton of the HFO modelling in Steel Slag studies

Results after the application of the HFO are shown on the following table:

*Table 3.- Results on modeling with HFO the retention of pollutants from leaching BSS*

Species	pH	12	L/S = 10	HFO modelisation				
	Conformity (mg/kg) [7]	Black Slag (mg/kg) [4]	Black Slag (mg/L)	Black Slag (mol/L)	Retention (%)	Black Slag (mol/L)	Black Slag (mg/L)	Black Slag (mg/kg)
Pb <sup>2+</sup>	0,5	0,17	0,017	8,20E-08	3,65E-01	8,17E-08	1,69E-02	1,69E-01
Zn <sup>2+</sup>	4	5,17	0,517	7,91E-06	7,73E-03	7,91E-06	5,17E-01	5,17E+00
Cu <sup>2+</sup>	2	0,12	0,012	1,89E-07	1,47E-02	1,89E-07	1,20E-02	1,20E-01
Cr <sup>3+</sup>	0,5	0,33	0,033	6,35E-07	7,29E-03	6,35E-07	3,30E-02	3,30E-01
Ba <sup>2+</sup>	20	4,11	0,411	2,99E-06	4,63E+01	1,61E-06	2,21E-01	2,21E+00

#### *Observations and discussion:*

With the results of modelling the retention of pollutants on HFO, this model it is only valid for enhancing the retention of Barium (retention of 46% on HFO surface). For the rest of metal ions, the retention is extremely low and inappreciable.

*Table 4.- Results on modeling with HFO the retention of pollutants from leaching WSS*

Species	pH	12	L/S = 10	HFO modelisation				
	Conformity (mg/kg) [7]	White Slag (mg/kg) [4]	White Slag (mg/L)	White Slag (mol/L)	Retention (%)	White Slag (mol/L)	White Slag (mg/L)	White Slag (mg/kg)
Pb <sup>2+</sup>	0,5	0,03	0,003	1,45E-08	6,46E-02	1,45E-08	3,00E-03	3,00E-02
Zn <sup>2+</sup>	4	0,17	0,017	2,60E-07	2,54E-04	2,60E-07	1,70E-02	1,70E-01
Ba <sup>2+</sup>	20	34,67	3,467	2,52E-05	8,79E+01	3,05E-06	4,19E-01	4,19E+00

#### *Observations and discussion:*

In this last situation, the reader can find the very specific utility in which HFO can be trusted. The retention of Barium is the real value that HFO can give. For other metal ions, retention still is very sensitiveless. In this case, though, the application of HFO in between the White Steel Slag (WSS) material can enhance and allow the usage of the material. This is because the equivalent effect on leaching through retention is to fit the WSS in the regulation. With a theoretical retention yield or almost 88% of the total Barium leached, here, HFO can provide a good solution to the utilisation of WSS.

Table 5.- Results on modeling with HFO the retention of pollutants from leaching BSS

Species	pH	11,5	L/S = 10	HFO modelisation				
	Conformity (mg/kg) [7]	Black Slag (mg/kg) [5]	Black Slag (mg/L)	Black Slag (mol/L)	Retention (%)	Black Slag (mol/L)	Black Slag (mg/L)	Black Slag (mg/kg)
Pb <sup>2+</sup>	0,5	1,85E-03	1,85E-04	8,92E-10	3,98E-03	8,92E-10	1,85E-04	1,85E-03
Zn <sup>2+</sup>	4	3,06E-02	3,06E-03	4,68E-08	4,57E-05	4,68E-08	3,06E-03	3,06E-02
Cd <sup>2+</sup>	0,04	2,83E-05	2,83E-06	2,52E-11	7,43E-09	2,52E-11	2,83E-06	2,83E-05
Hg <sup>2+</sup>	0,01	2,08E-04	2,08E-05	1,04E-10	5,92E-01	1,03E-10	2,06E-05	2,06E-04
Cu <sup>2+</sup>	2	1,70E-02	1,70E-03	2,68E-08	2,08E-03	2,68E-08	1,70E-03	1,70E-02
Ni <sup>2+</sup>	0,4	4,21E-03	4,21E-04	7,18E-09	1,68E-06	7,18E-09	4,21E-04	4,21E-03
Cr <sup>3+</sup>	0,5	4,23E-02	4,23E-03	8,14E-08	9,35E-04	8,14E-08	4,23E-03	4,23E-02
Ba <sup>2+</sup>	20	1,00E+00	1,00E-01	7,30E-07	1,74E+01	6,03E-07	8,29E-02	8,29E-01

*Observations and discussion:*

In this last table, it can be noticed that his BSS already fulfilled the requirements of regulation. At this point, there is no need to use any HFO to improve anything because the law allows using the material without problems. Nevertheless, the study on modelling HFO for metal ion sorption processes shows that at these little concentrations of the metal ions, the removal of the pollutants is useless. There is no practical removal yield. Values for sorption process are almost zero, except for Barium.

