

MASTER'S THESIS

DIPLOMARBEIT

Influence of Ageing in the Assessment of Leaching Behaviour of Electric Arc Furnace Slags

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ABSTRACT

Mining operations and the subsequent smelting and refining procedures result in large quantities of waste and by-products. After separating the valuable components, side components and impurities are bound in an artificial rock matrix, the slag, with elevated technical properties, which render them - in principle - feasible for constructive purposes.

However, slags from the Electric Arc Furnace contain, like slags from other processes and also natural rock material, a variety of trace elements, which can give rise to contamination of soils, lakes, rivers and coastal areas, at a certain level of release of these elements from the solid slag. The assessment criteria of the environmental impact at a material based level is often settled on leaching tests.

Electric arc furnace slags from two different production cycles in the same factory have been investigated with the one stage batch test according to EN 12457-4 at a liquid to solid ratio of 10 l/kg after prior aging for a total of three month in ambient, humid and aqueous conditions. Extractions were done at the freshly sampled slag from the factory and at intermediate steps at the age of 21, 42 and 91 days of aging. Their mineralogical composition was determined by a non-quantitative diffraction analysis and the influence of particle size distribution within the sample was evaluated.

The two investigated slags did not show relevant differences in their leaching behaviour, neither does their mineralogical composition, although differences in the content of Wüstite and Gehlenite are observed.

The Barium release of the material stored in ambient and humid conditions showed the expected decrease due to formation of Barite, whose tendency can be mathematically expressed as an exponential-3 parameter-fall, although this is only fulfilled for one of the two slags investigated. In aqueous conditions, the release is slightly higher and does not reveal a definite depletion.

Chrome, Copper, Lead and Zinc showed a similar up and down release tendency during the aging in ambient and humid conditions, which lacks of further explanation. During the storage in aqueous conditions these elements reveal a general peak at the age of 21-42 days, followed by a

decrease in release at the final extraction at the age of 91 days, what can probably be associated to the lower reduction potential at the end of the experiment.

Molybdenum appeared not to be influenced by neither of the aging methods applied, its release in both experiments did not show deflection in the time series established.

Vanadium was increasingly released after the aging in ambient and humid conditions, rising its leachability from 0,88mg/kg solid mass for the freshly sampled material in the factory to 1,58mg/kg after 91 days of aging and from 0,58 to 1,13mg/kg respectively.

Comparison regarding the particle size distribution showed a higher release tendency for the finer graded samples, this is more obvious for the anions than for the cations. However, all the samples had a similar grain size distribution with a maximum discrepancy of 17,7% in the fraction <2mm.

Assessment according to the European Landfill Directive (1999/31/EC) or the Austrian Landfill Directive 2008 excludes the slags from the classification “inert waste”, due to higher Chrome contents in the solid mass (only required in the Austrian Landfill Directive 2008) and higher leaching test results for Flour and Sulphate. Generally, this study does not provide sufficient information for a classification as inert or hazardous.

Keywords: EAF-slag, leaching, aging, carbonation.

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Chapter 1: INTRODUCTION

The smelting and refining process of iron ore and metallic scrap involves large quantities of raw products and similarly produces high amounts of secondary materials, these are slags and dust. For economic and environmental reasons the slags are traditionally recycled and applied primarily in the construction industry, as they fulfil the same requirements as natural aggregates.

The formation of slags can be compared to the genesis of volcanic rock materials, only the time scale is squeezed. Their structure is a similar mixture of mineral and vitrified phases, depending on the temperature (and pressure) conditions.

Although technical, economic and environmental reasons approve the utilization of slags as industrial aggregates, they cannot be as easily handled as their natural counterparts. The application of slags implicates a necessary precaution from the technical and environmental point of view.

Addressing the technical feasibility, restrictions caused by volume instabilities are given. These originate from the reaction of free lime and magnesium, which occur in steel-slags due to the employment of lime and dolomite in the steel mill, with water. Generally, this volume increase is encouraged by the distributor before the slag is applied on site by ageing the crushed slag in ambient conditions in order to guarantee its quality. This process at the same time influences the environmental impact of the finally installed slag by altering its chemical structure and therefore changing its release behaviour.

From the environmental point of view, slags can have a significant impact on soils and (ground) water by transmitting metals and other substances and consequently contaminating the surrounding (aquatic) environment. In this study the level of this contamination and its tendency during the aging process are investigated.

In most industrialized countries, recycling slag products is already state of the technology in order to provide sustainable resource management. Although steel producers in the north of Spain, particularly the Basque Country, have already initiated the recycling process of steel slags, the slag from the single steel plant in Catalunya in Castellbisbal, close to Barcelona, still lacks of

sufficient scientific proves to eliminate certain technological and environmental reservations, which would guarantee its launch on the market on a value basis.

From the environmental point of view this is an astonishing situation, being aware of the fact that in the south of Catalunya, the distribution of Municipal Solid Waste Incinerator Slag (MSWI-slag) is already successfully implemented, although for less valuable applications and below additional requirements.

Chapter 2: PURPOSE

The focus of this work is to evaluate and assess the influence of aging on the leaching behaviour of EAF-slag from the factory of CELSA in Castellbisbal, Spain on a material level. Additionally mineralogical composition and probable influences of the grain size distribution are determined for the discussion of the results. Finally the applied aging methods are discussed and recommendations for on-site and laboratory aging are given.

The first part of this study is dedicated on the description of slags, their properties, common treatment and application for engineering purposes. Furthermore, environmental regulation in different countries, crucial dependencies of the release behaviour and the basics of leaching tests are described based on literature studies.

The second part describes the practical laboratory work, the methods applied, the results obtained and a discussion of the results. The reader of this work should bear in mind, that the study was conducted by a civil engineering student with a limited base of knowledge in chemistry.

The main interest lies in the detection of trends concerning the release of selected cations and anions after leaving the material in ambient (oxidizing) and aquatic conditions for a total of three month. Especial attention is paid to the behaviour of Barium release, as the development of the carbonation process should be reflected there.

It should be stressed, that the results of this work only provide information for the environmental assessment in a very limited, material based level. The leaching behaviour in laboratory can only show possible long-term effects from a restricted point of view, as the system boundaries are too narrow. This aspect is described briefly in the chapter “Environmental issues concerning slags”.

PART 1: THEORY

Chapter 3: SLAGS FROM IRON AND STEEL PRODUCTION

Raw-steel is currently produced by mainly two types of processes: The Basic Oxygen Furnace (BOF) and the Electric Arc Furnace (EAF). The BOF, also known as LD converter, is charged with pig iron from the Iron Blast Furnace. The Blast furnace needs high amounts of coke for the reduction of the iron ore. Coking is the process of heating coal in coke ovens to drive volatile matter from it. As this process is very cost-intensive and produces high amounts of toxic gases, there further exist direct reduction processes like the COREX-process, the MIDREX-process, the FINEX-process and production in rotary kiln. Direct reduction processes are basically two-stage smelting reduction processes that produce hot metal on the basis of non-coking coal and iron ore.

After production in the primary process (BOF or EAF), the raw-steel has to be further refined to meet specific requirements of the chemical composition. This happens in the secondary process, where some elements are removed from the steel (e.g. Sulphur, Phosphorus and Carbon) and some are alloyed (e.g.: Manganese, Nickel, Chrome and Vanadium).

Slag is a by-product, which occurs in all the different steps mentioned before. Different types of slag originate from the different production processes and vary furthermore depending on the method used to cool the molten slag or further treatment.

The most important slags for the use of recycling according to their quantity within the iron and steel production and their technical properties are

- blast furnace slags
- steel slags (BOF and EAF).
- secondary steel slag

Addressing steel slags, the more common process in Europe is still Basic Oxygen with 61% of crude steel production in 2005 (91% in Austria), whereas in Spain, Italy, Portugal and Greece (all included in this number) more Electric Arc Furnaces are in service. In Spain 76% of the steel is produced by EAF, with most of the factories located on the north coast (1).

Probably the EAF steel production will expand in the future as raw material stocks rise whereas the crude material for the BOF is more difficult to obtain if mining activities are more restricted.

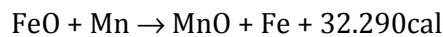
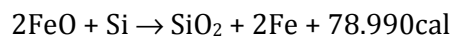
3.1. ELECTRIC ARC FURNACE SLAGS

The purpose of the EAF is for the re-melting of steel scrap, however, EAFs can be charged with limited amounts of iron scrap, pig iron and direct reduced iron. If 100% of the charge comes from the scrap, the steel quality is difficult to control, this is why the steel produced in EAFs is often used if less quality is required (steel for construction industry).

After charging the furnace with the scrap, graphite electrodes are lowered on the feedstock and switched on. The electrical power is transformed into heat, because of arcing between the electrodes and the scrap. When the feedstock starts to liquefy, lime (calcium oxide) and oxygen are added, the first to generate a slag layer on top of the molten steel and the last to oxidise the iron from the scrap with the following chemical reaction:

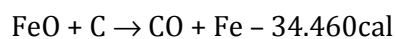


The iron oxide oxidises further silicon and manganese:



The oxides are removed to the slag, which is floating on the surface of the molten steel. Besides assimilating the oxides, the slag acts as a thermal blanket and helps to reduce erosion of the refractory lining.

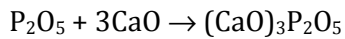
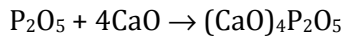
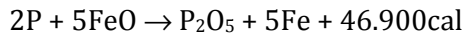
As soon as the temperature is high enough (about 1600°C) and sufficient FeO is assimilated in the slag, carbon is injected, which reduces the iron oxide to iron and to carbon monoxide, which causes foaming of the slag:



Foaming slag is used to increase the thermal efficiency of the furnace during the following refining period. Furthermore, the decreasing boiling of the slag indicates the end of the process. Like in the BOF, the fluxes (usually calcium oxide and/or magnesium oxide) are needed to protect the refractory from the acidic impurities and to remove them from the molten steel to

the slag. The slag formers (fluxes) are partly charged with the scrap, and partly added later in the refining period.

In the first phase, the fluxes are utilized to oxide the phosphorus from the molten steel:



The phosphorus oxides too are removed to the slag. During the foaming mentioned before, the EAF-slag is continuously pouring out through the slag door, by tilting the vessel and begins to solidify quickly into a rock-like product, the EAF-slag. On tapping, steel is drained from the furnace via a submerged taphole on the opposite (figure 3-1).

The slag still contains high amounts of metallic pieces, which are removed and recycled for the steel making process. The end-product, which is no more further recycled in the steel-making process, still contains some heavy metals, furthermore fragments from the graphite electrodes and the furnace shell, usually ceramic bricks (e.g.: carbon bounded magnesia bricks).

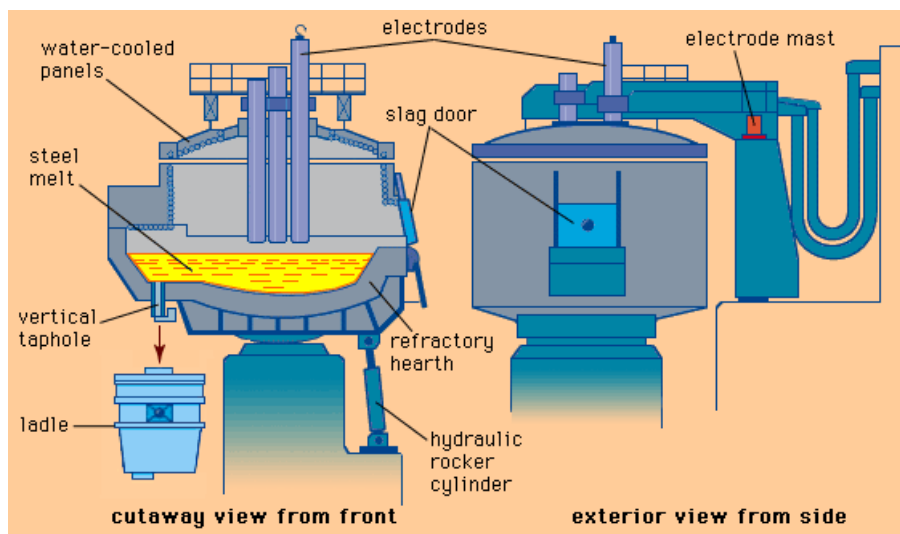


Figure 3-1: EAF (2)

The molten steel still contains high amounts of oxygen, sulphur and carbon. These impurities, additionally to obtain a specifically required chemical composition of the steel, are removed in the refine process.

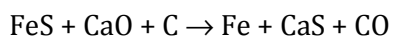
The refine process partly can take place in the EAF and is then completed in Secondary Steel Operations: Deoxidation takes place in the EAF, parallel the desulfurization starts, which is completed later in the Secondary Operations. Important to state that the slag obtained before

the refine process (the EAF slag – high amount of oxides) has different properties than the one obtained afterwards (usually called Ladle slag – essentially pure lime).

The refining process can partly take place in the EAF according to IHOBE (Eds.), 1999; the EAF in CELSA, Castellbisbal – Spain, does not include this step.

In the first phase of refining in the EAF, the liquid metal is covered with a reductive composition of lime, fluorspar and coke or graphite, forming a layer of slag on the surface. The simple contact provokes the molten steel to oxide the slag, decreasing the oxygen content of the steel (Deoxidation). The final deoxidation is achieved by adding manganese (Mn) and silicon (Si), which oxide to MnO and SiO₂ that again are assimilated to the slag.

The desulfurization is initiated too by the contact with the slag, which contains lime and carbon:



Per ton of steel about 120 to 150kg of EAF-slag is produced (5).

3.2. SECONDARY STEEL SLAG

In order to optimize the composition and further to obtain high-quality steel and meet specific chemical composition, the steel from the BOF or EAF is further treated in Secondary Steel Making facilities, where several types of furnaces are used. Generally, the refining process includes desulfurization and optimization of the oxygen content. If desired, the nitrogen and hydrogen quantity can be optimized, specific alloys added and the carbon content further reduced.

The molten steel is covered with the reductive slag of lime, fluorspar and coke or graphite, and is gradually stirred in order to homogenize bath composition and temperature, facilitate slag-metal interactions and accelerate the removal of inclusions in the steel. Stirring is achieved by argon bubbling the liquid steel or Electromagnetic Stirring (EMS).

The fluorspar is added to prevent the stiffening of the slag, consisting primary of lime without oxides.

Carbon and other impurities are removed in the Recirculation Degasser, using Argon for the movement of the steel and often oxygen to reduce the carbon.

The argon environment further allows the addition of alloys. During this step, Aluminium and oxygen are added, which react to Al_2O_3 under a strongly exothermic reaction and help to raise the temperature. The Al_2O_3 is later removed to the slag.

The slag produced in this steps (in literature referred to as Ladle Slag or Secondary Steel Slag) of refining is a white powdery material, with a high amount of free lime and some rests of BOF or EAF-slag (4).

Per ton of steel about 30kg of Ladle-slag is produced.

3.3. PROPERTIES

Slag properties are irregular, depending on the raw-materials charged, the type of operations in the steel-making process and further treatment. Therefore, even in the same plant and furnace properties are varying.

Especially the chemical composition of EAF-slag changes according to the scrap charged into the furnace: High amounts of chrome will occur if scrap with chrome-coating is charged, e.g. used for street lamps. However, evidence shows that the properties are generally comparable.

The EAF-slag has a partly crystalline, partly vitrified structure with a dark-grey colour. Quick cooling with water would develop a more vitrified structure, which obviously does not change the chemical composition, but the mineralogical structure. The grain sizes are usually between 0 and 150mm with the biggest part of 0/40. The particles are dense, angular and roughly cubical.

3.3.1. Technical Properties

Average values show, that aggregates of recycled slag fulfil the technical requirements of a wide range of construction applications including road construction (capping, subbase, base, binder course and surface course), concrete construction (both as aggregate: EAF slag - and as cement: Ladle slag, which has pozzolanic or even hydraulic properties), embankments, etc. Especially the high frictional resistance and resistance to rutting of EAF-slag enhance the use as aggregate in surface courses. Angularity and shear resistance qualifies the slag for different pavement layers (6).

The high level of strength, the rough surface texture, together with an high Polished Stone Value (PSV) and a binder adhesion > 90% qualify EAF-slags especially for asphaltic surface layers of high trafficked roads (7).

Table 3-1 gives a range of values found in different sources in comparison to natural granitic aggregates.

Table 3-1: Technical Properties of EAF-slags

Property	Unit	Cloos S.A. (company, LUX)	SLAG S.A. (company, FR)	Motz, H. (6)	Granite (<i>comparison</i>)
Bulk Density	[kg/dm ³]	3,7 - 4,0	3,6	3,5	2,5-2,6
Water Absorption	[Vol.-%]	3	3	0,7	< 0,5
PSV ⁽¹⁾	[-]	58-70	56	61	48
Micro Deval	[-]	5	10	n.a.	Mai.15
LA	[-]	12	14-17	n.a.	27-49
⁽¹⁾ PSV is equivalent to CPA*100 in the spanish standard					

Two facts concerning its technical properties must be taken in account when using EAF-slag as an aggregate: the high bulk-density and volumetric expansion.

The high bulk-density explains the resistance of the material, but make it economically less competitive as transport-costs raise. Furthermore, the granulometric curve must be recalculated, if the slag is only used for the coarse grains with natural aggregates completing the curve for the fine grains.

Volumetric expansion is caused by hydration of Calcium oxide (CaO) and Magnesium oxide (MgO), producing cracks if applied as aggregate for surface courses. The Calcium oxide hydrates quickly, whereas the hydration of Magnesium oxide takes place very slowly.

The expansion can be minimized by ageing the material with water for several month to hydrate the Calcium and Magnesium oxide, by controlling the chemical composition of the slag during the EAF process and minimizing the CaO and MgO content or by treating the slag with acid.

Although application as aggregate in rigid confined structures like concrete is not recommendable, due to its expansion behaviour, investigations concerning concrete made with EAF oxidizing slag show optimistic results if the slag is properly treated before entering in application (8).

3.3.2. Chemical and Mineralogical Composition

The chemical composition of EAF-slag is primary influenced by the scrap-composition and the fluxes added. The main components are therefore Calcium oxide, Silicium-dioxide and Magnesium oxide, with approximately 30, 20 and 10% respectively. Furthermore it contains

high amounts of Al_2O_3 , FeO , Fe_2O_3 , MnO and additional trace elements (Chrome, Phosphor, Vanadium, etc. see table 3-2).

The iron content increases during the production process (oxidation) and influences the density of the slag. The steel producer will seek to minimize the iron in the steel-slag in order to avoid losing primary material and minimizing the addition of lime, which is then necessary to inhibit the acid attack of the ferrous slag on the refractory.

The basicity of the slag is defined by the relation of CaO/SiO_2 , although it is sometimes referred to as $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ or $(\text{CaO}+\text{MgO})/\text{SiO}_2$. Due to its origin from calcium smelter, the EAF slag (equally to the other slags from iron and steel production) is generally basic with CaO/SiO_2 ranging from 1,3 to 2,6 (9). The basicity is used as an indicator for its volumetric stability. The higher the basicity, the higher values of expansion will be.

Table 3-2: Chemical composition of EAF-slags

	Cloos S.A. (company, LUX)	EAF from not/low alloyed steel (8)	EAF from high alloyed steel (8)	Motz, H. (6)	Granite (8) (comparison)
CaO	25-30	26-38	37-40	25-40	1,1
SiO_2	10-20	11-16	14-28	10-17	71,3
MgO	2-7	3-10	7-13	4-15	0,7
Mn_{tot}	n.a.	3,5-5,5	2,6-4,1	n.a.	< 0,1
Fe_{tot}	20-30	24-40	6-7	18-29	1,8
Al_2O_3	4-8	3-6	5-13	4-7	14,3
Cr_2O_3	n.a.	0,7-2,7	5-19	n.a.	< 0,01
P_2O_5	0,5-1,5	0,5-0,8	< 0,1	< 1,5	0,12
$\text{Na}_2 + \text{K}_2\text{O}$	n.a.	< 0,08	< 0,08	n.a.	8,6
S_{tot}	0,1-0,2	n.a.	< 0,4	n.a.	0,05
CaO/SiO_2	n.a.	1,9-2,6	1,3-2,3	n.a.	0,015
$(\text{CaO}+\text{MgO})/\text{SiO}_2$	n.a.	2,2-3,1	1,6-2,9	n.a.	0,025
Unit: [Mass-%]					

Apart from the chemical composition, least equally important factors for its characterisation are the phase composition and the material structure. Slags are composed of crystalline phases, which are generated similar to minerals in natural geological processes and amorphous substances like in volcanic glasses. The more slowly the slag is cooled down, the more the crystalline phases will dominate. Rapid cooling enhances the formation of amorphous materials, most typically by glass forming elements like silicon or aluminium.

As elements can be mineralogical bound into a structure by different ways, the chemical composition of a material does not allow drawing conclusions straight to its properties.

As the mineralogy of the slag may change, the total content of an element is not an appropriate indicator of the possible impact it can cause on groundwater and surface water. The leaching ability of an element depends – as one of its influences – on how it is captured into the matrix structure of the material.

Generally, an amorphous material is less soluble than a crystallized phase with a similar chemical composition, due to the very slow kinetics for a re-crystallization and reactions with the surrounding liquid media (10).

The typical mineralogical composition of EAF-slags found in different sources is shown in table 3-3. The data found shows little coherence, probably due to varying focus in investigation. All sources accede that the main mineral of EAF-slags is Dicalcium Silicate ($2\text{CaO} \cdot 2\text{SiO}_2$), which can be found as β -Dicalcium Silicate or γ -Dicalcium Silicate. γ -Dicalcium Silicate is rarely found in EAF-slags, but can occur in Ladle-slags, where they emerge during the cooling from the β -modification (9). The transition from β to γ -Dicalcium Silicate provokes a volume increase of 10% and is therefore of high importance for engineering applications.

Table 3-3: Mineralogical composition of EAF-slags

Mineral	Formula	Cloos S.A. (company, LUX)	EAF from not/low alloyed steel (8)	EAF from high alloyed steel (8)	Granite (comparison) major minerals
Gehlenite	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$		x	x	Quartz
Akermanite	$2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$		x	x	Feldspar
Merwinite	$3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			x	Glimmer
Tricalcium Silicate	$3\text{CaO} \cdot \text{SiO}_2$	x			
Dicalcium Silicate	$2\text{CaO} \cdot \text{SiO}_2$	x	x		
Bredigite	$2(\text{Ca}, \text{Mg})\text{O} \cdot \text{SiO}_2$		x		
Brownmillerite	$2\text{CaO} \cdot (\text{Al}, \text{Fe})_2\text{O}_3$		x		
Spinelle ⁽¹⁾	$\text{Me}^{2+}\text{O} \cdot \text{Me}^{3+}_2\text{O}_3$	x	x	x	
Wüstite	FeO_x	x	x		
Free lime	CaO				
Periclase/ MgO_{free}	MgO		x	x	
Mayenite	$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$		x		
⁽¹⁾ Me stands for different metallic cations; x = Mineral detected					

Drissen (11) shows in an investigation concerning the leachability of trace elements in BOF-slags, that chrome is mainly bound in ferrous minerals (Dicalciumferrit, Spinelle and Wüstite), which are not or very little leachable and therefore stable minerals for the capture of chrome. On the other hand, Vanadium is bound in Ferrous minerals and Calcium silicates. The test results showed that the high leachability of Vanadium occurs due to the solubility of Calcium silicates.

3.4. SLAG TREATMENT

Typically, the slag undergoes determined steps of treatment after cooling, which include magnetic separation of iron, sieving and classification by size, crushing, re-sieving and aging, which is normally achieved by simply leaving the slag outdoors in atmospheric conditions. It is important not to crush the slag after the period of aging, as fresh surfaces susceptible to hydration of lime and magnesia would be created (figure 3-2).

To achieve technical feasibility weathering is indispensable to transform the free CaO and MgO into its hydroxides. If sufficient storage space is given, leaving the slag without further intervention for some month, depending on the climate will produce the desired effect. To assure uniform aging, the piles should be intermixed periodically or the slag piled to moderate heaps.

To accelerate the process, the slag can also be sprayed with water. Some Japanese operators even store the slag in large containers and apply high temperature steam on the slag in order to save space and time of aging, which can be accomplished by this method within a few days (6).

The Thyssen Krupp Stahl AG in Duisburg, Germany installed a more sophisticated method to decrease the free lime and MgO content in the slag. In 1996, they installed an equipment in their Basic Oxygen Converter which injects oxygen and sand or glass powder (Silicium) into the liquid slag. The oxygen helps to increase the heat and dissolves the sand, which binds the free lime and magnesium.

By modifying the cooling conditions, the distribution of crystal and amorphous phases can be affected. Rapid cooling (e.g.: established by water granulation) results in formation of vitrified phases, which has positive effects on the volume stability by preventing the formation of β -Dicalcium Silicate, decreasing the free lime content and enclosing expanding phases in the glassy matrix and improves properties regarding the leaching behaviour (10).

Whereas for BF-slags various cooling procedures are applied, steel slags (BOF and EAF) are generally cooled on air (slow cooling, figure 3-2 and chapter 3.4).

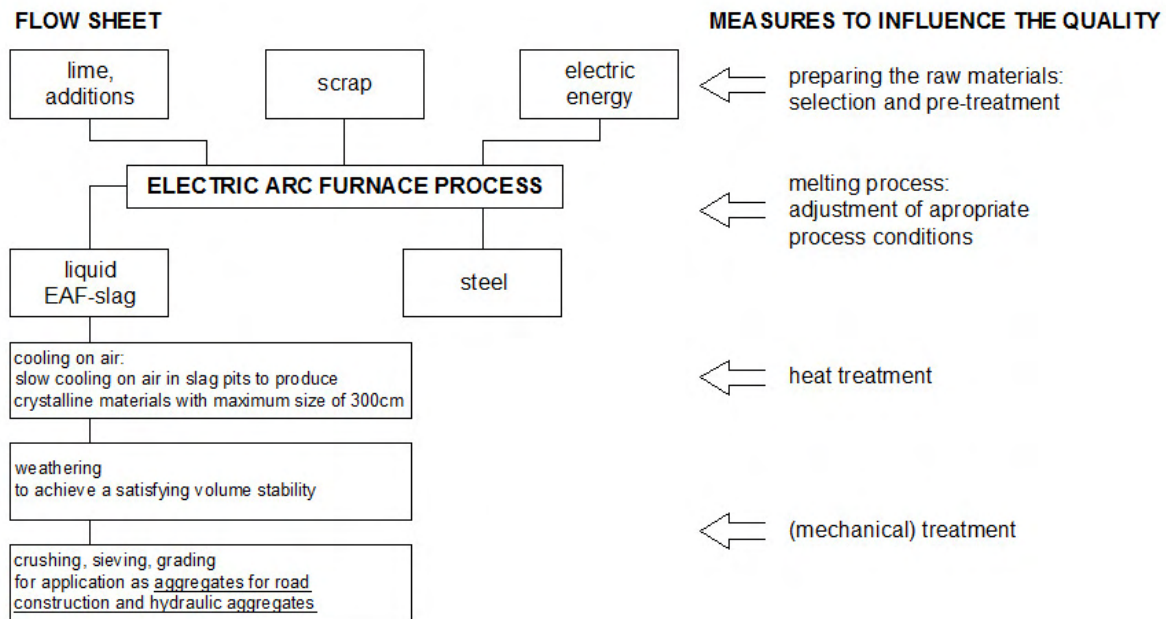


Figure 3-2: Typical slag treatment for EAF slags (12)

3.5. FIELDS OF APPLICATION

Utilisation of iron, steel and nonferrous slags in engineering applications is already standard in most industrialized countries. Knowledge and application priorities are varying slightly but generally head towards the same objectives.

Use instead of disposal obviously is desirable from an environmental and economic point of view. On the one hand, natural goods like aggregates are not renewable and every time more difficult to find in order of unrestricted mining and exploitation. In the region of Catalunya for example only three quarries for the mining of high-quality aggregates are left. On the other hand, metal production produces large amounts of by-product materials with similar properties to natural minerals, which demand plenty of space, another every time more valuable good on earth. Recycling of (appropriate) slags therefore maximises sustainability and minimizes waste.

The potential of marketing depends on the properties of the slag, the location of the steel mill, the volume produced, the relation between deposit costs and revaluating the slag and if there are other alternative, cheaper raw materials are available. For application in engineering, demands of volume tend to be high and the value of the product relatively low. These requisites can be easily fulfilled by slags, provided that the production location is close to the building site.

In Europe about 25 million tonnes of BF slag and 15 million tonnes of steel slag (BOF, EAF and SEM) were produced in 2004 (12). Calculating the volume with a raw density of 1,8 for BF slag and 2,2 for steel slag, the slag produced in Europe during one year can fill Viennese Stephansdom 100 times or heap up every 5 years a hill like Montjuic in Barcelona.

The factory Celsa produces 360.000 tonnes of slag per year, which is the total of 288.000 tonnes of EAF slag and 72.000 tonnes of SEM slag. By recycling this material 100.000 m³ less landfill volume would be needed per year.

On the other hand, the contribution to resource conservation – in particular aggregate conservation will be marginal, considering the total aggregate consumption in the region. According to Brunner (2003) gravel consumption can be estimated to account 4,6 tonnes per capita and year (13). This number is based on another study cited, it should be estimated here to reflect the situation in Germany 1994, when the construction industry held a 14,3% of the Gross Domestic Product (14), which is similar to the situation in Spain with 13,4% in the first semester 2007 (15). Hence recycling of 288.000 tonnes of EAF slag for construction purposes substitutes 0,89% of the total gravel consumption in Catalunya with 7,2 Mio habitants. Bearing in mind the actual production decline in the Spanish construction industry, a drop of 30% in production would increase the contribution of the slag to 1,24%.

Cross-checking this estimation by repetition with rough numbers for the European Union with approximately 500 million citizens and applying the production numbers for Europe cited before (25 million tonnes of BF and 15 million tonnes of steel slag), shows a similar result (figure 3-3). These numbers reveal that the recycling of the slag hardly collaborates to resource conservation.

