AN ENVIRONMENTAL STUDY OF THE USE OF STEEL SLAG AGGREGATE IN GABION CAGES

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ABSTRACT

The growing tendency of sustainable building and development is transforming the way in which construction projects are faced. These changes are saving the natural environment, as well as, minimising the quantity of industrial waste. In line with this initiative, the following project studies the potential recovery of Electric Arc Furnace Slag and its use as material fill in gabion cages.

From a sustainability point of view, the recovery of steel slag is positive from all perspectives. (a) Economically: steel slag is cheaper in comparison to natural rock considering that it does not need to be mined and if used steel companies do not have to pay a disposal tax. (b) Environmentally: natural resources are spared and space is being reserved in landfills. (c) Socially: steel slag is thought to have a low potential impact on human health and the environment.

The focus on gabion cages was chosen as the stability of the structure relies on the density of the material used to fill the metal cages. Additionally, gabion cages should be promoted as a sustainable solution to scour and erosion protection, as well as, retaining walls. These structures blend in with the environment and can even create a habitat for wildlife.

In order to verify this application, technical and environmental aspects have to be considered. A series of leaching tests, based on the developing European harmonised framework, have been carried out to determine the environmental impact of EAF Slag. Basic characterisation tests were used to determine the main leaching mechanisms of EAF Slag, whereas, conformity test verify the release of constituents in comparison with the limits defined by legislation.

Keywords: Electric arc furnace slag, Gabion cages, Environmental impact, Leaching.

RESUMEN

Cada vez más, hay una tendencia creciente a la construcción y desarrollo sostenible, que está transformando la forma de plantear y diseñar proyectos. Estos cambios protegen el medio ambiente y minimizan la cantidad global de residuos industriales. Siguiendo esta iniciativa, el trabajo presentado a continuación estudia la valorización potencial de la Escoria Negra y su uso como relleno en gaviones.

Des del punto de vista de la sostenibilidad, la valorización de la escoria de acería es positiva desde todas las perspectivas posibles. (a) Económicamente: escoria negra tiene un coste menor en comparación con roca natural considerando que no se tiene que extraer de la tierra, además, los productores del acero no tienen que pagar tasas de vertido. (b) Medioambientalmente: genera un ahorro de recursos naturales y reserva espacio en los vertederos. (c) Socialmente: se considera que la escoria negra tiene un impacto potencial mínimo sobre la salud humana y el medio ambiente.

El enfoque de este trabajo está centrado en gaviones, ya que la estabilidad de estas estructuras depende de la densidad del material utilizado como relleno. Asimismo, se tendría que promocionar el uso de gaviones como una solución sostenible para erosiones y socavaciones, además de muros de contención. Estas estructuras armonizan con el medioambiente y pueden generar un nuevo hábitat para fauna.

Para verificar esta aplicación, se tiene que considerar aspectos técnicos y ambientales. Una serie de ensayos de lixiviación, basados en el marco europeo armonizado en desarrollo, se ha llevado a cabo para determinar el impacto medioambiental de la escoria negra. Ensayos de caracterización básica determinan los mecanismos principales de lixiviación para el material, en cambio, los de conformidad verifican la liberación de componentes en comparación con los límites establecidos por la legislación.

Palabras Clave: Escoria Negra, Gaviones, Impacto medioambiental, Lixiviación.

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Chapter 1
INTRODUCTION

The growing tendency of sustainable building and development is transforming the way in which construction projects are faced. The production of steel has switch from the use of natural resources, iron ore, to the reuse of scrap metal. This change is saving the natural environment, as well as, minimising the quantity of industrial waste. To further optimise steel production, the energy consumption of furnaces needs to be minimised and the recovery of the steel slag promoted.

On an annual basis, over 21 million tonnes of steel slag is generated in Europe, of which approximately 2 million tonnes originates from Spain [1]. Steel slag is classified as a waste or a by-product in function of the legislation of the country, which restricts its potential use. Spanish legislation defines steel slag as a waste and determines leaching limits for its classification as an inert, non-hazardous or a hazardous material designated for landfill [2, 3, 4].

At present, Spanish construction companies may choose to use steel slag for specific infrastructure projects, as long as, an impermeable surface limits the interaction of the material with the environment. Other countries, such as Germany, directly consider steel slag to be a by-product which eliminates the difficulties of achieving End of Waste status for the material.

Electric Arc Furnace Slag, a type of steel slag, has been thought to have many potential applications due to its favourable mechanical and chemical properties. The materials high density, mechanical resistance and low concentration of potentially harmful substances are just some of its beneficial factors. A reduction in the cost of steel slag is due to the fact that the material is not mined or obtained from a quarry. This makes slag an ideal substitute for natural aggregates in load bearing layers or as erosion and stabilization control.

From a sustainability point of view, the recovery of steel slag is positive from all perspectives. (a) Economically: steel slag is cheaper in comparison to natural rock considering that it does not need to be mined and if used steel companies do not have to pay a disposal tax. (b) Environmentally: natural resources are spared and space is being reserved in landfills. (c) Socially: steel slag is thought to have a low potential impact on human health and the environment [5].

This study focuses on the potential use of Electric Arc Furnace Slag as a material fill in gabion cages. This application was chosen as the stability of the structure relies on the density of the material used to fill the metal cages. Additionally, gabion cages should be promoted as a sustainable solution to scour and erosion protection, as well as, retaining walls. These structures blend in with the environment and can even create a habitat for wildlife [6].

Regardless of all the positive aspects an outstanding issue still stands, the potential environmental impact which EAF Slag may have on the local area. To confront this issue a series of leaching tests have been carried out, based on the developing European

harmonised framework. Basic characterisation tests were used to determine the main leaching mechanisms, which then define the long term behaviour of the material in a specific application. Conformity tests verify the release of constituents in comparison with the limits defined by legislation and they act as a form of quality control for the material. The harmonization of leaching experiments is working towards the creation of an international database of materials for quick and easy comparison and simple validation of test results. Leach XS is an environmental assessment tool which has been developed to facilitate the creation of this database and the representation of results.

This study outlines what is currently known about EAF slag and the legislation which defines it within Spain. Followed by an outline of the principle characteristics and applications of gabion cages, along with the necessary properties of the material fill. The literature review ends with a focus on the potential environmental concern (leaching) related to this application. The material is then characterised and a specific methodology is used to determine its principle leaching properties, durability and expansion potential. Finally the results from these tests are presented and discussed in detail, from which conclusions will be drawn.

Chapter 2
OBJECTIVES

The principle objective of this study is to determine whether Electric Arc Furnace Slag is suitable to be used as a material fill in gabion cages. To obtain this objective, the material needs to comply with technical and environmental specifications established by regional legislation. For this reason the material need to be tested for its durability and resistance in extreme conditions, as well as, comply with the leaching limits established by the Catalan Decree [2].

To obtain the principle objective a series of secondary ones have been defined in order to focus on individual aspects of the material's behaviour. These were divided into blocks, corresponding to the various sections of this study.

- Determine the physical, chemical and mineralogical composition of the studied material.
- Study the durability of the EAF Slag with a focus on the materials resistance to weathering (through hydration and freeze/thaw testing) and its expansion potential.
- Define the total content of a constituent contained within the EAF Slag in relation to its potential release.
- Determine the leaching behaviour of EAF Slag in a gabion cage application, assuming the slag behaves as a granular material.
- Determine the leaching behaviour of EAF Slag in a gabion cage application, assuming the slag behaves as a monolithic material.
- Study the effect of the pH fluctuation on the release of constituents from the EAF Slag in various scenarios.

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Chapter 3
LITERATURE REVIEW

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The possible recovery of a metallurgic waste material to be used in a civil engineering application is the main focus of this study. Before the functionality and the environmental impact of this application can be defined, a brief introduction to the material (Electric Arc Furnace Slag) and the application in gabion cages is needed.

The present section is divided into three main parts. The first focuses on the production, characteristics and current uses of Electric Arc Furnace Slag, as well as, the legislation which defines its intended use and treatment. The common applications and advantages of gabion cages are discussed in the second part, along with the required properties of the material fill. The last section defines the potential environmental impact of using steel slag in a gabion cage, where leaching is the main concern.

1. Steel Slag

Steel Slag is a non-metallic by-product produced during the fabrication of metallic products. The properties of this rock-like material depend on a number of factors which intervene in the various stages of production. The main factors involve the selection of raw material or scrap metal, the maintenance and control of the manufacturing procedure, as well as, the choice of the appropriate cooling treatment [7].

1.1. History

Steel slag has been used in numerous applications ever since iron was first melted by humans. Starting in 1589, the Germans used this by-product to cast cannon balls, where the English were constructing wharf buildings (1652) and roads (1813) with the dense rock like material [8].

From the beginning of the twentieth century, the use of Steel Slag has been promoted with the introduction of sustainable development. Industrial by-products are now being used in various applications for economic and environmental reasons. The change in perspective regarding Steel Slag has led to modifications the steel making process in order to maximize its use and ensure compliance with specific standards and regulations.

1.2. Types of Slag

The manufacturing procedure of metallic products produces various types of ferrous slag, each with specific physical, mechanical and chemical characteristics. The main differences depend on the type of furnace and the phase in which the slag is produced. The principle types are defined as follows:

- *Blast Furnace Slag* obtained through the melting of iron ore in a blast furnace. The chemical reactions take place throughout the molten steel and not only on the surface. The main types of slag produced are known as air-cooled (ABS) or granulated (GBS).
- *Steel Slag* is characterised in two main types:
- *Basic Oxygen Furnace Slag* (BOS) is the conversion of hot metal to crude steel.

- *Electric Arc Furnace Slag* (EAFS) is obtained through the melting of scrap metal in an electric arc furnace to produce carbon steel (EAF C) or stainless/high alloy steel (EAF S).
- *Secondary Metallurgical Slag* is obtained after further refinement of crude steel. The most common type is Ladle Furnace Slag (LS).
- *Other Slags*, such as de-sulphurised Slag are also produced, but in smaller quantities.

This work is based on Steel Slag, in particular Electric Arc Furnace Slag obtained from the production of carbon steel, as this process is more common than that of stainless or high alloy steel.

1.3. Statistics

Steel slag production by type and the materials main uses has been registered in 2010 by the European steelworks and processing companies. This is done to give an idea of the percentages of the various types of slag which are being produced, *Figure 1*, and how they are being used, *Figure 2*, on a European level. Note that Electric Arc Furnace slag accounts for approximately a third of Steel Slag generation.

Currently, Spain has 24 Steel Mills that use an Electric Arc Furnace, 14 of which are in the Basque Country, which dominates the market with over 45 % of steel production. Approximately 75 % of the Spanish steel originates from Electric Arc Furnaces, which generate between 110 -150 kg of EAF Slag per ton of steel manufactured [9]. In 2011, 15,5 million tonnes of steel were produced in Spain, most of which corresponds to carbon steel (90 %) [10].
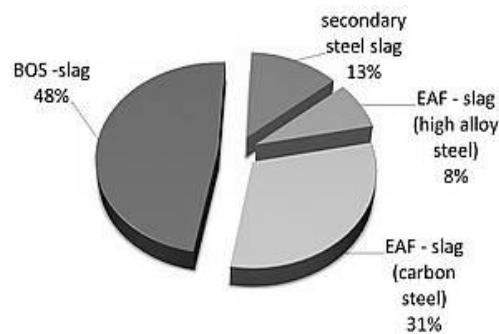
Figure 1: European steel slag production, 21,8 million tonnes in 2010 [11]
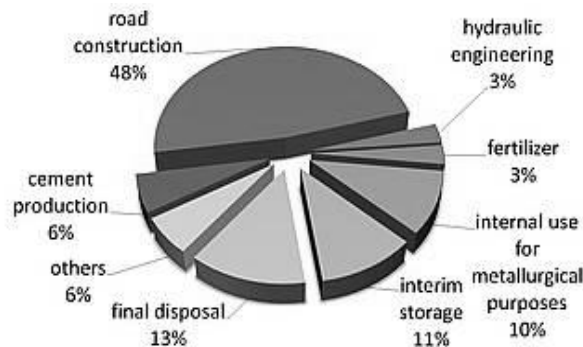
Figure 2: Use of steel slag in Europe for 2010 [11]

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2. Electric Arc Furnace Slag

Electric Arc Furnace Slag is a by-product of the steel making process and is formed by the melting of scrap metal with a small percentage of additives. Once the metal has been completely melted, the dense metal sinks to the bottom allowing the slag to be poured off and left to solidify in a similar manner to lava from a volcano. The EAF Slag is hydrated to accelerate the cooling process, as well as, the stabilization of the material [7]. Different grades of scrap and quantities of additives are used to produce carbon steel or stainless/high alloy steel, depending on the intended use of the final product. The steel slag tapped from these metals, shows variations in its chemical and physical properties.

2.1. Production

The Steel making process in an Electric Arc Furnace (EAF) is shown in *Figure 3*. The first step is to load raw materials into the furnace, which are mainly scrap metal with small amounts of mineral iron, ferroalloys and fluxes. Fluxes, such as lime and dolomite, are used to help eliminate the non-metallic components (impurities) contained in the melted steel. The first stage of this process is known as fusion or primary metallurgy, which results in EAF Slag and un-purified molten steel. Then a secondary refinement process follows on from the initial phase to remove the last impurities from the liquid steel. This process is carried out after the liquid steel has been tapped from the EAF into a Ladle Furnace, where the purification takes place and generates ladle slag [12].
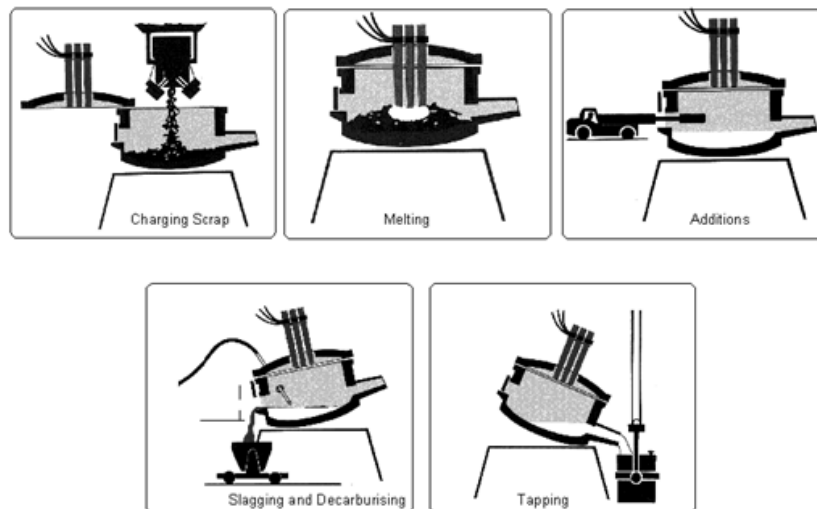
Figure 3: Electric Arc Furnace Steel making process [13]

Electrodes of graphite are used to melt the scrap metal and the additions. When the material has liquefied, a superficial layer of liquid slag is formed and acts as a thermal blanket. This benefits the chemical reactions within the steel and avoiding excessive heat loss. As mentioned before, lime is used to remove impurities from the steel, such as silicates and phosphorus. The use of lime and dolomite as fluxes also explains why the main components of EAF slag are calcium and magnesium oxide.

Oxygen is then injected into the molten steel, forming iron oxide, which makes the molten liquid bubble. Carbon in the form of coke is injected into the slag layer, which reacts with the iron oxide to form metallic iron and carbon monoxide. As this gas escapes the slag, it

forms a foamy substance which floats on the surface of the molten steel, improving the efficiency of the process.

Finally the liquid slag is tapped at temperatures of around 1600 °C [12], leaving the molten steel to continue with the refining process in the ladle furnace. The cooling process after extraction of the liquid slag can be carried out in various ways in function of the required properties. The faster the liquid slag cools the more vitreous and porous it will become. On the other hand, if the liquid slag is allowed to cool down slowly it will form a very hard, compact, crystalline structure. In most cases the slag is tipped out onto a large surface area and water may be used to speed up the cooling process. This is done to ensure the material has a large portion of vitreous material and can be broken down into smaller elements to be transported to its next destination.

Finally, once the slag has cooled, the rocklike material is then transported to a recovery plant, where the material is crushed and sorted into specific dimensions. At this stage metallic separation is used to recover pieces of steel to be taken back to the furnace.

2.2. Characterization

2.2.1. Physical and Mechanical Properties

Electric Arc Furnace Slag is dark grey in colour, porous and tends to cubical, sharp edges when crushed. Its physical and mechanical properties are comparable to those of natural rock and for this reason slag has started to replace natural aggregate in various construction applications. *Table 1* highlights some of the main properties of EAF slag and how it compares to typical natural aggregates.

Table 1: Comparison of EAF Slag to Natural Aggregate [8]

Property	EAF Slag	Basalt	Greywacke
Bulk density (g/cm³)	3,6	3,0	2,7
Compressive Strength (N/mm²)	200	300	200
Impact value (%)	17	17	20
Resistance to polishing (PSV)	57	50	56
Water absorption (%)	1	< 0,5	< 0,5
Resistance to freeze/thaw (%)	< 0,5	< 0,5	< 0,5

The mechanical characteristics of Electric Arc Furnace Slag make it an ideal construction material for road applications. It tends to have a Los Angles coefficient of 20-25% and values of 0,5 – 0,6 for the coefficient of accelerated polishing. Slag's relative bulk density lies between 3,3 – 3,8 g/cm³ and has a corresponding unit weight of 1600 – 1920 kg/m³ depending on the average diameter of the aggregate.

In contraposition to the values listed in *Table 1*, additional literature has measured values of water absorption which can reach 7 %, with normal values of around 3% in volume. High values of absorption can negatively influence the durability of the material in various freeze/thaw cycles [9].

Overall, EAF Slag can be considered a good substitute for natural aggregates in most cases. Its high density and compressive strength, good polishing and freeze/thaw resistance, as well as, its rough surface texture makes it an ideal candidate.

A study which analyses the effects and causes of the aging of EAF steel slag concludes that carbonation and oxidation are the main causes of aging [14]. This study compares the leaching results obtained from a ten year old tram of road and those from laboratory experiments, which were all influenced mainly by pH fluctuation linked directly to the carbonisation of the material.

2.2.2. Chemical Properties

The main chemical components of EAF Slag are calcium (CaO, 27 – 37 %), silica (SiO_2, 11 – 25 %), alumina (Al_2O_3, 1 – 6 %) and magnesium oxide (MgO 4 – 11 %) [8]. These substances originate from the flux used to favour the melting of the scrap metal. The content of iron oxide (FeO, 16 – 26 %) is also of importance in EAF slag. The combination of chemicals gives the slag a basic character, typically with a pH above 11. Pieces of iron are also present in the slag, which are recovered during the crushing and sieving of the by-product. The principle minerals detected in EAF Slag are dicalciumsilicate (Ca_2SiO_4), dicalciumferrite ($Ca_2Fe_2O_5$) and wuestite ($Fe_{1-x-y}Mg_xMn_y)O_z$ [8, 15].

An extensive study in North America [5], states that the metals detected in steel slag are tightly bound to the slag matrix which limits their leaching potential. From these findings the study concludes that slag is a non-hazardous material which is unlikely a source of ground water contamination.

Both the chemical and mineralogical composition of the material depends on the scrap metal used, as well as, the control of the melting process and the composition limits established for the liquid steel. The properties of the EAF Slag can be modified though changes in the chemistry of the molten steel, the cooling process and the post processing of the liquid slag once it leave the furnace. The quicker the slag is cooled, the more vitreous it will become, losing part of its crystalline structure.

Due to the free lime and magnesium oxide found within steel slag, the material has potentially expansive properties. Calcium oxide tends to change volume within a few weeks of hydration, whereas magnesium oxide has a slower expansive process. Another potential problem is the formation of carbonate precipitate, through the reaction of calcium hydroxide with the leachant, which may lead to the blockage of drains. Another point to consider is the basic character of the leachant (pH > 11) after being in contact with the material, which could lead to problems with the corrosion of aluminium tubes and steel [16].

2.2.3. Applications

Steel slag has been recovered and used since the invention of the blast furnace process in the 18th century. With the correct techniques and minimal processing, slag can be used in a variety of applications from construction to fertilisers. The physical properties of steel slag make it ideal for mechanically stable constructions. For this reason, steel slag is beginning

to replace natural materials as an ecologically sound and economically smart construction material [8].

One of the principal applications for EAF Slag is in road construction, due to its durability, Los Angeles coefficient and high skid resistance. The basic character of EAF slag shows good adhesion to bitumen to be used as a surface layer. Slag can also be used as the base or sub-base of road construction, as it has a large bearing capacity. It has been observed that the stiffness of the slag layer increases over time, due to its hydraulic properties [8]. This increases the service life of the road and reduces the need for maintenance.

The use of steel slag is being considered in construction projects, as part of the cement making process, the mortar or as an aggregate in the concrete. Many studies are being carried out with various types of slag to verify these applications. In the case of EAF slag, there is a potential problem due to its chemical composition as it is prone to expansion. On the other hand, this chemical composition can be used to re-mineralise soil and neutralize its acidity. In this sense, slag can be thought of as a replacement for agricultural lime [17].