## 6.2-Results on applicaton of the HFO modelling in the Aznalcóllar spillover studies

Results after the application of the HFO are shown on the following table:

Table 6.- Results on modeling with HFO the retention of pollutants from Aznalcóllar disaster leaching tests

Species	pH	6,7	L/S = 10	HFO modelisation			
	Aznalcóllar (mg/kg) [16]	Aznalcóllar (mg/L)	Aznalcóllar (mol/L)	Retention (%)	Black Slag (mol/L)	Black Slag (mg/L)	Black Slag (mg/kg)
Pb <sup>2+</sup>	3	0,3	1,45E-06	1,31E+00	1,43E-06	2,96E-01	2,96E+00
Zn <sup>2+</sup>	890	89	1,36E-03	2,71E-01	1,36E-03	8,88E+01	8,88E+02
Cd <sup>2+</sup>	23	2,3	2,05E-05	1,23E-03	2,05E-05	2,30E+00	2,30E+01
Cu <sup>2+</sup>	30	3	4,72E-05	7,44E-01	4,69E-05	2,98E+00	2,98E+01
Ni <sup>2+</sup>	2,4	0,24	4,09E-06	1,96E-04	4,09E-06	2,40E-01	2,40E+00

*Observations and discussion:*



In this scenario, it is intended to study the elimination of heavy metals from leaching sludge of the Aznalcóllar accident. Percentages of elimination do not even reach 1% at any case. This can be explained because of the little concentration in toxics that show leaching the sludge and also because of the pH that the sludge gives to the solution. When pH is neutral-low, the sorption processes are not favoured. In this sense, removal is not guaranteed at all. In fact, neither it was when pH was almost 12 for the last leaching tests results.

### 6.3-Results on application of the HFO modelling in iron fines studies

Results after the application of the HFO are shown on the following table:

*Table 7.- Results on modeling with HFO the retention of pollutants from Landfill leaching tests and comparison from retention via Iron Fines*

pH	7,6		HFO modelisation			
Species	Landfill (mg/L) [14]	Landfill (mol/L)	Retention (%) [14]	Retention (%)	Landfill (mol/L)	Landfill (mg/L)
Pb <sup>2+</sup>	3,70E-03	1,79E-08	0,04	5,35E-02	1,78E-08	3,70E-03
Zn <sup>2+</sup>	4,60E-02	7,03E-07	0,39	4,61E-04	7,03E-07	4,60E-02
Cd <sup>2+</sup>	2,00E-04	1,78E-09	4,4	3,52E-07	1,78E-09	2,00E-04
Hg <sup>2+</sup>	2,20E-05	1,10E-10	0,98	4,22E-01	1,09E-10	2,19E-05
Cu <sup>2+</sup>	1,30E-02	2,05E-07	0,054	1,07E-02	2,05E-07	1,30E-02
Ni <sup>2+</sup>	2,60E-02	4,43E-07	0,83	6,97E-05	4,43E-07	2,60E-02
Cr <sup>3+</sup>	8,20E-03	1,58E-07	0,48	1,22E-03	1,58E-07	8,20E-03
Sr <sup>2+</sup>	1,00E+00	1,14E-05	0,39	4,39E+01	6,40E-06	5,61E-01
Co <sup>2+</sup>	6,60E-03	1,12E-07	0,69	2,61E-06	1,12E-07	6,60E-03

#### Observations and discussion:

When comparing different iron species dealing with the removal of inorganic pollutants from an aqueous solution, the squared cells can show the similar values for which the HFO modelling and the laboratory test experiments [14] reach altogether. Retention is effective for big cations such as Strontium, with an elimination yield of almost 44%.

General observations and discussion about the results obtained in the previous tables:

It is remarkable that there is a big influence between the chemi-sorption (sorption on HFO) of within different d metals AT different concentrations. The more concentrated

the metal is in solution (because of leaching, of course), then, the more effective is the retention on HFO, according to the parameters of the model.