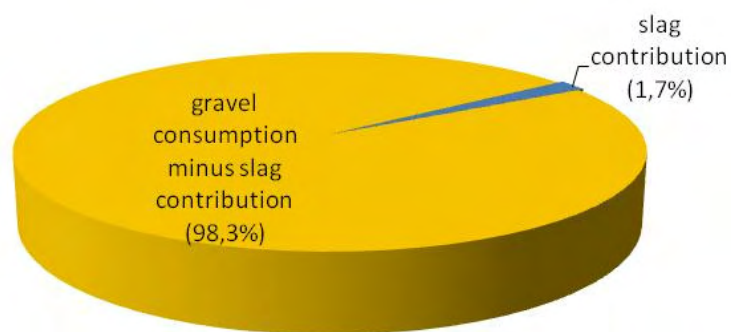


Figure 3-3: Gravel consumption and the contribution of recycling of iron and steel slags (estimation)

The longest tradition in recycling of slag surely can be assigned to slags from the iron production. The first furnaces are described in the 14th century; ever since metallurgical imagination treated to obtain benefits from the unavoidable product.

BF slag is utilized since the 19th century. First industrial use is reported from 1859, where it was applied in the production of bricks. In the second half of the 19th century its cementitious properties were discovered and the first cements produced at the end of the 19th century.

The total production of BF slag in Europe amounts to 25 million tonnes as mentioned before. Austria and Spain have a similar amount of generation of about one million tonnes. The far biggest part is employed in cement production, where granulated or pelletized BF slags are used.

The European standard for cements (EN 197-1) distinguishes 27 types of cements, 9 of them contain BF slag from 6 to 95% (CEM III/C). Blast-furnace cements are of especial interest for application in mass concrete structures, due to their lower temperature rise during hydration than Portland cement. This prevents cracks resulting from temperature stresses and increases the later age strength of the concrete structure. Additionally Blast-furnace cements have a higher resistance to chemical attack. These include alkali-aggregate reaction, sulphate attack and diffusion of chlorides into the concrete.

The manufacturing process for slag cement produces 44% less CO₂ emission than the process used for Portland cement production due to less limestone being burned (decarbonized) for slag cement fabrication than the amount required for Portland cement (16). As decarbonization during the cement clinker production is one of industries biggest emission source of CO₂, the ecologically compatible Blast Furnace cement is widely responsible to push the slag lobby reputation.

Besides of application in cement, great amounts of air-cooled BF slag are used in base layers for road construction, primary granular capping and unbound subbases. The high stability of air-cooled BF slag is additionally advantageous for application on grounds with low bearing capacity (17).

Although the main fields of application for BF slags are cement production and road construction, small parts are used for hydraulic engineering (river stabilisation, etc.) and for agricultural fertilizers. The basicity of Calcium and Magnesium improves the pH of acidic soils and serves as major plant nutrients. Additionally it brings along important trace elements like Copper, Zinc, Cobalt, Manganese and others.

Otherwise than BOF and EAF slags, the different influences of treatment after tapping the Blast Furnace is widely known and various cooling procedures applied. BF slag is either air-cooled, giving the slag time to perform a crystalline structure or foamed, pelletized or granulated to obtain a vitrified nature with different properties.

Foamed BF slag is cooled by addition of water, air or steam, producing a product with high porosity and low bulk density. Pelletizing is achieved by solidification with water and air quenching, whereas granulated BFS result by rapid water quenching.

Likely to natural geological formation, slow cooling results in a more crystalline structure, whereas rapid cooling provokes vitrification. For aggregate use a more crystalline structure is preferred and air-cooling applied. The glassy slag is utilized for production of mineral wool and cementitious application, where granulation is predominant (17).

Talking about the application of steel slags, generally little difference is made between BOF and EAF slags, as their properties are quite similar, although it has to be taken in account, that EAF slags have slightly better technical properties (PSV, CBR, LA abrasion,...) but bring along more environmentally important issues due to the input of scrap as primary raw material in the production process. On the contrary, SEM slags differ completely in their nature and feasibility in engineering applications and are therefore recycled separately, mostly reintroduced as a flux for BOF or EAF, as fertiliser or complement in cement production.

In Europe most steel is produced in the BOF, resulting in a total of 62% BOF slag. 29% are EAF slags, a steadily increasing number, as natural resources for the BOF, the iron ore, especially iron ore with low phosphate content, are minimizing, whereas the raw material for EAF (scrap) is rising. The 9% left are secondary steel slags from the subsequent refining process (figure 3-4) (12).

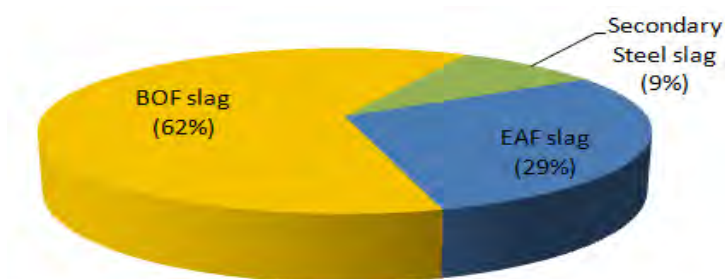


Figure 3-4: Slag from steel production, total amount of 15 million tonnes, 2004 (12)

The EAF process itself already presents a recycling process; furthermore reutilizing all of the out-coming products of this process can be seen as a further step of advancing sustainability.

Historically steel slag has been widely used for road construction and as a fill material implied by their ancestor the iron slag. Still around 45% of the steel slag produced in Europe in 2004 was used for the construction of roads (figure 3-4).

According to Euroslag (12) further 1% was used as additive in cement production, 3% for hydraulic engineering, 3% as fertilisers and 14% were internally recycled. Excluding 17% of the slag which was stored for the lack of employment fields and 11% which were finally discarded, a total of 72% of the steel slag was recycled in Europe in 2004 (figure 3-5).

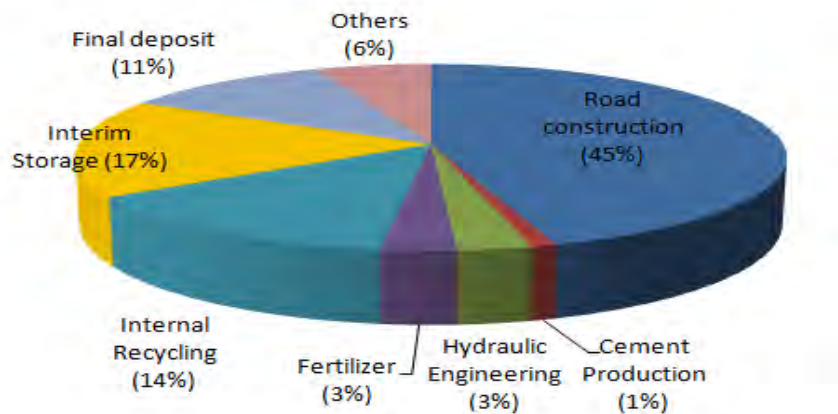


Figure 3-5: Use of steel slag in Europe in 2004 (12)

It follows a description of the application fields.

ROAD CONSTRUCTION

As observed before, the far greatest amount of steel slags is recycled in road construction, where angularity, high shear resistance, high bearing capacity and resistance to polishing make them suitable for several pavement layers (figure 3-6).

To take advantage of the steel slags most promising properties, the superior frictional resistance and the resistance to rutting, application is primary focused on bituminous surface course layers, these are hot-mixed asphalt pavement and cold mix or surface treatment (6). The increasing traffic and axle loads demand higher resistances of the pavement, where steel slags can provide a satisfying solution.

As the development of asphaltic pavements tends to higher void contents in order to accomplish noise reducing layers, steel slag aggregates can provide the properties to fulfil requirements of high resistance to abrasion and polishing.

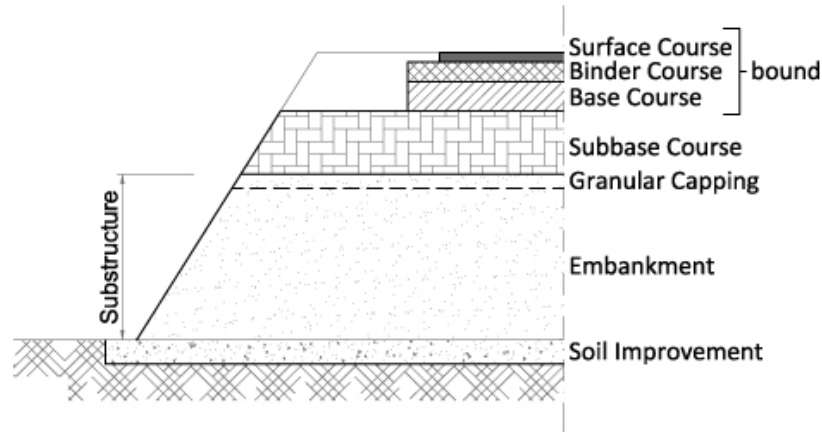


Figure 3-6: Pavement section

However, the high density of steel slags, which is 40 to 50% higher than the density of natural aggregates like granite, can make them economically unattractive, as transport costs rise. Another aspect of failure comes from the volumetric instability, which can cause surface cracking of the pavement.

In practice, besides of aging the crushed slag, expansion is tried to be avoided by exchanging the fine fraction of the steel aggregates by natural aggregates, e.g. granite, as the smaller particles show higher volumetric instability on the first sight. It should be stressed that this procedure is only effective on short-term, as the coarse particles are still expanding when the fine ones have already terminated their transformation. In the long-term, the contribution of the coarse grain will be an aliquot part of the total expansion.

The resistance to impact and crushing makes the slag feasible for other unbound road construction applications like granular base, subbase or embankments (figure 3-5), although the focus of slag merchandisers is on the more valuable top layers.

Construction of unbound low trafficked roads with steel slags, makes use of the carbonatic solidification of the particles, which leads to an increased bearing capacity, a stabile surface resistant to deformation and avoids dust even after long dry spells (18).

IHOBE (Eds.), 1999 describes that the execution on-site of granular courses with EAF slag might result inconvenient due to the porosity and angled shape of the particles and the missing of the fine fraction, and suggests adding natural aggregates to comply the proper granulometric curve (3). The missing of the fine fraction could be avoided by not excluding crushing from the production sequence, which is the case in the factory of Celsa in Castellbisbal, where the only

treatment so far is passing the slag through a sieve and therefore the granulometric curve is not properly adjusted.

A survey done by the organisation for Economic Co-operation and Development (OECD) in 1997 (6) shows, that steel slags are widely applied in hot-mixed asphalt in the participating countries (Aut, Bel, Can, Den, Fin, Fra, Jpn, Nl, Nor, Swe, Uk, Us) in the survey, followed by employment in subbase course, embankment, cold mix, surface treatment, fill, granular surface (unbound roads) and stabilising bases (soil improvement).

The same survey shows that application in confined constructions is not advisable and most countries reject its use in Portland cement concrete pavement, because of its potential of expansion.

“Slags must not be used in concrete” (6).

Bituminous matrixes are excluded from the term confined application, due to their ability to assimilate a small percentage of expansion.

On the other hand J.M. Manso (2004) describes that the traditional use in asphalt road pavements cannot absorb all the slag produced in a certain region with steel industry, and his investigation concerning EAF slag as a aggregate in concrete concludes that EAF slag can be efficiently applied in the production of concrete after correctly performed weathering for three month (19).

Regarding soil improvement measures, M. Barra (2001) showed that the employment of EAF slag as a part substitution of the soil in case of clay reduces the required cement input from 12 to 8%, by substitution of 50% of the soil, maintaining the same resistances (20).

From the environmental point of view, the impact from recycling slag in engineering applications depends by an elevated factor, on whether it is used in a loose form, like in embankments and granulate bases, or in a bound course, this can be a cementitious or bituminous matrix. Application in bound pavement inhibits theoretically the contact with water, although cracks and capillary pores have to be taken in account. Theoretically, neither rain nor groundwater can get in contact with the aggregate. This way the leaching behaviour of the slag changes drastically according to the way of employment.

At this point it should be emphasised that the simple “wrap-up” of the slag aggregate in bitumen or cement does in no way assure its environmental harmlessness. Although it might be involved perfectly in a bituminous matrix, this matrix one day will probably be destroyed, whether by human hand or natural influences. The surface course of heavy trafficked roads, for example, are approximately changed every 15 years. Although some part of the broken asphalt can be recycled internally and is reintroduced in a bituminous pavement, the far greatest amount does not have further application fields. If this destroyed pavement is then finally deposited and exposed to bitumen-destructive influences, the slag will be again available for leaching.

HYDRAULIC ENGINEERING

For application of slags in hydraulic engineering far less literature and investigation attempts than for road construction can be found. Whether this is caused by the greater economic interest in road construction and (Highway-) transport or by the fear of arising unknown ecologic parameters cannot be answered here.

According to Euroslag 3% of the 15 million tonnes of steel slag produced in Europe in 2004 were used for hydraulic engineering, including dams and dikes, stabilisation of river bottoms, refilling of erosion areas on river bottoms and stabilisation of river banks and shorelines.

“Mainly the high density, the high level of strength and abrasion as well as the rough texture of processed steel slag aggregates ensure a long term resistance to dynamic forces coming from waves and river flow” (18).

In countries with maritime access, attempts are encouraged to apply slags for coastal engineering. The BF or BOF slags are used to improve soft clay for marine foundations similar to the jet-grouting technique or applied to fill sunken sea-beds with a top sand capping or as a filling material for tidelands (21).

The Nippon Slag Organization claims to have positively tested a mixture of dredged clay and steel slag for the improvement of marine environment and insists on the positive effects of Ferrous Oxide (FeO) and Silicium dioxide (SiO_2) from the slag on the growth of algae and seaweed.

In New Zealand iron and steel slags are currently promoted and installed as aggregate filter beds in wastewater treatment plants. The prior emphasis is on removing suspended solids and algae, however it showed out to be capable of phosphorous reduction and contributed to the reduction of heavy metals, primary zinc and aluminium, although this effects decrease after some years of performance.

Comparison of two wastewater treatment plants in Waiuku (NZ), which was installed in 1993 and in Ngatea (NZ), 2002, after 13 and 4 years in operation, showed a satisfying removal of suspended solids, algae (>85%) and phosphorous (>50%). The retention of Zinc and aluminium dropped from 80 to 44% and 42 to 21% respectively (22).

The same paper (22) describes a current research on the feasibility of the use of iron and steel slags for the restoration of degraded lakes, as a material for the removal of nutrients.

Emphasis is also made on the effect on the pH of the water, which can increase to possibly unacceptable levels and on the (internationally compared) untypical slag, low in sulphur and Calcium oxide, which was applied (22).

AGRICULTURE

BF, BOF and SEM slags are widely used as lime fertilisers for agricultural utilisation, whereas EAF slags are not suitable as fertiliser. Although BF, BOF and SEM slags nowadays can contain less phosphate than the former Thomasslag, the ancestor of the Basic Oxygen Furnace, the treatment with soluble phosphates makes them match the requirements of industrial agriculture.

The basicity of the Calcium and Magnesium compounds increase the pH of acid soils and serve together with other trace elements as plant nutrients.

Although the slags contain certain amount of Chrome and Vanadium, Rex (2005) describes that “after an initial increase of both elements in the soil, continuation of liming did not cause any further accumulation of Chrome and Vanadium ... as they form insoluble strong bonds” (23).

INTERNAL RECYCLING

The simplest way of recycling slags, rich in CaO and MgO, is to reintroduce them within the steel production process and avoid further treatment and transport. As BF, BOF and SEM slags contain around 50% CaO+MgO, they can help to decrease the output of slags by reintroduction as raw-materials in the furnace.

By splashing the liquid steel slag on the walls of a BOF vessel, it can also be effectively utilized as a consumable refractory lining (24).

The main obstacle for recycling the slag internally is the phosphorous content of the slag, which can make up to 3% and is not adequate for being returned in the sinter plant. However, the phosphorous content is too low for the slag to be used as a fertiliser without further treatment.

A modelling study proposes a variation of the conventional basic oxygen steelmaking route to obtain a closed recycling process, where most of the slag is reintroduced, after passing a regenerating step, where the phosphor is again transferred from the slag to the metal, into the furnace during desiliconisation and dephosphorisation. The metal from the regenerator, high in phosphorous content, is transferred to an additional unit, where a synthetic slag accepts the phosphor from the metal and finally forms a slag with more than 10% P, which exits the process and is suitable as a fertiliser (24).

FURTHER APPLICATIONS

Apart from road construction, hydraulic engineering, fertilisers, cement and internal recycling, further bulky applications of slags include railroad ballast, foundations, landscape aggregate and after all fill material.

Literature studies hardly make any difference within steel-slags (BOF or EAF) when questions about their technical feasibility arise, but obviously less positive experimental results are found for EAF than for BOF slags when mentioning the more delicate subject of environmental harmlessness. A logic conclusion from comparing technical and chemical properties and assessing real application experiments is, that the most advantageous recycling of EAF slags lies in (bound road) construction. High Polished Stone Values (PSV ~60), low LA-values (LA ~10) and high mechanical strength (CBR~20) prove a superior quality for bound surface courses.

Chapter 4: ENVIRONMENTAL OBSERVATIONS

In the industrialized society, waste management and recycling are of gradually increasing importance. Inadequate activities in the past and the awareness of limited resources create an advancing consciousness for environmental affairs. Environmental effects from contaminants should therefore be in the responsibility of their producers and downstream users, who should be capable to figure out the most ecological way of carrying on business.

Sustainable management of resources implies that the rate of pollutant emission shall not exceed the capacity of pollutant absorption (25). The order of priority in the means of sustainability therefore favour avoidance of waste or by-products before reuse and reuse before disposal.

The goal of avoidance can be achieved by (25):

- process optimizing
- substituting input materials
- closing the material cycle in the plant
- developing of new production processes

Within the EAF steel production, possible activities for minimizing the slag output could include recycling of the slag in the plant after treatment or developing of resilient furnace shell materials.

The possibility of reuse is determined by the technical and environmental properties of the material. The technical aptitude of slags for reuse in construction applications was described in Chapter 3.3 and 3.4.

Addressing environmental affairs should include the assessment of the material in worst-case scenarios and long-term prediction. Thinking of the whole life-circle of a product or material, changes can occur within its proper chemical composition and its mineral phases, within environmental conditions and within its application field in case of “re-recycling”.

For long-term predictions, geochemical investigations are able to deduce borderline situations. In case of metals, information about long-term behaviour can be provided from “combined data of specially-designed elution experiments and extrapolations of the acid-producing potential under worst case conditions” (25).

4.1. REGULATION OF SLAGS

The legal key issue in the assessment of slags is the distinction between waste and by-product. The European Court of Justice has published several judgements dealing with this distinction. The European Waste Catalogue from the year 2000 contains two entries regarding slags:

10 02 01 waste from the processing of slag

10 02 02 unprocessed slag

Examples of slag processing accepted by the EU-Commission included granulation, pelletisation, foaming, proper solidification connected with a specified heat treatment, separation, crushing, sieving and milling (12).

However, the latest Directive of the European Parliament regarding waste (Directive 2006/12/EC) defines slags clearly as waste in Annex 1, categories of waste:

Q8 Residues of industrial processes (e.g. slags, still bottoms, etc.)

Nevertheless this categorization may be further developed, reintroducing the term of treated waste or recycled by-product (12). The definition as waste implicates an image loss and a discrimination of a by-product for the distributors of the slag and furthermore unclear legislation. If slags are defined as product, they will have to be registered under REACH (Registration, Evaluation and Authorization of Chemicals) and fulfil the same standards as their natural counterparts when used as aggregates. If they are defined as waste, they must be categorized for landfilling and/or satisfy the criteria for recycled materials construction application.

4.2. ENVIRONMENTAL ISSUES CONCERNING SLAGS

Obviously, the mentioned juridical distinction and following described environmental policies on a national basis are the most important aspects for producers, distributors and users. However, these aspects only provide a limited perspective of the national or global environmental issues concerned.

Certainly, the reutilization of industrial by-products can help to save natural non-renewable resources and decreases the solid waste in landfills. Nevertheless, to assure an equal quality of

the recycled material further natural resources or generally spoken, further energy has to be introduced into the system (26). In case of a treatment plant for steel slags this includes a minimum of transport, processing with heavy machinery, water consumption, especially in areas with low precipitation and can further require additional steps in the steel mill and asphalt plant if pavement application is desired. On a global basis these supplementary steps will probably represent a minor input of extra resources compared to the prevented natural resources and disposal of the slag in landfills, but contemplated within a local system can have a major impact.

This example shows how much influence the system definition has on the assessment of anthropogenic material flows. Following the principles of material flow analysis, Roth (26) proposes to investigate four different assessment levels concerning the use of industrial by-products like steel-slags and building materials in order to obtain a complete vision of the issues concerned (figure 4-1). Each level addresses different questions and has to apply varying evaluation methods.

Pursuing the framework shown in figure 4-1, it can be observed that the study of material characteristics like total chemical content and leaching behaviour focuses the narrowest point of view with a negligible perspective of material in- and outflow. However, expanding the system boundaries in time and space will provide further information and knowledge *“and address a much broader spectrum of environmental issues”* (26).

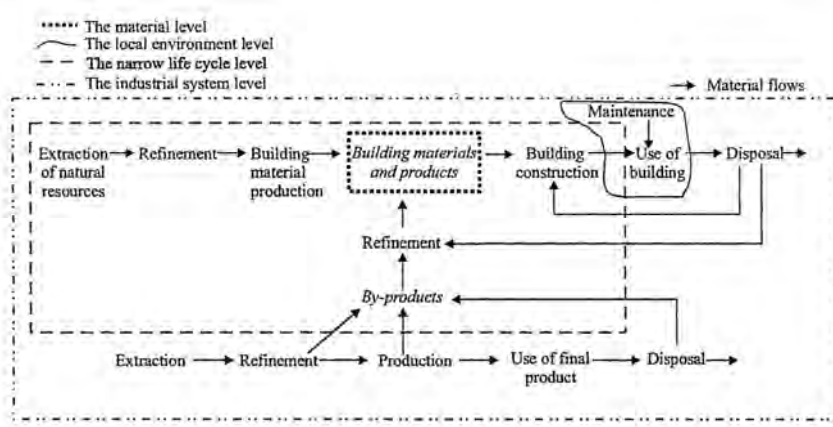


Figure 4-1: System boundaries for environmental assessment (26)

From a very general point of view, sustainable resource management will prefer recycling before disposal, but will all over prefer an optimum design of the steel plant processes with low immission and closed material flow cycles.

4.3. ENVIRONMENTAL POLICIES

No matter if the slag will be landfilled or utilized, it has to be characterized. The evaluation of the environmental impact is generally determined via leaching tests. So far the countries of European Union neither apply equal environmental laws, nor do exist standardized European guidelines for leaching tests or limit values linked to those tests.

In order to eliminate the difficult distinction between waste or not-waste, the Commission of the European Communities published in 2007 in the Communication from the Commission to the Council and the European Parliament on the Interpretative Communication on waste and by-products (27) a guideline how to interpret a materials legal status. In Annex I of this Communication (p.11), slags from the iron production are defined as by-products, whereas slags from the steel production (EAF and BOF) are judged as waste, as they are used for desulphurisation of the iron, therefore contain high amounts of Sulphur and are inappropriate for internal recycling.

Slags to be landfilled are classified according to the standards developed by CEN/TC 292, which is harmonizing leaching and extraction tests for waste. For aggregates, the chemical analysis is done according to EN 1744-1 and regarding the preparation of eluates following EN 1744-3.

4.3.1. Catalan Policy

The Catalan Residues Agency publishes in 2006 a policy regarding the validation and use of EAF-slags (28), which was planned to come into force in the year 2008. In this policy, the slag is valuable, if the eluates are below the limits (table 4-1). The policy fixes the compliance test from EN 12457-4 as test method, one of the test methods harmonized by CEN/TC 292.

The limits are applied following the European Council Decision from 2002 (2003/33/EC) for inert waste, without further restriction of the values.

Furthermore, the policy prohibits the use of iron and steel slag in areas of flood return periods of 100 years, in areas with the ground water level less than 2,5m below the surface and in areas with a distance less than 100m from drinking water wells.

Table 4-1: Catalan Leaching limits (28)

Parameter	Unit ⁽¹⁾	Limit	Parameter	Unit ⁽¹⁾	Limit
Arsenic	[mg/kg]	0,5	Lead	[mg/kg]	0,5
Barium	[mg/kg]	20	Antimony	[mg/kg]	0,06
Cadmium	[mg/kg]	0,04	Selenium	[mg/kg]	0,1
Chromium total	[mg/kg]	0,5	Zinc	[mg/kg]	4
Copper	[mg/kg]	2	Chloride	[mg/kg]	800
Mercury	[mg/kg]	0,01	Fluoride	[mg/kg]	10
Molybdenium	[mg/kg]	0,5	Sulfate	[mg/kg]	1000
Nickel	[mg/kg]	0,4			

⁽¹⁾ the unit corresponds to mg/kg of dry (solid) material

Until today the utilization of slags (in this meaning all types of slags) is environmentally regulated by the law which was published in the DOGC (Diari Oficial de la Generalitat de Catalunya) in 1996 (29) and specifies more accurately in which applications the slag can be used (sub-base, earth works and embankments). Additionally to the limitation close to the water sources mentioned in the (probable) future law, the slags can not be applied in “important thickness” in zones with materials of high permeability (karst and intense cracking), porous, not compacted materials and “altered surface layers of originally little permeable materials” (29).

A licit application is linked to the compliance of certain key values regarding the eluates but also the total composition (table 4-2).

Table 4-2: Catalan limits in force

Total Composition			Determination by DIN 38414-S4		
Parameter	Unit	Limit	Parameter	Unit	Limit
Soluble Fraction	[%] raw sample	3	Conductivity	[μS/cm]	6.000
Arsenic	[mg/kg] DM	250	Arsenic	[mg/l]	0,1
Cadmium	[mg/kg] DM	50	Cadmium	[mg/l]	0,1
Copper	[mg/kg] DM	6.000	Copper	[mg/l]	2
Chromium	[mg/kg] DM	3.000	Chromium IV	[mg/l]	0,1
Mercury	[mg/kg] DM	25	Chrome total	[mg/l]	0,5
Nickel	[mg/kg] DM	2.000	Mercury	[mg/l]	0,02
Lead	[mg/kg] DM	2.000	Nickel	[mg/l]	0,5
Zinc	[mg/kg] DM	8.000	Lead	[mg/l]	0,5
			Zinc	[mg/l]	2

Unit: mg substance/kg solid mass Unit: mg substance/l leachate

It can be observed, that the Catalan limits in force distinguish between the Total Chrome and the leaching of high toxic Chrome IV, whereas the recent proposal related above does not.

4.3.2. Austrian Policy

The Federal Waste Management Plan 2006, published by the Federal Ministry of Agriculture and Forestry, Environment and Water Management, specifies a classification by certain key parameters for the use of construction waste. The quality of the material is defined as class A+, A or B according to pH-value, electric conductivity and a selected list of eluates (table 4-3).

If there exist indications of further contaminants of a specific material or concerns arise due to its origin, additional parameters of eluate or total content have to be checked (table 4-4).

The shown limits are not specifically linked to a determined test method.

Most of the limits correspond the 2003/33/EC too. Grade B allows higher values for Antimony, Zinc, Chloride, Flour and Sulphate. Grade A+, which is allowed in all forms of application, has stricter limits for Chrome and Copper, but permits 50% more of Sulphates. Parameters for organic matter do not occur in steel slags and do not need to be discussed here.

Table 4-3: Classification of construction waste in Austria (30)

Parameter	Unit	Grade A+	Grade A	Grade B
Eluate with L/S 10				
pH value		7,5 - 12,5	7,5 - 12,5	7,5 - 12,5
Conductivity	[mS/m]	150/200	150/200	150/200
Chromium total	[mg/kg] DM	0,3	0,5	0,5
Copper	[mg/kg] DM	0,5	1	2
Ammonia-N	[mg/kg] DM	1	4	8
Nitrite-N	[mg/kg] DM	0,5	1	2
Sulphate-SO ₄	[mg/kg] DM	1.500	2.500	5.000
Carbonhydrate Index	[mg/kg] DM	1	3	5
Total Content				
Σ 16 PAH (EPA)	[mg/kg] DM	4	12	20
Unit: mg substance/kg solid mass				

The classification determines the permitted use, where differentiation is made between bound form respectively loose with a top layer, loose form without top layer and use as aggregate. Furthermore the hydrogeological conditions on site whether the material is appropriate or not (table 4-5). *A less hydrogeological area is defined by the availability of suitable impervious structures or sufficient distance from the groundwater (30).*

Table 4-4: Further parameters for the classification of construction waste in Austria (30)

Parameter ⁽¹⁾	Unit	Grade A+	Grade A	Grade B
Elate with L/S 10				
Antimony		0,06	0,06	0,1
Arsenic	[mg/kg] DM	0,5	0,5	0,5
Barium	[mg/kg] DM	20	20	20
Lead	[mg/kg] DM	0,5	0,5	0,5
Cadmium	[mg/kg] DM	0,04	0,04	0,04
Molybdenum	[mg/kg] DM	0,5	0,5	0,5
Nickel	[mg/kg] DM	0,4	0,4	0,4
Mercury	[mg/kg] DM	0,01	0,01	0,01
Zinc	[mg/kg] DM	4	4	18
Chloride	[mg/kg] DM	800	800	1.000
Fluoride	[mg/kg] DM	10	10	15
Phenol Index	[mg/kg] DM	1	1	1
DOC ⁽²⁾	[mg/kg] DM	500	500	500
TDS ⁽³⁾	[mg/kg] DM	4.000	4.000	8.000
Total Content				
Arsenic	[mg/kg] DM	20	30	30
Lead	[mg/kg] DM	30	100	100
Cadmium	[mg/kg] DM	0,5	1,1	1,1
Chromium Total	[mg/kg] DM	40	90	90
Copper	[mg/kg] DM	30	90	90
Nickel	[mg/kg] DM	30	55	55
Mercury	[mg/kg] DM	0,2	0,7	0,7
Zinc	[mg/kg] DM	100	450	450
⁽¹⁾ Significant CH content is only permitted on condition that this originates from primary construction materials and from oil contamination				
⁽²⁾ Can be investigated if own pH value or alternatively where L/S=10l/kg and pH value 7,5 to 8,0				
⁽³⁾ The values for totally dissolved solids (TDS) can be used instead of sulphate and chloride. However, sulphate must be determined in any case				
Unit: mg substance/kg solid mass				

Table 4-5: Minimal required grades depending on application (30)

Form of use	hydrogeologically less sensitive area	hydrogeologically sensitive area
In bound form or loose with capping	Grades A+, A, B	Grades A+, A
Loose w/o top layer	Grades A+, A	Grade A+
In loose form as aggregate	Grades A+, A, B	Grades A+, A, B

The Austrian classification addresses recycled construction waste (mineral construction waste, excavated soil, concrete waste, broken asphalt, etc.) which excludes slags from the iron and steel industry. The Waste Management program states (p.79) that adopting the principles of the ECJ

(European Court of Justice), *certain types of slag may be considered to be products in individual cases.*

4.3.3. Netherlands Policy

The Netherlands Waste Management program does not distinguish between new or recycled building materials regarding their quality requirements, including environmental issues. Materials, whether new or recycled, which are declared as building materials in the Dutch Building Materials Decree (31) have to fulfil the same limits concerning their environmental impact.