A continuation a list of the most common unbound applications of EAF Slag [8, 15]:

- Constructional layer: bearing layer to support the pavement and to spread the load of the traffic.
- Non-constructional layer: embankments and fill which may be used for erosion control or stabilization.
- Gabions and Riprap: used as retaining walls, erosion control and as a potential noise absorbing wall. Large aggregate size needed.
- Armourstone: used in hydraulic works for filter layers, ballast layers and erosion control. Maximum aggregate size 250 mm.
- Railway ballast
- Fill for drains in subsoil trenches
- Landfill cover material

Other more experimental applications are emerging, such as the use of EAF slag as a carbon dioxide capture and storage material or to neutralize mine and industrial discharge. Slag has also been used successfully to protect and restore coral reefs in deserted marine areas [17].

From all these possible applications, this study focuses on the potential use of Electric Arc Furnace Slag in gabion cages.

2.3. Legislation

Electric Arc Furnace Slag is considered differently in each country. While some classify the material as a waste product, others make use of most of its production as it holds the status of by-product [11].

This section classifies EAF Slag, compares the norms which define it within Spain and on a European level and make reference to the leaching limits defined by these respective norms.

2.3.1. By-product or Waste Material

Steel slag is classified as a By-product or as a waste material within the European member states. There was no official definition of By-product in European legislation, before the reform of the Waste Framework Directive (WFD) Directive 2008/98/EC in 2008 [18]. For this reason, up until 2008 most member states defined Steel Slag as a waste, a substance which the holder discards, intends to or is required to discard. These waste substances are classified by the European List of Waste 2000/532/EC [19]. Steel Slag is classified as a Waste from Thermal Processes (Class 10) under the group and subgroup:

10 02	**Waste from the iron and steel industry**
10 02 01	Waste from the processing of slag
10 02 02	Unprocessed slag

Note that if slag has been processed (granulation, pelletisation, foaming, solidification with specified heat treatment, separation, crushing or sieving) it is not covered by the European Waste Catalogue and has no corresponding number. The processes mentioned have no intention of changing the composition of the EAF Slag, they are only used to improve the materials properties [20].

Through changing tendencies in construction and the benefits of reusing steel slag, the materials classification is switching to a By-product status. In many cases, metallurgic slag meets the European requirements and specifications in relation to technical and environmental aspects of its intended use. EUROSLAG and European steel and slag industries are working towards this goal of achieving By-product status for steel slag on a European level, by providing the EU Commission with the necessary proof and reports they require. To this date, no environmentally harmful case has been reported where steel slag has been used in accordance to the relevant regulations [8].

To highlight just one of the multiple initiatives towards this change in classification is the European Regulation No. 1907/2006 for Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), [21, 11]. The REACH project intends to replace various national regulations with a single system managed by the European Chemical Agency (ECHA), in collaboration with the FEhS-Institute and Euroslag. This policy came into force on the 1st June 2007. Within this framework, steel slag has been registered as a Substance of Unknown and Variable composition, Complex reaction products or Biological material (UVCB substance). At this point in time and based on the available test results, steel slag does not release any dangerous substances above those establishes by the relevant European standards and Directives [8].

2.3.2. National and European Norms

To reuse steel slag in construction or other applications, it needs to meet the technical and environmental requirements established by harmonised European standards and regional norms.

The Official Journal of the European Union, Directive 2008/98/CE on waste [18], establishes the absolute minimum levels which all member states need to comply with when classifying waste materials. The objective of the policy is to minimize the negative

effects on the environment and human health with the correct management and disposal of waste materials. The limits defined in the directive may be maintained or incremented by regional norms in function of a country's specific environmental and geological conditions.

A harmonized European testing procedure is an initiative to optimise and simplify the classification of materials. The first step is to determine the basic characterization of the material, which is then followed by frequent and effective conformity tests which ensure the classified material has not altered its properties significantly. The basic characterization tests define the main properties and release behaviour of the waste material, classifying it as hazardous or inert. Periodical conformity tests, then measure the critical release quantities from these materials and ensure that they are below the limits defined by the European Directive. Note that the limits given within the European Directive [22] determine the suitability of the material for a specific type of landfill. The possibility of recovering materials for other applications is not contemplated in this Directive.

The current classification of slag as a waste product means that the material needs to obtain End of Waste status before it can be applied. This status is obtained when the material complies with Article 6 of the European Directive 2008/98/CE [18, 11]. This implies a series of tests to analyse the release limits and mechanical properties of the material, as well as, the paper work involved in reclassifying the material. Most of this time consuming procedure could be avoided if steel slag was considered a By-product on a European level.

On a national and regional level the directives are developed based on the EU directive and the best available technical and environmental knowledge. Within Spain on a national level, the General Specifications of road construction (PG-3) and the Concrete construction codes (EHE – 08, Art. 28) contemplates the use of Steel slag as part of projects National regulations are the first step toward an increase in the recovery of this waste material, but differences between autonomies communities are still present today. Note that none of the Directives (for example the Council Directive 89/106/EEC) which contemplate construction materials mention the use of steel slag.

Catalonia follows the limits defined in the European Directive, refer to chapter 5 section 3.3.1.1, with the exception of Fluoride whose leaching limit has been increased to 18 mg/kg of Dry Mass [2]. These values are determined for each material through the conformity test EN 12457-4:2002 (L/S = 10 l/kg). Once the steel slag has passed the leaching limit check, it can be used in one of the applications specified in the Directive with the corresponding limitations. A common restriction for projects involving steel slag is that they cannot be projected in floodable areas (T = 100 years), areas where the water table is less than 2,5 meters below the surface or 100 meters away from drinking water wells. The main applications of steel slag referenced in the Catalan Directive, focus on public infrastructure and are listed below:

- The construction of different road layers. A layer of pure slag may not exceed 70 cm in thickness and an impervious layer must be used on its surface.
- Urbanisation projects in industrial and commercial areas with the need for an impervious superficial layer.

- Levelling of land and creation of embankments, cannot be more than 2 meters in height and need to be covered in soil with a permeability below 9 – 10 m/s.
- Sub-ballast for laying train tracks, the slag needs to be confined and cannot be more than 50 cm thick.
- Filler of closed concrete cases, for use as part of dikes in a port.

In a similar way to Catalonia, Cantabria has based their Directive on that of the European Union. The Conformity test is used to determine the materials leaching limits, which coincided with the values in the European Directive [3]. The applications are the same as the before mentioned with the addition of the potential use of steel slag in cement and as an aggregate in concrete.

The Basque Region has a long history of steel making and handling of steel slag. Due to their experience, they have established their own leaching limits based on part 3 of the Conformity test, which determines the released constituents with a Liquid to Solid ratio of 8 l / kg [4]. For this reason, the limit values cannot be directly compared with those of the European Directive. Note that apart from the standard elements considered by the European Directive, Vanadium has also been included as a key element to monitor. The Basque Environmental Department classifies Steel Slag as an inert industrial waste. As before, the same applications and limitations are considered as those defined in the Catalan Directive.

2.3.3. Limit Leaching Values

The release limits defined by the various Directives are based on the Dutch Decree 'The Building Materials Decree'. As the front runners in sustainable development, the Dutch defined acceptable environmental impact limits based on the variation of local soil conditions. The principle idea behind the maximum releases values was to limit the change in soil properties and composition over a period of 100 years. This validation considers the first meter of soil as a reference and limits its variation to 1 % over the full time period considered [23].

Based on average soil properties within an area, a 1 % variation is calculated for each constituent. This quantity will be the total amount of constituent the material is permitted to release over a period of 100 years. If the material has been tested and it is believed to surpass the limit specified for any one of its constituents, then more extensive research need to be carried out to define the overall potential environmental impact.

Note that mathematical models are used to extrapolate test results over periods of 100 years, with the intention of predicting the total release of a constituent. This leads to results which give an initial approximation of the behaviour of constituents released from the material. The reliability of the estimates will depend on the accuracy of the laboratory results and the determination of the soil conditions, as well as, the analytical model used.

3. Gabion Cages

Gabion cages first appeared as wicker baskets filled with soil, at the beginning of the 16th century for military purposes and to reinforce river banks. The name comes from the

Italian word *gabbioni*, meaning 'big cage'. The concept has evolved over time to the modern day gabion cage, which can be thought of as wire-mesh basket filled with rocks. These baskets are then laced together to form a strong unified multipurpose structure.

Gabion cages are most commonly used as anti-erosion and earth retaining structures in civil engineering, road building, foundation construction, soil stabilisation and landscaping applications [24]. The main advantages of these structures are their flexibility, sustainability, durability and low cost. The structure's customization for each individual project is straight forward, due to its modular qualities.

The location of the project will define if a gabion is assembled and filled manually or by machine. The low cost of manual labour or the need for a neat exterior face finish will determine a manual assembly. For this reason, in developing countries gabion cages are a popular solution which in turn promotes the local industry [25]. Typically, the standardized wire mesh panels are transported to the project site where they are connected to create the box compartments. Locally sourced rock is then used to fill the cages, reducing the cost of transportation.

3.1. Characteristics

A gabion cage is a rectangular basket of woven mesh or welded galvanised steel wire with a diameter of 2 – 3 mm. These cages are usually supplied folded and flat to ease and economise transportation. Once on site, they are assembled manually using wire to lace the edges of the baskets. Diaphragms and internal connections are used to reinforce and strengthen the baskets.

The dimensions, properties and installation of gabion cages are customized for each project. Typically a designer would select the gabion size from the manufacturer's catalogue and then decide whether to use welded or woven steel panels. These choices are determined by the location of the project and the conditions the structure will need to withstand. Welding is carried out by specialised machinery and in regulation with specific standards and quality controls. The woven configuration needs to be double or triple twisted to prevent the wire from unravelling if cut or damaged [26], as seen in *Figure 4*.

Welded wire mesh gabions are as flexible as woven mesh ones when assembled, but they offer a higher tensile strength. Additionally, the welded configuration offers the same tensile strength in both directions, whereas the twisted wire can only withstand half of the tension in the direction perpendicular to its axis [27].
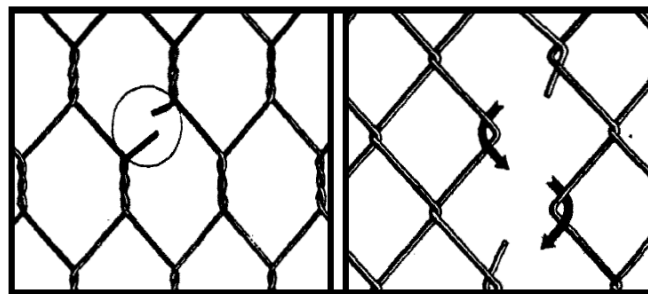
Figure 4: Woven Wire Mesh, double twisted compared to loosely woven [26].

As the welded panels are more rigid, they offer better dimensional accuracy once assembled. These panels are easier to handle as they do not stretch or bulge, as well as being self supporting which simplifies placement and filling. Preformed spiral binders, which evenly distribute stresses along the joint, are used to connect these welded panels. In the case of the woven wire mesh, a labour intensive process of lacing is used to join the components of the gabion basket.

Finally, a greater corrosion resistance can be achieved with prefabricated welded meshes than with the twisted option. This is because of the stretching and friction of the steel wires covered with the Polyvinyl Chloride (PVC) during the twisting process. The PVC coating allows the gabion cage to be in constant contact with water which increases their service life. A standard zinc coating gives a structure a lifespan of 35 years, whereas an additional polymer coating can extend this to 75 years [27].

Regardless of all the beneficial aspects of welded wire panels, the woven system is used in applications where the gabion needs to adapt to the shape of its foundations and where the aesthetic aspect is not of importance.

3.2. Gabion Cage Variations

Gabions have been classified into different groups depending on their dimensions and functionality. Listed below are the common names given to these structural blocks [27], which are then combined for use in varies applications, listed in the following section 3.3.

- Standard Gabion: mainly used to construct retaining walls. These structures are free draining and one of the most cost effective structures available. The standard dimensions are 1 meter high by 2, 3 or 4 meters in length.
- Trapion: is a gabion with a trapezoidal cross section. This solution is used to give the structure a sloped finish, rather than a stepped face. It is common to create these gabions by modifying the standard rectangular ones on site.
- Gabion Mattresses: have a relatively small height (15 – 30 cm) in relation to the lateral dimensions (2 – 6 m). The dimensions of the rocks used should not exceed 2/3 of the height of the mattress. They are generally used as slope stabilization, channel lining and as scour protection of riverbanks and coast lines. The main advantage of gabion mattresses is their adaptation to differential settlements while maintaining their functionality.
- Modular Wire Faced Wall Systems: Filled with compacted soil and not rock. Before the cages are filled they are lined with a Geo-textile to prevent the soil particles from escaping, while maintaining the permeable property of a gabion.
- Modular Block Faced Systems: The front face of the gabion cages is laid with coloured concrete blocks to create a neat appearance without losing the structural benefits of the gabions [27]. Easily combined with Anchor Mesh System to achieve retaining walls of heights which can exceed 15 meters.
- Gabion Cladding: Architectural concept, which uses smaller gabions to cover a structural wall. The average depth of the cages ranges between 20 – 30 cm.

3.3. Applications

Gabion cages and its variations have been used effectively in multiple applications over many decades. Erosion control and stabilization have been the principal functions of these structures. Below a more extensive list of applications with their key benefits are mentioned [27]:

- Retaining walls: are quick and cheap to install and can be done without specialized equipment or skilled labour.
- Green or Ecological Walls: environmentally beneficial and aesthetically pleasing as they promote the growth of vegetation.
- Mechanically Stabilized Earth Wall: combined with an Anchor Mesh System can be used to reach impressive heights as the strength and stability of the structure is improved.
- Weir and Spillway components: good energy dissipater due to the stones resistance. The structure gains strength as sediments are collected within the voids. The gradient of the river bed can be modified to slow down water flow and reduce erosion.
- Revetments: prevent erosion and stabilize slopes of river banks and coast lines. Their function is to dissipate the energy from incoming waves or heavy water flow.
- Scour Protection/Flexible Aprons: use gabion mattresses along the contour of structure to avoid progressive scouring.
- Coastal and Beach Protection: dissipate energy from waves on impact.
- Landslide control: in mountainous areas where rocks are abundant.
- Noise Barrier
- Landscaping and Architectural Purposes

3.4. Advantages and Disadvantages

Gabion cages can have many positive aspects when used in construction projects. In continuation a few of these beneficial aspects are highlighted [27], which are then followed by a few structural limitations.

- Flexibility: The cages allow for deformation without breaking. In other words, the gabions adapt to the grounds movements without losing its structural efficiency, as a monolithic structure would. The modular quality of these structures makes the project design very flexible.
- Strength: From the union of the individual gabion cages working together as a single structure. Tension is formed in the wire mesh, which reinforces the structure. The strength can be further improved with the use of diaphragms.
- Durability: Gabion efficiency increases with time. During the early stages of use, particles and vegetation will collect between the rocks, making the structure a naturally permanent part of the environment. For this reason, minimal maintenance is required.
- Environmental friendliness: The structure blends naturally into the environment with the use of local materials and the growth of vegetation between the rocks.

Additionally, these structures have a positive aesthetic appearance, as multi-coloured rocks can be used with different textures and shapes. [26].

- Permeability: Eliminates the need for a drainage system and prevents the build up of hydrostatic pressure. Making gabion cages an ideal structure for protecting slopes from erosion.

- Economic: Wire mesh gabions are less expensive than most construction materials, when the rock fill is sourced locally. Waste materials may also be used in place of natural stone. No specialized machinery or skilled labour is needed for the installation and minimal preparation is needed for the foundation of the structure. Where necessary the first layer of gabion cages can be laid in water or mud.

- Simple installation: Minimal preparation work is needed before installation starts. The work force is easy and quick to train.

- Immediate use: the structure can withstand the full load it has been designed for immediately, unlike concrete structures which need a number of weeks before they can be used to their full extent.

Having listed the strong points of gabion structures, one must also consider the limitations. Gabions may be placed directly on any type of soil, but care should be taken so that preferential flow does not form along this interface [25]. If this occurs it may lead to partial or total failure of the structure. This problem can be easily solved with the use of a geotextiles which act as a filter layer to retain fine particles [28].

Once all the necessary geotechnical considerations have been made, the only remaining concern is the maintenance of the gabion structure. The baskets are designed to be low maintenance, but vandalism or continuous abrasion of the steel wire could lead to the opening of a cage and the collapse of the structure.

3.5. Material and Filling

The most common natural materials used as fill in gabion cages are granite, quartzite, sandstone and intermediate species [26]. The choice of material depends on what is locally available to minimise the cost of transportation. The main characteristics required are a suitable compressive strength and durability to resist loadings, as well as the effects of water (frost resistance) and weathering throughout the design life of the structure.

A well graded stone mixture increases the density of the final structure, but dimension limitations are set to ensure the material does not escape the wire mesh and can be easily packed together. Both rounded and angular stones can be used in gabions as it has no effect on its functionality. The dimensions of the stones can be anything between 70 to 400 mm, depending on the separation in the wire mesh and the specific application. As a general rule, the dimensions of the stones should be more than 1,3 times the wire mesh grid (1,5 if the gabion is to be used in underwater conditions) [26, 25].
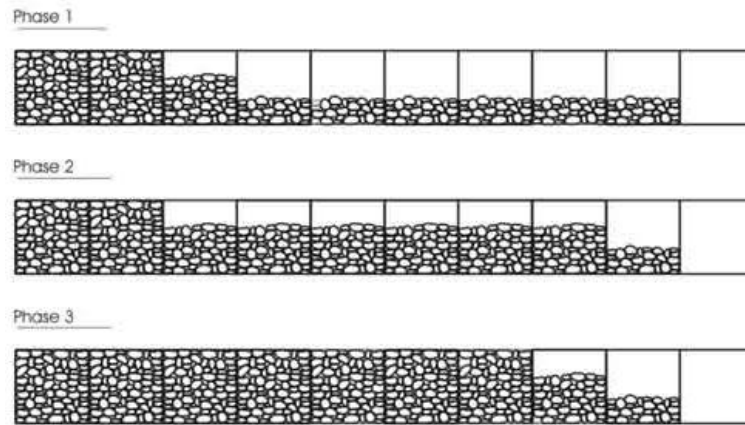
Figure 5: Staged Gabion filling process [26]

The filling of the gabion cages may be done by hand, mechanized or a combination of the two, in function of the project requirements. The goal of manual installation is to minimize the voids created between the stones and to produce a neat finish of the exterior face. Considering the average minimum required density of the material 2300 kg/m^3, the filling process should result in a minimum bulk density of at least 1750 kg/m^3 [26]. The void porosity can vary between 25 to 35 percent, in function of the chosen filling method. In the design of a retaining wall structure, a more conservative 40 percent is assumed [28].

The cells should be filled in stages, see *Figure 5*, to avoid local deformation. At no time shall a cell be filled more than a third of its adjacent cell, this is done to position and tension stiffeners, which strengthen the structure. In a 1 x 1 meter gabion, stiffeners are located at third points, see *Figure 6*. Note that the gabion structures should be securely connected to each other before the filling process begins. This ensures the individual cages work together as a single unit. Spiral binders, ties or lacing are used for this binding operation.
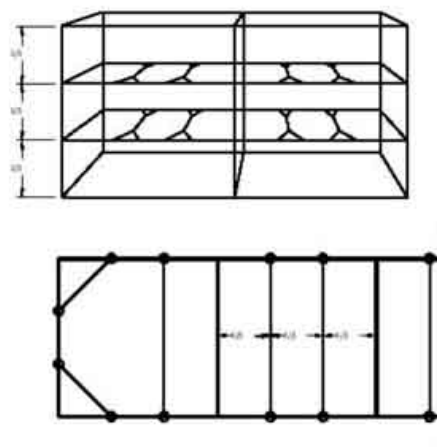
Figure 6: Supports and stiffeners within a Gabion Cage [26]

4. Environmental Impact

The main focus of this study is to determine the potential environmental impact of using Electric Arc Furnace Slag in gabion cages. So far, the origin and characteristics of the material have been defined, as well as, the requirements for the installation of gabion cages. Now, the focus falls on the potential environmental impact this application may have.

4.1. Leaching

The main concern with regards to the environmental impact of a material is the potential release of contaminants into the environment, due to the contact with water. This process is known as Leaching and may occur at any point in the full life cycle of the material, from production to final disposal. Not only is the release of constituents important, but also the migration of these elements with groundwater, surface water or their accumulation in the soil [29].

A study analysing the hydrogeochemistry of Alkaline Steel Slag Leachates in the UK showed low concentrations of potentially harmful or contaminating substances originating from steel slag [30]. This data had been collected over the past three decades at various points downstream from a steel slag disposal site. The main components of this site were blast furnace bottom and steel slag, resulting in an extremely alkaline (pH > 10) and potentially contaminant surface runoff. Differences in the chemistry of the ground water and the soil properties resulted in significant changes in the formation of precipitants, as well as, the distance travelled by the constituent. The study concludes that steel slag has a low concentration of potentially problematic trace elements and it is apt for use in passive treatment wetlands.

When considering a number of different materials used in various applications, a common methodology needs to be followed to determine the total release and/or peak concentrations of the individual constituents. These parameters will depend on the location of the construction project in relation to sources of drinking water. In order to define a series of tests to determine the leaching potential of various materials, one needs to consider the mechanisms and factors which define this release phenomenon.