The type of metal is determinant, as well on the retention yield. For example, in the previous tables, the metal that is most likely to be adsorbed are Barium ( $\text{Ba}^{2+}$ ), Strontium ( $\text{Sr}^{2+}$ ) and Mercury ( $\text{Hg}^{2+}$ ). This can be explained by the easy binding nature these elements present in general. These atoms are very big in comparison with the other ions, and then, the effect of the size can help polarizing the ions and attracting and attaching them to the HFO.

The effect on the pH is also a good factor to realize that has a special weight. The higher the pH is, it is shown that the more retained the ions are.

## **Chapter 7**

### **Conclusions**

## 7.-Conclusions

This study on the leaching phenomenon coupled with the study of a semi-empirical model to retain pollutants has reached the following conclusions:

Given the current environmental and economical situation of societies in relation with industries and regulations it is necessary to understand the behaviour of the materials to avoid their disposal and to be used as new raw material or reused/recycled material. In connection with this idea, leaching is a phenomenon that happens whenever a material touches water. In order to ensure the suitability of a material for a new usage, leaching tests are essential to be carried out in this field.

Leaching is a surface phenomenon very interesting to study because is almost inevitable every time that fluids come into touch with liquids. The factors and mechanisms for the leaching processes have been studied in this work, focusing on the processes that enhance leaching and those that help “reversing” leaching, in terms of retention.

Given the wide variety of studies about leaching, the novelty of some of them and the own nature of science, it is important to understand the need for harmonisation of leaching test so that new legislation frameworks could be easy to implement and spread around European Union, for example.

Given the current state of the art about leaching and the solution proposed on the utilisation of HFO to retain by complexation and sorption mechanisms, inorganic metal ion pollutants, it has been demonstrated that this is not enough because this model is only practical to apply in real cases if the concentration of the ions are quite high enough for the iron species to interact properly with metal ions and because of the difficulty of ion species to reach the surface by diffusion mechanisms through the layer that governs the previous step of reaching the surface of the minerals. However, for Barium, the HFO have proved to be a good solution for leaching.

Throughout the study process and the articles read it is worth to say that there are multiple studies running on leaching topics. Comparing the results or even the procedure followed on each study is a quite hard task because each author follows his/her own method to prepare the samples and his/her own method to perform the leaching tests. It is true that more science-based authors use to trust more in the availability tests, whereas more technological-based authors use to follow standardized tests following local, regional, national or international normatives/recommendations. This final paragraph does not pretend to say who is doing right and who is doing wrong but after studying the needs for harmonization the leaching tests and parameters, the possibility to work in a similar framework is more encouraging (when this is possible).

## **Chapter 8**

### **Need for further studies**

## 8.-Need for further studies

In this chapter some interesting uses for HFO are pointed out and as well the need to study in depth the purpose of the intended use.

Although in the previous chapter it has been affirmed the relatively bad behaviour of HFO when retaining heavy metal cations when those are found at low concentrations, it is interesting to focus on the applications for the metals with which HFO work properly. This is to say that for the Barium leaching, the HFO can be studied more in depth because of the goodness the model provides.

Of course, despite the model is based on semi-empirical studies and the sorption constants are calculated this way, it is always recommended to test the material in real conditions on a laboratory. In this line, in the future, for real HFO applications, it would be interesting to check its behaviour and also test it under different conditions in the laboratory.

In spite of the low effectiveness that the model showed, for high concentrations of metal cation, the HFO minerals can proof high efficiency and so, the HFO can be considered as a pre-treatment for any industrial or big-scale metal retention application. That is, though, another field for its application.

## **Chapter 9**

## **References**

## 9.-References

In this chapter the reader can easily find the relationship between literature consulted and the number of the references appearing at each section symbolized as [].

[1].- “Issues in environmentally conscious manufacturing and product recovery: a survey”. Gungor, A; Gupta, S.M; Computers and Industrial Engineering.Vol 36, issue 4, September 1999. 811-853.

[2].- “Borsa de subproductes de Catalunya”. Web source: [subproductes.com](http://subproductes.com). Last consulted date: 2013 August 30<sup>th</sup>.

[3].- “Euroslag”. Web source:[euroslag.com](http://euroslag.com). Last consulted date: 2013 August 30<sup>th</sup>.

[4].- “Estudio del impacto ambiental por lixiviación de la escoria de acería en capas granulares no ligadas”. Otegi, K; Department of Construction Engineering. Universitat Politècnica de Catalunya. June 2012.