Building materials in the meaning of the Decree are characterized by the presence of one or more chemical elements found in stony raw materials of natural origin. These elements are Silicon, Calcium and Aluminium, which declare a material as a building material if exceeding a total amount of 10% (excluding metallic aluminium) (31).

The Netherlands environmental policy includes:

- the limitation of the distribution of environmentally hazardous substances
- the removal of the obstruction for the reuse of (waste) products as secondary raw material insofar that obstruction was based on unclear issues related to environmental protection standards
- the decrease of the amount of primary raw materials to be extracted and the subsequent decrease/prevention of erosion

The Building Materials decree implements a general report rule, where “The party planning to use a building material on or in the soil shall notify the competent authority of this intention” (31).

A distinction is made between two categories of construction materials, including earth, new materials and recycled ones:

CATEGORY 1

Building material that do not exceed any of the established limits, neither composition values for organic substances nor emission values of inorganic substances. These materials may be used without application of isolating provisions.

CATEGORY 2

Building materials with the composition below the limits but which do have inorganic constituent emissions that would exceed the limits without additional environmental

protection measures. It is therefore, obligatory, to take isolation measures for this category of building materials, in such a way that the immission stays below the immission values. Application despite of insulation measures is allowed at minimally 0.5 meters above the mean highest groundwater level and demands a permit (31).

For these two categories, further distinction is drawn between moulded and unmoulded building materials, on the basis of their manner of leaching. Accordingly, a compliance test or diffusion controlling test is applied (31).

Additionally the Dutch Building Materials Decree specifies two extra categories for tarry asphalt granulate and MSWI (Municipal Solid Waste Incinerator) bottom ash.

The tests applied are adjusted to the material examined. For quick results the availability test according to NEN 7341 is used, which can be supplemented by a column test if doubts concerning the real behaviour of the material arise. For monolithic materials the tank test described in NEN 7345 is applied.

Limit values are implemented in reference to the calculated immission from the building material into the soil as a result of use of the building material. The calculation deduces the impact within 100 years on the soil from the laboratory test results applying correction factors for changes in-situ, extrapolation over 100 years, moistening period, differences in temperature and additional isolation measures.

Boundary requirements have been laid down for the minimum amounts that need further control measures. Construction materials belonging to category 2 demand specified control measures if applied to a minimum of 10.000 tons (with the exception of road-building, where a minimum of 1000 tons applies) (31).

Chapter 5: THE LEACHING PROCESS

The chemical and mineralogical composition of the slag is important to deduce certain properties like bulk density, which is highly influenced by the iron content or volumetric expansion, caused by hydration of Calcium and Magnesium oxides in contact with moisture.

However, the composition of the solid material helps to indicate but is insufficient to determine the environmental impact. Thus, information about the environmentally relevant concentration, which can be released during the application as construction material, is necessary.

Leaching is the process by which inorganic or organic contaminants are released from the solid phase into the waterphase under the influence of mineral dissolution, desorption, complexation processes as affected by pH, redox, dissolved organic matter and (micro)biological activity (32).

The leachant in natural ambiances is water from rain or groundwater. Basically, water can leach out the construction material in bound or unbound layers by 5 different scenarios. These are (33): unfavourable weather conditions during the construction period, flood, high ground water in combination with capillary rise, infiltration of rainwater through the banquet and fractures in old or badly compacted bituminous surface courses.

Depending on the leachant's origin, it will have a individual chemical signature as a result of biological activity, water-solid interactions and physical changes, which influences drastically in its leaching ability.

Due to the high temperature in the steel-production process, neither organic contaminants nor biological activity are found in the slag sampled in the factory and do not interfere in the leaching process performed in laboratory experiments.

It has to be taken in account that further chemical alterations will occur in the slag while being placed in a natural ambience, which include hydrolysis and formation of both, inorganic and organic complexes. Complexation of metal cations with inorganic or organic complex former can enhance the solubility of trace metals (34).

It is obvious that leaching is a highly complex process, were innumerable factors influence. Experimental investigation and geochemical assessment need to respect all this factors to establish a base for legislation. So far, there does not exist a complete European harmonized

standard to detect the leachability of a substance, but in order to classify waste work is in progress by the European Committee CEN/TC 292 (Characterization of Waste).

5.1. FACTORS CONTROLLING THE LEACHING PROCESS

The release of inorganic constituents to the water phase is a procedure controlled by several chemical, physical and biological processes. Generally, the combination of various mechanisms interacts and produces the release (figure 5-1).

Whereas geotechnical engineering studies the flow of water according to the hydraulic gradient, geo-environmental observations include the processes affecting the release, transport, chemical form and concentration of the contaminants.

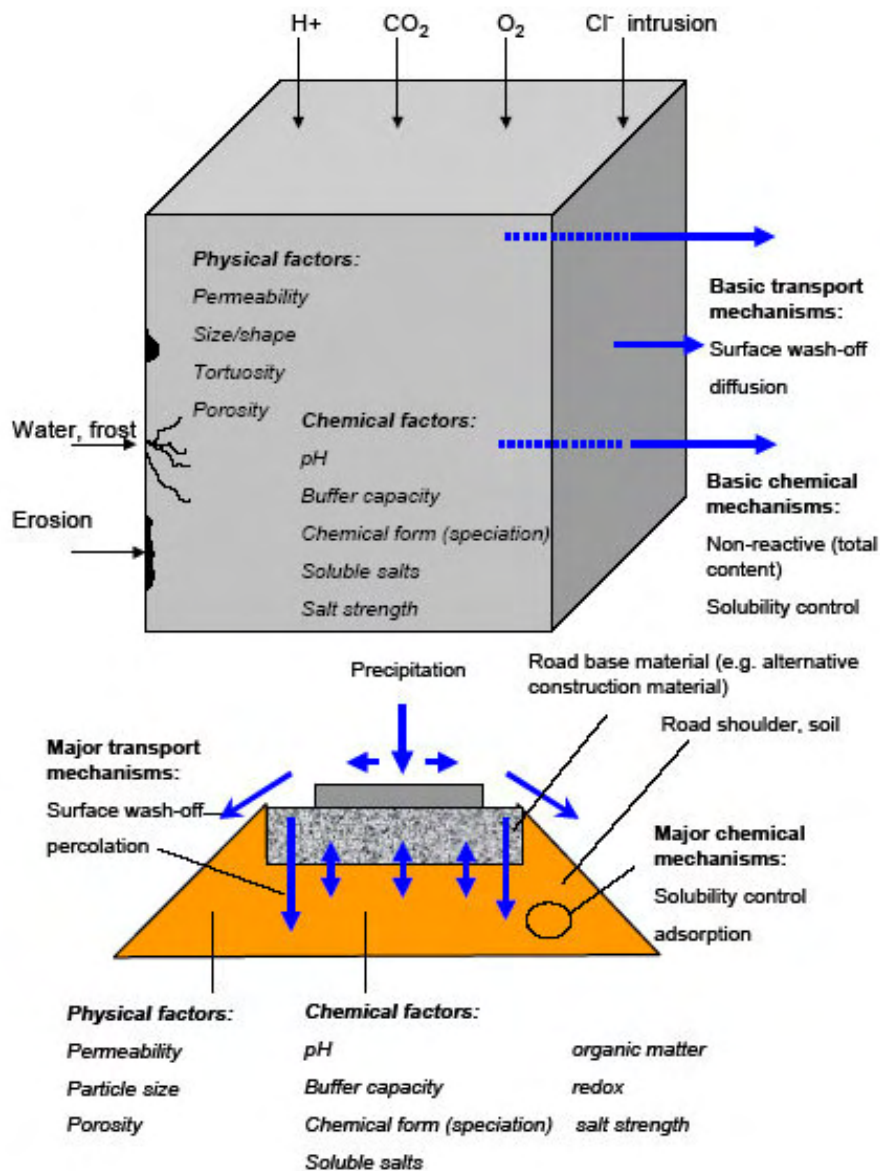


Figure 5-1: Factors controlling the leaching process (35)

Chemical mass transfer processes include sorption and desorption, dissolution and precipitation, oxidation and reduction, acid-base reactions, complexation, ion exchange, volatilization and hydrolysis. Physically there are two principal transport processes: advection and diffusion. Furthermore, surface wash-off and dispersion give a justification for changes in concentration. Explanation about biological activity and interaction with gases is not included in this work.

The leaching mechanisms controlling the quantity, concentration and the rate at which the release occurs in laboratory experiments are referred to as solubility, release and availability control (35). These are used to classify the leaching test applied and depend on the chemical, physical (and biological) processes.

5.1.1. Chemical mechanisms

The release of chemicals is controlled by three different chemical mechanisms. These are:

- Solubility Control
- Availability Control (Total Content)
- Release Control (35)

Solubility controlled systems release a maximum quantity under specific conditions. The leached quantity expressed as leachant concentration (mg/l) will then be proportional to the ratio of leachant volume to the mass of solid matrix (liquid to solid ratio L/S) (36).

Solubility is highly affected by pH, redox conditions, temperature, complexation and sorption.

In availability controlled systems a maximum quantity of a constituent is released under intense leaching conditions, thereafter no further release occurs. The leached quantity expressed as constituent release (mg/kg of solid material) will then be proportional to the liquid to solid ratio (36).

Release control gives reference to systems where porosity, permeability and tortuosity are significant for the mass transfer within the material and determine predominately its leaching habit. Diffusion and chemical interaction within the material matrix are the controlling factors then, in combination with species transfer across the solid-aqueous interface (36).

Solubility, Availability or Release controlled systems show typical release patterns which depend according to the release behaviour of the constituent on a variety of factors explained following.

INFLUENCES ON THE CHEMICAL MECHANISMS

- pH VALUE

The pH value, both of the product and the leachant, is one of the most important influences on the leaching process. The pH value of the surrounding leachant determines the maximum water phase concentration on that pH value, and each material has its own pH-dependent release curve. Release curves by pH value are similar for different groups of materials (figure 5-2).

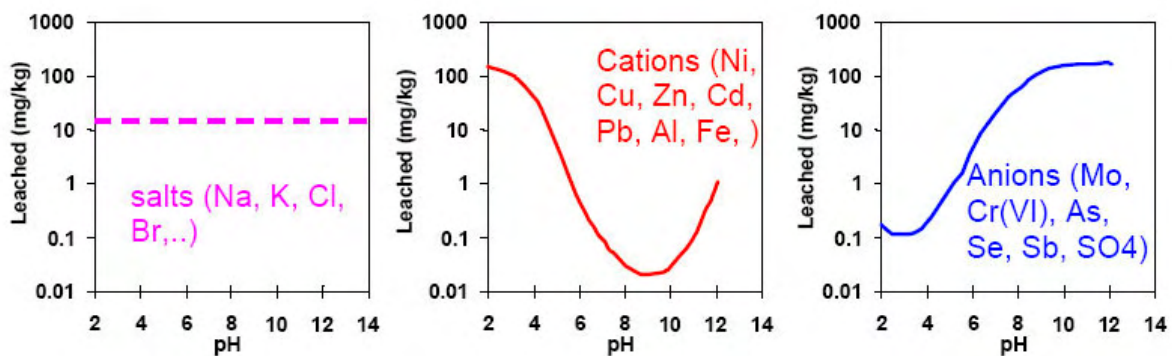


Figure 5-2: Release curves of Salts, Cations and Anions (35)

As solution and release controlled systems are pH dependent, the release of virtually all contaminants with exception of availability controlled salts, show pH depending leaching. The release behaviour for cations and anions shows a specific leaching pattern, which is very systematic, but differs in absolute levels. Most of the metals exhibit a marked increase at both low and high pH values, whereas anions generally show a high release at neutral to high pH values (figure 5-2).

The actual pH value at which the leaching takes place, depends on the pH of the material, the pH of the surrounding environment and the buffering capacity of the material (figure 5-3) (35).

The pH of steel slags is generally high due to its high content of CaO and MgO and approaches values around 11. This value lowers gradually when exposed to the atmosphere. Similar to prior high alkaline cementitious products, carbonatisation lowers the pH gradually; a typical example is the neutralization of under the influence of carbon dioxide from the atmosphere (35).

The buffering capacity determines how the pH develops over time under external influences. A liquid with a high buffering capacity has a stable pH value, which will not change significantly though external changes take place.

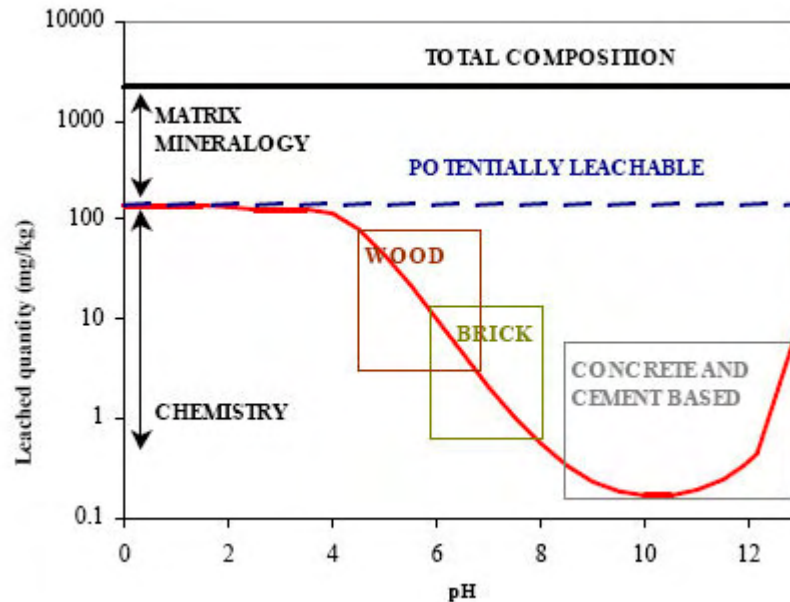


Figure 5-3: Influences of the composition and material-own pH values (35)

- CHEMICAL FORM OF THE CONSTITUENT IN THE PRODUCT (REDOX FORM)

The chemical form of the constituent determines its characteristic leaching behaviour. The contaminants may be present in oxidised or reduced form (e.g.: Chrome may occur as CrO_4^{2-} , hexavalent CrO_2^{+6} or trivalent Chrome $\text{Cr}_2\text{O}_3^{+3}$), which, as shown in figure 5-2, strongly influences its leaching behaviour.

For metals, the oxidation of an originally reduced material usually increases the release process, while reduction will have the opposite effect (35).

- TOTAL COMPOSITION AND MINERALOGIC MATRIX OF THE PRODUCT

Although the total (chemical) composition of a material indicates the potentially leachable substances, it has only limited influence on the actual quantity of the released elements. An exception would be non-reactive, soluble salts like NaCl. Concerning all the other constituents, the total amount rarely correlates with the released elements.

The distribution of the elements in the mineralogic matrix determines the potentially leachable amount (figure 5-3). As certain minerals are more susceptible to release in the water phase, the leaching of trace elements bound in this matrix depends on their location in the matrix too.

- COMPOSITION OF THE WATER PHASE AND IONIC STRENGTH

When other ions are available in a solution, the solubility of a solid will change from its value in pure water. Generally, an increasing ionic strength, which is the concentration of all the ions present in a solution, enhances the solubility of a solid.

Solubility may increase if unfamiliar ions are available and reduces its activity in solutions containing the same ions (common-ion effect).

Furthermore, other components in the solution may cause increased leaching due to complexation, such as metal complexes with chloride or carbonates (37).

- TEMPERATURE

Temperature increase generally enhances chemical reactions and leads to higher solubility, by accelerated movements of the elements (35).

- TIME

Time influences in various aspects on the leaching behaviour (35):

- by the time period the material will be used in the application (e.g.: 15-20 years for a bound surface course).
- by the rate of process-proceeding (flow-rate).
- by modifications of the material and environmental conditions over time (e.g.: cracks in the surface course of a road, compactation and crushing, unusual heavy rainfalls, etc.)

5.1.2. Physical factors

Two different transport processes can be distinguished:

- Advection
- Diffusion (35)

Additionally two phenomena: surface-wash off and dispersion (37) influence in variations of concentration.

Advection refers to the substance in movement within the water phase as result of a hydraulic gradient, which can be described by Darcy's law (37). Water percolation along the surface of the material causes advection, which has the most important role for rain. Percolation through a material only occurs in porous materials, like granular base courses.

The initial release of constituents is called Surface wash-off and is quite similar to advection but causing higher concentrations. It refers to the wash-off of monolithic materials eventually without flow of the water phase (35). Surface effects are more dominant for finely graded materials than for course graded materials due to their higher surface area to volume ratio.

After the initial wash-off, diffusion releases the constituents by the movement of molecules by the absence of flow, which is a result of a chemical concentration gradient. Diffusion can be described by Fick's law (37).

Diffusion is typical for stagnant groundwater in compacted base courses of roads. It depends both, on time and temperature and stops when a balance in concentration of the water and material is reached. Therefore, the release may stagnate until environmental circumstances cause flow of the water and constituents are taken away by further advection.

Leaching in laboratory experiments of materials with typical diffusion control is characterized by a flushing off at the beginning of the test (surface wash-off), followed by low emission (31).

INFLUENCES ON THE TRANSPORT MECHANISMS

- GRANULAR OR MONOLITHIC STRUCTURE

Unbound, granular materials release their constituents in a different way than bound structures. In granular materials, percolation is the main transport regime, whereas in monolithic structures diffusion dominates the leaching, sometimes after the initial surface wash-off.

Road sections with bound surface courses inhibit great part of the infiltration into the base courses, which therefore release their constituents in a similar way as a monolithic material (35).

- PARTICLE SIZE, PRODUCT SIZE AND SHAPE

The particle size, particularly the particle surface area to volume ratio, influences the release concerning granular materials. The smaller the particle, the faster the constituents are released, as the distance from the inside of the particle to the outside is smaller and the surface of the

particle increases exponentially with the decreasing particle size. Coarse grains tend to release their constituents by diffusion.

For monolithic products too, size and shape influence in the diffusion behaviour. Likely as for the particles, the greater the surface, the higher the release will be.

A monolithic product like the surface course of a road is thick enough to maintain the original concentration of constituents inside the product for a long time. This fact must be taken in account when testing the material with small samples in the laboratory, where the diffusion may take place till affecting the core of the sample and therefore showing decreasing release (35).

Finely grinding of the sample, like in the availability test according to NEN 7341, ensures that chemical rather than physical factors define the leaching behaviour.

- POROSITY

The more pores the material has, the higher the release will be. This corresponds both to granular and to monolithic materials. Additionally friction in the pores will hamper the velocity of release (37).

- PERMEABILITY

Low permeability tends to provoke release by diffusion, whereas high permeability allows the water to percolate along the material, hence leaching the constituents by advection (35).

- TORTUOSITY

The diffusion of monolithic materials is influenced by its tortuosity, which is defined as the quotient between the path length over which the constituent is transported and the straight length between this two points. The higher this quotient, the higher retardation in the release will be (35).

- SENSITIVITY FOR EROSION

Erosion provokes increased surface of the material disposed to the releasing waterphase, hence leads to higher release.

For material for road construction, erosion may take place during the handling and construction by creating higher amounts of fines and further during its lifetime by abrasion and cracking of the surface and in a limited amount by compacting and crushing of the base course (35).

5.1.3. Further External Factors

Chemical and physical state in field conditions influence widely in the release of the contaminants. Following the principles explained before, the main factors are climatic and hydrogeological conditions and the properties of the releasing medium (pH, Redox, Temperature). Further, depending on the application of the product the external factors have a varying influence.

Furthermore, gradual modifications change the exposure of the product. This can be fissures in the surface course of a road, which expose fresh area and increase the total area. For concrete surfaces, salt intrusion may severely damage the construction and expose constituents for susceptible release.

Another important factor for asphalt roads is the degradation of organic substances. The bitumen generally ages over time due to several factors, like UV-light, etc. This degradation of the bitumen enhances the exposure of the aggregates and frees its constituents for further release.

Besides of taking account of the existing conditions during the materials first field of application (e.g. aggregate for road construction), a comprehensive environmental assessment must involve the materials fate until the end of its lifetime. Especially the final sink – the place where the material will remain for a time > 1000 years (13) - will be crucial for the magnitude of the materials environmental impact.

In case of aggregates for bituminous surface courses, the materials will remain approximately 30 years on-site, suffering gradual modifications like explained before. According to the state of art, approximately 20% (increasing tendency) of the asphalt will be recycled for the replacement of the pavement. During execution of the asphalt-recycling, the material will be mechanically and thermally stressed, exposing new surfaces. Throughout the entire lifetime of the aggregate within the pavement, multiple recycling can take place, changing the materials properties and therefore its effects on the environment. Finally, the most important question will be, where the material will be deposited when its properties have changed so far, that recycling is technically and/or economically no more feasible. Deposition in landfills not only generates accumulation of materials but high concentrations of (toxic) substances (e.g. Chrome or Vanadium in steel slags), which can leave the landfill and find their final sink in the soil.

Chapter 6: LEACHING TEST METHODS

Leaching is the process where soluble components of a solid phase are released to a liquid phase. Various testing methods have been developed to detect the migration of these components from the material into the environment. These testing methods differ in the purpose for material application (waste, construction materials, etc.) and in their approach to a specific scenario (time, changing environmental conditions, etc.). The test chosen for an individual material and application should reflect as well as possible its true impact.

The first leaching tests were developed to detect the leaching behaviour of granular waste and sludge, usually to range them in different hazard classes and propose their handling, like the former Austrian standard öN S 2072 (leachate classes), which was dismissed in the year 2000. As slag is (still) seen as waste of the (steel)process and first specific standards of leaching for recycled material in construction did not exist, the same standards were applied, although both the material and the application differ decisively when used as an aggregates in road construction.

To understand the principles of leaching, its nomenclature is indispensable to understand:

leachee (material) + leachant → leachate (38)

Leaching methods vary in mass and particle size of the sample, in the type and volume of leachant, the leachant delivery method and time (38).

The methods can be categorized by whether the leachant is added only once (static extraction test) or is renewed (dynamic extraction test).

Test methods can furthermore be distinguished between batch methods, column or flow-through methods and monolithic or bulk methods (see examples in table 6-1). For pilot scale experiments, lysimeter systems are used, where a naturally produced leachate is collected and analyzed.

- Batch Methods

Batch methods treat with a generally small sample, which is placed in a leachant for a specific period of time. Most of those tests require agitation of the leachant, often leachee and leachant are in constant movement. Testing time is short with approx. 24 hours.

Batch methods can furthermore divided in one stage, serial or sequential tests, indicating that the properties of the leachant is changed (e.g. pH value) to observe the leachees behaviour (38).

Batch tests are generally used by regulatory agencies to determine whether a waste presents a potential leaching threat to groundwater and soils. The resulting concentrations of contaminants are therefore compared directly to groundwater limits or guidance concentrations.

- Column Methods

Column leaching tests simulate the flow of water through a porous layer of granular material. There exist both, down-flow or up-flow tests, with continued or intermittent flow. They can be conducted in saturated or unsaturated conditions or varying those.

These tests are able to simulate interception of rainwater or groundwater flow for several decades by accelerating the flow rate.

Results from Batch and Column leaching tests are generally expressed in [mg/kg] of dry mass. To evaluate the influence of solubility, results from the column leaching test can also be expressed in [mg/l]. If the constituents release is solubility controlled, a higher L/S ratio will lead to higher release (theoretically a linear function).

Batch and Column Tests are based on the assumption that chemical equilibrium is reached during the test. The equilibrium is reached when there is no concentration gradient between the boundary layer of the specimen and the free water (39).

- Monolithic and Bulk Methods

Monolithic methods are designed to evaluate the release of contaminants from a solid, massive structure, which (in case of concrete or bituminous asphalt) is controlled by diffusion after eventual initial surface wash-off (see chapter 5).

Bulk methods are tests with the same concept as monolithic tests but referring to the leaching of large samples in columns or heaps (38).

As the release by diffusion is a function of the surface area exposed to the leachant, the results from monolithic tests are expressed in $[\text{mg}/\text{m}^2]$.

Test parameters, which can be adjusted individually, are LS value (Liquid to Solid Ratio), pH of the leachant, redox potential, temperature, leachant agitation, testing time and number of extractions.

Due to the variety of applied leaching tests and diversity of data representation, comparison with other authors is sometimes difficult. Although a high amount of leaching test data concerning soils, sludge, sediments, waste and construction materials can be found in literature, relevant key information is not found easily and creates a need for harmonization of leaching test methods and data evaluation (36).

EXAMPLE OF BATCH TESTS: DIN 38414-4 AND THE MODIFIED DEV-S4 METHOD

A minimum of 100g of raw (dry) material with a maximum grain size of 10mm is poured in a glass or plastic bottle (depending on the parameters to be tested) and agitated with demineralised water in a constant overhead rotation for 24 hours. The liquid/solid ratio is 10:1 $[\text{l}/\text{kg}]$.

The conventional DEV-S4 method is little suitable to test building materials for road construction. First, the grain diameter is limited to 10mm, although aggregates can be far bigger, especially if tested for unbound layers. It is suggested to crush the material, hence changing the size spectrum and increasing the surface of the grains. The constant movement of the sample furthermore applies fractures and loss of surface particles. Least the sample size of 100g is far too small to get appropriate and meaningful results (40) (With a bulk density of 3,5 g/cm^3 one single grain of 70mm would make up the whole sample).

Table 6-1: Leaching Tests

Type		Standard	Description
Batch tests	one stage	EN 12457-1	Characterization of Waste - Leaching; Compliance test for leaching of granular waste materials and sludges - Part 1: One stage batch test at a liquid solid ration of 2l/kg with particle size below 4mm (without or with reduction)
		EN 12457-2	Characterization of Waste - Leaching; Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid solid ration of 10l/kg with particle size below 4mm (without or with reduction)
		EN 12457-4	Characterization of Waste - Leaching; Compliance test for leaching of granular and sludges - Part 4: One stage batch test at a liquid solid ration of 10l/kg with particle size below 10mm (without or with reduction)
		DIN 38414-4	German standard methods for the examination of water, waste water and sludge; sludge and sediments; determination of leachability by water
		modified S4	Modification of DIN 38414-4, nationally recognized in Germany
	two stage	EN 12457-3	Characterization of Waste - Leaching; Compliance test for leaching of granular and sludges - Part 1: Two stage batch test at a liquid solid ration of 2l/kg and 8l/kg for materials with high solid content with particle size below 4mm (without or with reduction)
		NEN 7341	Availability Test for granular material at pH 4 and pH 8
		pREN 14429	Characterization of Waste - Leaching behaviour test - Influence of pH on leaching with inical acid/base addition (pH stat)
Column tests		pREN 14405	Characterization of Waste - Leaching behaviour tests - Up-flow percolation test
		NEN 7343	Up-flow percolation test
Monolithic tests		EN 1744-3	Tests for chemical properties of aggregates - Part 3: Tank Leaching Test
		NEN 7345	Diffusion test for shaped building materials, monolithic and stabilized waste materials

Due to these disadvantages, the DEV-S4 method was modified for application on road construction materials. The current German policy refers therefore to the modified method described in the working-sheet FGSV 28/1 (40). In this modification, grain sizes of more than 22mm with a sample size of 2,5kg can be tested.

EXAMPLE OF MONOLITHIC TESTS: EN 1744-3 TANK TEST

Although the modified DEV-S4 method is more adapted on testing aggregates, there are still some disadvantages. First, testing aggregates in bound structures is not possible, second the same problem as in the conventional DEV-S4 method happens regarding fractures and crushing during the test phase, when the sample is in constant movement.

The main difference from the Tank Test to the DEV-S4 method is that only the water is moved, whereas the sample itself is not (figure 6-1). Therefore, the sample is not further stressed

mechanically. Furthermore, bigger samples can be tested easily and the test of bound structures does not need to change the handling with vessel or equipment.

The leachant to solid ratio of 10:1 and the testing time of 24 hours are similar to the DEV-S4 method. The sample size is approx. 2000g for unbound materials. For bound materials, different test pieces are suitable like the Marshall-specimen or a cube with 100x100x100mm. The leachant is, like in the DEV-S4 test, demineralised water (40). The magnetic stirrer rotates at 500rpm.