4.2. Mechanisms

Leaching mechanisms have become the main focus of regulations, instead of concentrating on individual material properties. This change in test development, limits the experiments to determining a few key parameters which are sufficient to define the release potential of a material. The dominant leaching mechanisms have a slight dependence to the scenario in which the material is used, but they are not dependent on the formal state of the material. The key processes which define the release of the material may be controlled by physical or chemical processes [29].

Release behaviour can be divided into two main groups, one refers to Monolithic materials and the other to Granular materials. This division is made as monolithic materials tend to have a diffusion controlled release, whereas granular materials are dominated by a percolation mechanism. Percolation can also be understood as filtration of a leachant through a granular material, causing surface wash-off and dissolution simultaneously.
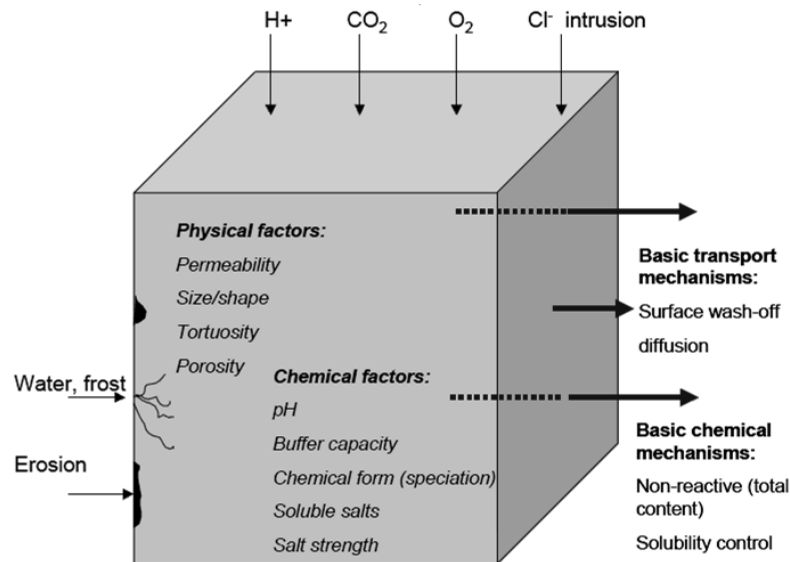
Figure 7: Leaching Mechanisms of a Monolithic Material [29]
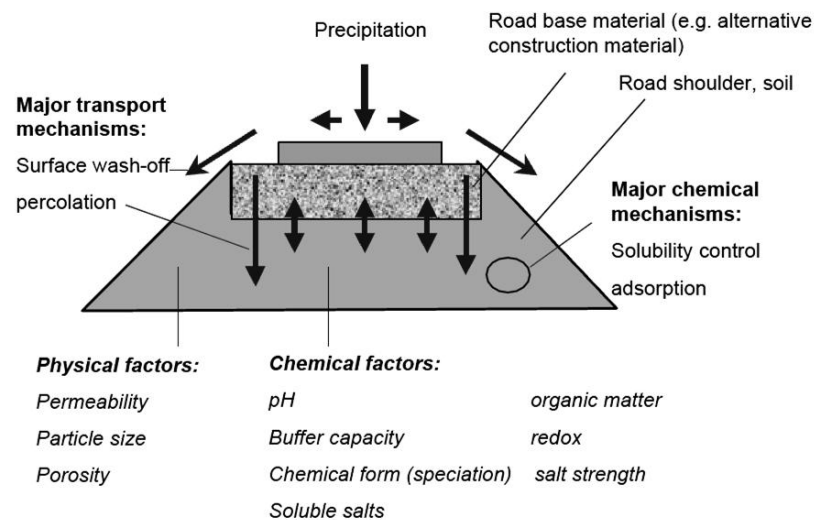
Figure 8: Leaching Mechanisms of a Granular Material [29]

Monolithic materials include products like concrete and brick, where examples of granular materials are sand and gravel. *Figure 7* and *Figure 8* represent these two categories of material, note that they are both influenced by the chemical and physical processes.

The distinction between chemical and physical factors has concentrated on the behaviour of inorganic constituents. Less information is available regarding the behaviour of organic substances, some effects are known but more research needs to be carried out in this field to determine the main release mechanisms [29]. Additionally, it is evident that external factors which originate in the specific application scenario influence the behaviour of the materials. Preferential flow paths and the flow rate are the main external factors.

4.2.1. Chemical Mechanisms and Factors

The three basic chemical mechanisms which control the release of constituents are listed below, followed by factors which influence their behaviour.

- Solubility Control: the capacity of a mineral to dissolve within its medium, the dissolution of a constituent.
- Sorption Control: affinity for adsorption to a reactive surface due to opposite charges. Normally appears as the dominate mechanism in granular materials.
- Total Content: when a constituent is not reactive, it simply dissolves in a medium, a good example of these constituents are salts. Tends to be the dominate mechanism in monolithic materials.

Now that the main chemical mechanisms are known, the following factors influence these mechanisms in both a positive and negative form.

The pH of the surrounding environment and that of the material itself plays a large role in the release of constituents. This is because the dissolution and sorption processes are pH dependent. Each material and each constituent released has its own unique release curve in function of the pH of the leachant, which defines the behaviour of the material in various situations. The chemical form of the constituent will also have an influence on its leaching behaviour, for example, the behaviour of an element changes if it is in an oxidized or a reduced form [29].

Laboratory tests have shown different pH values in comparison to lysimeter tests, which is believed to be caused by variations in the inflow of carbon dioxide (the samples contact with air) [31]. These finding make it clear that chemical conditions define the leaching behaviour, but they are incomplete without the appropriate geochemical model to back these results in real applications.
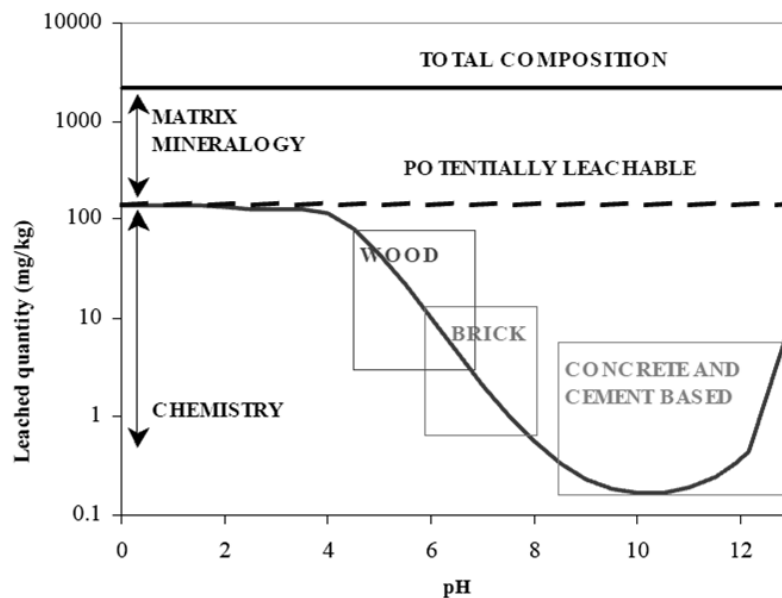
Figure 9: Comparison of Total Composition and real released quantity in function of the pH [29]

Figure 9 relates the total composition of a constituent within a material with the real released quantity of that constituent, as well as, the potentially leachable amount. Note that this is a counterintuitive relationship, the more of an element present within a material, does not necessarily mean this will be the element with the highest release. Soluble salts are an exception to the before mentioned.

Redox influences in the chemical form of the constituent, oxidation of a reduced material usually increases the leached quantity. Acid-base buffering or neutralization determines how the pH develops over time under the influence of external factors. Organic matter and Dissolved Organic Carbon (DOC) have the affinity to bind heavy metals and their presence within the material studied can increase leaching by several orders of magnitude [29].

The liquid phase of the leaching process is influenced by the concentration of the elements within the liquid and the interaction between these and the materials components. A rise in temperature increases chemical reactions and tends to lead to higher solubility. Finally, time must not be forgotten in the leaching process, as material properties may change over time influencing the outcome of a project.

4.2.2. Physical Mechanisms and Factors

In the same way as the chemical mechanisms, there are three basic transport mechanisms, which are then intensified or decreased by various physical factors. The three mechanisms which focus on the transfer of constituents from the material to the water phase are as follows:

- Advection or Percolation of constituents which are taken along with the water as it runs along or through the material, usually caused by rainfall.
- Diffusion occurs in the absence of flow, it is a process which refers to the movement of molecules due to concentration differentials. This mechanism is dominant in pores.
- Surface Wash-off is similar to advection, but the term refers to the initial wash-off of the soluble material.

These transport mechanisms are influenced by a series of physical factors, as well as, if the material is present in a granular or monolithic form. Typically, leaching of a granular material is percolation dominated, whereas for a monolithic material, leaching is controlled by diffusion.

The particle size determines the distance a constituent must travel to reach the water phase. In the case of small dimensions, depletion of an element may be achieved over a relatively short period of time. Porosity of a material can increase the transport rate of a constituent, which is directly related to a higher release. These factors are especially important in the case of monolithic materials, as the diffused quantity of a constituent is directly related to the surface area of the material [32].

The following factors have more relevance in relation to monolithic materials than to granular ones. Permeability defines how easily the water can enter the material and how fast

constituents will be released over time. Tortuosity defines the rate of diffusion, as the length of the path travelled by a constituent to exit the material over the distance in a straight line between the two points. Erosion or abrasion of the surface will increase the surface area and expose a new fresh surface of the material, both factors increase in release. Finally, the intrusion of an expansive salt or ice into the material may lead to cracking and the formation of new surfaces, which again increase the surface area of the material. [29]

4.3. Leaching Tests

The leaching mechanisms defined in the previous section classify the release behaviour of most construction materials. This classification has allowed a restructuring of the testing approach. Instead of analysing each individual scenario, a standardised testing method has been established. The goal of this method is to provide a simple process to classify a material and determine its potential environmental impact when used in a specific application. Two steps can be identified in this method, the source term and the impact scenario. The first, *the source term*, defines the release of the constituent. The second step is *the impact scenario*, where the specific location of the project is taken into consideration and the dispersion of the contaminant in that medium. To maintain a general overview of the environmental impact, this study has focused on the first step, the determination of the source term.

The harmonisation of test methods has led to the need to classify the basic leaching characteristics of a material through percolation, monolithic and pH-dependence testing [33]. The norms are designed to complement each other, as each one highlights a specific leaching mechanism. The results obtained from only one of these tests may lead to misinterpretation of the leaching mechanism and for this reason various tests need to be carried out in order to characterise the material. These tests define the dominating leaching mechanisms of a material, but they are time consuming procedures. For this reason a compliance test has been defined, which is quicker, easier and more efficient for checking and approving materials. This test assures the material falls within a reasonable range for which it was first classified. Once the results for the compliance test have been verified against the leaching limits of the region, the material is apt for use.

One major benefit from an international standardised testing scheme is that a common database of leaching results can be compiled with data from various laboratories and a number of different materials. This database would simplify future studies and avoid repetition of tests. Through the comparison of data, one can optimise processes to obtain better waste products and effective construction materials.

A hierarchic structure has been developed by CEN TC 292 *Characterisation of waste*, which is based on the concept of initially characterising the material's principle leaching behaviour. This stage is then followed by series of compliance and verification tests at more regular intervals [29]. These tests are described in detail below in sections, 4.3.1, 4.3.2 and 4.3.3.

To ensure the correct interpretation of the sections referring to leaching, it is important to have the correct definition of the following terms, as established by the Technical Committee CEN/TC 292 *Characterisation of waste*.

- *Eluate*: a solution obtained from a laboratory leaching test.
- *Leachant*: liquid that is brought into contact with the test portion in the leaching procedure, in most cases this will be demineralised water unless specified otherwise.
- *Liquid to Solid ratio* (L/S): litres of leachant per kilogram of dry matter.

4.3.1. Basic Characterization Tests

The objective of these tests is to characterise the release behaviour of the studied material. Common controlling factors or mechanisms are defined to easily categorise the materials tested. This procedure facilitates the judgement and definition of specified criteria of a material for a specific project. The key variables analysed in the basic characterisation, which will later be used to verify the compliance tests, are the liquid/solid ratio, leachant composition, pH dependence and the ageing of waste material. The variability of the test results may also be determined once a reasonable number of similar materials are registered in an international database.

The tests defined for the basic characterisation are as follows:

- Percolation test, EN 14405 [34], designed to determine the leaching behaviour of a granular material, tested at the natural pH of the material and with a L/S ratio of 10 l/kg to simulate a long term scenario.
- Tank test or Monolithic diffusion test [32], under development by CEN TC 292 and based on NEN 7345. This test consists in collecting and renewing leachants from a tank, where a monolithic specimen has been for a specified amount of time.
- pH dependence test, PrEN 14429 [35], defines the influence of pH on the release of constituents with a predefined acid or base addition. A crushed test sample is combined with the leachant with a L/S ratio of 10 l/kg until an equilibrium condition is met (48 hour period). This test gives an indication of the buffer capacity of the material.

More details referring to the methodology of the above tests can be found in Chapter 4, section 4.1.

4.3.2. Compliance Tests

The main purpose of compliance tests is to ensure that a material complies with the studied reference material used for the classification of the material, as well as, the limits defined in regulations. From a regulatory point of view, compliance tests are used to categorise materials as inert, not hazardous or hazardous. More information regarding the details of this test can be found in chapter 4, section 4.2.

Compliance testing is growing in popularity as it is quicker, cheaper and simpler than the full characterisation of the material. The main difficulty related to this method is the determination of an acceptable range for which a material is still considered the same as the reference material. To solve this problem, many tests need to be carried out on similar materials and relations need to be defined between characterisation and compliance testing.

At present, most Directives base the leaching limit values on the various parts of the EN – 12457: Conformity Test [36]. This assumes that the classification of the material, as apt for

the application, has been carried out with the basic characterisation tests at a prior point in time.

4.3.3. On-site Verification

On-site verification, also known as quality control, intends to determine if a material complies with its predicted behaviour. In general, quick and inexpensive controls are carried out, such as, visual checks and an administrative inspection [29].

4.4. Assessment

The determination or prediction of leaching quantities depends on the scenario in which the material tested will be applied. Predictions are made based on the results obtained from the experiments listed in the previous section. These tests are designed in such a way that the results can be transformed to a number of different scenarios and various applications [33].

To assist the analysis of the leaching data, Leach XS [37], an environmental impact assessment tool is used. This software is designed to estimate the short and long term release of constituents from a specific material designated for use, recycling or landfill purposes. Through the use of this tool, an international database is being developed in order to have a point of comparison for materials with similar properties and origin. For more information on the functionality of Leach XS refer to chapter 4, section 4.5.

The data obtained from laboratory experiments is evaluated in function of the materials dependence to pH and its reaction in acidic or basic environments. The constituent's reaction to other elements (ionic strength and dissolved organic carbon) within the leachant is also considered. Additional key parameters consider in these analyses are the release rate of the constituents and the liquid to solid ratio.

Chapter 4
MATERIALS AND METHODS

The objective of this chapter is to explain the methodology followed to characterise the physical, mechanical and chemical properties of Electric Arc Furnace Slag, as well as, the series of tests applied to determine its potential environmental impact. The results of these tests are analysed in chapter 5.

The experimental campaign is made up of three main blocks, each of which focuses on a particular aspect of EAF Slag and its potential use as a material fill in gabion cages. The first section explains how the material was characterised from a physical and chemical perspective, followed by a study of its durability and expansion potential. The final block focuses on determining the potential leaching mechanisms of the EAF Slag.

The whole experimental campaign has been carried out in the Construction Materials Laboratories (B1-004 and B1-S1) of the Department of Construction at the Polytechnic University of Catalonia (UPC), Barcelona, Spain.

1. Material

The Electric Arc Furnace Slag studied was provided by ADEC Global, S.L., Vallirana (Barcelona) a company which specializes in the recovery of steel slag. The steel slag originates from the electric arc furnaces of CELSA Barcelona, *Compañía Española de Laminación S.L.*, situated in Castellbisbal (Barcelona). CELSA is one of the largest steel producers in Europe and most of their production is common carbon steel.

CELSA Barcelona produces 2,4 million tons of steel annually all of which is produced in Electric Arc Furnaces. According to a report published by CEDEX [9], between 110 -150 kg of EAF Slag are produced for every ton of steel. This means that over 264 000 tons of waste material are produced on an annual basis in Catalonia alone.

1.1. Sampling

Approximately 250 kg of EAF Slag was collected from ADEC Global, S.L. at the beginning of October 2012. This quantity of material was needed to ensure a representative fraction for the whole experimental campaign, as defined in UNE – EN 932-1: Test for general properties of aggregates. Part 1: Methods for sampling. [38]. The objective of this norm is to obtain a representative sample of a material with the average properties of the entire batch. The sample was collected manually from piles of aggregate at different heights and depths. The aggregates had previously been separated into a group with a diameter of 80 – 140 mm. This dimension was chosen as an ideal fraction for use in gabion cages.

The age of the EAF Slag collected from ADEC is unknown, but from the moment of fabrication till the time of sampling, more than six months had passed. After collection the slag was stored in sealed plastic barrels until the start of each test.

1.2. Sample Reduction

The next stage was to reduce the sample through the methods specified in UNE – EN 932-2: Tests for general properties of aggregates. Part 2: Methods for reducing laboratory

samples [39]. Quartering was used to divide the total amount of material into subcategories for the individual series of tests.

Approximately a quarter of the total amount of EAF Slag collected was crushed and grinded to reduce the aggregates size in preparation for the experimental campaign. In function of the desired final diameter of the aggregate, more or less sample will need to be prepared to obtain the minimum representative quantity of subsample. Any metal flacks or pieces were removed with a magnet during crushing to minimize the possible damage of the equipment. The quantity of steel removed from the test samples was not recorded due to the large variability in findings.

A sample splitter and a rotating sample divider were used to separate the subsamples into smaller quantities for the individual tests. The rotating system was used for finer particles (less than 1 mm) and acts on vibrations and a rotating motion to split the sample into eight subsamples. The sample splitter was used with larger particles and divides the sample into two equal parts.

2. Characterisation

This section defines the tests used to characterise the physical properties of Electric Arc Furnace Slag, as well as, the material's chemical and mineralogical composition.

2.1. Size Distribution

The particle size distribution was determined based on UNE-EN 933-1 Test for the geometrical properties of aggregates [40]. This Norm is limited to a maximum aggregate diameter of 63 mm. For this reason, the sieving method could not be used to characterise the size distribution of the EAF Slag. Seven aggregates or test units were selected to represent the original test sample. These were then weighed and their dimensions measured individually using a Vernier Caliper, for higher accuracy and precision.

2.2. Density and Water Absorption

The Norm for determining the density and absorption of an aggregate, UNE-EN 1097-6 Tests for mechanical and physical properties of aggregates [41], faces the same limitation as that for the size distribution, particle sizes above 63 mm are not commonly considered. Annex B of this Norm relates to larger particles, where a test unit is defined as a single aggregate. Again seven aggregates or test units were selected to represent the original test sample.

2.3. Chemical Composition (XRF)

The chemical composition of the EAF Slag is determined through X-ray fluorescence spectroscopy (XRF). This technique identifies and quantifies the main chemical components present in the EAF Slag studied. Knowledge of the materials composition helps to identify elements which may have a negative environmental impact if present in large quantities.

A sample of EAF Slag was prepared for X-ray fluorescence by grinding the material down to below 0,063 mm followed by calcination at 1000ºC for an hour. The sample was analysed with a *Philips PW 2400* spectrophotometer.

2.4. Mineralogical Composition (XRD)

The elements identified in the chemical composition of the EAF Slag are present in the solid matrix of the material with a crystalline or amorphous structure. The form in which the chemical components are arranges is determined through X-ray Diffraction.

The test sample was ground down to below 0,063 mm and sent to the scientific-technical services of the University of Barcelona for an X-ray diffraction analysis. The specifications of the machine used are as follows: *ANalytical X'Pert PRO MPD Alpha1* powder diffractometer in *Bragg-Brentano* $\theta/2\theta$ geometry of 240 millimetres of radius Cu Kα_1 radiation ($\lambda = 1.5406$ Å).

The crystalline components were then identified on the Spectrum using the data base from the International Center for Diffraction Date, Powder Diffraction File Search Manual, 1998. The following specialized software, X'Pert HighScore 2.0 [42], was used to interpret the results from the diffraction spectrum.

3. Durability

These tests were carried out to determine the durability and potential weathering of the EAF Slag. This series of tests was chosen and modified to represent the natural conditions of aggregates used in gabion cages.

3.1. Autoclave

NLT-361/91 Determine the degree of aging of Steel Slag [43] is a norm developed for road construction, but will be used to determine the aging characteristics of the EAF Slag in gabion cages. Seven test units of whole aged aggregate were selected. Each unit was subjected to five cycles in the Autoclave to ensure full hydration of the material. Each cycle lasts 4 hours, in which the Autoclave reaches temperatures of 135°C and 2 atm of pressure. This process is thought to accelerate the hydration of any remaining calcium and magnesium oxide. The hydration of the material produced in one cycle is similar to that which occurs during one year of exposure to the elements.