[5].- “An environmental study of the use of steel slag aggregate in gabion cages”. Richter, T; Department of Construction Engineering. Universitat Politècnica de Catalunya. May 2013.

[6].- “EU Norms”. Web source: [ec.europa.eu/environment/waste/framework/pdf/guidance doc.pdf](http://ec.europa.eu/environment/waste/framework/pdf/guidance_doc.pdf). Last consulting date: 2013 August 30<sup>th</sup>.

[7].- “Decret 32/2009, de 24 de Febrer, sobre la valorització d’escòries siderúrgiques”. Diari Oficial de la Generalitat de Catalunya. 5328-27.02.2009.

[8].- “Decreto 34/2003, de 18 de febrero, por el que se regula la valorización y posterior utilización de escorias procedentes de la fabricación de acero en hornos de arco eléctrico, en el ámbito de la Comunidad Autónoma del País Vasco”. Departamento de ordenación del territorio y del medio ambiente; BOPV. 26.02.2003.

[9].- “Nordic recommendations for leaching tests for granular waste material”. Wahlström, M. The Science of the Total Environment 178 (1996) 95-102.

[10].- “Harmonization of Leaching/Extracting tests”. Van der Sloot, H.A; Heasman, L; Quevauviller, Ph. Elsevier. Studies in Environmental Sciences. Vol. 70. 1997.

[11].- “Leach XS”. Web source: [leachxs.com](http://leachxs.com). Last consulted date: 2013 August 30<sup>th</sup>.

[12].- “The Essential Guide to Environmental Chemistry”. Schwedt, G. Wiley Editorial. 2<sup>nd</sup> Edition 2007. (Adapted from Atlaslexikon at the same time).

[13].- “Handbook of solid waste management”. Tchobanoglous, G; Kreith, F. Second edition. Mc Graw Hill. 2002.



- [14].-“Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines”. Modin, H; Persson, K. M; Andersson, A; van Praagh, M. *Journal of Hazardous Materials* 189 (2011) 749-754.
- [15].-“Prediction of the impact of the Aznalcóllar toxic spill on the trace element contamination of agricultural soils”. Vidal, M; López-Sánchez, J.F; Sastre, J; Jiménez, G; Dagnac, T; Rubio, R; Rauret, G. *The Science of the Total Environment* 242 (1999) 131-148.
- [16].-“Remediation of metal-contaminated soils with the addition of materials – part II: Leaching tests to evaluate the efficiency of materials in the remediation of contaminated soils”. González-Núñez, R; Alba, M.D; Orta, M. M; Vidal, M; Rigol, A. *Chemosphere* 87 (2012) 829-837.
- [17].-“Phytoextraction: the use of plants to remove heavy metals from soils”. Kumar, N; Dushenko, V; Motto, H; Raskin, I. *Environmental Science Technology*. (1995) 29 1232-1238.
- [18].-“Treatment of Contaminated Soil – Fundamentals, Analysis and Applications”. Stegmann, R; Brunner, G; Calmano, W; Matz, G. Springer Editorial. 2001.
- [19].-“Cation binding by humic substances”. Tipping, E. Cambridge Environmental Chemistry Series, 12. Cambridge University Press. 2002.
- [20].-“Surface Complexation Modeling – Hydrous Ferric Oxide”. Dzombak, D. A; Morel, F. M. M. John Wiley&Sons Editorial. 1990.
- [21].-“Use of steel slag in subgrade applications”. Yildirim, I. Z; Prezzi, M. Joint transportation research program. Purdue University. 2009.
- [22].- “Unión de Empresas Siderúrgicas”. Web source: unesid.org. Last consulting date: 2013 August 30th.
- [23].- “Physical Chemistry” Atkins, P; de Paula. J; Editorial panamericana. 8th Edition. 2008.
- [24].-“Inorganic Chemistry”. Shriver&Atkins. Overton, Rourke, Weller, Armstrong. McGrawHill. 2008
- [25].-“Curso De Ingeniería Química”. Costa, J; Cervera, S; Cunill, F; Esplugas, S; Mans, C; Mata J. Editorial Reverté. 2004.
- [26].-“Apunts de Reactors Químics”. Cunill, F; Iborra, M; Tejero, J. Catàlisi i Cinètica Aplicada. Departament d’Enginyeria Química. Universitat de Barcelona. 2010.
- [27].-“CRC Handbook of Chemistry and Physics”. Several Authors. (Ed. Haynes, W. M.). 93<sup>rd</sup> edition. 2013.
- [28].-“Waste Water Engineering. Treatment and Reuse”. Metcalf&Eddy. Fourth Edition and International Edition. McGrawHill. 2004.