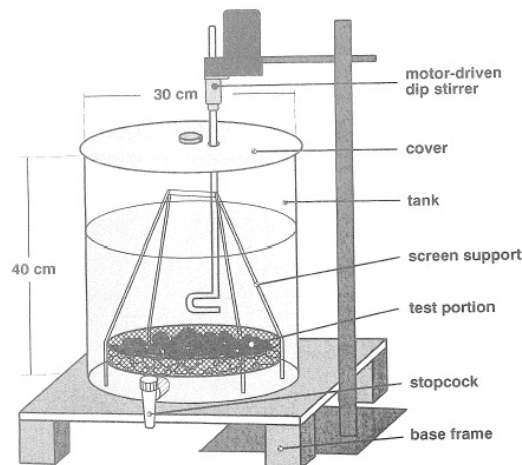


Figure 6-1: Tank leaching test (18)

EXAMPLE OF COLUMN TEST: CEN/TS 14405

Neither the batch methods nor the monolithic methods simulate the dynamic of the leaching process, which is an important aspect to evaluate the influence of time in natural ambience.

To study the leaching of a pollutant in function of time, Percolation tests or pH-stat methods are applied. Although testing of bound structures is not possible, these methods achieve results to examine the release of contaminants of substructures, according to the influence of time and variations of climatic conditions.

The various substructure-layers are placed in a lysimeter and compacted. At the top and at the bottom of the vessel a filter ensures that the fine particles are not washed out.

The sample is then watered with demineralised water in up-flow mode until the liquid/solid ratio of 10:1 is reached (figure 6-2). The leachate is extracted and evaluated in seven determined steps.

Percolation tests with predetermined, acid pH value can simulate “acid rain”, which can have a pH value of down to 4 and will therefore mobilize cations more easily.

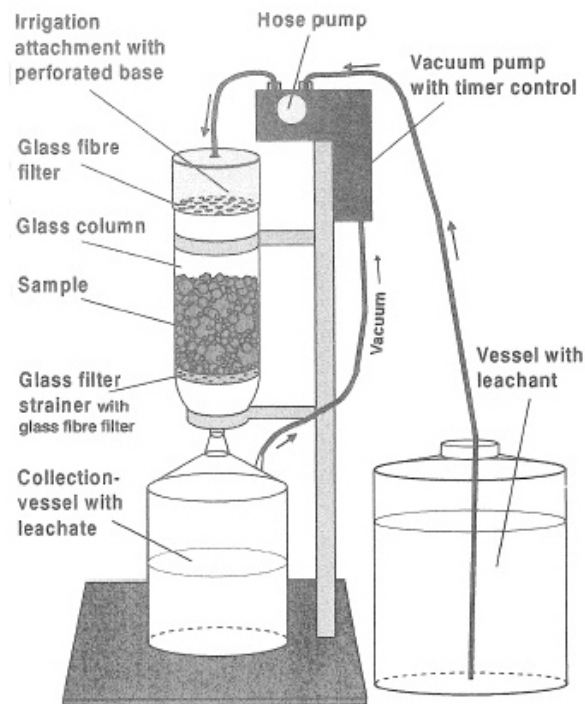


Figure 6-2: Percolation test (18)

6.1. HIERARCHY IN TESTING

The European Directive for Waste at Landfills (2003/33/EC) frames three steps for the evaluation of waste:

- Basic characterization
- Compliance testing
- On-site verification

In the meaning of the Directive, the first assessment of the material in a specific environment is done by the basic characterisation of the material, information about its behaviour, rating its constituents against limit values and highlighting the key parameters for further compliance testing. The Directive requires data about the compositional range of the waste, its range and variability of characteristic properties, key variables to be tested on a regular basis and (if necessary) the leachability by a batch leaching test and/or percolation and/or pH dependence test.

In the second step, the compliance testing, the objective is to check periodically, whether the key parameters are still fulfilling the behaviour evaluated in the characterisation tests. This helps to save time and costs, as the characterisation tests can be more simple (generally batch tests) and only the key parameters need to be tested.

On-site verification includes visual control and administrative checks (at the landfill).

Applying the principles of waste assessment from the European Directive on the assessment of the environmental impact of steel-slag as recycled by-product in road construction, the Basic characterisation should include an ample testing period to obtain information on the short and long term leaching behaviour, evaluating the influences of a wide spectrum of parameters.

PART 2: PRACTICAL WORK

Chapter 7: LABORATORY TESTING

7.1. Program design and Experiments

The advancing standardization in most European countries regarding the leaching behaviour of secondary raw materials generally determines a simple compliance test for their valuation. The national limit values are generally based on this testing method too, in order to establish basic comparability.

Although the influences of weathering and aging of steel slags concerning their volumetric stability is widely investigated, the effects of aging on their leaching behaviour still lacks of scientific research. Laboratory testing in this research include standardized leaching tests of two types of EAF-slag (c-A and c-55) weathered in different conditions (c1 and c2) and a non-standardized test, where small samples of EAF-slag are stored in demineralised water to determine the total amount of release in unaltered laboratory conditions.

The leachate is analysed from the material directly sampled from the furnace ("0 days") and after ageing at 21 days, 42 days and 91 days. Equally, the leachate from the water-stored slag is analyzed at the corresponding dates (table 7-1). The final testing date of 91 days was chosen in order to coincided with the maximum ageing period in the future treatment plant. The intermediate experiments at 21 and 42 days serve as an indication for the trend of the release behaviour during the ongoing aging process and were selected to provide a convenient sampling schedule (they are multiples of seven, hence sampling was done on a determined week-day).

It was not possible to store the slag longer than three month, therefore this study does not provide conclusions about the behaviour after longer aging periods.

The company CELSA in Castellbisbal, close to Barcelona in Catalunya, produces six types of steel, differing in grades of pureness and alloys. The mixtures are fabricated by assembling various combinations of the scrap used. For the experiments it was chosen to test two types of slag, what allows first conclusion about if mentionable differences between the slags exist and second if the release pattern is comparable.

The slags tested are named c-55 (“carga 55”), which made up 53,80% of the production in July 2006 and represents generally the majority of output from the factory, and c-A (“carga A”), production-rate of 34,50% in July 2006 and supposed to be the most contaminating slag. The steel from c-55 is further refined for the fabrication of steel-beams, the one from c-A is used to fabricate reinforcement bars.

Table 7-1: Planning of conservation

EAF-slag	conservation type	days of weathering/aging			
		0 ⁽¹⁾	21 ⁽²⁾	42 ⁽²⁾	91 ⁽²⁾
c-A	c1	x	x	x	x
	c2		x	x	x
	BOT	x	x	x	x
c-55	c1	x	x	x	x
	c2		x	x	x
	BOT	x	x	x	x

⁽¹⁾testing done by six replications, ⁽²⁾testing done by triple

After sampling in the factory, the material is stored in permeable sacks with 1x1m² surface area and placed upon wooden pallets. Approximately each sack contains three tons of slag.

The sampling of the material “0 days” is done immediately and hence has never been in contact with water. The slag is then weathered simulating possible aging-methods in a treatment plant:

- c1: The material of conservation type c1 is rained with deoxidized water simulating average precipitation in Catalunya of 750mm per year. As the for the future planned treatment plant is designed to receive heaps of approx. 4m of height, the added water is multiplied with a height factor $k = \frac{h}{4}$, where h is the actual height of the heaped material in meters. The raining is done every two weeks, which therefore corresponds to the following amount of water: $w [l] = \frac{750 \frac{mm}{year} * h [m] * 1 m^2 * 2 weeks}{52 \frac{weeks}{year} * 4 m}$
- c2: Conservation type c2 simulates a humid climate by storing the slag under permanent wet covering. Furthermore, the slag is rained regularly with deoxidized water until saturation is reached.
- BOT: 90g of slag from the sampling “0 days” are stored in a closed vessel together with demineralised water in a L/S ratio of 10 after crushing to a diameter < 10mm and reducing sample-size according to EN 932-2.

At the corresponding dates 40kg of the untreated slag ("0 days") and the one aged after 21, 42 and 91 days of weathering are sampled according to EN 932-1. After drying during 24 hours at 105°C the slag is crushed to a diameter of < 22,4mm, then reduced in its amount by quartering according to EN 932-2 and a representative sample of 2kg for the leaching tests and about 3kg for the granulometric curve separated. The representative samples are further crushed to < 10mm (figure 7-1).

The specimen for determination of Chemical Composition and Mineralogy are sampled from the remaining material for lixiviation. Therefore a amount of approximately 200g is crushed to a diameter of <0,063mm before preparing the specimen.

It should be noted here, that, at the time the program design was planed and started, insufficient attention was paid to the influence of crushing the slag after the aging process. Furthermore, at this time the possibilities regarding the crushing equipment were limited to a small laboratory jaw-crusher, which did not have enough capacity to crush all the material sampled. Therefore, all the results of this study should be treated with caution, considering the fact, that the relation between actually aged surface to freshly opened surface of each sample is unknown.



Figure 7-1: Sample c-A/N/42d/c1, grading sizes during sample preparation

7.1.1. Major constituents in the Total Composition

The total composition of the EAF slag is detected by X-ray Fluorescence (XRF), a method of X-ray Spectroscopy which is based upon measurement of fluorescence of electromagnetic radiation. Like a genuine optical spectroscopic equipment, the instrument of XRF includes *a source, a device for restricting the wavelength range to be employed, a sample holder, a radiation detector or transducer and a signal processor and readout* (41).

The total composition was determined for the samples c-55 / N / 0d and c-A / N / 0d by two duplications. Therefore a fine grained sample (particle size <0,063mm) of approx. 7g was weighed and heated at 1000°C for 2 hours. Reweighing determines the destruction of potential organic contaminants and Calcium. 0,3g are then mixed with Lithium Tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), which serves as a flux, in a proportion of 1/20 and heated at 1100°C to form a glassy pearl which is finally inserted in the XRF equipment.

Results are expressed in oxides and give an overall determination of the major constituents.

Principle

As a source for XRF X-Ray tubes are used, in which a tungsten filament represents the cathode and a metal plate (tungsten, copper, Chrome, or other) the anode. The X-rays are produced by an electron bombardment, are directed at the sample (a small sample of 4g is ground to fine powder <0,063mm and melted into glass) and interact with the electrons in the sample. The incident X-ray ejects the tightly bound electrons from the inner shells of the atoms in the sample, whose vacant positions are filled with electrons from the outer-shells. This event provokes an emission of fluorescent X-rays, which can be detected either by their energy or by their wavelength, where the energy is characteristic for each element and is inversely proportional to the wavelength (figure 7-2) (42).

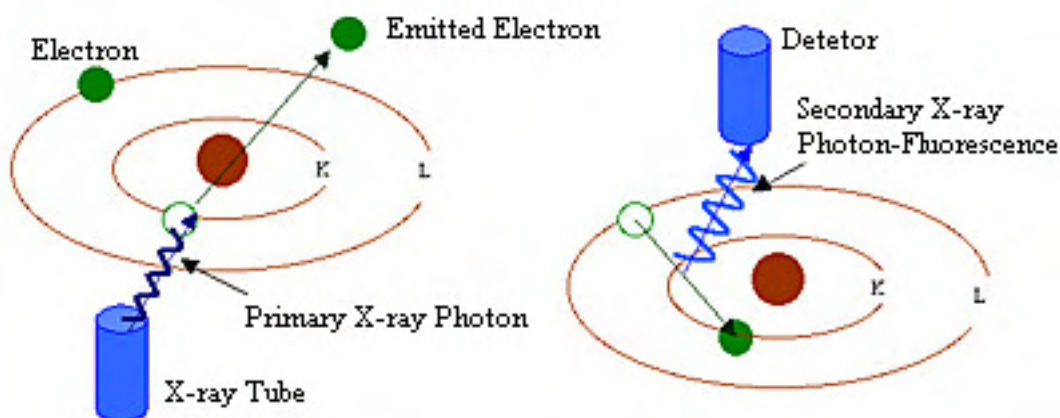


Figure 7-2: XRF principle (42)

7.1.2. Leaching Tests

The leaching test is performed according to EN 12457-4. Therefore 90g of the representative sample are separated and filled in polyethylene bottles with a nominal volume of 2l. 900ml of demineralised water are added, obtaining a L/S ratio of 10:1. The slag without aging ("0 days") is tested by six duplicates, together with two blank samples. As the results from the analysis of this

samples showed low deviation, the following tests (21, 42, 91 days) were performed by triple. The BOT-tests (aging in water – reduced conditions) were carried out by double.

Principle

The extraction is executed in a constant overhead rotation for 24 hours at 5rpm. The leachate is then treated according to EN ISO 5667-3, although in some cases the storage times were exceeded.

First the leachate is filtered with a 0,45µm membrane filter. 100ml are stabilized with 1ml (1%) of HNO₃ (nitric acid) and guarded in cooled conditions (< 5°C) for the analysis with Inductively Coupled Plasma/Mass Spectrometry (ICP-MS). Another 100ml are filtered for the determination of pH, electric conductivity and anion analysis. The pH and the electric conductivity are determined immediately with electrochemical sensors. In cases when the anion-analysis cannot be performed at once, the leachate-samples are stored in cooled ambience. The anion analysis (F⁻, SO₄²⁻ and Cl⁻) is done by High Performance Liquid Chromatography (HPLC).

7.1.3. Detection of Anions – Solid sample and Leachate

For the detection of F⁻, SO₄²⁻ and Cl⁻ in the solid sample and in the leachates of this study, High Performance Liquid Chromatography (HPLC) was applied.

For application on the solid sample 3g of fine grained particles (<0,063mm) are dissolved in an acid mixture of 21ml HCl and 7ml HNO₃ (agua regia) for six hours, which is then diluted and serves as a liquid sample for the HPLC equipment.

Principle

Analytical Chromatography is used to separate mixtures by passing the mixture dissolved in a mobile phase through a stationary phase. It determines the existence and possibly also the concentration of analytes in a sample. The components are transported through the system at different rates, hence provides separation. The retention time is the characteristic time for a particular component to pass through the system. Strongly attracted components move more slowly than those with weak attraction. An inert component which will not be immobilized passes through the system in the same time as the mobile phase (43).

During chromatographic separation, various physical and chemical interactions occur between the components of the mixture and the mobile and the stationary phase. Mostly separation is

achieved by adsorption on the surface of a solid stationary phase and distribution between two not mixable liquid phases. Furthermore, ion exchange, sieve effects and others play a secondary role in the separation process (43).

When emerging the system, the different components are collected and analyzed by detecting a property, which is related to the characteristics of the chemical component. The output from the detection is the chromatogram, where the x-axis corresponds to the retention time and the y-axis a signal from the eluting system. Different peaks are the signal for the components. Generally, the peaks are not shown in a theoretical sharp curve, but do follow a systematic pattern (43).

An example how the principles of chromatography work is shown in figure 7-3. It shows a liquid phase, which carries two components (A and B) down the column. The separation can be observed in (b) and at a later point in (c) where the component A is moving at a faster rate than B. The first peak in the chromatogram corresponds to A followed by B (43).

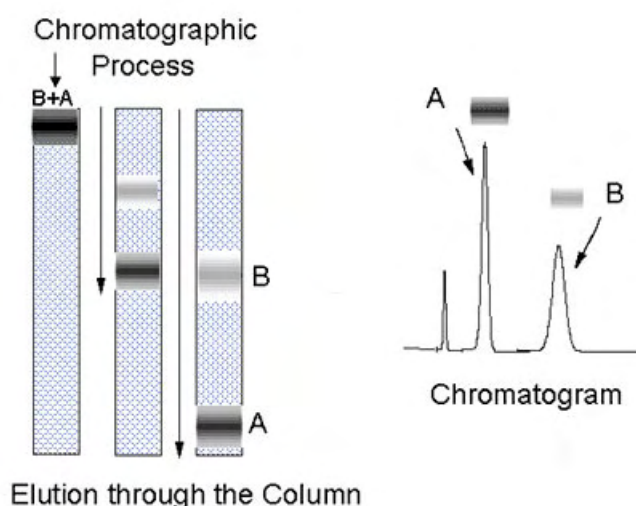


Figure 7-3: Example chromatographic separation (43)

There exists a range of techniques for chromatographic separation. According to the chromatographic bed shape we distinguish between column chromatography and planar chromatography (paper and thin layer), according to the physical state of the mobile phase we distinguish between gas (GC), liquid (LC) and supercritical fluids (SFC), which is a fluid close to its critical temperature and pressure.

In accordance with the separation mechanism, we furthermore distinguish between ion exchange chromatography and size exclusion chromatography (43).

HPLC utilizes a tube as a recipient for the stationary phase (a column), which is composed of very small packing particles. The mobile phase is a liquid, which is forced through the column together with a small sample at pressure. Originally, this execution pressures were very high, where the original name comes from (High Pressure LC).

The basic principle of HPLC is the same as in the example described before: each component takes a specific time to pass the column. Else than ordinary column chromatography, the application of pressure in HPLC allows the utilization of very small particles for the stationary phase, which enables better separation. Furthermore shorter columns can be used and the total separation process proceeds more quickly (44).

The equipment of a HPLC is shown in figure 7-4. It consist of the (steel)column packed with the stationary phase, the liquid mobile phase (eluent), the pump to pass the mobile phase more quickly, a sample valve (PV), where the sample is added to the mobile phase and a detector.

The second mobile phase is an eluent, which can pass the column more quickly than the first one. It is therefore used to wash out the slow components, which would take a long time for their trajectory in the column with the fist mobile phase. Wide and unclear peaks or even fusion with neighbour peaks could occur. Practically even more than two eluents can be utilized (44).

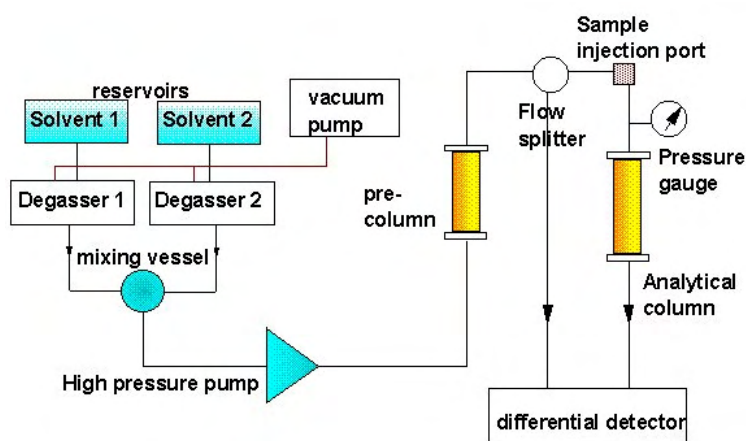


Figure 7-4: HPLC equipment (44)

7.1.4. Detection of Cations – Solid sample and Leachate

For the detection of cations in the solid sample and in the leachates of this study, Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) was applied.

For application on the solid sample 3g of fine grained particles (<0,063mm) are dissolved in an acid mixture of 21ml HCl and 7ml HNO₃ (agua regia) for six hours, which is then diluted and serves as a liquid sample for the ICP-MS equipment (see chapter 7.1.3).

Principle

Inductively Coupled Plasma (ICP) was developed in the early 1960's and is nowadays primary employed for the detection of trace elements in environmental samples. The principle is based on the measurement of a characteristic wavelength, which is emitted by the elements (41).

A so-called ICP torch, the centrepiece of an ICP equipment, consists of three centric tubes, which are situated within a water-cooled coil powered by a radio frequency generator. Three gases, generally Argon, flow inside these tubes, which activates the generator and makes the gas close to the coil-region electrically conductive. This sequence of events forms the plasma, used for the ionization of the elements in the sample, needed to detect the elements with Mass Spectrometry (MS).

The outer gas maintains the plasma, stabilizes its position and thermally isolates it from the outer tube. The inner gas carries the sample to the plasma. The elements to be detected must be in solution. A nebulizer transforms the aqueous solution into an aerosol (41).

ICP equipments are often combined with other analytical instruments, such as MS (see figure 7-5). ICP-MS is employed since the 1980's and is preferably used in the environmental field, where low concentrations and interfering elements require high sensitivity of the instruments (41).

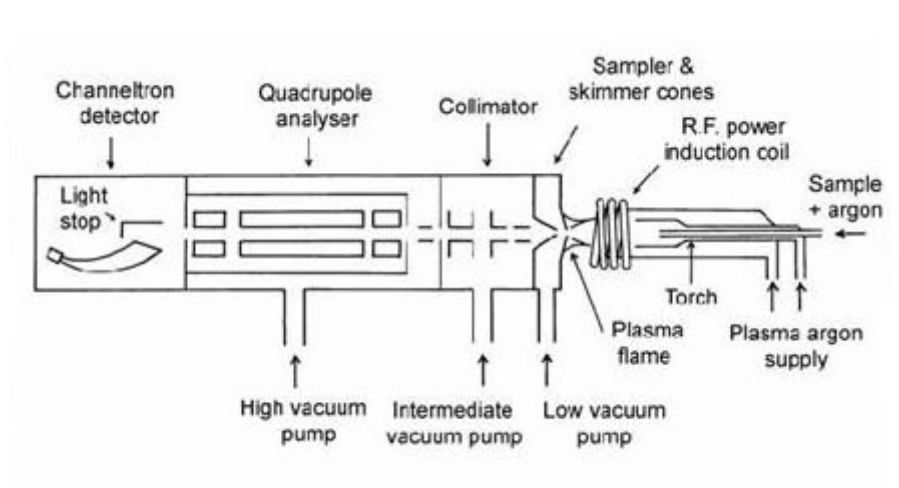


Figure 7-5: ICP-MS (45)

The ICP provides the following MS equipment with the ions and their associated electrons. A mass spectrum is obtained by separating these ions on the basis of their mass-to-charge ratio.

The ions pass from the ICP torch to the analyzer by interfaces used to extract the ions into the low pressure MS. The ions pass through two (or sometimes three) sampling cones, where the gas expands and the ions are then directed into an analyzer, most commonly a quadrupole mass analyzer (41).

The heart of a quadrupole MS is compound of four metal rods, which serve as the electrodes of the mass filter. The ions are accelerated and injected into the space between the rods. Each pair of rods are connected electrically to each other, one to a positive, the other one to a negative dc source, additionally to a variable radio-frequency ac potential (figure 7-5) (41).

If positive ions pass through the quadrupole, they will converge in the centre of the channel during its trajectory in the positive phase of the ac cycle and diverge during the negative phase. The magnitude of deflection depends on voltage and frequency applied and the ion mass. While ions with high mass will converge and follow the middle axe due to the higher influence of the dc potential, ions with low mass will diverge and strike the rod, where the positive charge will be neutralized and the resulting molecule carried away.

The second pair of rods, connected to the negative dc, holds the light ions in the middle axe during the positive phase of the ac voltage and deflects the heavier ones, as they are more attracted by the negative dc voltage. Therefore one pair of rods let pass the light ions to the analyzer, while the other pair serves to catch the heavier ones (41).

The ions are then collected according to their mass. An electron multiplier triggers a current, which indicates the intensity of the specific ion. This current can be drawn in a graph, the mass spectrum (41).

7.1.5. Grain size distribution

The granulometric curve of each sample was determined according to EN 933-1 in order to evaluate a probable influence of the particle size distribution or surface area respectively, on the release.

The applied method was wash-out of particles <0,063mm before screening. The sieve sizes following indications in the standard were 10, 8, 4, 2, 1, 0.5, 0.25, 0.125 and 0.063mm.

According to a study from J.J.R. Goumans (46) concerning MSWI bottom ash, 40% of the metals and anions are released from the particles <2mm, which in this study composed a quarter of the total mass.

This can be explained considering the higher surface to volume (or mass respectively) ratio of the smaller particles than the bigger ones. Presuming that the grain size distribution is given that way, that each sieve holds back the same mass, 98,36% of the surface is attributed by the particles <2mm. Presuming that one quarter of the mass concerns to the particles <2mm and three quarters to the particles between 2 and 10mm (given an equal distribution), 94,62% of the surface corresponds to the particles <2mm (table 7-2).

Table 7-2: Distribution of surface area within grain size distribution

Sieve	Ø (mean value)	Mass	Volume	Surface						
[mm]	[mm]	[g]	[cm ³]*	[cm ²]		[Vol.-%]		[%]**	[%]***	
10	10	M ₁₀	M ₁₀ x	0,27	M ₁₀ x	0,82	M ₁₀ /M _{total} x	0,19	1,34	5,38
8	9	M ₈	M ₈ x		M ₈ x	0,91	M ₈ /M _{total} x	0,21		
4	6	M ₄	M ₄ x		M ₄ x	1,37	M ₄ /M _{total} x	0,31		
2	3	M ₂	M ₂ x		M ₂ x	2,74	M ₂ /M _{total} x	0,63		
1	1,5	M ₁	M ₁ x		M ₁ x	5,47	M ₁ /M _{total} x	1,26	98,66	94,62
0,5	0,75	M _{0,5}	M _{0,5} x		M _{0,5} x	10,95	M _{0,5} /M _{total} x	2,51		
0,25	0,375	M _{0,25}	M _{0,25} x		M _{0,25} x	21,89	M _{0,25} /M _{total} x	5,02		
0,125	0,1875	M _{0,125}	M _{0,125} x		M _{0,125} x	43,79	M _{0,125} /M _{total} x	10,04		
0,063	0,094	M _{0,063}	M _{0,063} x		M _{0,063} x	87,34	M _{0,063} /M _{total} x	20,04		
0	0,0315	M ₀	M ₀ x		M ₀ x	260,64	M ₀ /M _{total} x	59,79		
		M _{total}			M _{total} x	435,92		100,00		
* specific weight 3,654g/cm ³										
** for: M ₁₀ = M ₈ = ... = M ₀ ; Unit: [Vol.-%]										
*** for: (M ₁₀ + M ₈ + M ₄) = 3/4 M _{total} and (M ₂ + ... + M ₀) = 1/4 M _{total} ; Unit: [Vol.-%]										

Additionally to the increase of the specific surface area of the particles, the size reduction may give rise to an increasing pH value, what is again linked to the release behaviour of (earth) alkali-metal (hydr)oxides (36).

7.1.6. Mineralogical Composition

The mineralogical composition of the EAF-slag was determined with X-ray Diffraction (XRD), using a Siemens D-500 diffractometer with Cu-tube, for each sample. It was expected to find the explanation for changes in the leaching behaviour by comparing the modification of the mineralogical structure during the aging.

Sample preparation consisted in graining to a diameter <0,063mm.

The diffractometer was adjusted to operate in an angle range of 4 to 70° with steps of 0.05° every three seconds.

Principle

XRD is another X-ray Spectroscopic method like the XRF explained in chapter 7.1.1 which uses X-rays as a source for the identification of the sample.

XRD has a wide range of application in geology, material science, environmental science, pharmaceutical industry among others, where it is applied to identify minerals, as well as other crystalline materials, although it does not provide quantitative data.

X-rays are produced in the X-ray tube, described in chapter 7.1.1. The interaction of the X-ray photons with the electrons from the sample produces a deflection of the incident X-ray beams, similar to the reflection of natural light in a mirror. The diffracted waves give information about the distribution of atoms in the material, by deducing the lattices inter-plane distance. This is described by Bragg's law (figure 7-6).

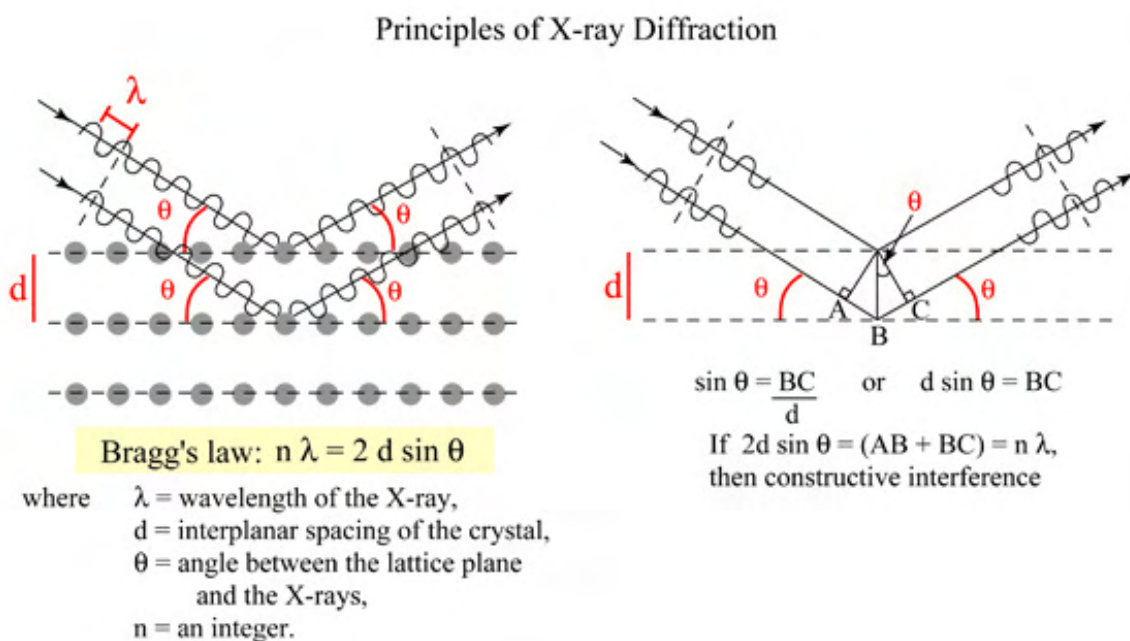


Figure 7-6: Principles of XRD

Unlike to normal light in a mirror, not every wave will be reflected, only the ones striking the atoms in a certain angle θ . This fact requires continuous variation of the wavelength λ or the entrance angle θ in order to provide sufficient information. This can be achieved by using a

range of X-ray wavelengths, by rotating the (single-)crystal or using a powder or polycrystalline sample (47).

For the diffraction analysis in this study the Powder XRD was applied. The sample was grained to a fine powder (<0,063mm), consequently the crystalline structure is randomly oriented in the sample by multitudinous crystals, and exposed to monochromatic light. The sample was rotated in an angel of 4 to 70 degrees with a dwell period of three seconds in every step of 0,05 degrees.