3.2. Accelerated Expansion

Section 19.3. of the Norm UNE-EN 1744-1 Tests for chemical properties of aggregates. Part 1: Chemical analysis [44], refers to a method which determines the potential expansion of steel slag.

EAF Slag was crushed into a range of dimensions and sieved to fit a specific size distribution curve. The test was duplicated with 4,5 kg of material in each case. The EAF Slag was compacted into cylindrical moulds and placed on a water vapour generator. As the steam passes though the compacted sample, it generates optimal hydration conditions for elements of free lime and/or magnesium oxide. The volumetric variations of the test samples were continuously recorded at the centre point of the sample during seven days.

3.3. Weathering

The main objective of UNE-EN 1367-2: Tests for thermal and weathering properties of aggregates. Part 2: Magnesium sulphate test [45] is to determine the behaviour of a material subjected to a series of freeze/thaw cycles. The dimensions of the test sample were not

reduced as required by the Norm. It was decided to test the reaction of the whole test unit as it would be used in gabion cages.

Four aggregates were selected for this experiment, for which 12 litres of dissolution was prepared with distilled water and 18 kg of crystalline salt. The test consists of cycles made up of 16 hours of hydration in the saturated magnesium sulphate dissolution and 24 hours of drying at 105ºC in an oven. The cycle was repeated five times as specified by the norm to simulate the freeze/thaw process of water within the pores of the material. Once the cycles were complete, the crystallised salt is removed from the test samples. A visual inspection was then carried out to highlight any signs of disintegration or fractures.

3.4.   Los Angeles Abrasion Test

The following test was carried out to comply with the requirements of the material used to fill gabion cages, UNE-EN 1097-2 Tests for mechanical and physical properties of aggregates. Part 2: Methods for the determination of resistance to fragmentation [46]. This norm applies to larger dimensions of natural or artificial aggregates which are used in construction and civil engineering. The Los Angeles Abrasion Test determines a coefficient which represents the percentage in mass of the sample that has been crushed to below 1,6 mm after a series of rotations with abrasive material balls.

The test portion consists of material with a particle size between 10 and 14 mm, of which 60 % passes through the 12,5 mm sieve. Any fine particles were washed off the individual material fractions. These were then dried and weighed separately to ensure the correct percentage in the total test portion of 5 000 ± 5 g of dry mass.

A Los Angeles Abrasion Test machine was loaded with the test portion and 11 steel balls of 47 ± 2 mm in diameter and 400 – 445 g in mass. The rotating drum turns 500 times at a constant velocity of 32 ± 1 r.p.m. At the end of the test, the material is removed from the drum and passed through a 1,6 mm sieve. The retained test portion is then washed and dried at 105 ºC until constant mass is reached.

4.   Leaching

Various European norms have been analysed, characterised and assessed to determine the chemical components which are being released from waste materials. The focus of this process is to create a homogeneous European test structure to define the dominant leaching mechanisms that characterise waste materials, for further information refer to chapter 3, section 4.3. The reason for focusing this initiative on leaching is to avoid harming the natural environment, as well as, human health.

This section describes the main points of the Norms used to carry out the Basic Characterisation and Compliance Tests, as well as, the difficulties faced in their application. The attack of Aqua Regia, the Total Content of Chrome, Chlorides and Sulphates will also be carried out to determine the quantities of the potentially leachable constituents. These tests are not specific of waste material characterisation, but their outcome will be useful for the analysis and discussion of the results. This will be followed by a detailed description of how the physical and chemical characteristics of the eluates are obtained through ICP-MS,

HCLP and the measurement of the conductivity and pH. And finally, a presentation of the functionality of Leach XS an environmental impact assessment tool.

In order to ensure an adequate analysis of the eluates, they need to be stored and preserved correctly. From each fraction of eluate collected, 200 ml will be stored in labelled plastic bottles for later analysis. This volume is divided into two bottles, one for ICP-MS and the second for HCLP. In order to avoid the segregation of chemical components, 1 % of nitric acid (1 ml) is added to the eluate sample being sent in to ICP-MS.

The dry residue of the waste material is a value needed in almost all of the leaching tests. According to UNE-EN 1097-5 [47], the dry residue (w_{dr}) of a material is determined through its mass once the material had reached a constant value in an oven at 105 ± 5 ℃. The dry residue is calculated as follows:

$$w_{dr} = \frac{m_d}{m_r} \cdot 100 \qquad [\%]$$

Where

w_{dr} Dry residue of waste expressed in percentage [%]

m_r Mass of the un-dried test proportion expressed in grams [g]

m_d Dry mass of the test portion expressed in grams [g]

All of the following tests have been carried out at room temperature 20 ± 5 ℃, unless specified otherwise.

4.1. Basic Characterisation Tests

The basic characterization tests carried out in this experimental campaign refer to both granular and monolith materials as it is unclear which will dominate the use of EAF slag in gabion cages.

4.1.1. Percolation

The following Norm CEN/TS 14405 Characterization of waste [34] was used to determine the leaching behaviour of the EAF Slag under specified conditions in the up-flow percolation test. The test is designed to determine the leaching behaviour of inorganic constituents from granular waste materials. The norm does not intend to represent a specific scenario, but the hydraulically dynamic conditions can be thought of as the infiltration of rainwater through the granular waste material. Continuous vertical up-flow is implemented, instead of down-flow, to ensure the material in the column remains saturated. As the leachant is pumped through the column at a constant flow rate, eluate is collected in several separate factions which will each have a specific Liquid to Solid (L/S) ratio.

4.1.1.1. *Equipment*

Three plastic columns with a diameter of 5 cm and a length of 30 cm were fitted with a top and bottom piece, as well as, filters to avoid fine particles from leaving the column. An adjustable volumetric pump was used to control the leachant flow rate through the material. A series of plastic bottles supplied the leachant (demineralised water) to the system while others collect the eluate once it has passed through the material. The test setup is shown in *Figure 10*.

Figure 10: Percolation test set-up in accordance to CEN/TS 14405

4.1.1.2. Sample Preparation

EAF Slag was reduced to below 4 mm to be apt for this test. Approximately 2,5 kg of material was prepared for each column or test (7,5 kg in total). Ideally the material should have been tested with its naturally aged surface at its original size, but due to the diameter of the column and the fact that the norm does not consider aggregates of this dimension, the material was modified.

4.1.1.3. Test Procedure

Firstly the columns (including the top and bottom connections) and the plastic bottles were rinsed with nitric acid and demineralised water consecutively, to clean them of any unwanted residues. The dry weigh of the three columns including the filters was noted before the start of the blank test.

Blank tests verify that no contamination has occurred during the test process. For this the pump was attached via capillaries to the empty columns which were then filled with leachant. The system was left to stabilize for 48 hours before emptying through the base and collecting the first blank eluate. This process was then repeated to obtain the second blank eluate, the conductivity of which was less than 0,2 mS/m allowing the test to continue. The blank eluates were preserved and the second blank from each column was sent for an ICP-MS analysis to ensure the concentration of chemical components is below that specified by the norm.

The columns were filled to a total height of 30 ± 5 cm in five consecutive layers. Each layer was introduced in 3 sub-layers and levelled. The layers were compacted with a rammer (125 g) which was dropped three times from a height of 20 cm. A free space of 1 mm was left between the material and the top section, as EAF slag is known to have potential expansive properties.

The linear velocity was set to 15 ± 2 cm per day, according to the following relationship:

$$\emptyset = 0,0104 \cdot v_L \cdot \pi \cdot d^2$$

Ø	Leachant flow rate [ml/h]
v_L	Linear velocity of the leachant through the empty column [cm/day]
d	Diameter of the column [cm]

This relationship results in a fixed flow rate of approximately 13 ml/h, which was used throughout the test. To verify the equilibrium condition, the columns were saturated and left stationary for three days at the start of the test. After this time, the pump was started and 15 ml of eluate was collected to measure its pH. A further 15 ml were pumped into a separate container to verify the pH deviation was less than 0,5 pH units between the two samples. Equilibrium was reached in all three cases and so the test could proceed to collect the first eluate fraction, *(0,1 ± 0,02)· m_0,* including the 30 ml used to verify the pH. m_0 refers to the dry mass of the test portion in each column, this value is important as it determines the amount of eluate which needs to be obtained to ensure a L/S ratio of 10.

Table 2 shows the remaining fraction to be collected to complete the percolation test. Each stage was performed in the same way as the first eluate, without the initial verification of the equilibrium conditions. A set flow rate was used throughout the test and the eluates corresponding to each fraction were collected in separate containers. The test took a total of approximately 40 days to complete.

Table 2: Collection of eluate fractions for Percolation test [34]

Fraction Number	Fraction Volume [l]	Cumulative L/S ratio [l/kg]
1	(0,1 ± 0,02)·m_0	0,1 ± 0,02
2	(0,1 ± 0,02)·m_0	0,2 ± 0,04
3	(0,3 ± 0,05)·m_0	0,5 ± 0,08
4	(0,5 ± 0,1)·m_0	1,0 ± 0,15
5	(1,0 ± 0,2)·m_0	2,0 ± 0,3
6	(3,0 ± 0,2)·m_0	5,0 ± 0,4
7	(5,0 ± 0,2)·m_0	10,0 ± 0,1

Once the total volume of the eluate fraction had been collected and the pH and conductivity were measured, the eluates were stored (100 ml for HPLC and an additional 100 ml with 1% of Nitric Acid for ICP-MS) at a low temperature in sealed plastic bottles for further analysis.

4.1.1.4. Representation of Results

The results of the percolation test are typically expressed as the cumulative release of a constituent in milligrams per kilogram of dry mass of the studied material. To calculate this cumulative quantity, first the individual releases of a constituent per eluate fraction needs to be found as follows:

$$U_i = \frac{V_i \cdot c_i}{m_0}$$

Where

      i   Index of the eluate fraction (1...7)

      U_i Released quantity of a component in eluate fraction i [mg/kg DM]

      V_i Volume of eluate fraction i [l]

      c_i Concentration of a component in the eluate fraction i [mg/l]

      m_0 Dry mass [kg]

Once all the U_i values have been determined for each constituent, the complete series of fractions are added to determine the cumulative released quantity. These results are then introduced into the software, Leach XS, to be represented in relation to their L/S ratio.

4.1.2. Monolithic

The following procedure is based on the Norm CEN/TS 15863:2012 Characterization of waste through the dynamic monolithic leaching test with periodic leachant renewal, under fixed test conditions [32]. This test characterises the waste material as a monolithic specimen where leaching is surface area related and not dependent on equilibrium conditions. For this reason, it is important that the test specimen has a quantifiable surface area and of a sufficient dimension.

The aim of this experiment is to determine the release of inorganic constituents, as a function of time, from the monolithic waste when it is put into contact with a leachant (demineralised water). The volume of leachant used in the test is determined by the liquid to surface area ratio (L/A ratio expressed in ml/cm^2), at a specific temperature and renewed at predefined intervals. The specific test conditions do not intend to simulate a real situation, but are used to determine the main leaching mechanism.

4.1.2.1. Equipment

An individual leaching vessel is needed for each test portion or unit. Plastic tanks with a lid were used to minimize contact with air. The dimensions of the container need to be large enough to ensure a minimum of 2 cm of free space all around the test portion. Base supports made from an inert material guaranteed this minimum distance with the bottom of the vessel.

A saw table was used to cut half of the test portions to simplify the calculation of their surface area and compare the effects of new and aged surfaces. And finally a vacuum filtration device was needed to filter the eluate over a 0,45 μm membrane filter , as part of the preparation for further analysis.

4.1.2.2. Determination of the Surface Area

EAF Slag has a similar appearance to volcanic rock where a number of pores and extrusions cover its surface. Due to the complexity of determining its surface area, two different methods were implemented. One in which the EAF Slag was cut into parallelepipeds and another involving computer imagery to determine the surface area. Six test units were selected to represent the sample of EAF Slag, all of which exceed the minimum dimensions of 40 mm in all directions, established by the norm.

The first and simplest method consisted in cutting the three test specimens into parallelepipeds so that their geometric surface area could be easily determined. This procedure exposed new surfaces which could lead to changes in the leaching properties of the waste material. The height, length and width of the geometric shapes were measured with a Vernier Caliper to maximise precision and accuracy. Note that even after cutting the aggregate into a geometric shape, multiple pores are still present, as seen in *Figure 11*.

The aim of the second method was to capture the original, porous, uneven surface of the EAF Slag. The reason for testing the material with its unmodified aged surface was to compare the leached results with those of the samples with freshly cut surfaces.

Determining the surface area of EAF Slag test samples was done with the help of graphic software and image processing. The idea was to produce a 3D scanned model of each test unit, from which the surface area could then be determined.

The 3D model was achieved through the overlapping of approximately 100 photographs taken at different angles. These images were then uploaded into Autodesk 123D Catch [48], a piece of image processing software which pins together photos to generate a 3D model. *Figure 12* illustrates the workspace of this programme with one of the test samples made up of a very fine triangulated mesh.

This mesh was then imported into AutoCAD 3D Civil [49] with the corresponding scale. Transforming this triangulated mesh into a single object and with the functions embedded in AutoCAD, the surface area could be determined.
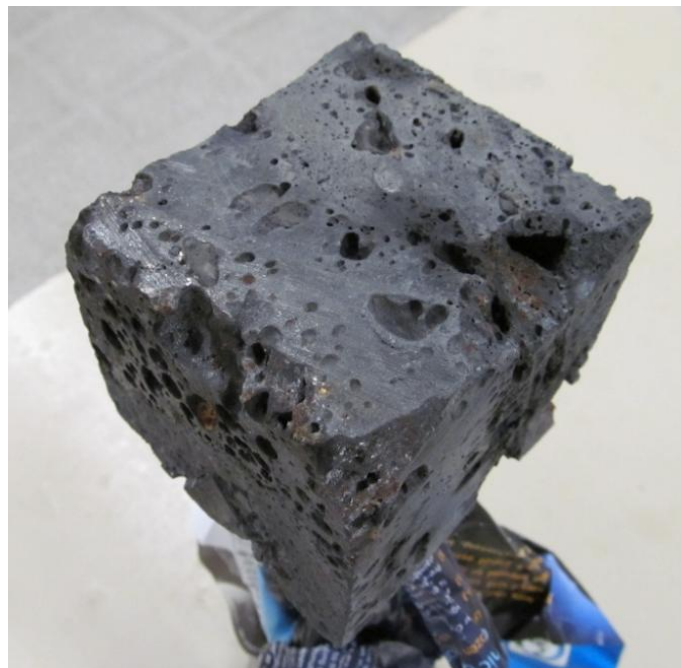

Figure 11: EAF Slag cut into geometric shape to easily determine surface area
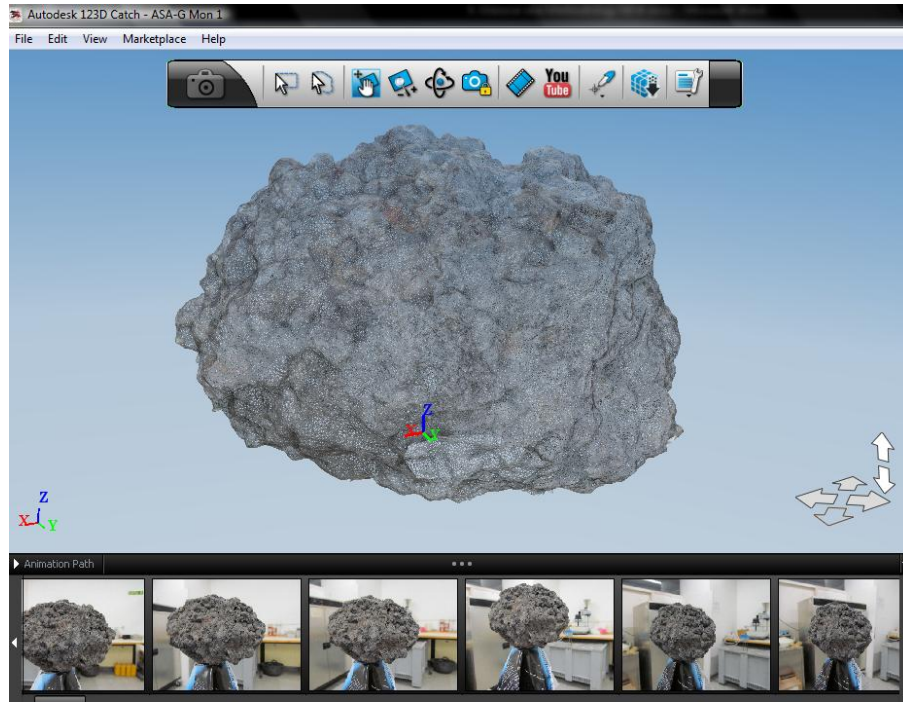
Figure 12: Workspace in Autodesk 123D Catch [48]

4.1.2.3. Test Procedure

Before the start of the experiment, blank tests were carried out to detect any possible contamination of the equipment or reagents used. For this procedure, each of the six leachant vessels were filled completely with demineralised water and left for 24 hours. After this time, the first blank eluate was collected, filtered and stored for later analysis. This process was repeated to obtain the second blank eluate. The pH and conductivity of the blank eluates were measured after filtration. Once the conductivity of the second blank eluate was verified as less than 0,2 mS/m, the monolithic test could begin.

The first stage of the test was to place the samples into the leaching vessels and ensure that the material was more than 2 cm away from all boundaries. The vessels were then filled with a specified volume of leachant V_1, which depended on the surface area of the studied material, as defined below:

$$V_1 = (8 \pm 0,1) \cdot A$$

Where

  V_1 is the volume of the leachant [ml]
  A is the surface area of the test portion [cm^2]

Once filled the leaching vessels were covered and the time (t_0) was noted as the start of the test. The test units were left for $2 \pm 0,1$ hours as the first stage of the leaching process. After this time, the eluate was drained without removing small parts which may have fallen off the test portion. The next stage begins immediately after the drainage of the previous eluate. The drained eluate was passed through a 0,45 µm membrane filter with the help of a

vacuum filter device. Its pH and conductivity were measured before its preparation for storage and posterior analysis.

Table 3: Time intervals for eluate collection in Monolithic test [32]

Step/Fraction	Duration of the time interval [days]	Duration from the start of the test (t_0) [days]
1	0,08 ± 5 %	0,08 ± 5 %
2	0,92 ± 5 %	1,00 ± 5 %
3	1,25 ± 5 %	2,25 ± 5 %
4	5,75 ± 5 %	8,00 ± 5 %
5	6,00 ± 5 %	14,00 ± 5 %
6	1,00 ± 5 %	15,00 ± 5 %
7	13,00 ± 5 %	28,00 ± 5 %
8	8,00 ± 5 %	36,00 ± 5 %

The same procedure was followed for the subsequent steps of the test, modifying only the duration of each time step as specified in *Table 3*. The volume of leachant V_1 remains constant throughout the test.

Note that none of the test units showed any signs of material loss by the end of the experiment. This shows that Electric Arc Furnace Slag is a durable material with clear monolithic properties when used in its natural form and when cut.

4.1.2.4. *Representation of Results*

The results from the Dynamic Monolithic Leaching Test are expressed in terms of area related release. This means that the accumulative amount of the constituent released per time step is expressed in relation to its geometric surface area [mg/m^2]. These values are then expressed as a function of cumulative time, starting at the beginning of the first time step.

Results can also be represented in function of the concentration released in each time step [mg/l]. If done so the results can only be compared with other test specimens of the same shape and size.

The following equations are used to calculate the cumulative release of a constituent in the dynamic monolithic leaching test, relative to the materials geometric surface area:

$$r_i = \frac{10 \cdot c_i \cdot V}{A} \qquad\qquad R_n = \sum_{i=1}^{8} r_i$$

Where

i	Index relating to each step (i = 1 − 8)
r_i	Released quantity of a constituent in step i [mg/m^2]
V	Volume of the leachant [ml]
c_i	Concentration of a constituent in the eluate in step i [mg/l]
A	Geometric surface area of test portion [cm^2]
R_n	Cumulative release of a constituent in the full 8 steps [mg/m^2]

Note when c_i is below the detection limit, the worst case scenario was considered, where the concentration is equalled to the detection limit of the specific constituent.

4.1.3. pH Dependence

The European Standard, prEN 14429 Leaching behaviour tests – Influence of pH on leaching with initial acid/base addition [35], specifies a pH dependent leaching test as part of a series of complementary standards which are used to determine the leaching behaviour of granular waste materials. This test determines the relationship between various pH values and the release of inorganic constituents from a material. These relationships are defined by the chemical behaviour trends and the levels of availability of these components. The results obtained can usually not be linked directly to the concentrations observed in real life scenarios, but an idea is given about the tendency of the material's leaching behaviour.

The results of the pH dependence test are used to make long term predictions and estimate the behaviour of a material in a specific application. The pH is one of the key parameters used to define the release of a material, as it affects many factors related to leaching. Redox and Dissolved Organic Carbon (DOC) can also affect the leaching behaviour of a material, but these factors have not been considered in this study.

The test also provides a measure of the acid/base neutralization capacity (ANC/BNC) of the material, to determine if it may act as a buffer. The potentially leachable quantity of a constituent may also be determined from the pH dependence test in extremely acidic conditions.