- [29].-“Anàlisi Química Quantitativa”. Daniel C Harris. Translation from the 6<sup>th</sup> American Edition. Reverté.
- [30].-“Leaching Environmental Assessment Framework”. Web source: [vanderbilt.edu](http://vanderbilt.edu). Last consulted date: 2014 April 28<sup>th</sup>
- [31].-“CEN/TS 15863:2012 Characterization of waste – Leaching behaviour test for basic characterization – dynamic monolithic leaching test with periodic leachant renewal, under fixed test conditions” CEN, Brussels, 2012
- [32].- “Use of alternative materials as secondary fuels and raw material for cement clinker production (Cluster 1)”. Web source: [eco-serve.net](http://eco-serve.net). Last consulted date: 2014 April 28<sup>th</sup>
- [33].-“Developments in the characterization of waste materials for environmental impact assessment purposes”. Van der Sloot, H; Meeussen, J; Van Zomeren, A; Kosson, D. Journal of Geochemical Exploration, vol 88, 72-76. 2006.
- [34].-“Sorption of Co, Cu, Ni and Zn from industrial effluents by the submerged aquatic macrophyte *Myriophyllum spicatum* L.”. Lesage, E; Mundia, C; Rousseau, D.P.L; Van de Moortel, A.M.K; Du Laing, G; Meers, E; Tack, F.M.G; De Pauw, N; Verloo, M.G. Ecological Engineering, 30. 320-325. 2007.
- [35].-“Reaction rates of heavy metal ions at goethite: relaxation experiments and modeling”. Pohlmeier, A; Lustfeld, H. Journal of Colloids and Interface Science, 269. 131-142. 2004.
- [36].-“Rapid adsorption of arsenic from aqueous solution by ferrihydrite-coated sand and granular ferric hydroxide (GFH)”. Mähler, J; Persson, I. Applied Geochemistry 37. 179-189. 2013.
- [37].-“Surfaces”. Attard, G; Barnes, C. Oxford University Press. 1998.
- [38].- Picture from “Taula Periòdic dels Elements”. Societat Catalana de Química. Institut d’Estudis Catalans (IEC). 2013.
- [39].- Guidelines for drinking-water quality [electronic resource]: incorporating 1st and 2nd addenda, Vol.1, Recommendations. – 3rd ed. World Health Organisation. WHO.
- [40].-“Biological Inorganic Chemistry: Structure and Reactivity.” Bertini, I; et al. University Science Book. 2007.
- [41].-“Metodologia Analítica per a l’Especiació del Mercuri en mostres del Medi Aquàtic”. Ibáñez, C. Tesi Doctoral. Departament de Química Analítica. Facultat de Química de la Universitat de Barcelona. 2012.
- [42].-“Influence of the carbon/nitrogen/phosphorus ratio on polycyclic aromatic hydrocarbon degradation by *Mycobacterium* and *Sphingomonas* in soil”. Leys, N. M; Bastiaens, L; Verstraete, W; Springael, D. Applied Environmental Biotechnology. 66. 726-736. 2005.



## Annex

In this Annex the reader will find the relation of constants used for the calculation of the HFO sorption model as well as the acidity constant and the molecular weights used.

*Table 8.- Values of HFO sorption constants, acidity constants and molecular weights in relation to the heavy metal cations studied [20].*

Species (M <sup>n+</sup> )	Molecular Weight (g/mol) [23]	Sorption Constant Value: log(K <sub>HFO</sub> ) [20]	Acidity constant K <sub>ac</sub> <sup>HFO</sup> [20]
Pb <sup>2+</sup>	207,2	4,65	5,13E-08
Zn <sup>2+</sup>	65,39	0,99	
Cd <sup>2+</sup>	112,411	0,47	
Hg <sup>2+</sup>	200,59	7,76	
Cu <sup>2+</sup>	63,546	2,89	
Ni <sup>2+</sup>	58,6934	0,37	
Co <sup>2+</sup>	58,9332	-0,46	
Cr <sup>3+</sup>	51,9961	2,06	
Sr <sup>2+</sup>	87,62	5,01	
Ba <sup>2+</sup>	137,327	5,46	