If a X-ray beam strikes the powdered specimen, a multitude of beams is diffracted. The more dispersed this beams are, the more they can be observed as continuous cones, which can emerge in all directions, forwards and backwards. If the sample is placed in the centre of a circle of a film to record the diffraction pattern, the cones are plotted on the film as arcs with a determined distance from the beam entry or exit spot (figure 7-7) (47).

When the film is laid flat, the diffraction lines can be measured (figure 7-7). From the distance of each diffraction line, we associate every single arc with a particular type of cubic structure and further a value for its lattice parameter. These two dates provide sufficient information to determine a specific crystal (element) (47).

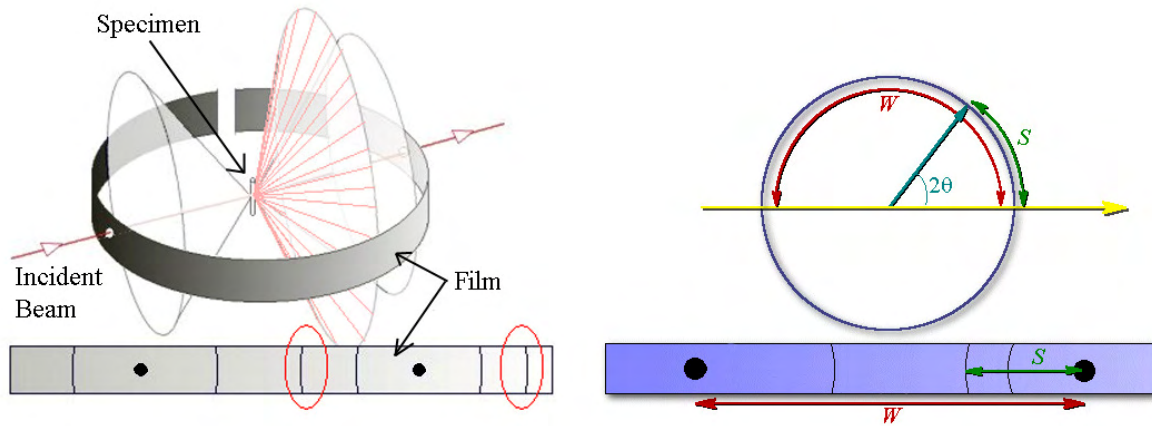


Figure 7-7: Indexing the XRD Pattern

From geometric coherence the angle θ can be deduced. 2θ is the angle between the incident X-ray plane and the one diffracted (figure 7-6).

$$\theta = \frac{\pi \cdot S}{2 \cdot W} \quad (47)$$

From Bragg's law the inter-planar spacing can be derived:

$$d = \frac{n\lambda}{2\sin\theta}$$

In the most simple case of cubic crystals, the equation of inter-planar spacing is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (47)$$

where a is the lattice parameter and $\sqrt{h^2 + k^2 + l^2}$ the triangular of a cubic shaped crystal.

7.2. RESULTS

Composition Solid Sample

Percentages of the major constituents of the slags sampled at age “0 days” obtained by X-ray Fluorescence are shown in Table 7-3. The results are expressed in oxides and do not show if and how the elements are bound in the structure. Table 7-4 shows the mass-% of each element within the sample, by partition of the oxides in Table 7-3 according to their relative atomic mass.

The two slags (c-55 and c-A) show similar values concerning their composition, with predominant constituents of Iron Oxides, CaO, SiO₂ and Al₂O₃, similar to the values found in literature (see chapter 3.3.2).

The results concerning iron, manganese, potassium and sodium are lower or higher than the calibration limits determined in the adjustment of the XRF equipment and therefore not completely reliable. Especially the values for iron should be discussed with precaution.

The basicity, defined as the relation of Calcium oxide to quartz, is higher for the slag c-55 than for c-A:

- c-55: $\text{CaO/SiO}_2 = 2,06$
- c-A: $\text{CaO/SiO}_2 = 1,68$

Table 7-3: Major Constituents in the solid samples – 1

	c55/N/0D-1 [Mass-%]	c55/N/0D-2 [Mass-%]	c55/N/0D mean value	cA/N/0D-1 [Mass-%]	cA/N/0D-2 [Mass-%]	cA/N/0D mean value	<LL	>UL
Fe ₂ O ₃	35,12	35,86	35,49	34,16	34,61	34,39	0,07	25,65
MnO	4,75	4,83	4,79	5,08	5,12	5,10	0,01	0,35
TiO ₂	0,58	0,61	0,60	0,65	0,66	0,66	0,01	2,71
CaO	26,75	27,09	26,92	25,19	25,68	25,44	0,04	49,00
K ₂ O	0,00	0,01	0,01	0,03	0,01	0,02	0,05	12,81
P ₂ O ₅	0,44	0,45	0,45	0,40	0,40	0,40	0,01	15,70
SiO ₂	12,90	13,22	13,06	15,05	15,25	15,15	1,13	90,40
Al ₂ O ₃	9,26	9,36	9,31	10,36	10,46	10,41	0,15	59,20
MgO	2,70	2,73	2,72	2,39	2,43	2,41	0,12	43,51
Na ₂ O	-0,01	0,01	0,00	0,33	0,13	0,23	1,00	10,59

Calibration Limits: LL (lower limit), UL (upper limit)

The selection of scanned trace elements in the solid sample was carried out in accordance with the constituents evaluated in the leaching extracts. The results achieved by ICP-MS are shown in Table 7-5. The content of trace elements sums 0,6 Mass-% for both slags, with main parts of Barium and Chrome.

The sulphur content of the slag was studied elsewhere and represents 0,06% of the total mass content.

Table 7-4: Major Constituents in the solid samples - 2

Element	C55 / N / OD		CA / N / OD	
	mean value [Mass-%]	standard deviation	mean value [Mass-%]	standard deviation
Fe	24,82	0,37	24,05	0,22
Mn	3,71	0,04	3,95	0,02
Ti	0,36	0,01	0,39	0,00
Ca	19,24	0,17	18,18	0,25
K	0,00	0,01	0,02	0,01
P	0,19	0,00	0,17	0,00
Si	6,10	0,11	7,08	0,07
Al	4,93	0,04	5,51	0,04
Mg	1,64	0,01	1,45	0,02
Na	0,00	0,01	0,17	0,10
O	32,33	0,42	33,22	0,28
TOTAL	93,33		94,20	

An interesting result shows the comparison of the values obtained in this study with the contents presented in a study by Tossavainen (2005). Whereas the results for the main constituents and all the trace elements with exception of Chrome are in a similar range, the values for Chrome in the study of Tossavainen are ten times higher than the values obtained in this study (32.700 mg/kg and 26.800 mg/kg respectively).

Table 7-5: Proportion of trace elements in the solid samples

	c55/N/0D-1	c55/N/0D-2	c55/N/0D		cA/N/0D-1	cA/N/0D-2	cA/N/0D	
	[mg/kg]	[mg/kg]	mean value	standard deviation	[mg/kg]	[mg/kg]	mean value	standard deviation
As	5,45	6,73	6,09	0,91	6,94	7,26	7,10	0,23
Ba	1977,48	2051,69	2014,59	52,47	2259,48	2382,78	2321,13	87,19
Cd	nd	nd			nd	nd		
Cr	2767,19	2776,83	2772,01	6,82	2317,86	2429,67	2373,77	79,06
Co	5,77	5,74	5,76	0,02	5,08	5,94	5,51	0,61
Cu	253,41	255,50	254,46	1,48	246,35	151,93	199,14	66,77
Hg	nd	nd			nd	nd		
Mo	23,71	23,74	23,73	0,02	18,61	19,15	18,88	0,38
Ni	20,50	20,68	20,59	0,13	24,53	24,43	24,48	0,07
Pb	13,62	15,59	14,61	1,39	16,24	14,36	15,30	1,33
Sb	0,96	1,15	1,06	0,13	1,18	1,16	1,17	0,01
Se	nd	nd			nd	nd		
Sn	11,69	12,14	11,92	0,32	12,01	12,38	12,20	0,26
V	474,63	489,01	481,82	10,17	450,75	473,82	462,29	16,31
Zn	438,43	456,35	447,39	12,67	226,39	217,59	221,99	6,22

* not detected

Leachate Analysis

The results of ICP-MS and HPLC concerning the leachates obtained by testing the slag after the aging process on air described in chapter 7.1 are shown in Table 7-6 (slag type c-55) and Table 7-7 (slag type c-A). For better readability, elements, which are not detected in neither of the replicas are shown blank.

A blank sample, which was done by duplicate, was subjected to the same process as the slag samples and serves as a proof for the correctness of the testing and the cleanness of the equipment applied. It should show a pH slightly beyond 7, because of slight reception of CO₂, and no release of contaminants.

The results obtained show basicity of the blank samples, which can be explained by the fact that the vessels used for the blank samples, contrary to the slag samples, were not properly cleaned after application of genuine soap. The vessels used for the slag samples have been unused before employment for this study. On the other hand, the high release of Sulphate from the blank samples does so far not have an explanation.

It should be noted, that especially the release of SO₄²⁻ of the samples “Blank 0 days” and “c-55 / N / 0 days” reveal very high deviation.

The results of ICP-MS and HPLC concerning the leachates obtained by testing the slag after aging in water (L/S=10) without exposure to ambient air described in chapter 7.1 are shown in Table 7-8 (slag type c-55) and Table 7-9 (slag type c-A). Here again, in order to provide better readability, elements, which are not detected in neither of the replicas are shown blank.

It should be stressed, that the results obtained have to be treated with caution, especially the ones concerning the leaching behaviour of the Anions, as they show very high deviation within the replications.

Although Flour and Chloride did not show up in the samples c-55 / 0d and c-A / 0d, this is very unlikely to be true. Additionally, half of the replications done for the sample c-55 / 0d do not show significant release of Sulphur, although the other half does and steel slags are typically reach in Sulphur, due to the desulphurisation of the metal during the steel-making process. Therefore, in the mean value of the sample c-55 / 0d only three of six replications were included.

A complete table with the result of every single value of the replicates for both experiments can be observed in **Annex I**.

Table 7-6: Leaching results c-55 / N, aging on air (c1 and c2)

	Blank 0 days		c-55 / N																Detection limit
			0 days ⁽¹⁾		21 days ⁽²⁾				42 days ⁽²⁾				91 days ⁽²⁾						
					c1		c2		c1		c2		c1		c2				
	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	
pH	8,53	0,23	10,28	1,97	513	61	407	141	10,78	0,45	11,03	0,28	10,76	0,59	11,32	0,03			
Conductivity (µS/cm)	47	1	504	29					412	64	440	51	392	120	483	13			
[Cl ⁻] (mg/Kg)					186,20	45,92	61,98	23,00	96,29	28,82	97,95	33,81	68,47	2,55	59,23	11,19		5,00	
[F ⁻] (mg/Kg)					16,65	8,60	12,85	6,78	72,07	86,80	13,76	0,55	86,33	117,72	15,49	4,32		5,00	
[SO4 ²⁻] (mg/Kg)	386,80	434,74	1503,72	345,74	251,65	65,94	120,48	55,19	191,01	54,28	164,79	11,26	128,34	4,95	111,63	22,24		5,00	
[As] (mg/Kg)			0,01	0,00														0,02	
[Ba] (mg/Kg)	0,06	0,05	11,86	0,79	5,09	0,33	4,46	0,59	4,34	0,78	3,40	0,57	4,18	2,60	5,05	1,18		0,2	
[Cd] (mg/Kg)																		0,01	
[Cr] (mg/Kg)			0,07	0,06	0,19	0,04	0,15	0,01	0,04	0,08	0,05	0,08	0,19	0,32	0,29	0,11		0,1	
[Cu] (mg/Kg)	0,04	0,00	0,11	0,08	0,28	0,03	0,18	0,06	0,15	0,06	0,10	0,10	0,22	0,29	0,34	0,14		0,1	
[Hg] (mg/Kg)																		0,01	
[Mo] (mg/Kg)			0,13	0,06	0,24	0,06	0,12	0,04	0,16	0,03	0,12	0,01	0,12	0,02	0,09	0,01		0,02	
[Ni] (mg/Kg)			0,01	0,00														0,2	
[Pb] (mg/Kg)			0,02	0,02	0,07	0,01	0,09	0,04	0,07	0,03	0,05	0,03	0,10	0,10	0,10	0,07		0,01	
[Sb] (mg/Kg)			0,01	0,00														0,02	
[Se] (mg/Kg)			0,01	0,01														0,5	
[V] (mg/Kg)			0,88	0,37			0,73	0,55	0,98	0,19	1,05	0,08	1,39	0,28	1,58	0,12		0,1	
[Zn] (mg/Kg)	0,01	0,01	0,12	0,06	1,03	0,06	1,09	0,20	0,94	0,35	0,71	0,26	1,64	1,29	1,54	0,89		0,1	

⁽¹⁾ Six duplicates, ⁽²⁾ three duplicates, blank = not detected, Unit: mg/kg solid slag mass

Table 7-7: Leaching results c-A / N, aging on air (c1 and c2)

	Blank 0 days		C-A / N																			
			0 days ⁽¹⁾		21 days ⁽²⁾				42 days ⁽²⁾				91 days ⁽²⁾				Detection limit					
					c1		c2		c1		c2		c1		c2							
	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation						
pH	8,53	0,23			9,60	0,52	28	432	409	35	318	77	0,61	10,54	1,32	28	377	411	102	360	97	0,56
Conductivity (µS/cm)	47	1																				
[Cl ⁻] (mg/Kg)									35,42	1,90	27,01	14,85	6,38	42,85	6,38			52,99	17,47	28,74	7,33	5,00
[F ⁻] (mg/Kg)									12,88	8,94	6,88	4,15	2,82	8,61	2,82			10,04	1,67	7,54	0,88	5,00
[SO4 ⁼] (mg/Kg)	386,80	434,74		1214,84	504,18		164,69	42,66	125,12	53,26		61,53	241,50	63,47	7,80			199,87	3,00	134,54	7,66	5,00
[As] (mg/Kg)				0,01	0,00																	0,02
[Ba] (mg/Kg)	0,06	0,05		4,61	0,68		9,89	7,45	4,17	0,32		0,38	3,08	0,28				3,12	2,68	3,69	0,49	0,2
[Cd] (mg/Kg)																						0,01
[Cr] (mg/Kg)				0,04	0,01		0,14	0,04														0,1
[Cu] (mg/Kg)	0,04	0,00		0,11	0,02		0,38	0,22	0,17	0,01		0,02	0,13	0,02				0,24	0,11	0,10	0,09	0,1
[Hg] (mg/Kg)																						0,01
[Mo] (mg/Kg)				0,23	0,02		0,15	0,01	0,12	0,01		0,02	0,17	0,05				0,17	0,01	0,13	0,01	0,02
[Ni] (mg/Kg)				0,01	0,01																	0,2
[Pb] (mg/Kg)				0,04	0,01		0,15	0,05	0,06	0,02		0,02	0,09	0,00				0,18	0,09	0,09	0,03	0,01
[Sb] (mg/Kg)				0,01	0,00																	0,02
[Se] (mg/Kg)				0,04	0,01																	0,5
[V] (mg/Kg)				0,58	0,06		0,99	0,09	0,81	0,01		0,08	0,77	0,04				0,94	0,08	1,13	0,03	0,1
[Zn] (mg/Kg)	0,01	0,01		0,49	0,49		1,42	0,86	0,74	0,12		0,31	0,82	0,12				0,95	0,36	0,52	0,09	0,1

³¹⁾ six duplicates, ³²⁾ three duplicates, blank = not detected, Unit: mg/kg solid slag mass.

Table 7-8: Leaching results BOT c-55 / N, aging in water

	BOT c-55 / N ⁽¹⁾								Detection limit
	0 days		21 days		42 days		91 days		
	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	
pH	4,45	0,05	10,17	0,28	11,54	0,35	11,49	0,10	
Conductivity (µS/cm)	319	24	351	11	556	163	472	66	
[Cl ⁻] (mg/Kg)	115,24	9,70	43,65	12,90	14,24	0,83	11,01	0,66	5
[F ⁻] (mg/Kg)	6,62	0,00	5,62	3,73	5,18	2,62	4,78	1,03	5
[SO4 ⁼] (mg/Kg)	123,29	11,23	24,46	0,64	21,99	0,22	14,51	1,70	5
[As] (mg/Kg)	0,01	0,00							0,02
[Ba] (mg/Kg)	9,53	1,93	22,41	6,25	17,44	7,64	11,28	1,69	0,2
[Cd] (mg/Kg)									0,01
[Cr] (mg/Kg)	0,02	0,01	0,38	0,03	0,20	0,14	0,12	0,03	0,1
[Cu] (mg/Kg)	0,09	0,03	0,15	0,04	0,73	1,03			0,1
[Hg] (mg/Kg)									0,01
[Mo] (mg/Kg)	0,06	0,01	0,12	0,01	0,11	0,01	0,06	0,01	0,02
[Ni] (mg/Kg)									0,2
[Pb] (mg/Kg)	0,01	0,01	0,03	0,01	0,06	0,07			0,01
[Sb] (mg/Kg)									0,02
[Se] (mg/ Kg)									0,5
[V] (mg/Kg)	0,19	0,02	0,93	0,14	2,73	1,26	1,73	0,25	0,1
[Zn] (mg/Kg)	0,64	0,19	0,43	0,16	0,84	0,84	0,29	0,06	0,1

⁽¹⁾ two duplicates, blank = not detected, Unit: mg/kg solid slag mass

Table 7-9: Leaching results BOT c-A / N, aging in water

	BOT c-A / N ⁽¹⁾								Detection limit
	0 days		21 days		42 days		91 days		
	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	mean value	standard deviation	
pH	3,66	0,82	10,95	0,35	10,39	0,45	11,51	0,40	
Conductivity (µS/cm)	420	42	394	108	395	14	553	143	
[Cl ⁻] (mg/Kg)	111,36	26,59	17,23	9,50	10,53	1,89	7,58	0,50	5
[F ⁻] (mg/Kg)	3,62	5,11	10,58	4,95	4,97	2,74	3,54	1,97	5
[SO4 ⁼] (mg/Kg)	235,74	75,92	28,97	29,74	25,82	9,27	15,18	2,10	5
[As] (mg/Kg)	0,01	0,00							0,02
[Ba] (mg/Kg)	1,71	0,01	4,85	6,14	8,27	1,32	8,36	1,68	0,2
[Cd] (mg/Kg)									0,01
[Cr] (mg/Kg)	0,02	0,01			0,07	0,10	0,09	0,12	0,1
[Cu] (mg/Kg)	0,08	0,01	0,08	0,11	0,20	0,00	0,16	0,23	0,1
[Hg] (mg/Kg)									0,01
[Mo] (mg/Kg)	0,17	0,06	0,10	0,13	0,16	0,01	0,12	0,01	0,02
[Ni] (mg/Kg)					0,34	0,48			0,2
[Pb] (mg/Kg)	0,03	0,01	0,03	0,03	0,05	0,02	0,06	0,06	0,01
[Sb] (mg/Kg)	0,01	0,00							0,02
[Se] (mg/ Kg)	0,03	0,01							0,5
[V] (mg/Kg)	0,18	0,00	0,62	0,88	1,22	0,13	0,79	0,95	0,1
[Zn] (mg/Kg)	0,20	0,16	0,37	0,28	0,65	0,01	0,40	0,39	0,1

⁽¹⁾ two duplicates, blank = not detected, Unit: mg/kg solid slag mass

Grain Size Distribution

The grain size distribution of each sample can be observed in **Annex II**. The results refer to the grain sizes before realization of the leaching tests, which cause certain crushing of the particles.

The particle size distribution is compared to the leaching test results, in order to assess its influence. Comparison can only be done for samples of the same age and therefore provide contrasts of four different samples at each age (e.g.: for age 42 days: c-55 / c1 and c2, c-A / c1 and c2; at this point the different conservation types are neglected as they did not show significant differences).

Annex III shows the comparison described. For each age two particle size distributions and their associated leaching behaviour are chosen according to the percentage of particles <2mm. The comparison is done for the sample with the highest and lowest percentage of particle size <2mm.

X-Ray Diffraction

The mineralogical composition, analyzed by X-Ray diffraction, of each single sample is shown in **Annex IV**. The slags are composed of a complex phase composition with a mixture of amorphous phases, which are shown as the base line in the graphs, and crystallized phases, which correspond to the peaks. Many crystallized phases cannot be identified with confidence due to the presence of amorphous phases and complex compositions, which result in overlapping peaks. However, the main peaks can be identified without doubt and reveal high contents of Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and iron oxide (FeO). For c-55 the Wüstite content is higher than the one of Gehlenite, while for c-A the Gehlenite content predominates likewise as found in different literature studies (10) (18). Further minerals found are Magnetite (Fe_2O_4), Dicalcium-silicate (Ca_2SiO_4), Calcite (CaCO_3), Lime (CaO), Calcium hydroxide (Ca(OH)_2), Periclase (MgO), Brucite (Mg(OH)_2) and a Silicate complex with potassium and magnesium.

Gehlenite and Dicalcium-silicate are cement minerals and react with water. This transformation, taking place during the aging process, can facilitate the leaching of heavy metals. During the aging process, lime and Periclase form in contact with water Calcium hydroxide and Brucite respectively.

7.3. DISCUSSION

The main task of this work consists in the evaluation of changes in the leaching behaviour after aging the slag in different conditions and discovering development of pH and similar leaching patterns of the constituents.

For better understanding, a legend for the following diagrams:

c-55, c-A	different slags
c1	aging on air with regular raining
c2	aging on air in humid conditions with regular raining
BOT	aging in water (L/S=10)

The results are expressed in mg of released constituent of kg solid (dry) slag [mg/kg].

The substances examined more closely are Chloride, Sulphate, Flour, Barium, Chrome, Lead, Zinc, Copper, Molybdenum and Vanadium, as the other elements analysed do not show up in the majority of the extractions.

7.3.1. Aging on air

The trend of pH is particularly influenced by the reaction of oxides in the slag (CaO, MgO and BaO), first with H₂O creating a hydroxide and later with carbon dioxide from the environment what leads to the formation of Calcium carbonate.

Other than expected, the pH development does not show a decrease caused by carbonatisation, but a slight increase for all the samples (figure 7-8). Probably the time scale of the experiment was too small, so that the formation of Calcium carbonate still not exceeded the reaction of CaO with H₂O, which actually leads to a decreasing pH value.

The generally high pH is most likely caused by the release of Calcium and Magnesium, (neither element was analysed in the leaching tests) and indicates a high buffering capacity. However, this pH can be changed drastically, as described by Tossavainen (10), who showed a drop to pH 4 in the leachate from a lysimeter-experiment concerning Blast Furnace slag, due to the oxidation of the reduced material containing sulphur.

Especially the different pH of the samples c-55 / 21d / c1 and c-55 / 21d / c2 deserves special attention, as their pH differs in two units. Comparison with the other samples shows, that c-55 / 21d / c1 not only has a lower pH (9,11), but also reveals higher conductivity (figure 7-9) and a remarkably higher release for Chloride (figure 7-10 a) and Molybdenum (figure 7-15).

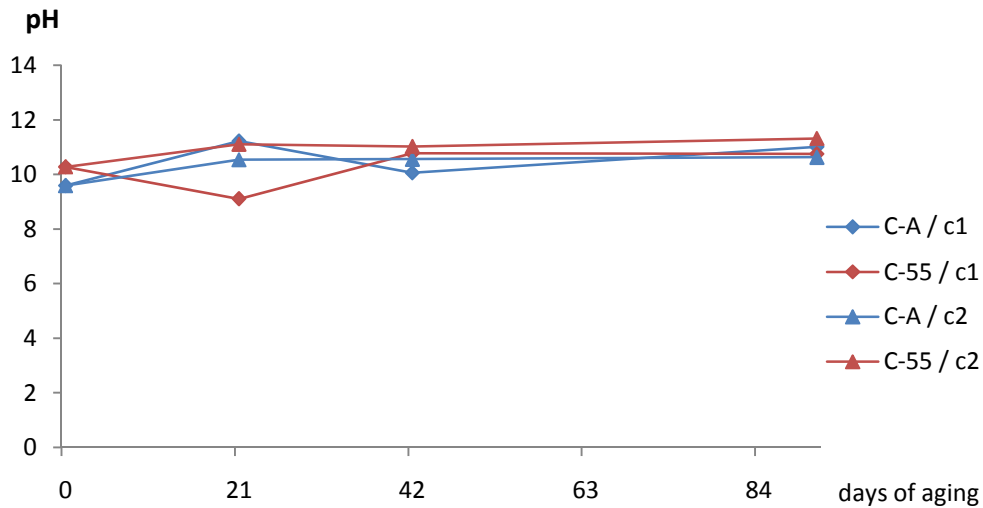


Figure 7-8: pH development, aging on air

The development of the conductivity is shown in figure 7-9.

The conductivity is proportional to the concentration of dissolved ions. More accurately it depends on the type, concentration and charge of the ions and is highly affected by temperature. At very high concentrations of ions, the conductivity is not proportional anymore, as the ions hinder themselves in their movements.

The samples present a general decrease of conductivity after 21 days of aging followed by a slow increase for the further aged material, with exception of slag c-55 / c1, where the conductivity increases slightly after 21 days and drops afterwards.

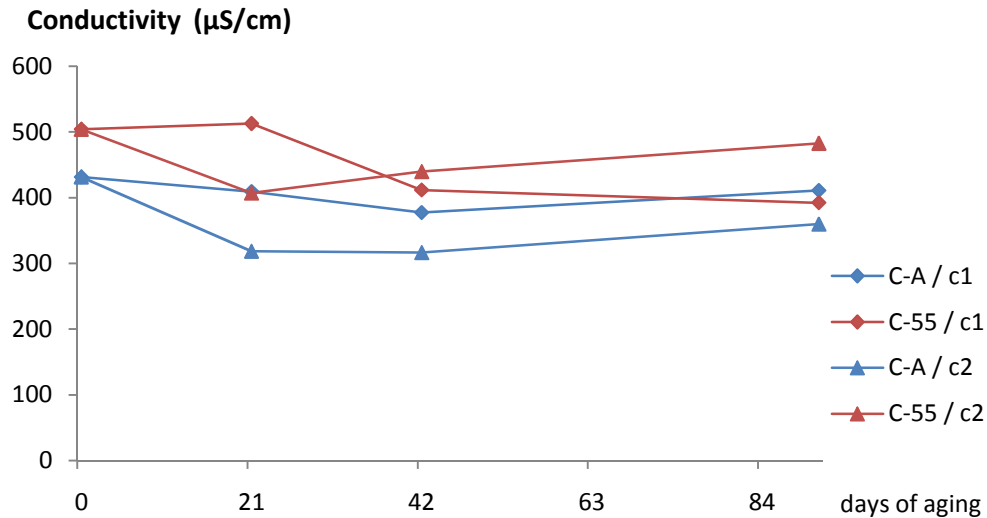


Figure 7-9: Conductivity development, aging on air

Anions

The release curves for the anions Flour, Chloride and Sulphate are shown in figure 7-10 (a-c). Dates for c-55 / c1 are not reliable and therefore not presented in the diagram. Flour and Chloride are released in a higher amount from the slag c-55 than from c-A.

An hypothesis for the dispersion of results concerning the “0 days” samples of Sulphate is based on the assumption of precipitation of Sulphate with Barium to Barium sulphate, also called barite (BaSO_4).

A precipitation results in the formation of salts, which are compounds of metal- and non-metal ions. They are water soluble and electric conductors in solutions (48).

If a solution contains Barium ions and Sulphate ions, solid Barium sulphate will begin to precipitate, as soon as the product of Barium and Sulphate ions exceeds the solubility product of BaSO_4 (48), what can be expressed in another way:

if $[\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] > K_{\text{sp}}(\text{BaSO}_4)$, the solution is oversaturated

if $[\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] < K_{\text{sp}}(\text{BaSO}_4)$, the solution is unsaturated

if $[\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] = K_{\text{sp}}(\text{BaSO}_4)$, the solution is saturated (equilibrium).

Calculation for each sample concerning the ion concentration of Barium sulphate reveals that the solubility product for the samples c-55 / 0d / 1-3 and for c-A / 0d / 1-6 is exceeded. The applied value for the solubility product K_{sp} of BaSO_4 is $1,9\text{E}-09 \text{ mol}^2/\text{l}^2$ according to H. Knoblauch

(1995). This value varies slightly depending on the author and is expressed normally for the standard temperature of 25°C. As storage temperature of the leachate is 4°C the solubility will be less than the indicated value, but this effect can be neglected for Barium Sulphate (49).

The maximum solubility of Barium and Sulphate respectively is

$$[Ba^{2+}] = [SO_4^{2-}] = \sqrt{1,9 * 10^{-9}} = 4,36 * 10^{-5} \text{ mol/l}$$

However, the sulphate concentrations for the samples mentioned are higher than the maximum solubility of 4,3E-05 mol/l and range in the order of 1E-03 mol/l.

The reason for this incoherence can lie in the fact, that there was not sufficient time for the Barium Sulphate to precipitate, although this is not likely as the leachates are stored for some days before the analysis. Eventually other precipitates with a lower solubility are formed.