The representations of pH in function of leached constituents, results in three main behavioural groups: Cations, Anions and Soluble Salts. Each group has a distinctive leaching pattern, marking the release of constituents in function of a defined pH value, shown in *Figure 13*. Note that these tendencies are ideal representations of the constituents' behaviour.

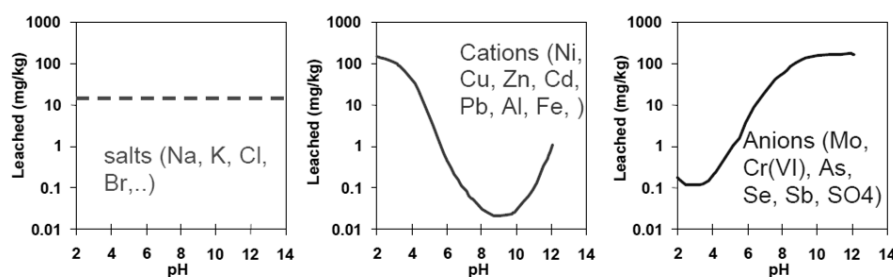*Figure 13: Three main leaching behaviours in function of pH* [29]

The goal of this norm is to obtain at least eight final pH-values which cover a range from below a pH of 4 to above a pH of 12. The maximum difference between two consecutive pH values shall not exceed 1,5 pH units. These eluate pH-values are obtained by mixing an acid or base leachant with a specific amount of test proportion to ensure a L/S ratio of 10.

The material used in this experiment has been crushed to below 1 mm. The size reduction produces fresh surfaces which accelerates the obtaining of the required equilibrium condition.

4.1.3.1. *Equipment and Reagents*

An end-over-end tumbler agitation device is needed to mix the suspension. The leachant and test portion will be placed in 2 litre sealable plastic bottles. The equipment used is illustrated in *Figure 14*. At the end of the test a vacuum filtration device will be used to pass the leachant over a 0,45 μm filter membrane to remove fine particles.

Demineralised water is the most common reagent in this test. Nitric acid with a concentration of 3 mol/l was used to create the acidic leachants and sodium hydroxide, NaOH, at 1 mol/l was diluted for the basic leachants.
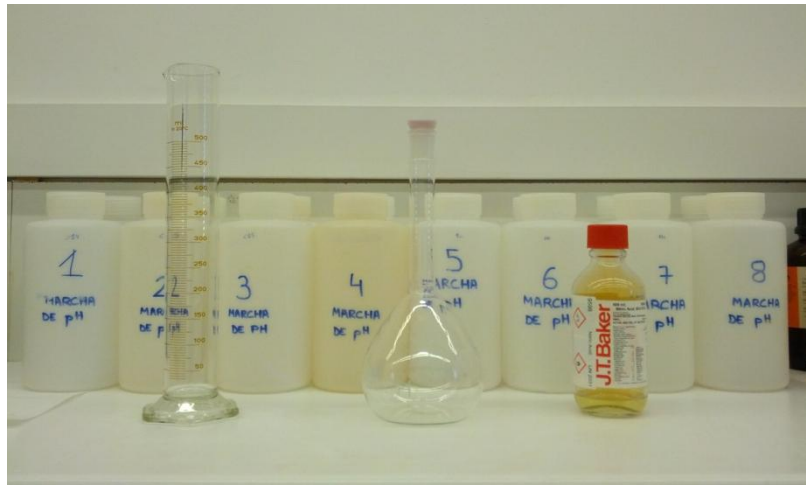
Figure 14: pH Dependence test equipment in accordance with prEN 14429

4.1.3.2. *Test Procedure*

The test bottles used in the experiment needed to be rinsed thoroughly with nitric acid and demineralised water consecutively to minimize possible contamination, before the start of the test.

For the pH dependence test, at least eight test portions were needed, each of which with the same dry weight of laboratory sample. One kilogram of dry mass was ground down to less than 1 mm in diameter and separated into eight equal parts with a rotating splitting device.

In each bottle, 60 g of material was placed with its corresponding acidic or basic leachant. The total leachant volume V including the volume of acid or base was calculated as follows:

$$V = (10 \pm 0{,}2) \cdot M_d$$

Where

        V   is the total volume of liquid in the test [ml]

        M_d is the dry mass of the test portion [g]

The total volume of leachant is made up of demineralised water and a solution of concentrated acid or base in function of the pH required. How to obtain the volume of acid used to prepare the acid adjusted leachant is shown below:

$$V_L = V_{demin} + V_A \qquad\qquad V_A = \frac{A \cdot M_d}{C_A}$$

Where

V_L is the volume of prepared leachant [ml]

V_{demin} is the volume of the demineralised water used [ml]

V_A is the volume of acid needed [ml]

A is the acid consumption for the pH [mol H^+/kg dry mass]

M_d is the dry mass of the test portion [g]

C_A is the concentration of the acid [mol/l]

In the case of the base adjusted leachant, the above calculations are the same, just substitute the concentrated acid for base.

The leachant was added to the test portion in three different stages. A third of the total at is added at the start of the test, t_0, followed by the second third at t_0 + 30 minutes and finally the last part at t_0 + 2 hours. The pH was measured before the addition of the second and third fraction of leachant, as well as, after t_0 + 4 hours, t_0 + 44 hours and t_0 + 48 hours. The test ends after the final pH measurement at t_0 + 48 hours once the equilibrium conditions have been acquired (pH variation < 0,3 pH units between the final two measurements).

A sample with the natural pH of the waste material (leachant of demineralised water only) was also included within the eight eluates obtained. Three blank tests were carried out to assess any possible contamination of the system. The blank tests follow the same test procedure described above but without the test portion of waste material. The three tests consisted of the maximum concentration of acid and base used, as well as, a traditional blank test with demineralised water only.

The filtration of the eluates through a 0,45 µm membrane filter, as part of the preparation for further analysis, was problematic. As the dissolution filtered, the suspended particles formed a thick paste blocking the filter. For this reason the dissolution was filtered twice, once through a filter with medium sized pores and then through the 0,45 µm membrane. Two bottles of 100 ml of eluate each were preserved for later analysis.

4.2. Compliance Tests

The key parameters and leaching behaviour of EAF Slag defined by the basic characterization tests are verified in a compliance test. The purpose of a compliance test is either to classify material in relation to the release values defined by Directives or as quality control, ensuring that the released chemical constituent fall within a defined interval. If this is the case, the release of a material's constituents can be classified without having to carry out the series of basic characterization tests defined in the previous section.

In this study, the limit values used originate from the Catalan Decree [2] which specifically defines the release limits of EAF Slag to be classified as inert. Apart from the defined

constituents, the release of Calcium is also monitored. This is done because of the high concentration of Calcium in EAF Slag and to determine the potential variation in pH of the surroundings in contact with the material.

4.2.1. Conformity

Part 2 of the European Standard EN 12457-2 Characterization of waste – Compliance test for leaching of granular waste materials and sludges [36] has been used in this section. Part 2 refers to a one stage batch test with a liquid to solid ratio (L/S) of 10 l/kg of dry matter for materials with a particle size below 4 mm. It was decided to use part 2 of the compliance tests as the material size is comparable with that of the percolation test, as well as, being the worst case scenario with a smaller aggregate diameter. The single batch leaching test assumes that equilibrium is achieved by the end of the test, between the leachant and the test sample.

The purpose of this test is to determine the release of inorganic constituents from granular waste materials under specific environmental conditions.

4.2.1.1. Equipment

Four 2 litre plastic bottles were used for this test. An end-over-end tumbler (shown in *Figure 15*) and a vacuum filtration device with 0,45 µm membrane filters will be needed to complete this experiment. All the equipment needs to be rinsed with nitric acid and demineralised water before the start of the test.

Figure 15: Conformity test samples (EN 12457-2) in the end-over-end tumbler

4.2.1.2. Test Procedure

At least 2 kg of dry material with a diameter below 4 mm were needed to have a representative amount of the laboratory sample. This material was then quartered and split into test portions, to have three samples of 0,090 ± 0,005 kg of dry mass.

These test portions were placed into bottles with the corresponding amount of leachant to obtain a liquid solid ratio of L/S = 10 l/kg ± 2 %, corresponding to the calculations below:

$$L = \left(10 - \frac{MC}{100}\right) \cdot M_D$$

$$MC = 100 \cdot (M_W - M_D)/M_D$$

Where

      L   is the volume of leachant used [l]

      M_D is the dry mass of the test portion [kg]

      MC   is the moisture content ratio [%]

      M_W is the mass of the un-dried test portion [kg]

The bottles were sealed and agitated for $24 \pm 0{,}5$ hours in the end-over-end tumbler. The dissolution was left for the particles to settle for 15 ± 5 minutes. The eluate was then filtered over a 0,45 µm membrane filter to remove the remaining suspended particles.

The fourth plastic bottle was used for the black test to verify the procedure. In this case, 0,95 litres of leachant were added to the empty bottle and submitted to the entire test.

The pH and conductivity was measured of the filtered eluates, which were then prepared for storage in a cool place for further analysis.

4.2.1.3. *Representation of Results*

The Conformity test results are expressed in milligrams of released constituent for every kilogram of dry mass of the material. This released amount of constituent is determined from the following expression:

$$A = C[(L/DM) + (MC/100)]$$

Where

      A   Released amount of constituent [mg/kg of Dry Mass]

      C   Concentration of constituent [mg/l]

      L   Volume of leachant [l]

      DM Dry Mass [kg]

      MC Moisture content ratio [%]

4.3. Total Content of Constituents

A number of tests have been used to determine the total content of the principle constituents defined by legislation. No single test or detection method exists with the capacity of determining all the specified constituents, as they are present in various concentrations within the EAF Slag. For this reason, various tests are carried out to determine the total content of constituents contained in the EAF Slag each with their own detection method.

4.3.1. Attack by Aqua Regia

The attack by Aqua Regia is used to determine the total content of the constituents within EAF Slag. These results are used as reference values in the leaching tests to mark an absolute maximum released amount corresponding to each element.

In order to compare these results with those from the lixiviation tests, a L/S ratio of 100 ml/ 3 g of dry mass is used. The test was duplicated and followed the Norm ISO/CD 11466 [50].

4.3.2. Total Content of Chlorides

A potentiometer was used to determine the total content of chlorides in the EAF Slag. The method consists in attacking the sample with heat and nitric acid. After which the solution is filtered and diluted for further analysis. A potentiometer was used to perform this analysis with the help of a titrator. Silver nitrate was used as the reactive in this process.

The results of this test are expressed in percentage of chlorides over the total mass of the test sample.

4.3.3. Total Content of Sulphates

Section 12 of the Norm, UNE-EN 1744-1 Determine the soluble sulphates in acid [44], was used to determine the total content of sulphates in EAF Slag. Gravimetric methods were used to determine the amount of sulphate extracted from a test sample after dissolution with diluted hydrochloric acid.

The first step is to combine 2 g of test portion with 90 ml of distilled water. While mixing the dissolution energetically, add 10 ml of concentrated hydrochloric acid. The solution is then filtered, diluted further and heated. Barium chloride is added to form barium sulphate precipitate, which was separated from the solution and calcinated. The concentration of sulphate ions is then expressed as a percentage of the total mass of the test sample.

4.3.4. Total Content of Chrome

The total content of chrome was determined via Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) with previous preparation of the sample through alkaline fusion. The test was duplicated for increased reliability.

The method consists in placing 0,1 g of sample, with a particle size bellow 0,063 mm, in a zirconium crucible with 5 ml of hydroxide of sodium (NaOH). The solution was left to evaporate on a sand bath. Then 1 g of sodium peroxide (Na_2O_2) was added and placed into a muffle for 15 minutes at 450 ºC, until fusion occurred. Once again over the sand bath, the melted material was mixed with hot water and 15 ml of hydrochloric acid (HCl). The dissolution was brought to the boil and left for more than an hour, until the solution turns transparent. Finally the container is filled to 100 ml with demineralised water and sent in for an optical ICP analysis. According to this procedure, the L/S ratio is equal to 1000 l/kg of dry mass.

4.4. Chemical and Physical Characterization of the Eluate

This section describes the various ways in which the eluates were analysed in order to obtain the chemical and physical characteristics of these liquids. The pH and conductivity of the eluate were determined immediately after the end of each test, whereas, the analysis of ICP-MS and HPLC were performed at a later stage.

An electron microscope was also used to amplify a sample before and after an attack by an acidic leachant, to try and determine the reason for the formation of the paste like substance which limits filtration.

4.4.1. pH Measurement

A pH measurement defines how acid or basic a substance is, which in reality refers to the concentration of hydrogen ions. The pH scale is logarithmic and extends from 0 to 14, with 7 marking a neutral pH.

Most of the leaching mechanisms are linked to the pH value, for this reason the pH of all the eluates has been recorded for later interpretation. A pH-meter (brand *Crison*) was used to determine this property and calibrated on a daily basis.

4.4.2. Conductivity

Conductivity is the ability of a solution to carry a current. Pure water cannot carry a current, whereas ions suspended in this liquid can. These ions are principally dissolved chemical components which originate from the test sample. Therefore conductivity can be thought of as a measurement of the concentration of ions present in the eluate.

An electrical conductivity meter (brand *Crison*) was used to measure the conductivity of the eluates and calibrated on a daily basis.

4.4.3. ICP-MS

Inductively coupled plasma – mass spectrometry (ICP-MS) is a method which aims to quantify and determine the isotopic composition of chemical elements.

The samples are vaporized with argon gas forming an aerosol. As this aerosol dries, molecules are dissociates leading to the removal of elections and the formation of singly-charged ions. The mass spectrometer acts as a filter, selecting a mass-to-charge ratio to pass on to the electron multiplier. This multiplier is a detector for the electrons impacting against it, the intensity of which determines the concentration of the element.

The ICP-MS *PerkinElmer, modelo Elan-6000* was used to carry out this analysis. The chemical components measured were as follows: barium, arsenic, chrome, copper, molybdenum, nickel, lead, selenium, zinc, cadmium, mercury and antimony.

4.4.4. HPLC

High performance liquid chromatography (HPLC) is a chromatographic technique used to separate samples in order to identify and quantify their individual components.

HPLC pressurises and pumps a liquid sample through a column filled with a sorbent. The sorbent is referred to as the static phase and is usually made of micro-particles of silica. The mobile phase or the pressurised liquid interacts with the sorbent as it passes through the column, leading to a separation of components. The interactions are based on the attraction forces between polar and non-polar molecules, as well as, the formation of hydrogen bonds (Van der Waals forces). The stronger the attraction force with the mobile solvent phase the quicker a particular component will pass through the column. Finally, a

detector generates a signal proportional to the amount of sample emerging from the column, which allows for a quantitative analysis of the sample.

The ionic interchange chromatograph used in this analysis is from Metrohm, model IC Compact 761. The elements measured via this technique were fluoride ions, chloride and sulphate. The results of the contents of these elements are expressed in mg/l.

4.4.5. Scanning Electron Microscope

A Scanning Electron Microscope was used to identify the changes in the EAF Slag test sample after it had been attacked by an acidic leachant. A test sample of EAF Slag (particle size below 0,063 mm) was prepared for analysis, by drying in a furnace after being attacked by an acidic leachant. No further preparation of the sample was needed.

A thin beam of electrons interacts with the surface of the sample, reflecting electrons which are then captured by detectors within the Scanning Electron Microscope. This moving signal defines the topography and composition of the test sample [51].

The analysis was carried out by the Scientific-technical services of the University of Barcelona. The Scanning Electron Microscope used was the ESEM Quanta 200 FEI, XTE 325/D8395 with an integrated EDS detector to acquire the data needed to produce the X-ray diffraction spectrum.

4.5. Leach XS

Leach XS [37] is a leaching environmental assessment framework tool that allows the evaluation and characterization of constituents in various types of materials. The programme combines leaching tests to give a clear representation of the fluctuation of released chemical elements as they are tested in different conditions. One of the goals of this software is to compile an international database of waste materials, to facilitate future leaching assessments.

Leach XS distinguishes between granular and monolithic materials as they tend to be characterised by different leaching tests. One constituent from multiple materials can be represented for analysis or alternatively multiple constituents from a single material. The results are expressed graphically in function of the key parameters for easy interpretation of the main leaching mechanism.

The values resulting from HCLP and ICP-MS were incorporated into the Leach XS database as release concentrations expressed in µg/l. If the detected concentration of a constituent was below the detection limit of the analyzing equipment, a worst case scenario was considered. In other words, all concentrations below the detection limit were rounded up to this value. Note that this is a highly conservative approach, especially when the cumulative released quantity of a constituent is considered.

Chapter 5
RESULTS AND DISCUSSION

The following section summaries the results obtained from the characterisation, durability and leaching tests presented in chapter 4. These values have been analysed, discussed and compared to draw conclusions about the use of Electric Arc Furnace Slag in gabion cages.

The presentation of the test results follows the same structure as in Chapter 4 Materials and Methods. The characterisation of the material defines the average physical properties, as well as, the chemical and mineralogical composition. The durability and weathering resistance of the EAF Slag is then discussed in the context of gabion cages. Finally and most importantly, the potential environmental impact of the EAF Slag is debated. Here the accumulative concentrations of the released components are compared with the limits set by Directives for the materials classification and potential use.

1. Characterisation

The characterisation of the material is divided into two main parts, the physical and the chemical properties of EAF Slag. The dimension, density and absorption of aggregates used to fill gabion cages are fundamental properties, as they define the potential applications of the cages. Apart from the physical aspect, the chemical and mineralogical composition of EAF Slag has also been determined.

1.1. Size Distribution

The test fraction was obtained from ADEC, which had previously sorted the material by size to restrict its dimension to between 80 – 140 mm. Seven test units were chosen to represent the sample, from which the size distribution of the EAF Slag was determined.

Nine measurements were taken of each test unit, three per orthogonal direction, from which the average values were determined. The second largest dimension was selected to define the size distribution of the sample of EAF Slag, these are shown in *Table 4*.

These results show that the material is confined within the fraction 80 – 140 mm as established by ADEC, with the majority of the test samples concentrated in the upper limit of the fraction.

This fraction is ideal for filling gabion cages as it is large enough to be retained by the wire mesh baskets. The variation in the size distribution allows the particles to fit together within the cage to form a compact structure.

Table 4: Size Distribution of test units

Test Unit	1	2	3	4	5	6	7
Diameter [mm]	128	139	134	84	104	135	132

1.2. Density and Water Absorption

Table 5 summarises the results obtained from the application of the norm UNE-EN 1097-6 [41]. In addition to these particle densities, the unit weight of the material was determined from a 0,3 x 0,5 x 1,0 m^3 gabion cage, manufactured by ADEC. This cage weighs 340 kg, resulting in a unit weight of approximately 2267 kg/m^3.

Table 5: Densities and Absorption of EAF Slag

Apparent Bulk Density [kg/m^3]	Dry Density [kg/m^3]	Saturated Surface Dry Density [kg/m^3]	Unit Weight [kg/m^3]	Absorption [%]
3167	3034	3076	2267	1,4

In comparison to natural rock, see chapter 3 section 2.2.1, EAF Slag is typically a denser material making it very suitable for gabion cage applications. The average apparent bulk density of Electric Arc Furnace slag is between 3,3 – 3,8 g/cm^3 [9]. In the case of large dimensions (80 – 140 mm), the average apparent bulk density obtained is lower. The absorption measured is also low, due to the fact that the material is covered in large superficial pores which do not retain water.

The average volumetric density was calculated, which resulted in a porosity of 18 %. Note that the property of EAF Slag is not directly represented through the values obtained for its density or absorption. This may be due to a large quantity of internal porosity within the matrix of the solid material, which is isolated from the exterior.

Article 659 Fabrication of Gabion Cages [52] from the Spanish General Specifications of road and bridge construction (PG-3) limits the absorption of the material used in gabion cages at 2 %. EAF Slag complies with this absorption limit.

1.3. Chemical Composition

The results obtained from X-Ray Florescence representing the percentage of oxides contained in EAF Slag are shown in *Table 6*. Iron, calcium, silicate and aluminium oxide are the main components (Chemical composition > 10 %) detected in the studied sample of EAF Slag. Secondary components include manganese, magnesium and chrome oxide, as well as, traces of other elements.

Note that the test sample sent in for analysis showed an increase of 2,6 % in mass. Loss on ignition or calcination usually results in a loss of mass which occurs after placing the sample in a furnace at 1000 ºC. This loss is caused by the transformation of carbonates contained in the material, which result in the release of CO_2. The gain in weight observed may be due to the oxidation of iron oxide.

Table 6: Chemical Composition in Oxides of EAF Slag

Chemical Compound	Percentage
Fe_2O_3	32,69%
CaO	27,58%
SiO_2	15,76%
Al_2O_3	11,10%
MnO	5,33%
MgO	3,16%
Cr_2O_3	2,44%
TiO_2	0,71%
SO_3	0,60%
P_2O_5	0,35%
K_2O	0,14%
SrO	0,08%
ZrO_2	0,03%
Nb_2O_5	0,03%

1.4. Mineralogical Composition

The mineralogical composition of the material was determined through X-Ray Diffraction. The principle minerals detected in the Electric Arc Furnace Slag are listed in *Table 7*. These components were determined with X'Pert HighScore 2.0 [42] from the XRD spectrum of the sample, see *Figure 16*.

Note that the mineralogical compounds do not show signs of potentially expansive elements (MgO and CaO) observed in the oxide composition of the material. Other studies have shown that EAF Slag has a complex and heterogeneous composition, with a wustite-type solid as the principle identified mineral. In function of the cooling conditions of the steel slag, the Larnite mineral compound shows the most variations in its overall total content within the material [7].

Table 7: Mineralogical Compounds in EAF Slag

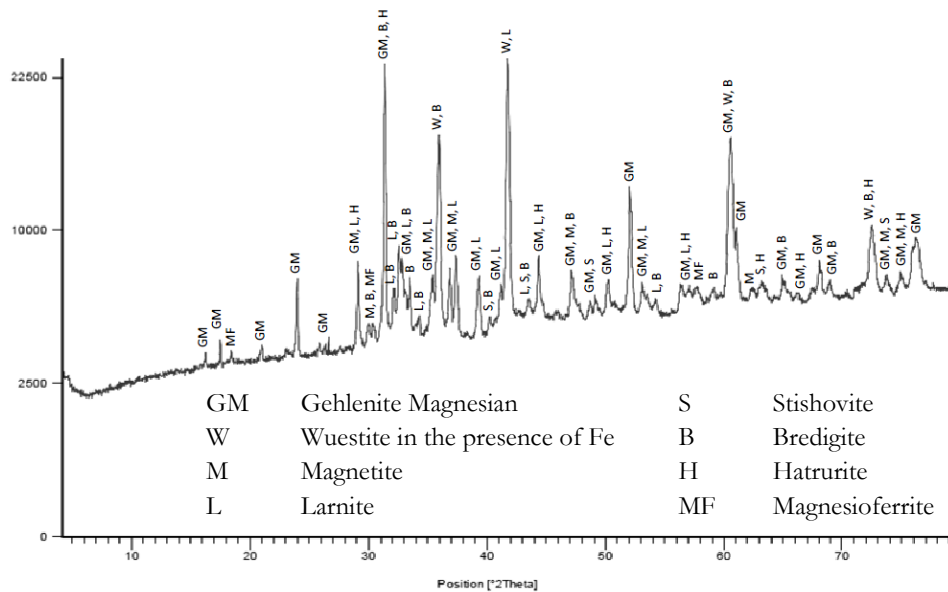| Ref.	Compound Name	Chemical Formula
GM	Gehlenite Magnesian	$Ca_2(Mg_{0,25} Al_{0,75})(Si_{1,25} Al_{0,75} O_7)$
W	Wuestite in the presence of Fe	FeO
M	Magnetite	$Fe_{2,957} O_4$
L	Larnite	$Ca_2 SiO_4$
S	Stishovite	SiO_2
B	Bredigite	$Ca_{1,7} Mg_{0,3} SiO_4$
H	Hatrurite	$Ca_3 (SiO_4) O$
MF	Magnesioferrite	$MgFe_2 + 3 O_4$

Figure 16: XRD Spectrum with main mineral compounds of EAF Slag

2. Durability

The durability and resistance tests carried out in this section intend to analyse the potential weathering of Electric Arc Furnace Slag. The objective of the following experiments is to have an understanding of the potential behaviour of the material when exposed to the elements in a specific application. In the long term, a direct relation between the behaviour of the material and the test results cannot be made. For this reason, a study was carried out to reproduce ten years of EAF Slag aging in a road application [14], where real data was available. This study showed few changes in EAF Slag behaviour over the 10 year period.

The following section will analyse aspects of hydration, expansion, freeze/thaw and resistance of the material.

2.1. Autoclave

A visual inspection was carried out after each cycle in the Autoclave. All seven test units showed no signs of fracture or cracking after the 5 full cycles. Minor loses of particles were recorded, none of which exceeded 5 g or 0,5 % in mass of the test unit.

On average a 0,25 % increase in weight was observed, which may be due to the oxidation of iron, as seen in *Figure 17*. In the test samples analysed, the formation of this mineral did not cause any cracking of the EAF Slag, though orange-brown points appeared on the material's surface. To ensure water had penetrated to the centre of the test sample, one of the samples was split open. *Figure 18*, shows the split test unit after the 5 cycles in the autoclave, where effectively water had reached the interior without showing signs of cracking.

These samples of EAF Slag show good resistance to the potential effects of hydration. This may be due to the fact that the material contains a low concentration of potentially expansive elements (MgO o CaO) or that the aging of the material has counteracted these

effects. In the long term, it is not expected that the material will undergo any major changes caused by hydration.

An exception to the above defined occurs when magnesium or calcium oxide concentrates in a weak point within the matrix of the EAF Slag. This effect was observed in one of the collected test samples, see *Figure 19*, concentration of MgO or CaO indicated by the white point in the centre right. Here it is supposed that fractures occurred due to the hydration of these expansive components, leading to the aggregate to split in half.

Figure 17: EAF Slag with clear signs of oxidized iron (orange-brown points, centre left)

Figure 18: Test sample split open after 5 cycles in the Autoclave, with water penetration to its core

Figure 19: Concentrated point of hydrated CaO/MgO (white point, centre right) within an EAF Slag matrix

2.2. Accelerated Expansion

Section 19.3. of UNE-EN 1744-1 [44], was used to determine the potential expansion of EAF Slag. Initially for more than 24 hours after the start of the test, no expansion was detected. After approximately 35 hours, the material shows signs of expansion, which quickly slows and tends towards a constant value of approximately 1,5 % in volume by the end of the test (7 days in total). The results for the two samples tested are shown in *Figure 20*. The limited expansiveness observed in the material, may be due to the hydration of specific minerals. It is believed that Iron oxide may be the main cause of the observed expansion, as low concentrations of Calcium and Magnesium oxide were detected in the mineralogical composition of the EAF Slag.
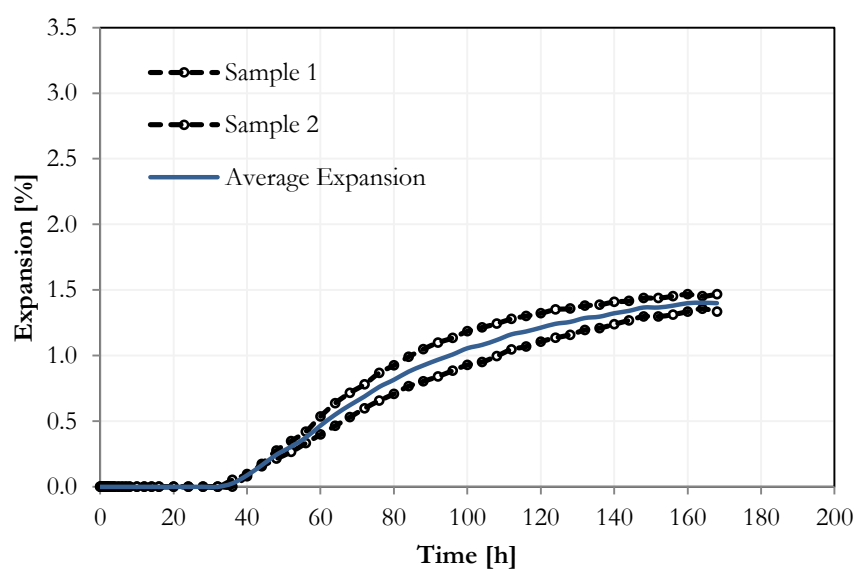
Figure 20: Accelerated Expansion test of EAF Slag

Norms which refer to the material fill of gabion cages do not restrict the expansiveness of the material. As gabion cages are flexible and allow for minor deformations, the potential expansive properties of EAF Slag are not seen as a barrier.

2.3. Weathering

The objective of UNE-EN 1367-2: Tests for thermal and weathering properties of aggregates. Part 2: Magnesium sulphate test [45] is to simulate water freezing within the material. Five test cycles were carried out to observe any potential changes due to internal expansive forces within the slag. These forces are derived from the crystallization and rehydration of magnesium sulphate within the pores of the test sample.

A visual inspection was carried out, where photographs from the beginning and the end of the test were compared. Minor losses of superficial particles were noted, but no major cracks or fractures appeared on the surface of the test units. A total weight loss of between 0,2 – 1,2 % of dry weight was recorded.

This result shows that the material has the potential to withstand many years of exposure to cycles of freeze/thaw.

2.4. Los Angeles Abrasion Test

The Los Angeles Coefficient is a measure of a materials resistance to fragmentation. In the case of gabion cages, the Spanish technical specifications PG-3 [52], states that the coefficient should be below 50 %.

The results of the test are shown in *Table 8*, where a total mass reduction of 817 g results in a Los Angeles coefficient of 16,3 %. This low coefficient complies with technical specifications, making EAF Slag apt for use in gabion cages.

Table 8: Los Angeles Coefficient of EAF Slag

Material	Total weight loss	Los Angeles Coef.
EAF Slag	817 g	16,3

3. Leaching

The following section characterizes the leaching behaviour of EAF Slag as both a granular and a monolithic material, through the percolation and monolithic tests respectively. These results are complemented by those of the pH dependence test to obtain the principle leaching mechanisms of EAF Slag. The total content of constituents detected within the material has also been defined. Note that these test results cannot be directly related to the material's true behaviour in a specific application.

Finally, the aim of this section is to determine whether the studied Electric Arc Furnace Slag is suitable to use as fill for gabion cages from an environmental point of view. This was determined by categorising EAF Slag as an inert material, through the comparison of the conformity test results to the current Catalan Directive [2].

3.1. Total Content of Constituents

Attack by Aqua Regia was the method used to determine the total content of the most of the chemical constituents of the EAF Slag. The total content of Chlorides, Chrome and Sulphate were determined as part of a separate procedure to provide more reliable results. As shown in *Figure 9*, the total content of a constituent does not necessarily have to coincide with its potentially leachable quantity.

Table 9 shows the quantities of constituents obtained in the EAF Slag. Note that the results obtained below the detection limit of the specialised equipment have been indicated by their respective upper bound values.

Table 9: Total Content of Constituents in EAF Slag

Constituent	Detected Quantity [mg/kg]
Antimony (Sb)	< 0.0002
Arsenic (As)	< 0.0005
Barium (Ba)	105.8
Cadmium (Cd)	< 0.0001
Chloride (Cl-)	207192.0
Chromium (Cr)	12569.8
Copper (Cu)	10.1
Lead (Pb)	0.293
Mercury (Hg)	< 0.0002
Molybdenum (Mo)	0.622
Nickel (Ni)	< 0.01
Selenium (Se)	< 0.005
Sulphate (SO4)	224665.0
Zinc (Zn)	< 0.02

3.2. Basic Characterisation Tests

The results presented below are designed to predict the main leaching mechanisms of EAF Slag in a specific scenario over the long term. The pH dependence and conductivity variation in time have also been represented.

3.2.1. pH – Time Dependence

The average value of the eluate's pH is represented for the monolithic and percolation tests as a function of time in *Figure 21*. For both tests, the resulting pH tends towards a common value (pH = 11 – 11,5). As the L/S ratio is below 10 l/kg and no external factors are considered, the waste material is determining the pH of the eluates.

Figure 21 initially shows the pH values obtained from the percolation test are higher than those from the monolithic test. This may be due to the fact that the EAF Slag has been ground down to below 4 mm, resulting in a greater surface area which increased the initial leaching potential of some constituents.
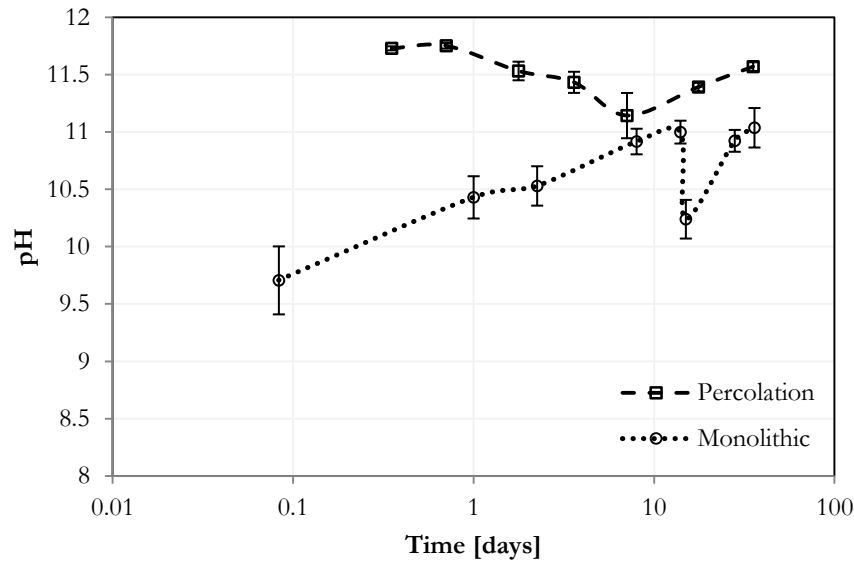
Figure 21: Variation of pH with time for the Percolation and Monolithic test on EAF Slag

3.2.2. Conductivity – Time Dependence

The conductivity of the eluates from the crushed granular EAF Slag (Percolation test) was compared with that of the monolithic material over time, represented in *Figure 22*. As conductivity is proportional to the total quantity of ions dissolved in the eluate, it is clear that the average value of released constituents is superior in the percolation test. Through the constant renewal of leachant, the conductivity for the percolation test reduces over time. After approximately 10 days, the conductivity measured in the percolation test tends towards that obtained in the monolithic test (250 – 500 µS/cm).
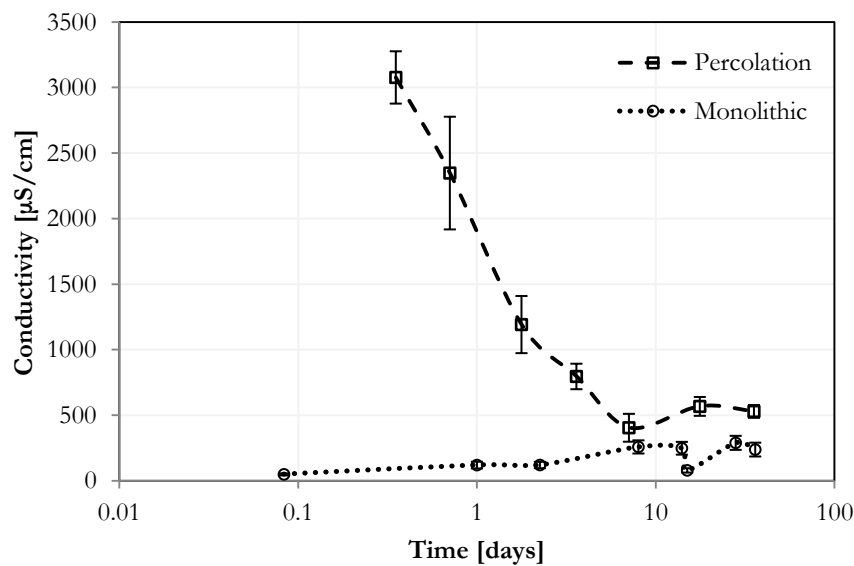
Figure 22: Variation of conductivity over time in the Percolation and Monolithic test of EAF Slag

3.2.3. Percolation

Before the results of the percolation test, CEN/TS 14405 Characterization of waste [34], are presented some important points are highlighted with regards to the choices made for the testing of EAF Slag.

- Reduction of particle size (<4 mm): Apart from being a requirement of the Norm to achieve local equilibrium, the crushing of the material generates new surfaces which may alter the characteristics of the leaching behaviour.

- Local equilibrium condition: Is only mandatory at the start of the test to enhance robustness. This condition may not be maintained throughout the test due to the flow rate and the constant renewal of leachant.

- Liquid to Solid ratio of 10 l/kg of Dry Mass: This ratio is representative of a long-term situation. Considering 640 mm as the average annual precipitation in Barcelona [53] and a gabion retaining wall of 5 m in height and a unit weight of 2267 kg/m^3 as determined in chapter 5 section 0, it would take more than 175 years to reach a liquid to solid ratio of 10 l/kg.

- Nature of the leachant: Distilled water was used as there is little difference in results when using rain water as the release of constituents is controlled predominately by the composition of the material, when the L/S ratio is below 10 l/kg of Dry Mass.

3.2.3.1. *Granular Release*

The results obtained from the percolation test only show a clear leaching mechanism for six of the constituents analysed. To simplify the representation of these results, average values have been used for the three test replicas. Barium, Calcium and Fluoride show signs of solubility control, meaning that a similar amount of constituent is dissolved in each test fraction. *Figure 23* shows how these elements tend towards a line with a slope equal to 1, which represents a constant release rate. Note that the solubility controlled release of Barium from EAF Slag had been verified in field tests [31].
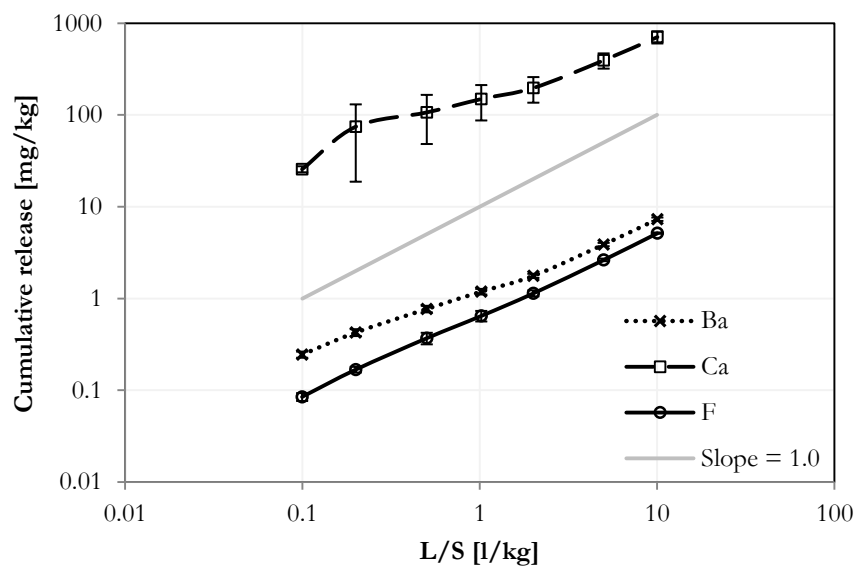

Figure 23: EAF Slag Constituents which show signs of Solubility Control obtained in Percolation test
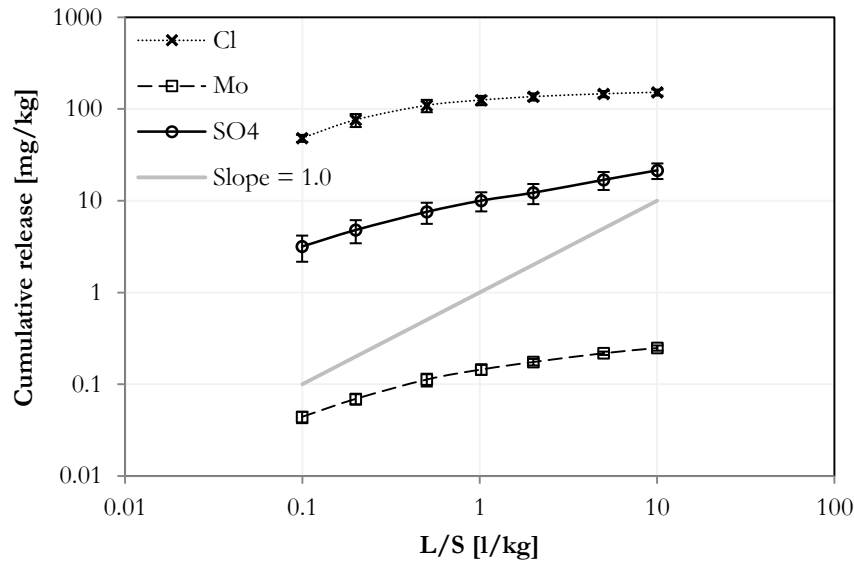
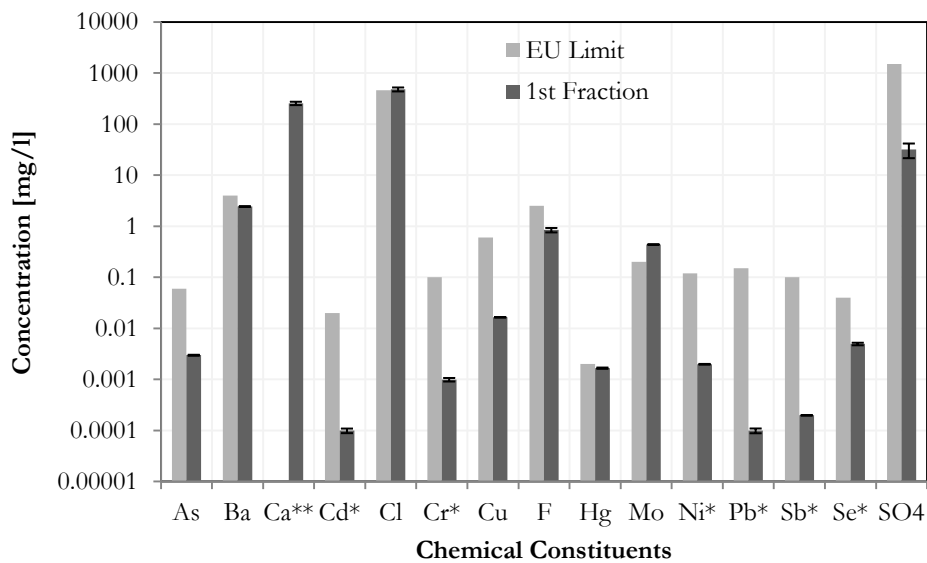*Figure 24: EAF Slag Constituents which show signs of Wash-Out in Percolation test*

Figure 25: Concentration of Constituent in 1st Fraction (L/S = 0.1) of Percolation Test compared to EU Limit

Note: *   Worst case scenario, detection limit has been used as concentration

On the other hand, Chloride, Molybdenum and Sulphate are subjected to washout. This mechanism is characterised by an initially high release rate which reduce with an increase in the L/S ratio. *Figure 24* shows how the cumulative release curve tends away from the constant slope, which represents the depletion of these constituents in the test unit. The leaching behaviour of Chloride and Molybdenum are backed up by the findings of a study focused on the environmental aspects of alternative materials [54], in which these constituents shows signs of the same leaching mechanisms.