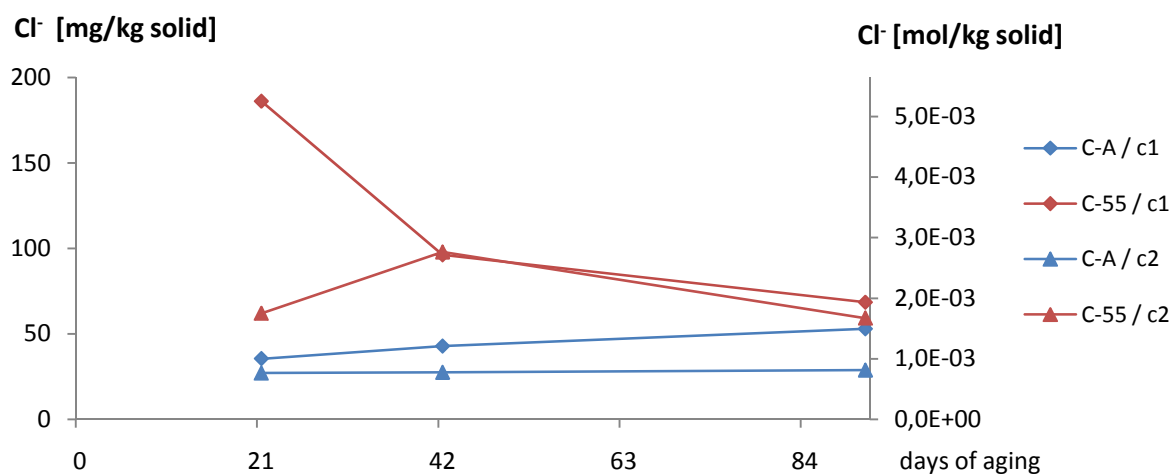


Fig. 7-10 (a)

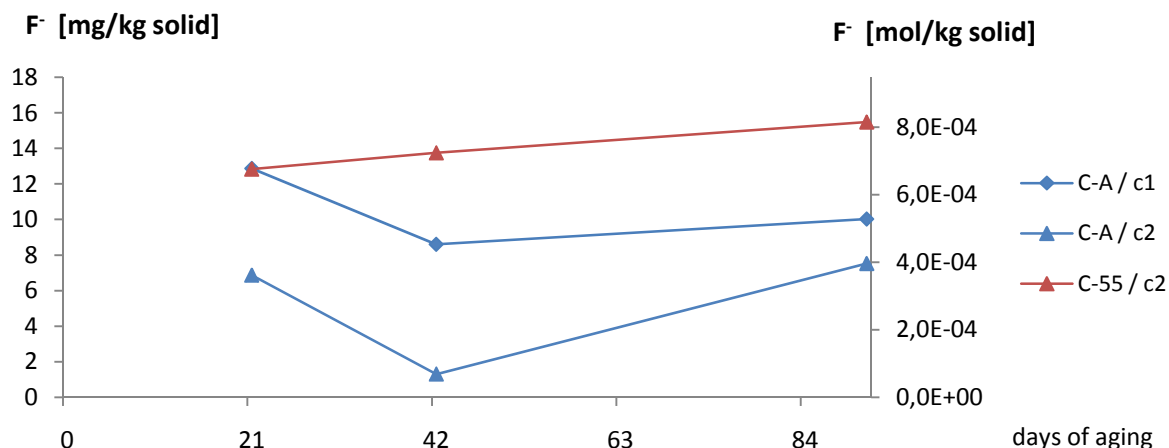


Fig. 7-10 (b)

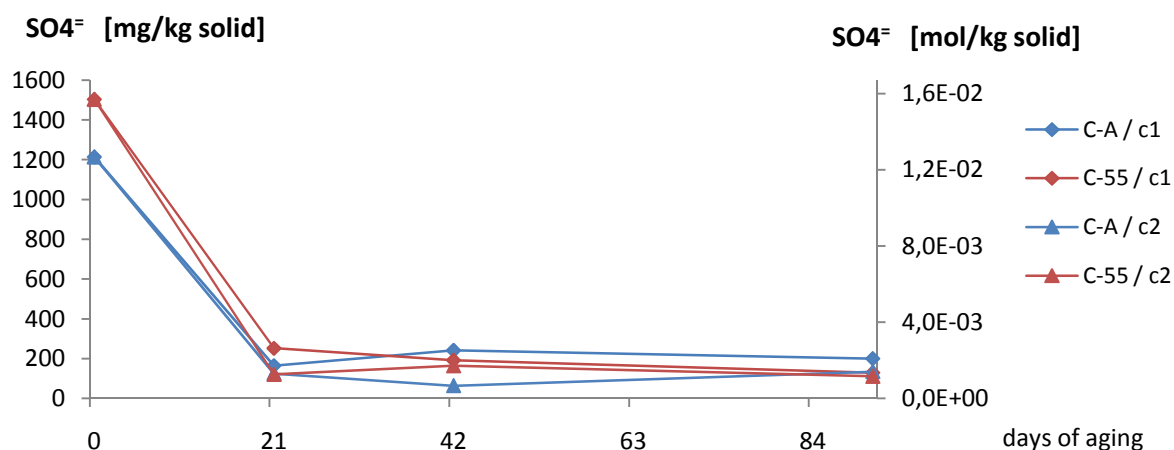


Fig. 7-10 (c)

Figure 7-10: Development in the release of anions, aging on air

Barium

The release curve for Barium is shown in figure 7-11. The trend shows evidence of the carbonatisation of BaO to BaCO₃ for the samples of c-55, which especially influences the slag within the first three weeks of aging.

Although the total Barium content in the solid sample is similar for c-55 and c-A (table 7-5) the release of Barium referred to slag c-A does not show the same effect. As release is even low for the not aged slag, the Barium in c-A might be present in a less soluble form than in c-55.

The replications for the sample c-A / 21days / c1 reveal a high dispersion (table 7-7), where the value for replica c-A / 21days / c1-1 causes the peak shown in figure 7-11. If the replica is neglected, the trend of c-A / c1 and c2 become comparable.

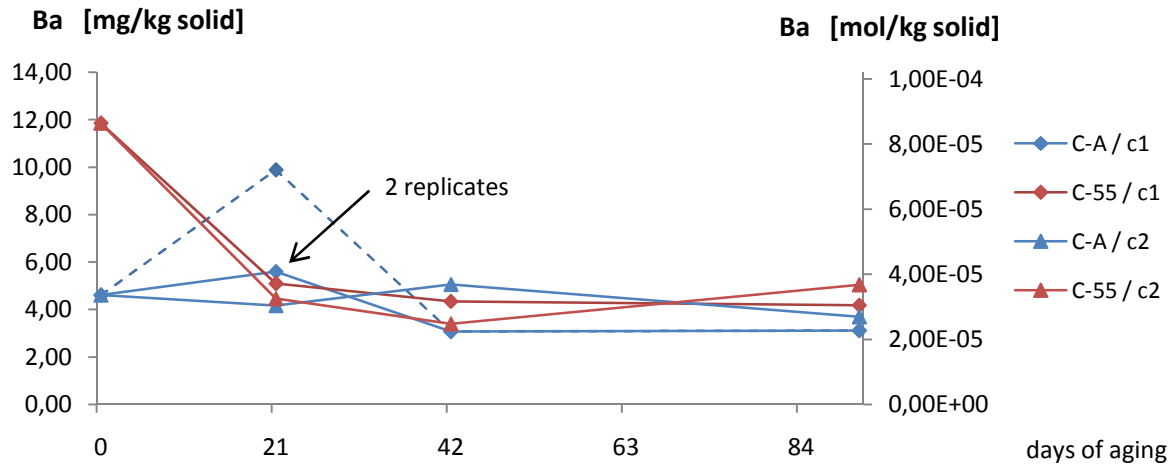


Figure 7-11: Development in the release of Barium, aging on air

A regression analysis for the trend of Barium release from c-55 reveals good adaption to an exponential-3 parameter-rise (or fall), which can be written like:

$$f(x) = y_0 + a * e^{(-b*x)}$$

The regression analysis is done with the program “SigmaPlot” and adjusted to a 95% confidence range.

Table 7-10 shows the statistical summary for the data of c-55 / c1, which shows a poorer adjustment to the non-linear regression than the data of c-55 / c2. This is caused by the value of replica c-55 / 91days / c1-3 and its effect on dispersion of the 91 days data. Neglecting this value would provide a similar probability of the model.

The relative high P-value for the variable b reveals a low contribution for the prediction of the concentration, although R^2 , the coefficient of determination is close to 1, which reveals a good prediction of the model (figure 7-12).

Table 7-10: Statistical summary table and Anova for regression Barium c-55 / c1

Variable	Coefficient	Standard Error	LL	UL	t	P
y ₀	4,200	0,631	3,569	4,832	6,654	0,0002
a	7,656	1,150	6,505	8,806	6,655	0,0002
b	0,102	0,055	0,048	0,157	1,874	0,0978
Analysis of Variance						
	Degrees Of Freedom	Sum of Squares	Mean Square			
Regression	3	467,63	155,88			
Residual	8	15,00	1,87			
Total	11	482,62	43,88			

Table 7-11 shows the statistical summary for the data of c-55 / c2. The regression model fits appropriately the given data (figure 7-13), as the coefficient of determination is close to 1, the residuals reveal a non-correlation and the regression passes the constant variance test, which is not given for c1.

Again, the high P-value for the variable b reveals a low contribution for the prediction of the concentration.

Table 7-11: Statistical summary table and Anova for regression Barium c-55 / c2

Variable	Coefficient	Standard Error	LL	UL	t	P
y ₀	4,239	0,424	3,815	4,663	10,002	<0,0001
a	7,618	0,833	6,785	8,451	9,149	<0,0001
b	0,179	0,195	-0,016	0,374	0,919	0,385
Analysis of Variance						
	Degrees Of Freedom	Sum of Squares	Mean Square			
Regression	3	447,65	149,22			
Residual	8	8,22	1,03			
Total	11	455,87	41,44			

Both models pass the normality test, which reveals if the values are distributed normally around the regression. This fact is probably given by the low amount of data available.

The resulting equation for c-55 / c1 is

$$\text{Concentration} \left[\frac{mg}{kg} \right] = 4,20 + 7,66 * e^{(-0,10 * \text{time} [days])}$$

and for c-55 / c2

$$\text{Concentration} \left[\frac{mg}{kg} \right] = 4,24 + 7,62 * e^{(-0,18 * \text{time} [days])}$$

revealing similar values for the independent variables.

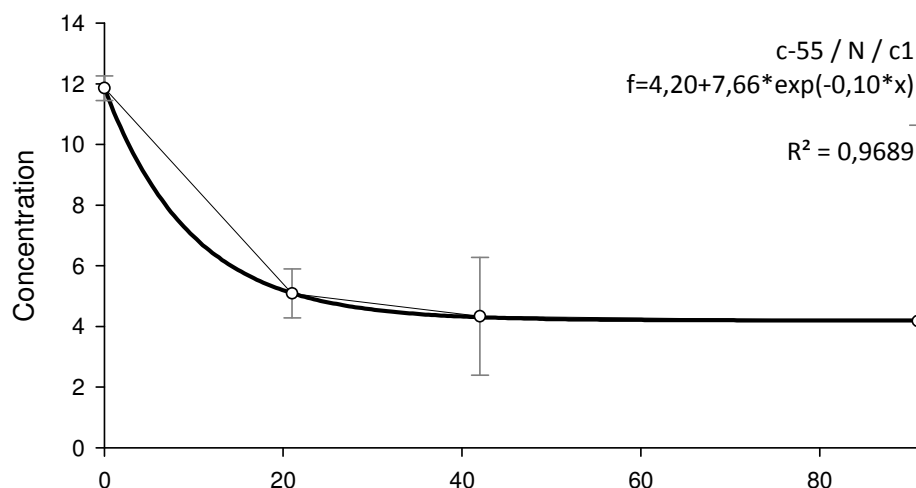


Figure 7-12: Regression c-55 / c1

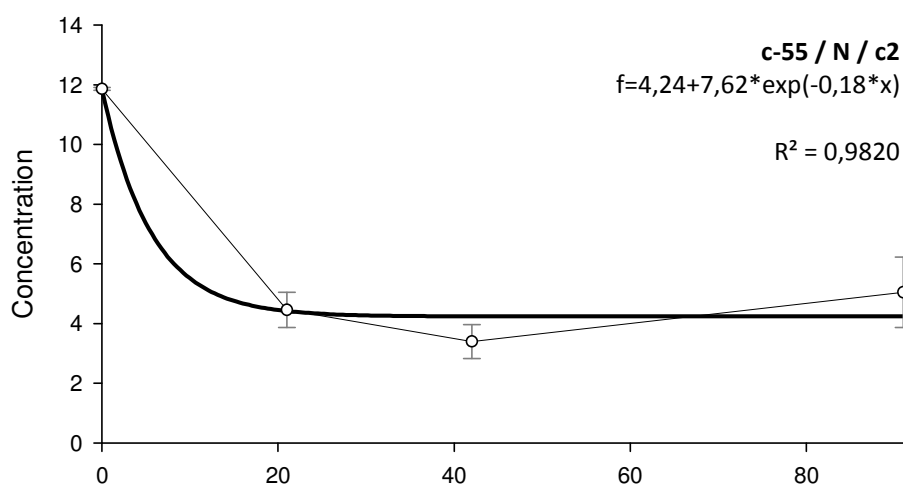


Figure 7-13: Regression c-55 / c2

Chrome, Zinc, Lead, Copper

The ageing-process provokes an interesting phenomena concerning the release behaviour of Chrome, Zinc, Lead and Copper (figure 7-14 (a-d)). These cations tend to show low release without aging, increase their leachability after the first three weeks of ageing, decrease again after six weeks and increase when tested after three month.

c-A indicates a lower release for the aging in humid conditions (c2) than in simulation of ambient conditions (c1) similar to the behaviour of Flour and Chloride, although this effect cannot be observed for c-55.

The analysis provides no distinction between hexavalent and trivalent Chrome. According to D. M. Proctor (50) hexavalent Chrome is not produced during the steel making process due to its

reducing conditions, but is formed at low concentrations during the aging process under oxidizing conditions. It can be assumed that 0,04% of the Chrome in the solid sample after 91 days of aging exists as hexavalent Chrome and that a similar value represents the part of Cr(IV) in the leachates.

A study dedicated on the oxidation of solid Chrome(III)-Oxide in FerroChrome and stainless steel production (51) likewise affirms the gradual oxidation to the hexavalent form in ambient conditions and depicts a similar scenario with 0,1 to 1% of Chrome being oxidized to Cr(IV) within 6-9 month of free contact with oxygen. The study further concludes, that the oxidation process decreases exponentially and ceases within 12 month.

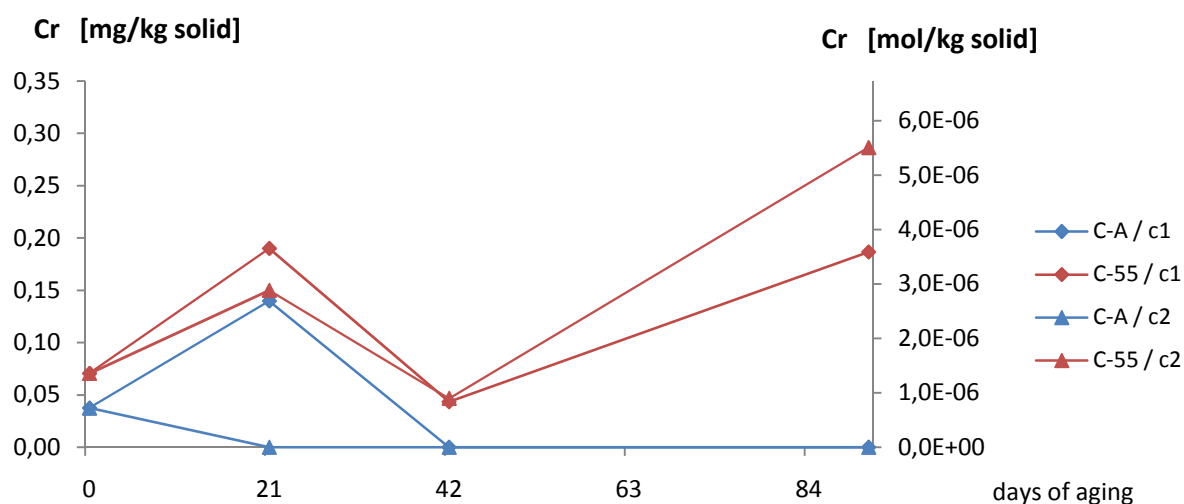


Fig. 7-14 (a)

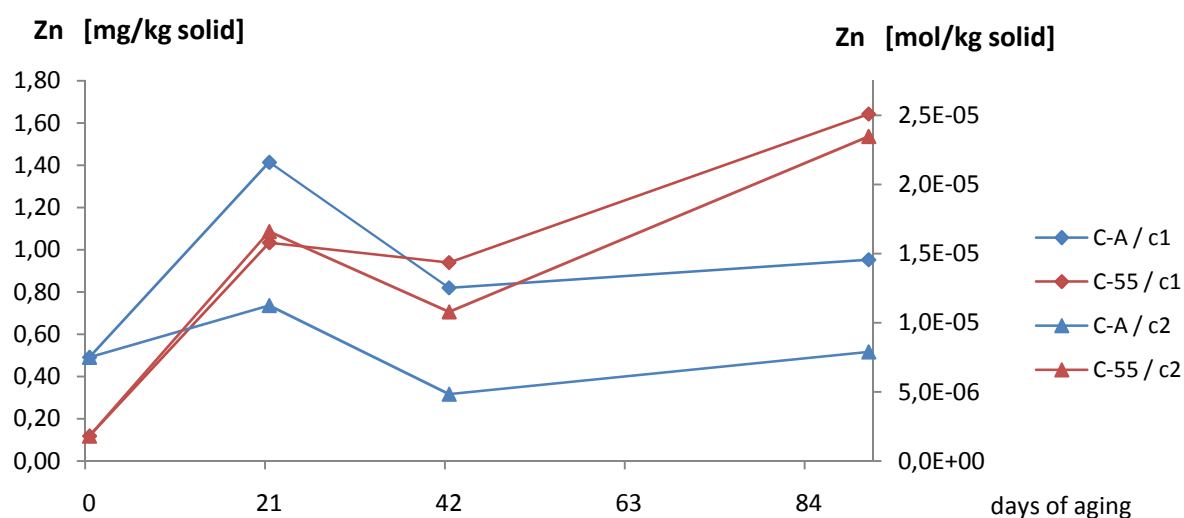


Fig. 7-14 (b)

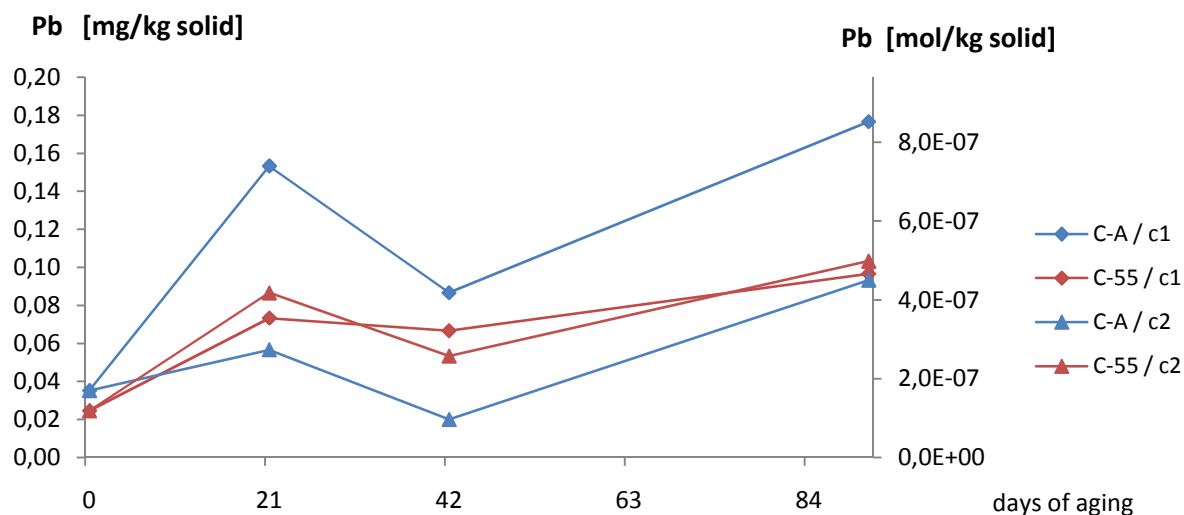


Fig. 7-14 (c)

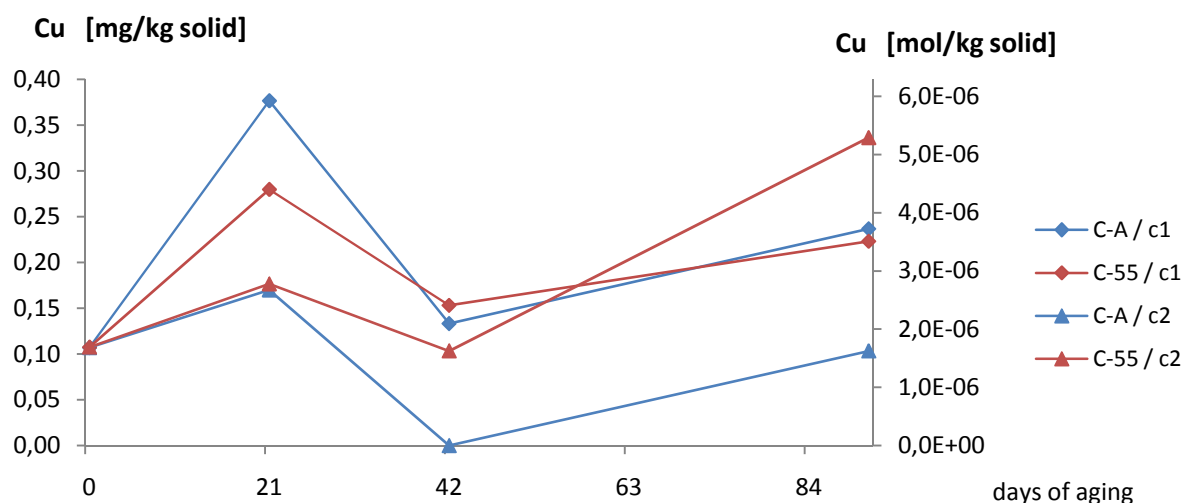


Fig. 7-14 (d)

Figure 7-14: Development in the release of Cr, Zn, Pb and Cu, aging on air

Molybdenum

Release of Molybdenum reveals a very slight fall in the release behaviour along the ongoing ageing process, appreciating the mean trend for c-55 and c-A. Contemplating every single release curve, no obvious increase or decrease can be observed; the release of Molybdenum is rather not influenced by the aging process.

According to Tossavainen (10) the contact with water at a high pH (10-12) and a slightly oxidizing atmosphere results in the formation of MoO_4^{2-} , what could explain a decreasing release tendency.

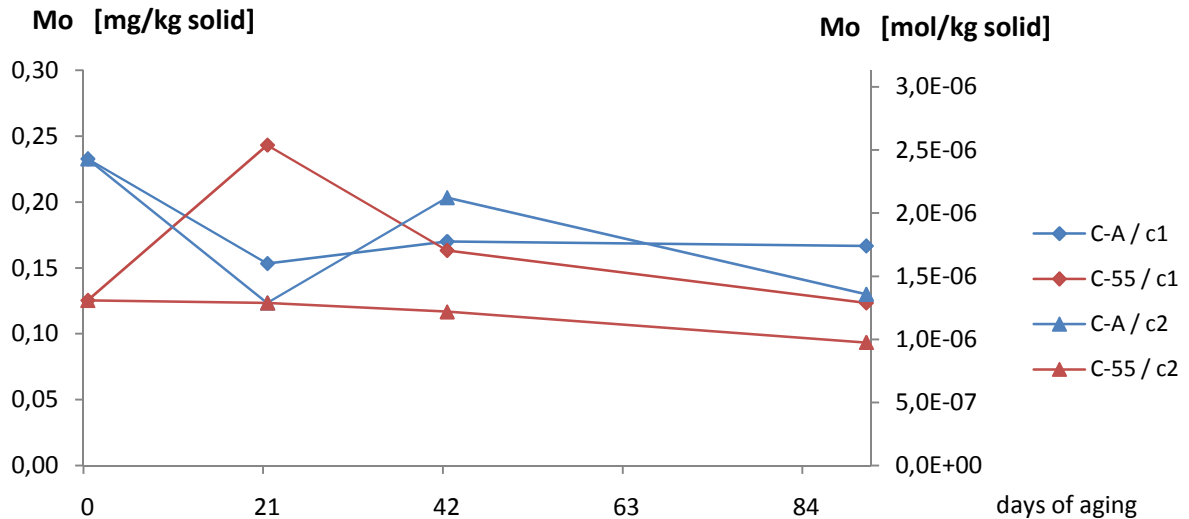


Figure 7-15: Development in the release of Molybdenum, aging on air

Vanadium

Although statistical ambiguity due to the low replication number in this study might create certain doubts regarding the significance of the results, all of the slags show a well-defined increase of Vanadium release with the proceeding aging (figure 7-16).

Vanadium exists in oxidation states from 0 to +5, its toxicity usually increases with increasing valence. In slags, Vanadium is most likely found as V^{3+} - V^{5+} , where V^{4+} is the most stable (10) and predominate form in BOF steel slag, according to Chaurand P. (52); a fact which is very likely applicable for EAF slags too.

The same study (52) suggests, that the predominate, tetravalent Vanadium becomes oxidized during aging in ambient conditions to the more toxic pentavalent form.

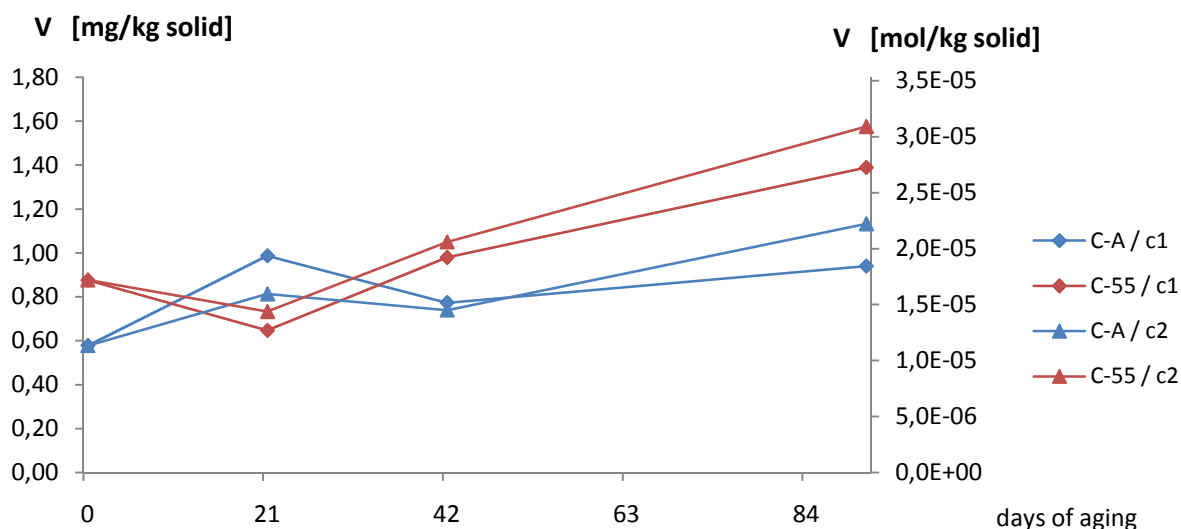


Figure 7-16: Development in the release of Vanadium, aging on air

7.3.2. Aging in water

The trend of pH is shown in figure 7-17. The results should be treated with caution as electric pH sensors are generally susceptible for failure and manual control with litmus paper was not conducted. The first analysis, after leaving the slag for 24 hours without agitation in deionized water, shows an acid pH. This phenomena can probably be caused by a rapid release of metal ions in absence of appropriate ligands.

Consequent the pH rises to approx. 10,5 after 21 days and finally 11,5 after 91 days of water-aging, a slightly higher value than the pH established by genuine aging on air.

For both experiments (aging on air, aging in water) it can be assumed, that the slag in contact with water develops reducing conditions, which has been ascribed to sulphide species released from the solid material (53). It should further be assumed, that the redox potential is even lower for the aging in water experiments than for the standardized 24h test (aging on air), based on the fact, that during the aging in water more time to develop reducing conditions is given.

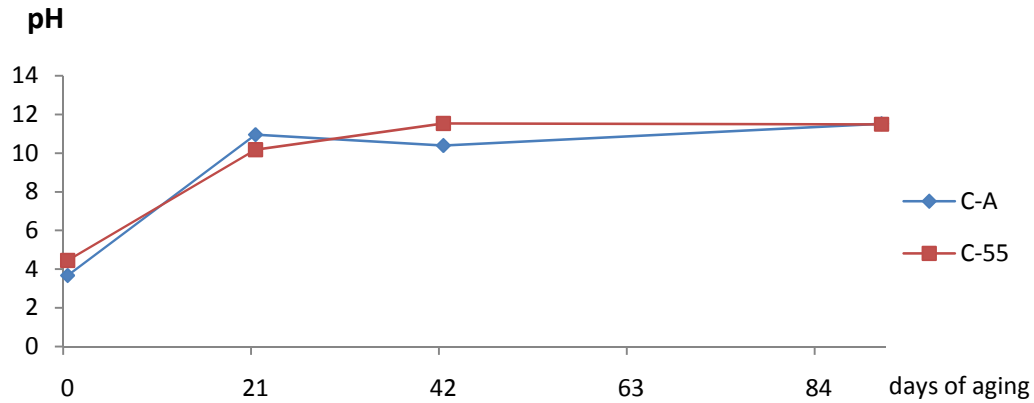


Figure 7-17: pH development, aging in water

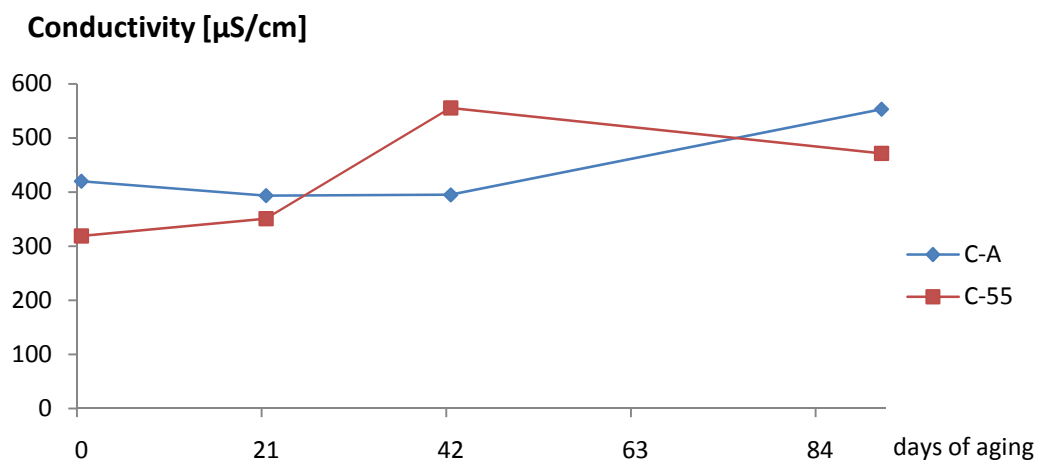


Figure 7-18: Conductivity development, aging in water

The diagrams regarding the release of trace elements in the “reducing-conditions” experiment express, beyond the results obtained at the specific time, the cumulative trends and a linear regression line (black colour) for both slag types (figures 7-19 to 7-21). The slope calculated for the linear regression indicates whether the release of an element is solubility controlled and shows the retention potential for the element.