The remaining constituents analysed (As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Zn) were below their respective detection limits in the majority of the test fractions. For this reason no leaching mechanisms could be defined for these constituents. On the other hand, the results can be used to give an indication of pore water concentrations, released from EAF Slag. The pore water concentration is comparable to the first eluate collected with a L/S = 0,1 l/kg of Dry Matter. *Figure 25* represents these values and compares them to the release limits established in the Official Journal of the European Union [55], for inert waste landfill materials.

Chloride and Molybdenum are slightly above the initial detection limits determined in the Official Journal of the European Union [55]. As both of these elements are dominated by Wash-Off, their initial concentration is the maximum obtained and the concentration of the constituent is reduced over time.

3.2.4.   Monolithic

The released values of constituents were obtained by following the norm CEN/TS 15863:2012 Characterization of waste through the dynamic monolithic leaching test [32]. The leachant renewal frequency is designed to determine the dominant leaching mechanism, solubility or diffusion controlled release, from the analytical results. In the case where the concentration of a constituent does not vary between fractions, the constituent is controlled by solubility. Whereas, if variations occur the release is diffusion controlled and tends towards a line with a slope of 0,5. The short duration of step 6 (1 day) is used to verify check this classification.

3.2.4.1.   Monolithic Release

An average concentration of the three test replicas has been used to represent the results, maintaining the distinction between the cut test samples (cubes) and the unmodified samples (rocks).

Barium and Calcium show clear signs of diffusion control with similar behaviours between the original and the cut samples. This leaching behaviour can clearly be identified in *Figure 26*, as the cumulative release of the constituents tends towards a line with a slope of 0,5. The pendent of the slope refers to the rate of diffusion with time. In both cases, no signs of surface wash-off or tendencies to solubility control were observed.

Figure 27 shows signs of the constituent's depletion. Initially, Chloride and Sulphate were detected in the eluates, but with each time step their concentration decreases. The cumulative release of the constituents tends towards a line with a slope of less than 0,5.

Most of the remaining concentrations measured in the eluates were below the established detection limits, meaning that no leaching mechanisms could be identified. These constituents were the following As, Cd, Cr, Cu, F, Hg, Mo, Ni, Pb, Sb, Se and Zn.
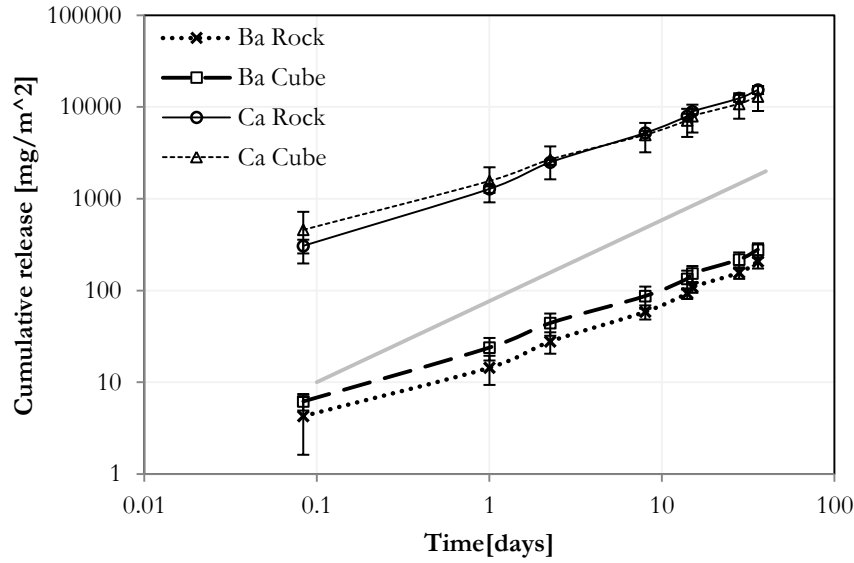
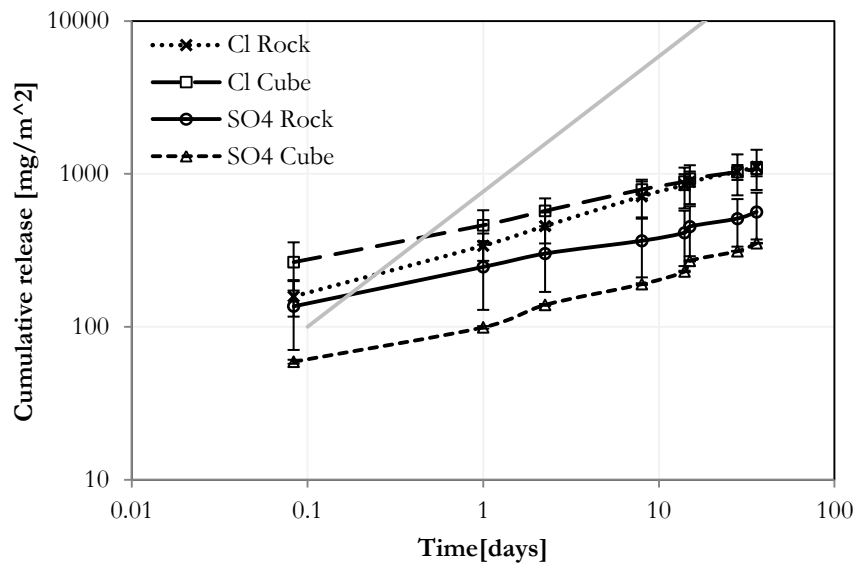*Figure 26: Diffusion Controlled constituents from EAF Slag determined by Monolithic Leaching Test*

Figure 27: Depletion of constituents from EAF Slag determined by Monolithic Leaching Test

3.2.5. pH Dependence

The pH Dependence test, prEN 14429 Leaching behaviour tests – Influence of pH on leaching with initial acid/base addition [35], provides information on one of the main factors defining the constituent release of a material. These results are used to define a Neutralization Curve which can determine a material's sensitivity to leaching in specific applications.

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3.2.5.1. *Neutralization Curve*

The pH values of each eluate fraction can be expressed directly in function of the concentration of acid or base in the leachant, forming the neutralization curve of EAF Slag shown in *Figure 28*. Negative values on the cardinal axis refer to an addition of base [mol of OH⁻] and positive values are acid additions [mol of H⁺]. Note that the pH of the eluate in contact with the material fluctuates smoothly with changes in acidity of the surrounding medium. No clear buffering effect is observed within the studied pH values (4 – 12). The materials natural pH has been indicated in black, in *Figure 28*.
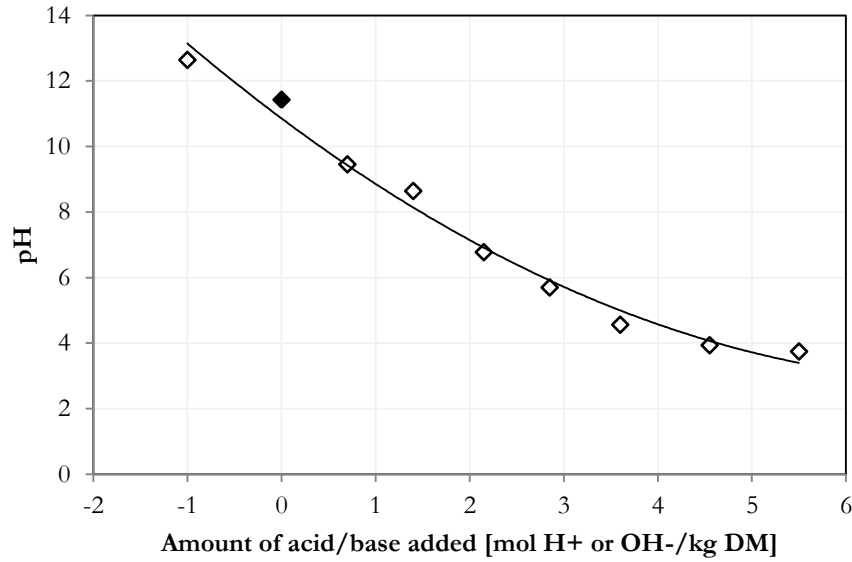
Figure 28: Neutralization Curve of EAF Slag, materials natural pH marked in black

3.2.5.2. *pH Dependant Release*

The following section relates the release results obtained from various tests on EAF Slag as a granular material for each individual constituent. The pH dependence is thought to define the material's release tendency within a specific scenario. In a real application, the eluates pH would be determined by the pH of the surrounding area (the acidity of the soil and the rain water), as well as, that of the material itself. In laboratory conditions, two dimensions were given to the release quantities. The first based on the variation of the pH of the leachant and the second based on the natural pH the eluate achieves when in contact with the material (percolation test carried out with demineralised water, pH = 7).

Figure 29 to *Figure 36* show the fluctuation of constituent release in function of the eluates pH, the natural pH of the material is indicated in the figures with a black square. The results from the percolation and conformity tests have been included where possible to show the tendency of release. Note that the conditions for each of these tests are unique, in relation to the L/S ratios, as well as, the flux and renewal of the leachant. The total content and the limit value of release (corresponding to the pH dependence test, pH = 4) as defined in chapter 5 section 3.1, have also been represented in these figures. The legal limit

refers to the value defined by the Catalan Decree [2] for each constituent. Note that this limit is based on the released amount obtained from the conformity test.

In the case where the material is the defining factor of the resulting pH of the eluate (pH = 11,5 approx.), all the test results represented in *Figure 29* to *Figure 36* tend toward a unique value. In some cases the results for the percolation, conformity or total content are not represented in the figures, this is due to the fact that the released quantities measured were below the detection limit defined. Antimony, Arsenic, Cadmium, Mercury and Selenium are not detected as a released constituent from EAF Slag for any of the above mentioned tests.

The release measured for the eluate at pH = 4 does not necessarily have to be the worst case with maximum release of constituents. Chromium and Lead show peak release with the second eluate (pH = 5 approx.). Whereas, the release of Molybdenum is lowest at high acidity levels and peaks at a pH = 9 approximately.

The release behaviour of constituents in function of an eluates pH and the properties of the constituent itself are represented in *Figure 13*. These behaviours have been categorised into three groups, cationic, anionic and soluble salts. In the case of EAF Slag, Barium, Calcium, Copper, Nickel, Lead and Zinc tend to show signs of a cationic behaviour.

In some cases, the release from the Conformity test is below the legal limit set by the Catalan Decree [2] with a higher release of the constituent for the remaining pH levels, as seen for Barium, *Figure 29*. Note that this observation should not influence validating the compliance of the material as the Conformity test is carried out with demineralised water meaning the final pH depends on that of the EAF Slag.
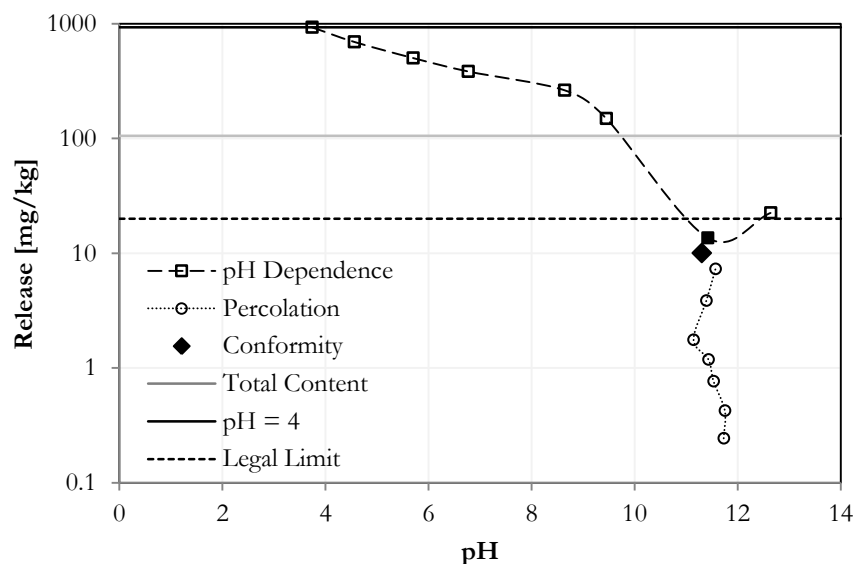

Figure 29: Release of Barium in function of pH, related to total content, percolation and conformity tests
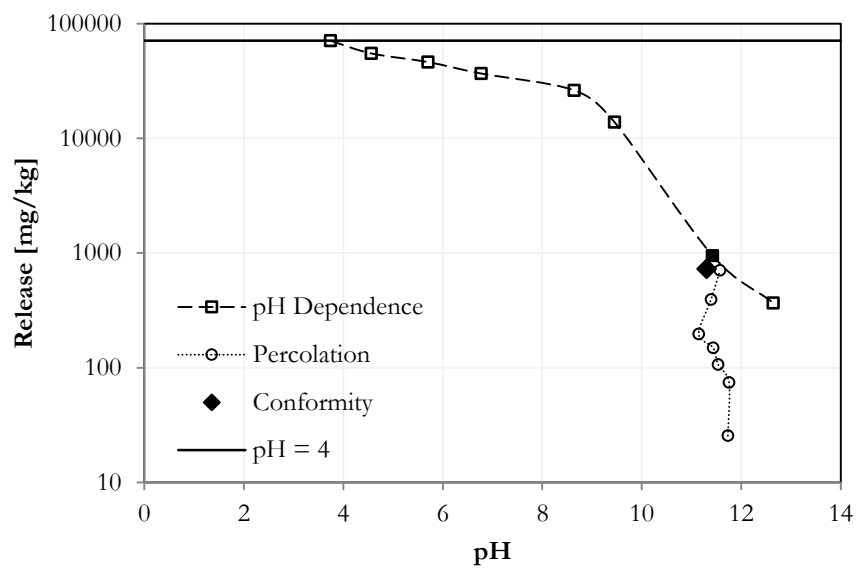
Figure 30: Release of Calcium in function of pH, related to total content, percolation and conformity tests
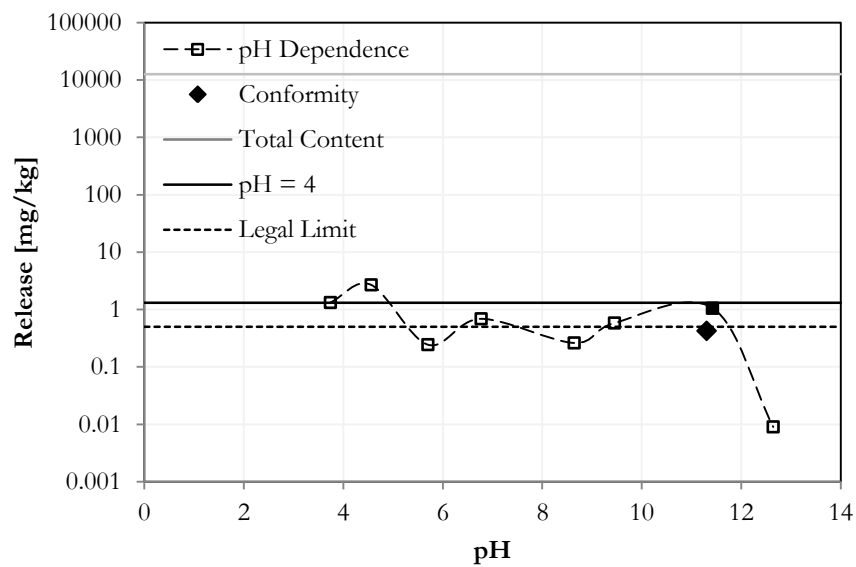

Figure 31: Release of Chromium in function of pH, related to total content and conformity tests
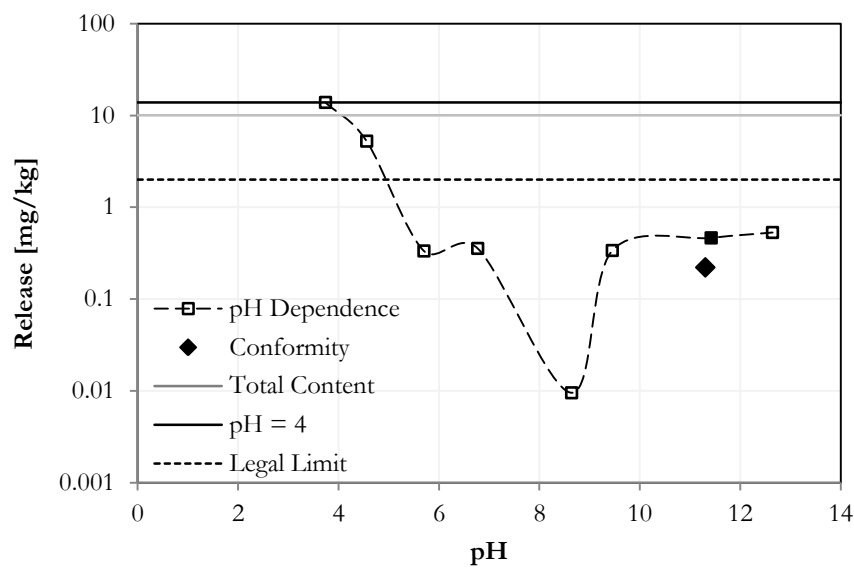
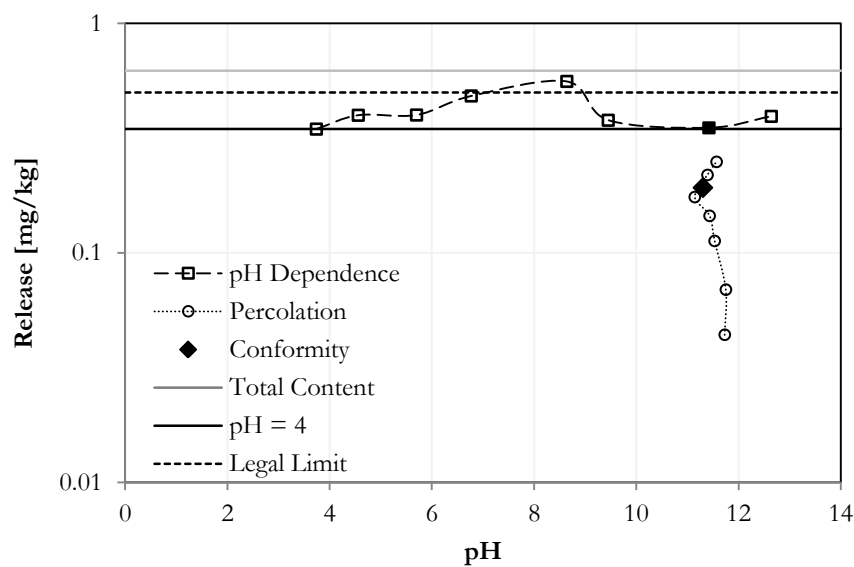*Figure 32: Release of Copper in function of pH, related to total content and conformity tests*

Figure 33: Release of Molybdenum in function of pH, related to total content, percolation and conformity tests
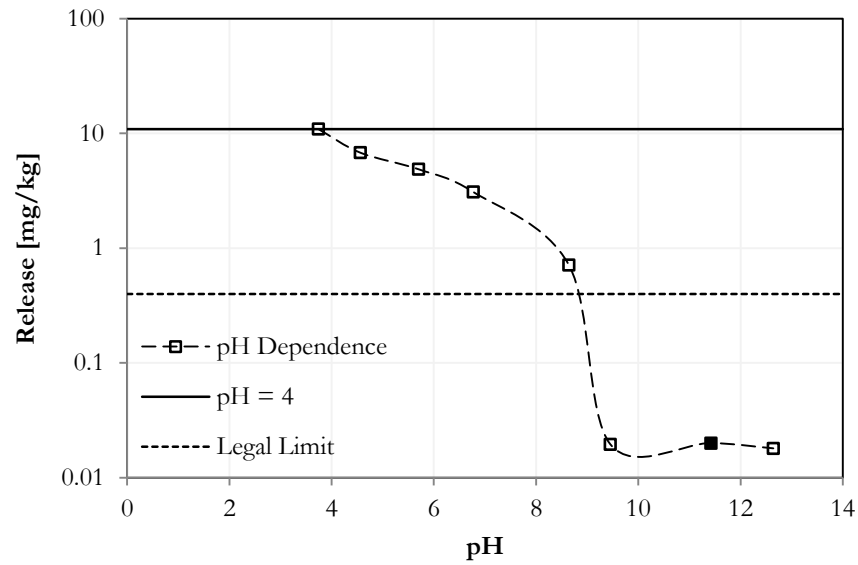
Figure 34: Release of Nickel in function of pH, related to total content and conformity tests
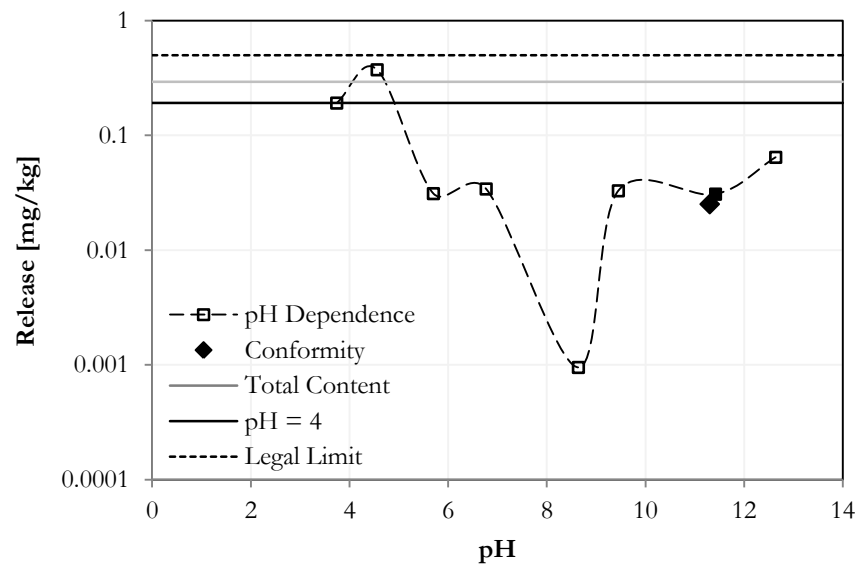

Figure 35: Release of Lead in function of pH, related to total content and conformity tests
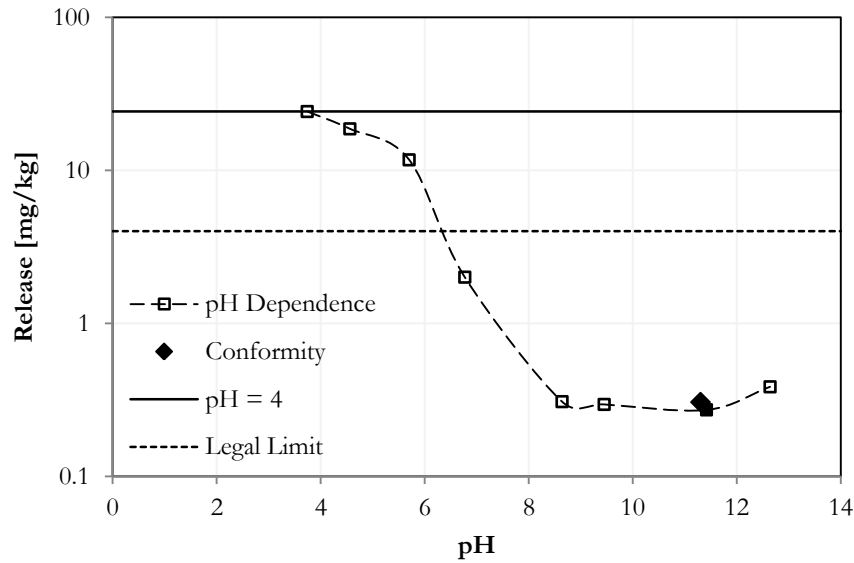
Figure 36: Release of Zinc in function of pH, related to total content and conformity tests

3.2.6. Comparison of Granular and Monolithic Behaviour

The release mechanisms and constituents resulting from the monolithic and percolation tests show various similarities. For this reason, the cumulative release of Barium, Calcium, Chloride and Sulphate have been represented in function of the tests specific L/S ratio in *Figure 37* to *Figure 40*. The L/S ratio was chosen (instead of time for example) as it is one of the key leaching parameters, which can be easily transformed to represent conditions relating to different applications.
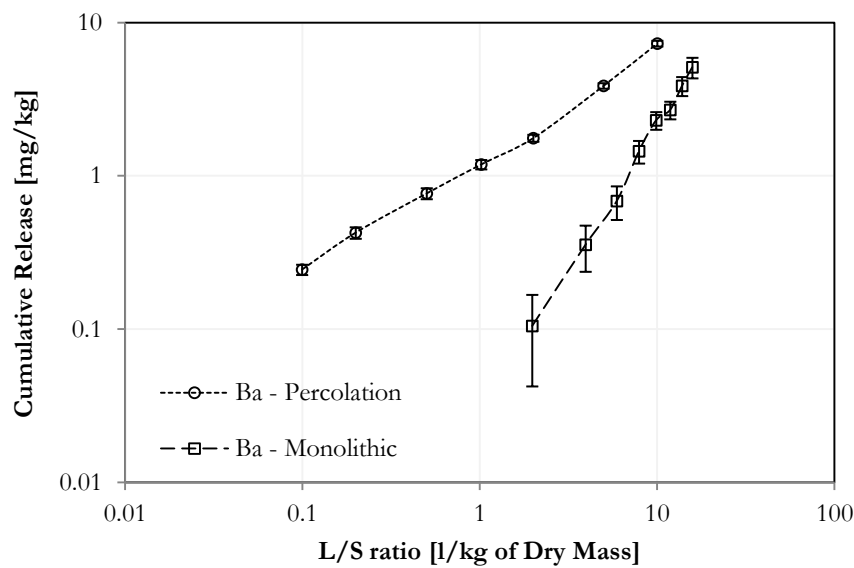

Figure 37: Release mechanisms of Barium from granular and monolithic tests

The size of the test particle plays a large role in the initial released quantity of a constituent. Recall that the particle size for the percolation tests is below 4 mm, whereas the monolithic test units are the original dimensions (80 – 140 mm). This difference gives the percolation test a significantly larger surface area through which the leaching occurs. *Figure 37* and *Figure 38* show the solubility and diffusion controlled leaching mechanisms of Barium and Calcium. *Figure 39* and *Figure 40* show the comparison between the leaching mechanisms, wash out and depletion for Chloride and Sulphate.
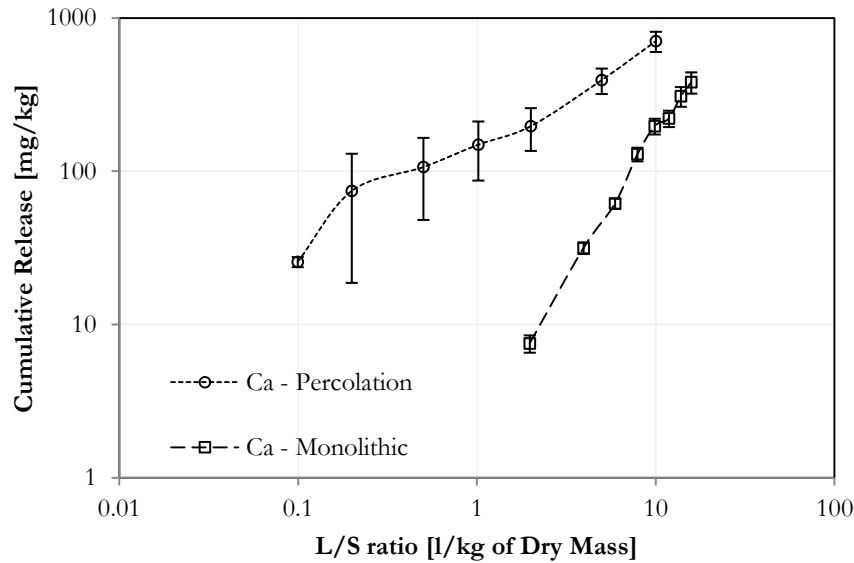

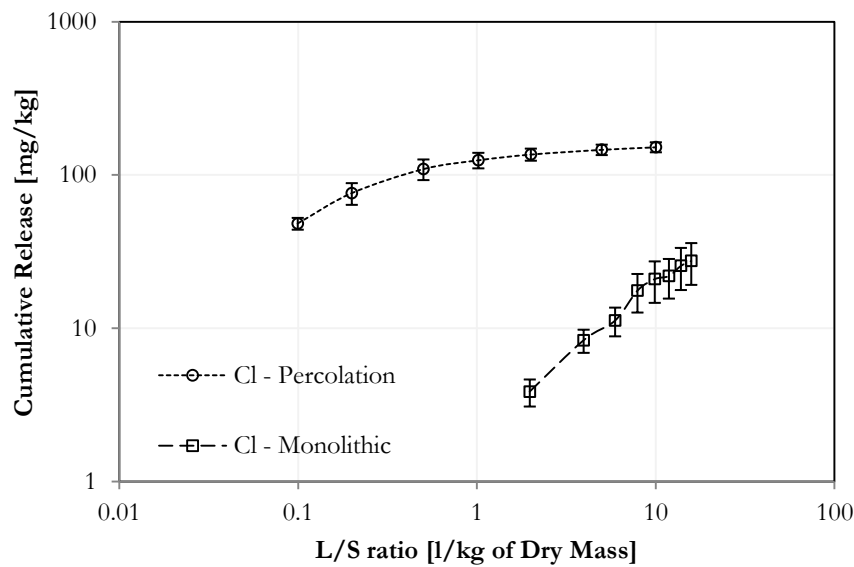*Figure 38: Release mechanisms of Calcium from granular and monolithic tests*

Figure 39: Release mechanisms of Chloride from granular and monolithic tests
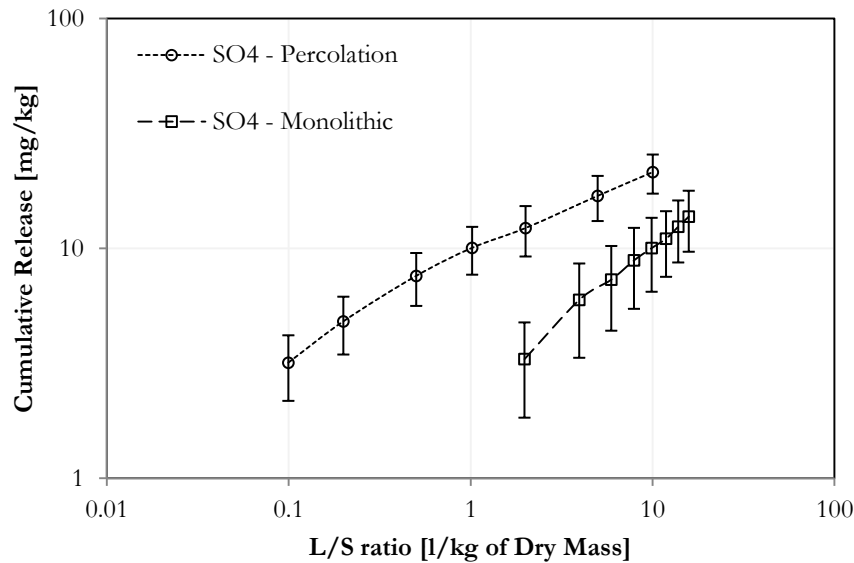
Figure 40: Release mechanisms of Sulphate from granular and monolithic tests

3.3. Compliance Tests

The main purpose of compliance tests is to categorise materials as inert, non-hazardous or hazardous in function of the leaching limits established by legislation. In this study, the regional legislation Official Journal of the Catalan Government, No. 5328, Decree 32/2009 [2] has been used to classify the studied EAF Slag. Apart from the constituents defined in the Decree, the total content of Calcium is measured to determine its potential influence on the pH of the surroundings which is in contact with the EAF Slag.

3.3.1. Conformity

Part 2 of the Norm EN 12457 Characterization of waste – Compliance test for leaching of granular waste materials and sludges [36], was used to determine the material's constituent release.

3.3.1.1. Results

Figure 41 represents the average leached quantities obtained through the Conformity Test compared to the legal limits defined by the Official Journal of the Catalan Government, No. 5328, Decree 32/2009 [2]. All of the constituents analysed from the eluates are below the limits specified. From these results, EAF Slag can be classified as an inert waste which will not have any direct negative effect on the environment.
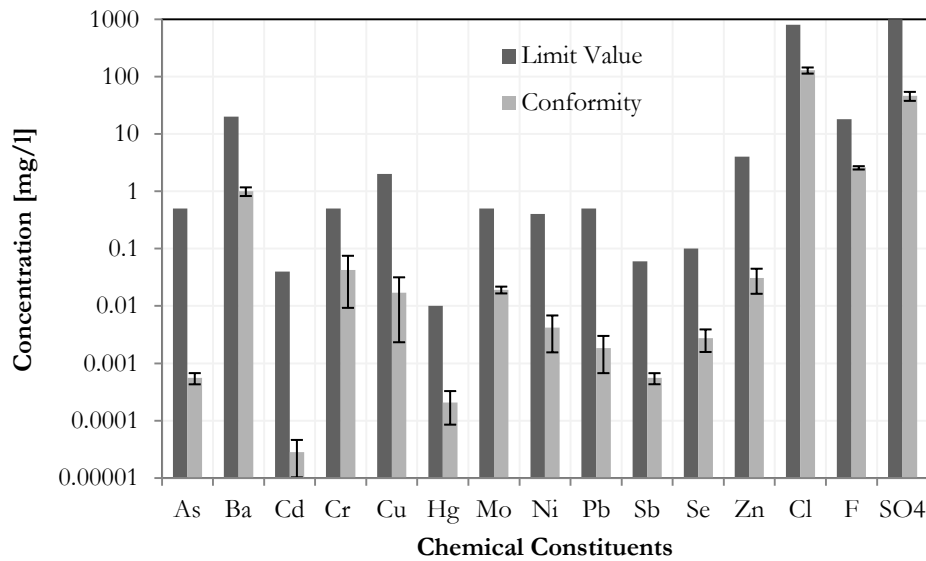
Figure 41: Verify the release of constituents is below the legal limit defined in the Decree 32/2009 [2] *for EAF Slag*

3.4. Effects of Acidic Attack

Due to the difficulties observed in the filtration process of dissolutions of EAF Slag and acidic leachants, a Scanning Electron Microscope (SEM) was used to compare the particles of a sample with those which had been attacked by acid.

Figure 42 and *Figure 43* compare a pulverised test sample (particle size < 0,063 mm) of EAF Slag, before and after an attack from an acidic leachant. The reference sample shows disperse ground particles, whereas after the acidic attack, these particles form agglomerations. The larger agglomerated particles and the formation of string-like particles may be the cause of the difficulties in the filtration process.
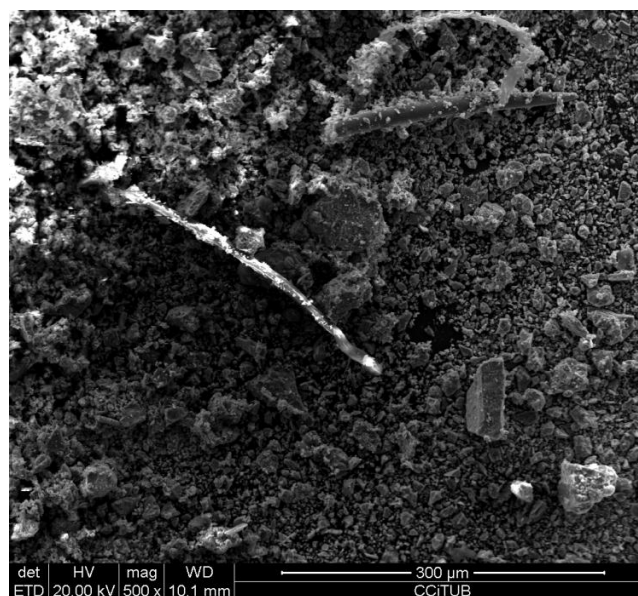

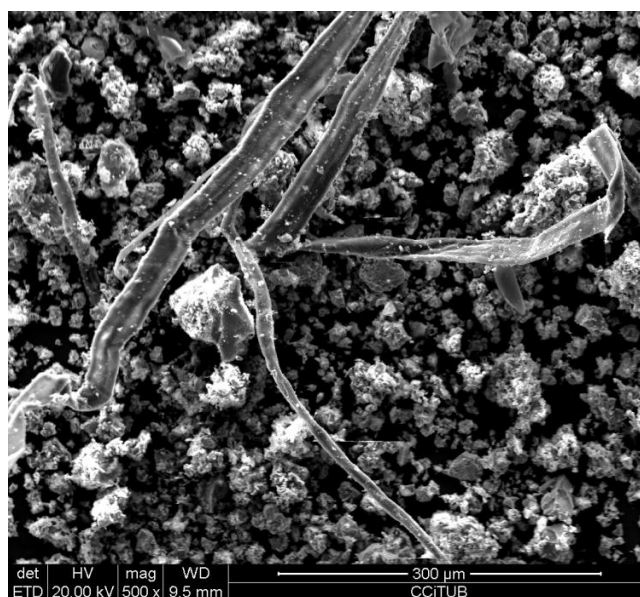*Figure 42: SEM image of reference sample of pulverised EAF Slag*

65

Figure 43: SEM image of pulverised EAF Slag after an acidic attack

Chapter 6
CONCLUSIONS

A full experimental campaign was carried out to determine the potential recovery of Electric Arc Furnace Slag with the intention of being used as the material fill in gabion cages. For this particular application, EAF Slag with a large diameter was considered and tested to ensure compliance with technical and environmental specifications established by regional legislation.

The study concludes that Electric Arc Furnace Slag can be used as a material fill in gabion cages in place of natural rock, as it complies with the principle technical and environmental specifications defined by legislation. In particular, the material is durable and can resist extreme weather conditions, as well as, complying with the leaching limits established by the Official Journal of the Catalan Government, No. 5328, Decree 32/2009 [2].

Within the global conclusion, a number of secondary points have been defined, which focus on the individual aspects of the material's behaviour.

- The EAF Slag fraction studied (80 – 140 mm) has an average unit weight of 2267 kg/m^3 and an absorption of 1,4%. The material's chemical composition showed signs of potentially expansive constituents CaO (27,6 %) and MgO (3,2 %), whereas, the mineralogical composition showed that these elements were not present in the form of oxides.

- EAF Slag is a durable material, as it showed resistance to hydration (Autoclave test) and freeze/thaw testing (Magnesium sulphate test). The Los Angeles Abrasion Coefficient obtained (16,3 %) is below the limit value specified by legislation [52]. The material shows an expansion potential of approximately 1,5 % in volume which stabilizes after the initial hydration of chemical constituents (CaO, MgO and potentially FeO) after a period of approximately 7 days.

- The total content and release potential of the constituents detected in EAF Slag have been obtained and represented in *Figure 29* to *Figure 36*.

- Assuming the EAF slag aggregate behaves as a granular material in a gabion cage application: Barium, Calcium and Fluoride show signs of solubility control, while Chloride, Molybdenum and Sulphate are subjected to washout. These results were obtained from the Percolation Test [34] for which the material was ground, creating a larger surface area for potential release.

- Assuming the EAF slag aggregate behaves as a monolithic material in a gabion cage application: Barium and Calcium show clear signs of diffusion control, whereas, Chloride and Sulphate are controlled by depletion. These results were obtained from the Monolithic Test [32] for which the material was tested in its original state, as well as, with freshly cut surfaces. No conclusive comparison could be made based on the results obtained from the aged and freshly cut surface of the test samples.

- The neutralization curve of EAF Slag, *Figure 28*, obtained from the pH-Dependence Test [35] shows no clear signs of a buffer effect caused by the material's

composition in the pH range considered [4 - 12]. The release of each constituent in function of the pH variation has been represented in *Figure 29* to *Figure 36*.

Electric Arc Furnace Slag could behave both as a granular or monolithic material over the life cycle of its application in gabion cages. Over time (high values of liquid to solid ratios, L/S = 10 l/kg) the leaching mechanisms tend toward similar accumulative results, meaning both potential behaviours would be acceptable for the application of EAF Slag as a material fill in gabion cages.

Chapter 7
FUTURE LINES OF INVESTIGATION

This study contributes to the existing research and knowledge on the recovery of EAF Slag and the use of alternative materials in gabion cages. Apart from the gained knowledge, future lines of investigation have also been defined based on the observed test results from the experimental campaign.

With reference to gabion cages, an optimal granulometric curve could be defined to obtain the most compact disposition of the EAF slag particles. This optimal size distribution would need to have a lower and upper bound limit in function of the wire mesh used and the size of the gabion cage.

From a material and an analytical point of view, more in-depth testing may be carried out to determine the influence of the material's surface age. This can be done to determine whether the size and shape of the aggregate influence the release quantities of a constituent, as well as, if the test surface is aged or freshly cut. The influence of Redox and Dissolved Organic Carbon (DOC) in the eluate can also be tested to determine if these parameters have any potential effects on the release of constituents from the EAF Slag.

The release results from the Basic Characterisation Tests can be combined with geochemical data of a specific area to obtain long term predictions in real applications. These release models would allow for estimates of an overall potential environmental impact within a region over a certain period of time, which can then be adjusted according to obtained lysimeter and field data.

The need for the development of an extensive international database of materials showing their leaching potential is a key point to consider and one which has been mentioned throughout this study. A database would allow for comparison and validation of leaching and characterisation test results between various materials with similar release mechanisms.

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