The high cumulative dilution in the experiment ($\sum L/S = 40$) minimizes solubility limitations. Therefore, the effect of solubility can be observed clearly. A completely solubility controlled release would show a trend line with a slope of $k=1$. In order to compare the slopes in diagrams of different elements, the absolute release of every element has to be taken in account, as the variables for the regression increase linear with the concentration in the leachate. Hence, the value $|k/a|$ is calculated for each element according to:

$$y = k * x + a$$

with x representing the liquid to solid ratio and y the concentration of the addressed substance.

The value $|k/a|$ provides comparability for the regressions obtained; the lower $|k/a|$, the higher the retention potential for the addressed substance.

The linear regression (see figure 7-19 to 7-21) leads to the following $|k/a|$ values:

<u>Anions:</u>		<u>Cations:</u>	
- Chloride:	0,016	- Barium:	0,213
- Flour:	1,130	- Chrome:	0,164
- Sulphate:	0,014	- Zinc:	0,434
		-Lead:	0,184
		- Copper:	0,130
		- Molybdenum:	1,679
		- Vanadium:	0,098

Anions

The release of anions is shown in figure 7-19. Chloride and Sulphate show a high initial release, which decreases rapidly in the further extractions. The $|k/a|$ values, 0,016 for Chloride and 0,014 for Sulphate are the lowest of all the focused substances. This prior high release can be ascribed to a quick initial surface wash-off, as these substances are easily soluble. However, the later extractions continuously reveal further, decreasing release, what does not a priori demonstrate a high retention potential for Chloride and Sulphate, but rather attributes to the surface wash-off in the first extraction, hereafter the leachant was renewed and/or to precipitation reactions.

On the other hand Flour ions are extracted in a nearly continuous flow, which can be observed in the far more inclined regression line with $|k/a| = 1,130$ and shows a low retention potential for Flour.

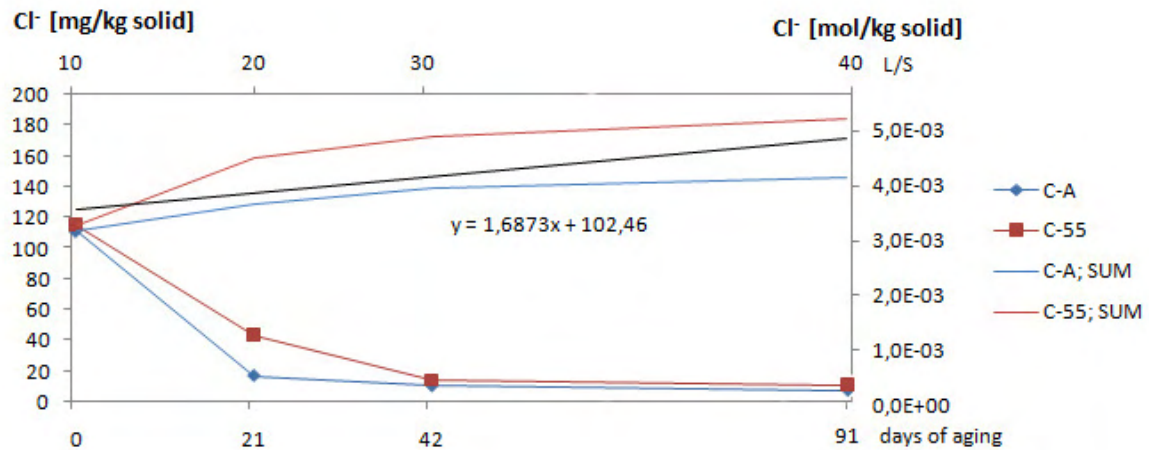


Fig. 7-19 (a)

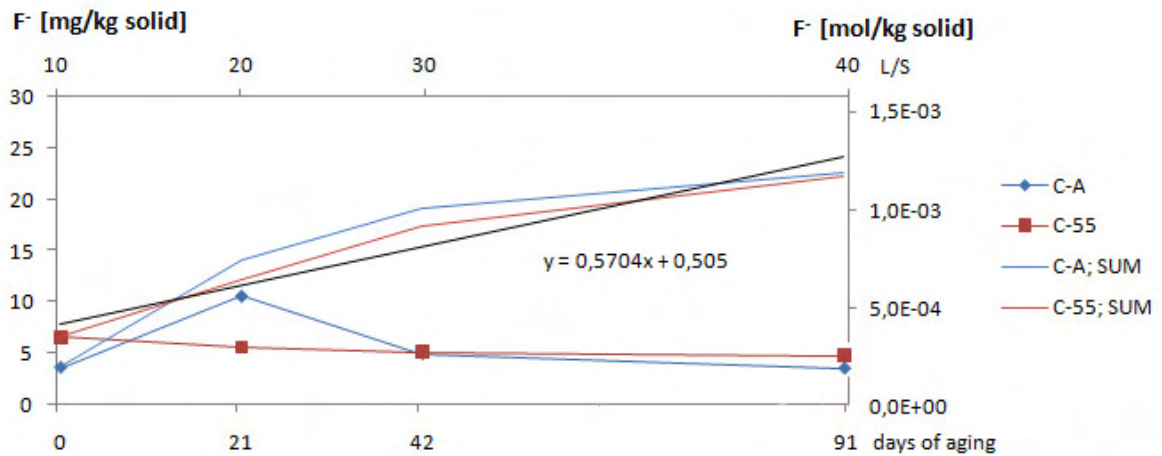


Fig. 7-19 (b)

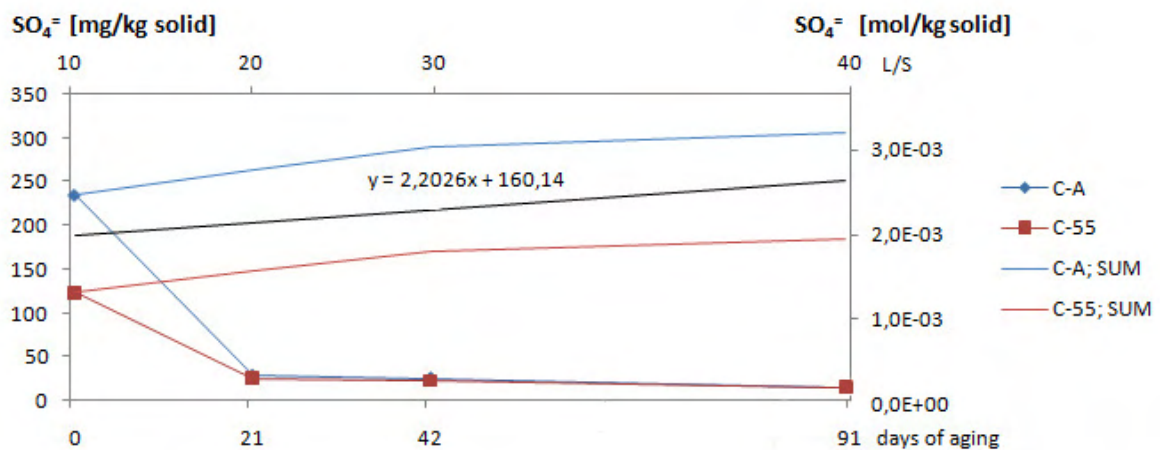


Fig. 7-19 (c)

Figure 7-19: Development in the release of anions, aging in water

Barium

The release curve for Barium is shown in figure 7-20.

Barium solubility, as described before, is limited by BaSO_4 . Therefore, the mobility of Barium increases with a decreasing redox potential, where the Sulphate is reduced (53). Without knowledge of the actual redox conditions and assuming the lowest redox potential for the extraction at 91 days, the trend of c-A, increasing its mobility during the aging fulfils this affirmation, whereas c-55 does not. On the other hand the release for c-55 is definitely higher in the “aging in water” experiment than after extraction of the slag aged in ambient conditions (figure 7-11), confirming the explanations from B. N. J. Comans (53), that Barium “*increases its release substantially under reducing conditions*”.

With $|k/a| = 0,213$ the slag reveals a relatively low retention potential for Barium compared to the other substances discussed, most probably due to the neo-formation of minerals and precipitation as BaSO_4 .

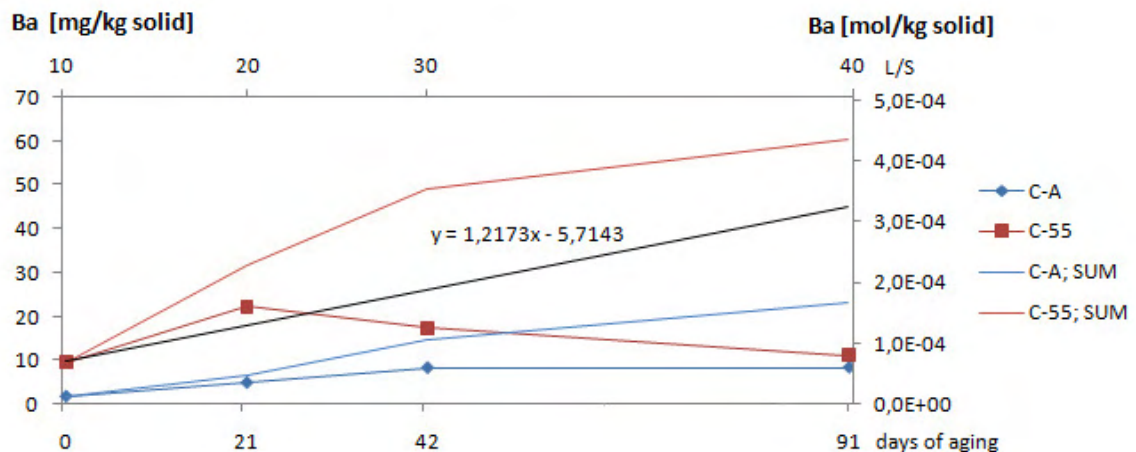


Figure 7-20: Development in the release of Barium, aging in water

Chrome, Zinc, Lead, Copper, Molybdenum and Vanadium

The development in release for the selected metals (Cr, Zn, Pb, Cu, Mo and V) is shown in figure 7-21 (a-f). In general, they show a peak at the age of 21 or 42 days. Very likely, the time span afterwards (until the extraction at 91 days) was sufficiently long to create strongly reducing conditions, whereas the metal leachability drops significantly.

The reference value for the retention capacity $|k/a|$ reveals a similar retention for the metals discussed with $|k/a| = 0,164$ for Chrome, $0,434$ for Zinc, $0,184$ for Lead, $0,130$ for lead and $0,098$ for Vanadium. Considering the time series for the metals in the figure 7-21, depletion cannot be observed.

Both slags show the lowest retention potential for Molybdenum, with both trends similarly horizontal and a combined $|k/a|$ of 1,679. Remembering the trend of Molybdenum during the “aging on air” experiments (figure 7-15), which was not affected by the aging conditions neither, reveals precisely, that the release of Molybdenum does not depend on storage conditions or neo-formation of minerals.

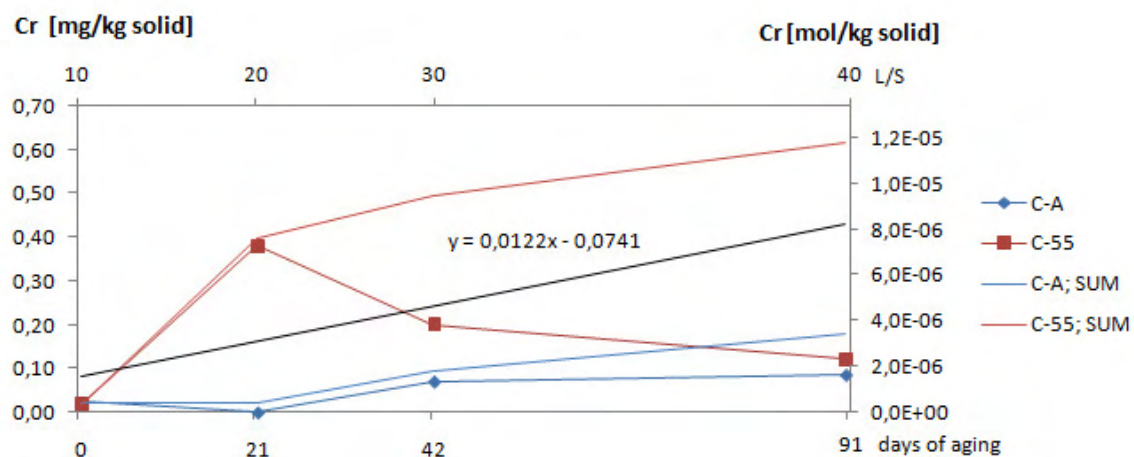


Fig. 7-21 (a)

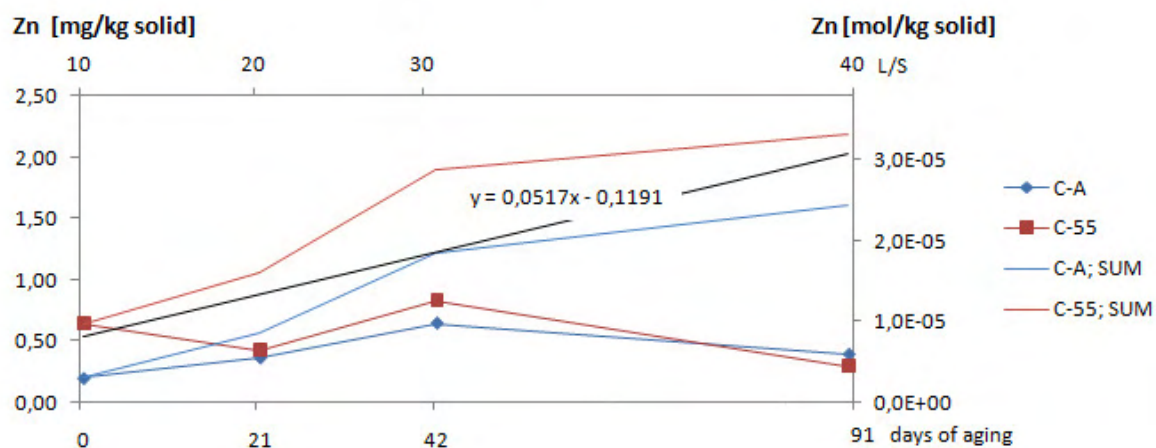


Fig. 7-21 (b)

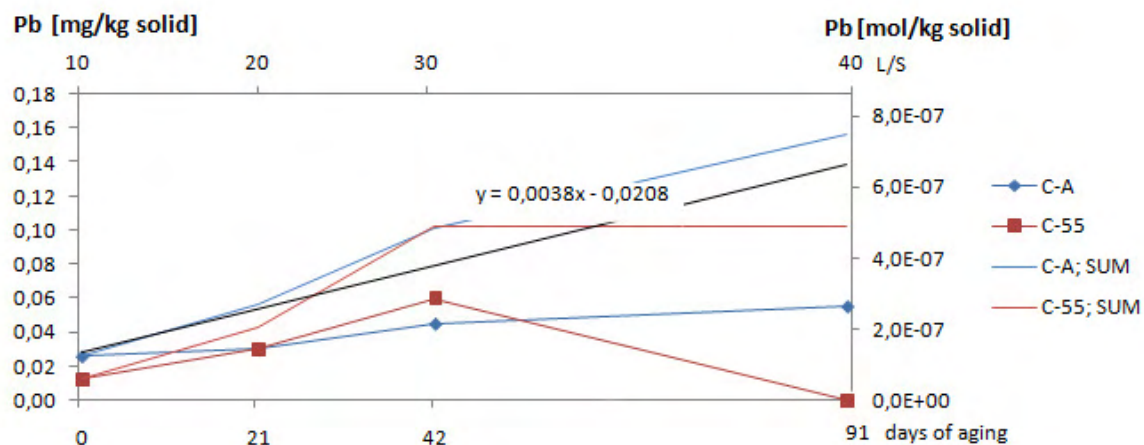


Fig. 7-21 (c)

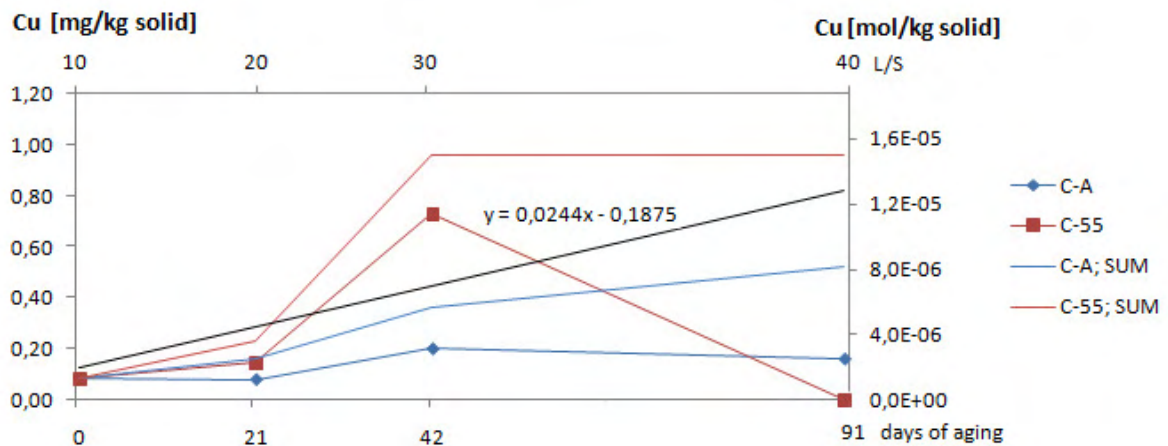


Fig. 7-21 (d)

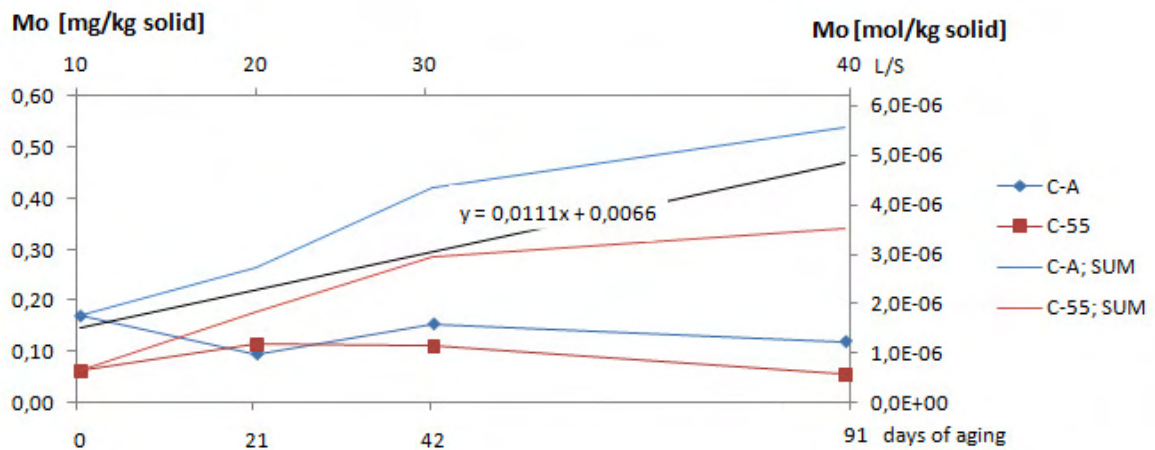


Fig. 7-21 (e)

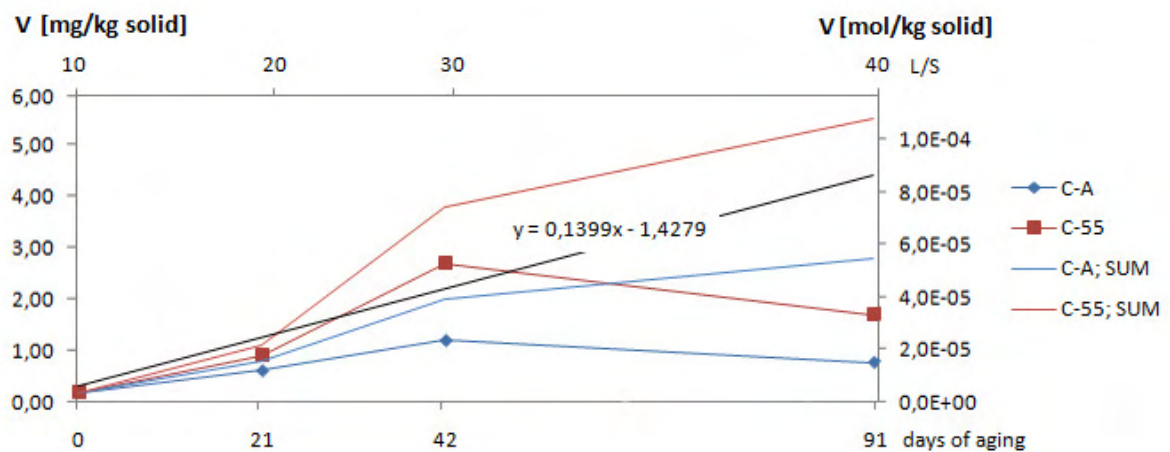


Fig. 7-21 (f)

Figure 7-21: Development in the release of Cr, Zn, Pb, Cu, Mo and V, aging in water

7.3.3. Availability and Comparison of the experiments

The concentration of the cations in the leachates is represented as a percentage value of the total concentration in table 7-12 (see also tables 7-5 to 7-9 for reference). This value indicates if an element is tightly bound in the slag matrix or shows mobility at the slag-water interface.

Arsenic, Chrome and Copper show a low availability, whereas Barium, Molybdenum and Lead are readily released during the test. Nickel hardly shows mobility for c-55 but increases its mobility during the aging in water for c-A to more than 1 percent. Antimony, although not discussed concerning its trend, reveals high mobility for both slags, especially for the untreated slag.

Obviously the rate released is generally higher for the “0 days” samples, subjected to the standard process described in EN 12457-4 (column 1 and 4 in table 7-12) than for the “0 days, aging in water” samples (column 2 and 5). Although the aging state is equal, the samples were not in movement during the second experiment. The difference therefore has its seeds in the agitation of the sample.

Table 7-12: Availability of selected metals (% released of total content)

	c55/N/0D		c55/N/0-91D (SUM)	cA/N/0D		cA/N/0-91D (SUM)
	LEACHATE (aging on air)	LEACHATE (aging in water)	[Mass-%]	LEACHATE (aging on air)	LEACHATE (aging in water)	[Mass-%]
	[Mass-%]	[Mass-%]		[Mass-%]	[Mass-%]	
As	0,09	0,08	0,08	0,17	0,18	0,18
Ba	0,59	0,47	3,01	0,20	0,07	1,00
Cr	0,00	0,00	0,02	0,00	0,00	0,01
Cu	0,04	0,03	0,38	0,05	0,04	0,26
Mo	0,53	0,26	1,44	1,23	0,90	2,86
Ni	0,04	0,00		0,04	0,01	1,40
Pb	0,14	0,09	0,70	0,23	0,17	1,02
Sb	0,62	0,00		1,20	0,71	0,71
V	0,18	0,04	1,16	0,12	0,04	0,61
Zn	0,03	0,14	0,49	0,22	0,09	0,72

7.3.4. Influences of Particle Size Distribution

Comparison regarding influences of the grain size distribution could only be done for four slag samples (see **Annex III** for the results). The samples “0 days” compared do not comply the presumption of higher release for higher fraction of small particles (<2mm). c-55 is composed of 10% less fines than c-A, but shows higher release for all the elements analysed.

The comparison done for the samples “21 days” with a difference of 18% in the amount of the fine fraction fulfils in a better way the assumption. With exception of Vanadium, all the elements analyzed show a higher release for the finer graded sample. Especially the anions are released in far higher amounts, with an increase of 100% for Sulphates, 590% for Chloride and 140% for Flour.

The following contrast for the samples “42 days” (16% difference in the amount of the fine fraction) shows the expected habit for the anions (+280% Sulphates, +55% Chloride and +550% Flour), but in a less obviousness for the cations. Likewise the sample “c-55/c1, 91 days” with 14% more in the fraction <2mm, presents an increase in the leached contaminants, again with one exception, in this case the Sulphates.

A simple comparison of the number of times when an element follows the assumed increase in leaching, when the sample has a higher percentage of the fraction <2mm, shows more obvious results. From a total of 40 cases (bearing in mind Ba, Cr, Cu, Mo, Pb, V, Zn, SO₄²⁻, Cl⁻ and F⁻ at the ages of 0, 21, 42 and 91 days), 27 times the finer grained slag has a higher release, whereas 9 times the behaviour is reverse.

7.3.5. Influences due to Surface changes

X-ray diffraction analysis was performed on every sample in order to detect surface changes due to the reactions with water and carbon oxide during the aging process.

Generally, c-A contains a higher amount of Gehlenite than c-55 and the later contains higher amounts of Wüstite than c-A.

Most of the minerals do not show visible differences in the peak heights with the proceeding aging process. However, comparison regarding the Gehlenite-content, reveals lower amounts of the cement forming material in the older samples, although its transformation into more stable hydrated phases is not testified due to the lack of increase of Calcite.

The increasing trend of Chrome in the “aging on air” experiments can probably be explained by differences in the Wüstite-content. If Chrome is preferentially bound in Dicalciumferrit, Wüstite and Spinell, as stated by Drissen (11), the lowering content of Wüstite in the c-55 samples could be the reason for the increasing Chrome release with the ongoing aging process, assuming that Wüstite is further oxidized to more soluble, amorphous compositions (Iron Hydroxides), which do not show up in the diffraction analysis.

It should be noted here, that the differences recognized in the peak heights might also result from the interaction of the high amount of minerals in the slag and that these affirmations need to be confirmed by further studies regarding the mineralogical matrix of the slags (e.g. by SEM).

7.3.6. Comparison with legal limits

The results obtained from the leaching tests in this study do not allow to declare de slag feasible regarding the limits in force in Catalunya, as they are based on a different testing method. The total content limits in this directive from the year 1996 (see table 4-2) are comparably high, hence neither of the elements exceeds the established limits for As, Cd, Cu, Cr, Hg, Ni, Pb or Zn.

In 2006 the “Agencia de Residuos de Catalunya” published a proposal of the new legal limits, which are established on the base of the European Council Decision from 2002 (2003/33/EC) regarding inert waste (see table 4-1). Accordingly, the slag would neither be valuable for construction purposes nor acceptable at landfills for inert waste, due to higher concentrations of Sulphate (sample c-55 / 0d and c-A / 0d) and Flour, where c-55 exceeds the limit of 10mg Flour per kg solid mass in each sample and c-A exceeds in the samples c-A / 21d / c1 and c-A / 91d / c1, although very slightly in both samples. The slag fulfils for each sample the requirements for non-hazardous waste (limit value for Flour is 150mg/kg dry solid substance and for Sulphate 20.000mg/kg dry solid substance).

Application of Austrian law regarding the classification of construction waste (see table 4-3, and 4-4) would reject the tested slags for recycling due to exceeding contents of Chromium and Zinc in the dry solid mass. The Chromium content is 2800mg per kg solid mass for c-55 and 2400mg per kg solid mass for c-A, which is higher than the classification limit for Grade B (lowest classification), which allows a maximum of 90mg/kg solid. The Zinc content is 450mg respectively 220mg per solid mass, exceeding the classification limit for Grade A+ (100mg/kg solid) but fulfils the limit for Grade A and B (450mg/kg solid).

Applying the new Austrian Landfill directive from 2008, the slags do not fulfil the limit values for inert waste landfills due to the higher solid mass content of Chromium (>500mg/kg solid) and higher concentrations in the leaching tests for Flour (>10mg/l leachant) and Sulphate (>1000mg/l leachant), however, the slag can be accepted for construction waste landfills (54).

8. SUMMARIZED CONCLUSIONS

The environmental impact of steel slags is generally based on the assessment of its leaching behaviour, which depends on a variety of chemical and physical factors, reflected in different testing conditions of a wide range of standardised leaching tests.

In this study a simple compliance test with a liquid to solid ratio of 10 and demineralised water as leachant was applied, in order to investigate how

- the age of the slag (0-91 days),
- different storage conditions (ambient, humid and aqueous),
- its mineralogical composition and
- the grain size distribution of the sample

influenced in the release behaviour of a list of selected substances, which coincide with those adopted by the Catalan environmental regulation. Following the major conclusions are summarized:

- The two slags analyzed do not show significant differences in their composition or release behaviour with exception of Flour and Chloride, which are more easily released from c-55 than from c-A.
- The release of Sulphate drops remarkably after a short time of aging, whether in ambient or aqueous conditions: after three month of storage approx. 85, respectively 90% less Sulphate is released, probably due to surface wash-off effects. Furthermore, Sulphate leaching is highly influenced by Barium precipitation, hereafter it does not show up in the analysis method applied.
- During the aging process on air Barium Oxide is carbonated to less soluble Barium Carbonate, decreasing the release 61% after 91 days in ambient conditions for c-55 but only 26% for c-A. Storage in water implies a lower redox potential, hampering the leachability of Barium. In the latter ambient, Barium is released steadily, revealing a low retention potential of the slag concerning this element, which leads to a total release of 1-3% of the solid mass after a total liquid to solid ratio of 40.

- Accordingly, two major forces regarding the Barium release are presented in this study: First the carbonation process during the storage of the slag and second the precipitation of Barium sulphate, which takes place during the leaching test.
- Chrome, Zinc, Lead and Copper reveal a similar release pattern after storage in air: increase after the first 21 days, decrease after the next 21 days and a peak after the last extraction at the age of 91 days. Furthermore, the Wüstite content of the single samples shows a contrary trend in the time series. As Chrome is foremost bound in these crystals and a lower Wüstite content presumes a higher content of soluble Iron Hydroxides, a higher release of Chrome is probably caused by aging. However, this affirmation probably does not apply for Zinc, Lead and Copper, whose mineralogical binder should be investigated.
- Vanadium increases its leachability by about 70-80% after aging on air for 91 days. This is probably related to the neo-formation of Calcium-Silicates, which are assumed to bear the majority of the Vanadium.
- Molybdenum does not show deflection in the time series, hence reveals no certain dependency on the neo-formation of the minerals, applicable for aging on air and in water. After subjecting Molybdenum to the total liquid to solid ratio of 40, up to 2,8% of the solid mass content were released.
- Very little attention was paid to the particle size distribution during the experiments, therefore its influence lacks of verification. However, higher proportions in the fine fraction (<2mm) definitely led to higher release of the investigated substances. Especially the anions revealed an increasing release (+55 – 590%), when the fine fraction changed in magnitude. This encourages the hypothesis concerning the release controlling force, whereupon surface wash-off effects are mainly responsible for the leaching of anions.
- In order to reduce the influence of freshly opened surfaces of the material on the test results, it is indispensable to crush the slag prior to subjecting it to the aging process. In this study this fact was despised, provoking an uncertainty concerning the distribution of actually carbonated surfaces to freshly opened slag particles in every single sample. This equally counts for on-site aging in order to achieve reliable conditions both environmentally and technically.

- Due to the leachate concentrations of >10mg/l leachant of Flour and >1000mg/l leachant of Sulphate, the slags cannot be classified as inert waste according to the European landfill directive and neither fulfil the limit values established for valuable construction waste according to the Federal Waste Management Plan 2006. For the last-mentioned, the solid mass content of Chromium, which amounts to 2800, 2400mg/kg solid dry mass respectively, further exceeds the legal limits. Comparison to Catalan limits in force is not possible, as different testing methods were applied.

After all, considering the deviation in the results of the Anions, a general conclusion cannot be drawn; the slag can neither be declared inert nor hazardous during the time span of three months after sampling in the factory.

9. RELEXIONS AND SUGGESTIONS FOR FURTHER WORK

During the execution of leaching tests, it is important to be aware of the impact of a wide range of interconnected variables. For the assessment of one single variable, it should be accurately checked, that the residual conditions are not altered. In this context, the slag should not be crushed after the aging process and a constant grain size distribution should be guaranteed for each single sample.

Enhanced control of the leachability of trace elements in slags is provided by better knowledge of the trace element bearing major phases and their transformation during the aging process (including transformations caused by changing cooling conditions). Microscopic methods (Optical microscopy, Electron microscopy) are widely used in order to detect, how an element is bound in the matrix and can complement the diffraction analysis.

Another important chemical aspect in the assessment of the leaching behaviour is to determine the valence state of the released trace elements, which determines its toxicity, and after all the elements fate in the environment, where it is placed.

In order to identify the elements fate but also the slag behaviour in a long-term scale, the leaching test results need to be reflected in a wider context. Wisely, worst-case scenarios should be applied and effects of accumulation on sensitive deposits needs to be discussed.

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REFERENCES

- [1] **Eurofer, (European Confederation of Iron and Steel Industries).**
<http://www.eurofer.org>. [Online] [Cited: 09 08 2008.]
- [2] **Britannica, Encyclopedia.** <http://www.britannica.com>. [Online] [Cited: 16 11 2007.]
- [3] **IHOBE, (Sociedad Pública Gestión Ambiental).** *Libro Blanco para la minimización de residuos y emisiones, Escorias de Acerías*. Pais Vasco : Gobierno Vasco, 1999.
- [4] **Steeluniversity.** <http://www.steeluniversity.org>. [Online] [Cited: 30 11 2007.]
- [5] **FEhS.** <http://www.fehs.de/dtpages/schlacken/schlacken.html>. [Online] [Cited: 15 01 2008.]
- [6] **OECD, (Eds.).** *Recycling strategies for road works*. Paris : s.n., 1997. (Organization for Economic Co-operation and Development: Road Transport Research).
- [7] **Motz, H.** *Products of Steel Slags, An Opportunity to save natural Resources*. 2000.
- [8] **Manso, J.M., et al.** Durability of concrete made with EAF slag as aggregate. *Cement and Concrete Compositions*. 2006, Vol. 28, Issue 6, pp. 528-534.
- [9] **Drissen, P.** *Eisenhüttenschlacken-industrielle Gesteine*. Duisburg : FEhS, 2004.
- [10] **Tossavainen, M.** *Leaching Results in the Assessment of Slag and Rock Materials as Construction Material*. Lulea : Lulea Technical University, 2005.
- [11] **Drissen, P.** *Mineralische Bindung von Spurenelementen in Stahlwerksschlacken*. Duisburg : FEhS, 2006.
- [12] **Euroslag, (Eds.).** *Legal Status of Slags*. Duisburg : Euroslag, 2006.
- [13] **Brunner, Paul H. and Rechberger, H.** *Practical Handbook for Material Flow Analysis*. Florida, USA : Lewis Publishers, 2003.
- [14] **Hauptverband_der_deutschen_Bauindustrie_eV.** www.bauindustrie.de. [Online] [Cited: 06 12 2008.]
- [15] http://www.cincodias.com/articulo/economia/construccion-aporta-puntos-PIB-media-ultimos-anos/20071119cdscdseco_3/cdseco/. [Online] [Cited: 06 12 2008.]
- [16] **Global_Slag_Staff.** Slag in Japan. *Global Slag Magazin*. 2006, November 2006.
- [17] **Chesner, W. H. ao.** *User Guidelines for Waste and by-product materials in pavement construction*. New York : Chesner Engineering, 1998.
- [18] **FEhS, (Eds.).** *Iron and Steel Slags – Properties and Utilisation*. Duisburg : Forschungsgemeinschaft Eisenhüttenschlacken, Reports from 1974-2000.
- [19] **Manso, J.M., Gonzales, J.J. and Polanco, J.A.** Electric Arc Furnace Slag in Concrete. *Journal of Materials in Civil Engineering*. 2004, Vol. 16, 6.
- [20] **Barra, M.** *Estabilización de suelos con escorias de acería y cement*. Salamanca : s.n., 2001.

- [21] **Nippon_Slag_Organization.** Current State of Use of Iron and Steel Products in Japan. Duisburg : FEhS, 2007.
- [22] **Bourke, B.** *Water Improvement Initiatives in New Zealand Using Melter Slag Filter Beds.* Auckland, New Zealand : SteelSerLtd.
- [23] **Rex, M.** *The use of BF, converter and ladle slags in European agriculture – benefits or risks.* Duisburg : FEhS, 2005.
- [24] **Dippenaar, R.** *Industrial uses of slag – The use and re-use of iron and steelmaking slags.* s.l. : The South African Institute of Mining and Metallurgy, 2004.
- [25] **Förstner, U.** *Integrated Pollution Control.* Berlin, Heidelberg : Springer, 1995.
- [26] **Roth, L. and Eklund, M.** Framework for Environmental Assessment of Using Industrial By-Products and Used Building Materials. *International RILEM Conference on the Use of Recycled Materials in Buildings and Structures.* 2004.
- [27] **Commission_of_the_European_Communities.** *COM (2007) 59 - on the Interpretative Communication on waste and by-products.* Brussels : Communication from the Commission to the Council and the European Parliament, 2007.
- [28] **ARC, (Agència de Residus de Catalunya).** *Projecte de Decret sobre valorització d'escòries procedents de la fabricació d'acer den forn elèctric.* Barcelona : Generalitat de Catalunya, 2006.
- [29] **DOGC, (Diari Oficial de la Generalitat de Catalunya).** Utilització d'escòries valoritzables. 1996. Vols. Número 2181 – 13.3.1996.
- [30] **BMLFUW.** *Federal Waste Management Plan 2006.* Vienna : Federal Ministry of Agriculture and Forestry, Environment and Water Management, 2006.
- [31] **Sdu Uitgevers, Eds.** *Building Materials Decree, Texts and explanatory notes.* The Hague : s.n., 1999.
- [32] **Sloot, H. A. van der.** <http://www.leaching.net/leaching/>. [Online] [Cited: 31 07 2008.]
- [33] **Holnsteiner, R.** *Praxisgerechte Prüfung des Auslaugverhaltens von industriellen Nebenprodukten und Recyclingbaustoffen.* Vienna : BM für wirtschaftliche Angelegenheiten, 1997.
- [34] **Bourg, A. C. M.** Speciation of Heavy Metals in Soils and Groundwater and Implications for their Natural Provoked Mobility. [book auth.] W. Salomons (Eds.). *Heavy Metals, Problems and Solutions.* Heidelberg : Springer, 1995.
- [35] **Sloot, H. A. van der and Dijkstra, J. J.** *Development of horizontally standardized leaching tests for construction materials: A material based or release based approach?* 2004.
- [36] **Sloot, H. A. van der, et al.** *Harmonization of Leaching/ Extraction tests.* Amsterdam : Elsevier, 1997.

- [37] **Sharma, H. D. and Reddy, K. R.** *Geoenvironmental Engineering*. New Jersey : John Wiley & Sons, 2004.
- [38] **Kim, A.G.** *Leaching Methods Applied to the Characterization of Coal Utilization By-Products*. Pittsburgh, Pennsylvania : National Energy Technology Laboratory, US Department of Energy.
- [39] **Fällman, A.M.** Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *The Science of the Total Environment*. 178, 1997.
- [40] **Mesters, K.** *Untersuchungen zur übertragbarkeit von Grenz- und Richtwerten des Schüttelverfahrens nach DEV-S4 auf Trogverfahren*. Bochum : BM für Verkehr, 1997.
- [41] **Skoog, D. A. and Leary, J. J.** *Principles of Instrumental Analysis*. Orlando : Saunders College Publishing, 1992. Vol. Fourth Edition.
- [42] **Innov-X_Systems**. <http://www.innov-x-sys.com/technology/fluorescence>. [Online] [Cited: 31 07 2008.]
- [43] **Carrier, R. and Bordonaro, J.** <http://www.rpi.edu/dept/chem-eng/Biotech-Environ/CHROMO/chromintro.html>. [Online] 1994. [Cited: 31 07 2008.]
- [44] **Kohlmann, R. von H.**
http://www.med4you.at/laborbefunde/techniken/chromatographie/lbef_chromatographie_hplc_gc.htm. [Online] [Cited: 31 07 2008.]
- [45] <http://www.onafarawayday.com/Radiogenic/Ch2/Ch2-2.htm>. [Online] [Cited: 31 07 2008.]
- [46] **Goumans, J. J. J. M.** Leaching potential of MSWI Bottom Ash as a function of particle size distribution. [book auth.] J. J. J. M. Goumans, H. A. van der Sloot and Th. G. Aalbers. *Waste Materials in Construction*. Amsterdam : Elsevier, 1991, pp. 135-143.
- [47] **P. Goodhew, A. Fretwell.** <http://www.matter.org.uk/diffraction>. [Online] 2000. [Cited: 31 07 2008.]
- [48] **Knoblauch, H. and Schneider, U.** *Bauchemie*. Düsseldorf : Werner, 1995.
- [49] **Kolthoff, I.M. and Sandell, E.B.** *Análisis químico cuantitativo*. Buenos Aires : Nigar, 1975.
- [50] **Proctor, D.M., et al.** Physical and Chemical Characteristics of Blast Furnace, Basic Oxygen Furnace and Electric Arc Furnace Steel Industry Slags. *Environmental Science and Technology*. 2000, Vol. 4, 8.
- [51] **Pillay, K., Blottnitz, H. von and Petersen, J.** Aging of Chromium(III)-bearing slag and its relation to the atmospheric oxidation of solid Chromium(III)-oxide in the presence of calcium oxide. *Chemosphere*. 2003, Vol. 52.
- [52] **Chaurand, P., et al.** Speciation of Cr and V within BOF steel slag reused in road construction. *Journal of Geochemical Exploration*. 2006, Vol. 88.

- [53] **Comans, R.N.J., et al.** Chemical Processes at a Redox/pH Interface arising from the use of steel slag in the aquatic environment. [book auth.] J. J. M. Goumans, H. A. van der Sloot and Th. G. Aalbers. *Waste Materials in Construction*. Amsterdam : Elsevier, 1991, pp. 243-254.
- [54] **BMLFUW.** *Deponieverordnung 2008*. Vienna : Federal Ministry of Agriculture and Forestry, Environment and Water Management, 2008.

Applied standards:

EN 12457-4	Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction)
EN 932-1	Tests for general properties of aggregates. Part 2: Methods for sampling
EN 932-2	Tests for general properties of aggregates. Part 2: Methods for reducing laboratory samples
EN 933-1	Test for geometrical properties of aggregates. Part 1: Determination of particle size distribution – Sieving method.
EN ISO 5667-3	Water quality. Sampling. Part 3: Guidance on the preservation and handling of water samples.

ANNEX I

Detailed list of leaching test results

Comments:

- The experiments c-55 / N / 0d and c-A / N / 0d were carried out with six replications, the two results for the pH values indicated in the columns concerning the replicas correspond to the mean value of three replicas (result 1 = mean value of replica 1, 2 and 3; result 2 = mean value of replica 4, 5 and 6). All the other experiments were carried out with three replications (c-55 and c-A) or two replications (BOT c-55 and BOT c-A).
- In case that a substance is not detected in non of the replicas within one sample, the corresponding cells in the tables are left in blank, in order to provide better readability. If a substance is not detected in one or more replicas but at least shows up once in the experiment, the corresponding cells are assigned "nd".
- The experiments at the age "0 days" were carried out with a lower detection limit than the experiments "21 days, 42 days and 91 days". The detection limits indicated in the tables comply with the last-mentioned.
- It is important to be aware of the Anions high standard deviation. Accordingly, for the mean value of Sulphate in the experiment c-55 / N / 0d only the first three replications are considered, as the last three are highly implausible (see remark in chapter 7.2 Results)

ANNEX I: Detailed list of leaching test results

	Blank 0 days				c-55 / N																Detection limit									
					0 days ⁽¹⁾								21 days ⁽²⁾																	
	1	2	mean value	standard deviation	1	2	3	4	5	6	mean value	standard deviation	1	2	3	mean value	standard deviation	1	2	3		mean value	standard deviation							
pH	8,69	8,37	8,53	0,23	8,89*				11,67*				10,28				1,97	9,33	9,15	8,84	9,11		0,25	10,91	11,11	11,3	11,11		0,20	
Conductivity (µS/cm)	46	48	47	1	484*				525*				504				29	450	572	517	513		61	315	337	570	407		141	
[Cl ⁻] (mg/Kg)													138,92 230,63 189,06 186,20 45,92								52,27 45,43 88,24 61,98 23,00								5,00	
[F ⁻] (mg/Kg)													7,38 18,19 24,37 16,65 8,60								20,36 7,18 11 12,85 6,78								5,00	
[SO4 ²⁻] (mg/Kg)	79,39	694,20	386,80	434,74	1697,67	1104,55	1708,95	< 11	nd	nd	1503,72	345,74	183,04	314,54	257,38	251,65	65,94	95,02	82,62	183,81	120,48	55,19	5,00							
[As] (mg/Kg)					0,01	0,01	0,01	nd	nd	0,01	0,01	0,00	4,84 5,46 4,97 5,09 0,33				4,36 3,92 5,09 4,46 0,59				0,02									
[Ba] (mg/Kg)	0,03	0,10	0,06	0,05	11,19	11,52	12,76	12,20	10,85	12,62	11,86	0,79									0,20									
[Cd] (mg/Kg)													0,22 0,15 0,2 0,19 0,04								0,16 0,15 0,14 0,15 0,01								0,10	
[Cr] (mg/Kg)													0,25 0,29 0,3 0,28 0,03								0,17 0,12 0,24 0,18 0,06								0,10	
[Cu] (mg/Kg)	0,05	0,04	0,04	0,00									0,19 0,3 0,24 0,24 0,06								0,1 0,1 0,17 0,12 0,04								0,02	
[Hg] (mg/Kg)																													0,2	
[Mo] (mg/Kg)																													0,01	
[Ni] (mg/Kg)																													0,2	
[Pb] (mg/Kg)																													0,01	
[Sb] (mg/Kg)																													0,02	
[Se] (mg/Kg)																													0,50	
[V] (mg/Kg)	0,01	nd	0,00	0,00	0,86	0,97	0,92	0,90	0,22	1,38	0,88	0,37	0,78	0,5	0,66	0,65	0,14	1,19	0,117	0,89	0,73	0,55	0,10							
[Zn] (mg/Kg)	nd	0,02	0,01	0,01	0,13	0,09	0,12	0,24	0,06	0,07	0,12	0,06	1,06	0,96	1,08	1,03	0,06	0,91	1,05	1,3	1,09	0,20	0,10							

⁽¹⁾six duplicates, ⁽²⁾three duplicates, blank or "nd" = not detected, na = not available, * = mean value of three duplicates

	c-55 / N																			Detection limit	
	42 days ⁽²⁾										91 days ⁽²⁾										
	c1					c2					c1					c2					
	1	2	3	mean value	standard deviation	1	2	3	mean value	standard deviation	1	2	3	mean value	standard deviation	1	2	3	mean value		standard deviation
pH	10,57	10,48	11,3	10,78	0,45	10,77	11	11,33	11,03	0,28	10,14	10,82	11,31	10,76	0,59	11,35	11,33	11,29	11,32	0,03	
Conductivity (µS/cm)	401	354	480	412	64	395	429	496	440	51	312	335	530	392	120	496	483	470	483	13	
[Cl ⁻] (mg/Kg)	129,04	74,81	85,01	96,29	28,82	82,03	75,04	136,78	97,95	33,81	65,54	70,17	69,71	68,47	2,55	50,49	55,35	71,84	59,23	11,19	5,00
[F ⁻] (mg/Kg)	171,61	32,44	12,16	72,07	86,80	14,37	13,6	13,3	13,76	0,55	221,9	27,1	9,98	86,33	117,72	20,2	14,54	11,72	15,49	4,32	5,00
[SO4 ²⁻] (mg/Kg)	252,53	149,87	170,63	191,01	54,28	161,74	155,37	177,27	164,79	11,26	133,16	123,26	128,59	128,34	4,95	86,09	122,02	126,77	111,63	22,24	5,00
[As] (mg/Kg)											nd	nd	0,02	0,01	0,01						0,02
[Ba] (mg/Kg)	4,96	3,46	4,59	4,34	0,78	3,29	4,01	2,89	3,40	0,57	2,56	2,79	7,18	4,18	2,60	4,55	4,2	6,39	5,05	1,18	0,20
[Cd] (mg/Kg)																					0,01
[Cr] (mg/Kg)	nd	nd	0,13	0,04	0,08	nd	0,14	nd	0,05	0,08	nd	nd	0,56	0,19	0,32	0,24	0,21	0,41	0,29	0,11	0,10
[Cu] (mg/Kg)	0,11	0,13	0,22	0,15	0,06	0,12	0,19	nd	0,10	0,10	nd	0,12	0,55	0,22	0,29	0,23	0,29	0,49	0,34	0,14	0,10
[Hg] (mg/Kg)																					0,01
[Mo] (mg/Kg)	0,2	0,14	0,15	0,16	0,03	0,12	0,12	0,11	0,12	0,01	0,11	0,14	0,12	0,12	0,02	0,08	0,1	0,1	0,09	0,01	0,02
[Ni] (mg/Kg)																					0,2
[Pb] (mg/Kg)	0,05	0,05	0,1	0,07	0,03	0,05	0,08	0,03	0,05	0,03	0,03	0,05	0,21	0,10	0,10	0,07	0,06	0,18	0,10	0,07	0,01
[Sb] (mg/Kg)																					0,02
[Se] (mg/Kg)																					0,50
[V] (mg/Kg)	0,76	1,08	1,10	0,98	0,19	0,96	1,12	1,07	1,05	0,08	1,18	1,28	1,71	1,39	0,28	1,47	1,55	1,71	1,58	0,12	0,10
[Zn] (mg/Kg)	0,66	0,83	1,33	0,94	0,35	0,73	0,95	0,44	0,71	0,26	0,44	1,49	3,00	1,64	1,29	1,02	1,02	2,57	1,54	0,89	0,10

⁽¹⁾six duplicates, ⁽²⁾three duplicates, blank or "nd" = not detected, na = not available, * = mean value of three duplicates

ANNEX I: Detailed list of leaching test results

	Blank 0 days				c-A / N																	Detection limit								
					0 days ⁽¹⁾								21 days ⁽²⁾																	
	1	2	mean value	standard deviation	1	2	3	4	5	6	mean value	standard deviation	1	2	3	mean value	standard deviation	1	2	3	mean value		standard deviation							
pH	8,69	8,37	8,53	0,23	9,23*								9,96*		9,60		0,52	11,14	11,24	11,29	11,22		0,08	10,34	10,06	11,23	10,54		0,61	
Conductivity (µS/cm)	46	48	47	1	452*								412*		432		28	371	416	441	409		35	281	267	407	318		77	
[Cl ⁻] (mg/Kg)													35,82		37,09		33,35		35,42		1,90	20,16	16,83	44,05	27,01		14,85	5,00		
[F ⁻] (mg/Kg)													23,1		9,03		6,51		12,88		8,94	5,65	nd	8,1	6,88		4,15	5,00		
[SO4 ²⁻] (mg/Kg)	79,39	694,20	386,80	434,74	899,73	1007,65	2158,00	1171,16	738,03	1314,50	1214,84	504,18	200,09	176,64	117,33	164,69	42,66	98,56	90,36	186,43	125,12	53,26	5,00							
[As] (mg/Kg)					0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,00															0,02			
[Ba] (mg/Kg)	0,03	0,10	0,06	0,05	3,97	3,86	4,14	5,18	5,21	5,29	4,61	0,68	18,48	6,02	5,17	9,89		7,45	4,54	3,95	4,01	4,17		0,32	0,20					
[Cd] (mg/Kg)																											0,01			
[Cr] (mg/Kg)					0,04	0,03	0,03	0,04	0,05	0,05	0,04	0,01	0,18	0,11	0,13	0,14		0,04							0,10					
[Cu] (mg/Kg)	0,05	0,04	0,04	0,00	0,12	0,08	0,12	0,09	0,09	0,14	0,11	0,02	0,62	0,3	0,21	0,38		0,22	0,16	0,17	0,18	0,17		0,01	0,10					
[Hg] (mg/Kg)																											0,01			
[Mo] (mg/Kg)					0,21	0,23	0,24	0,24	0,26	0,22	0,23	0,02	0,15	0,16	0,15	0,15		0,01	0,13	0,12	0,12	0,12		0,01	0,02					
[Ni] (mg/Kg)					0,01	nd	0,01	0,02	0,01	0,01	0,01	0,01													0,2					
[Pb] (mg/Kg)					0,05	0,02	0,02	0,03	0,04	0,04	0,04	0,01	0,18	0,18	0,1	0,15		0,05	0,08	0,04	0,05	0,06		0,02	0,01					
[Sb] (mg/Kg)					0,01	0,01	0,01	0,02	0,02	0,01	0,01	0,00													0,02					
[Se] (mg/Kg)					0,03	0,05	0,06	0,04	0,05	0,04	0,04	0,01													0,50					
[V] (mg/Kg)	0,01	nd	0,00	0,00	0,60	0,53	0,49	0,62	0,59	0,64	0,58	0,06	1,09	0,91	0,96	0,99		0,09	0,81	0,82	0,81	0,81		0,01	0,10					
[Zn] (mg/Kg)	nd	0,02	0,01	0,01	1,39	0,14	0,70	0,18	0,26	0,28	0,49	0,49	nd	2,02	0,81	1,42		0,86	0,88	0,66	0,67	0,74		0,12	0,10					

⁽¹⁾six duplicates, ⁽²⁾three duplicates, blank or "nd" = not detected, na = not available, * = mean value of three duplicates

	c-A / N																				Detection limit
	42 days ⁽²⁾										91 days ⁽²⁾										
	c1					c2					c1					c2					
	1	2	3	mean value	standard deviation	1	2	3	mean value	standard deviation	1	2	3	mean value	standard deviation	1	2	3	mean value	standard deviation	
pH	10,34	8,63	11,23	10,07	1,32	10,11	10,34	11,24	10,56	0,60	10,89	10,84	11,32	11,02	0,26	10,36	10,26	11,28	10,63	0,56	
Conductivity (µS/cm)	358	365	409	377	28	272	287	390	316	64	379	329	525	411	102	300	307	472	360	97	
[Cl ⁻] (mg/Kg)	48,08	44,73	35,74	42,85	6,38	23,54	26,11	32,59	27,41	4,66	44,41	41,47	73,09	52,99	17,47	26,01	23,16	37,04	28,74	7,33	5,00
[F ⁻] (mg/Kg)	11,62	8,19	6,03	8,61	2,82	0	0	3,93	1,31	2,27	11,97	9,18	8,97	10,04	1,67	6,9	7,17	8,54	7,54	0,88	5,00
[SO4 ²⁻] (mg/Kg)	286,95	266,07	171,48	241,50	61,53	67,75	68,2	54,47	63,47	7,80	196,44	202,04	201,12	199,87	3,00	137,77	125,8	140,06	134,54	7,66	5,00
[As] (mg/Kg)																					0,02
[Ba] (mg/Kg)	3,19	2,65	3,39	3,08	0,38	4,94	5,38	4,85	5,06	0,28	0,436	3,13	5,8	3,12	2,68	3,72	3,19	4,17	3,69	0,49	0,20
[Cd] (mg/Kg)																					0,01
[Cr] (mg/Kg)																					0,10
[Cu] (mg/Kg)	0,13	0,12	0,15	0,13	0,02						0,23	0,13	0,35	0,24	0,11	0,15	nd	0,16	0,10	0,09	0,10
[Hg] (mg/Kg)																					0,01
[Mo] (mg/Kg)	0,18	0,18	0,15	0,17	0,02	0,20	0,25	0,16	0,20	0,05	0,17	0,16	0,17	0,17	0,01	0,13	0,12	0,14	0,13	0,01	0,02
[Ni] (mg/Kg)																					0,2
[Pb] (mg/Kg)	0,09	0,07	0,10	0,09	0,02	0,02	0,02	0,02	0,02	0,00	0,16	0,10	0,27	0,18	0,09	0,11	0,06	0,11	0,09	0,03	0,01
[Sb] (mg/Kg)																					0,02
[Se] (mg/Kg)																					0,50
[V] (mg/Kg)	0,77	0,70	0,85	0,77	0,08	0,73	0,71	0,78	0,74	0,04	0,94	0,86	1,02	0,94	0,08	1,12	1,11	1,17	1,13	0,03	0,10
[Zn] (mg/Kg)	1,10	0,88	0,48	0,82	0,31	0,42	0,34	0,19	0,32	0,12	1,05	0,55	1,26	0,95	0,36	0,59	0,41	0,55	0,52	0,09	0,10

⁽¹⁾six duplicates, ⁽²⁾three duplicates, blank or "nd" = not detected, na = not available, * = mean value of three duplicates

ANNEX I: Detailed list of leaching test results

	BOT c-55 / N															Detection limit	
	0 days				21 days				42 days				91 days				
	1	2	mean value	standard deviation	1	2	mean value	standard deviation	1	2	mean value	standard deviation	1	2	mean value		standard deviation
pH	4,41	4,48	4,45	0,05	10,37	9,97	10,17	0,28	11,29	11,78	11,54	0,35	11,42	11,56	11,49	0,10	
Conductivity (µS/cm)	302	336	319	24	343	359	351	11	440	671	556	163	425	518	472	66	
[Cl ⁻] (mg/Kg)	108,38	122,10	115,24	9,70	34,53	52,77	43,65	12,90	13,65	14,83	14,24	0,83	11,48	10,54	11,01	0,66	5
[F ⁻] (mg/Kg)	6,62	6,62	6,62	0,00	2,98	8,26	5,62	3,73	3,32	7,03	5,18	2,62	4,05	5,50	4,78	1,03	5
[SO ₄ ²⁻] (mg/Kg)	131,23	115,35	123,29	11,23	24,00	24,91	24,46	0,64	21,83	22,14	21,99	0,22	15,71	13,31	14,51	1,70	5
[As] (mg/Kg)	0,01	nd	0,00	0,00													0,02
[Ba] (mg/Kg)	8,16	10,89	9,53	1,93	17,99	26,83	22,41	6,25	12,03	22,84	17,44	7,64	10,08	12,47	11,28	1,69	0,2
[Cd] (mg/Kg)																	0,01
[Cr] (mg/Kg)	0,02	0,01	0,02	0,01	0,36	0,40	0,38	0,03	0,20	nd	0,20	0,14	0,14	0,10	0,12	0,03	0,1
[Cu] (mg/Kg)	0,11	0,06	0,09	0,03	0,17	0,12	0,15	0,04	nd	1,46	1,46	1,03					0,1
[Hg] (mg/Kg)																	0,01
[Mo] (mg/Kg)	0,07	0,06	0,06	0,01	0,11	0,12	0,12	0,01	0,10	0,12	0,11	0,01	0,05	0,06	0,06	0,01	0,02
[Ni] (mg/Kg)																	0,2
[Pb] (mg/Kg)	0,02	0,01	0,01	0,01	0,04	0,02	0,03	0,01	0,01	0,11	0,06	0,07					0,01
[Sb] (mg/Kg)																	0,02
[Se] (mg/Kg)																	0,5
[V] (mg/Kg)	0,21	0,17	0,19	0,02	1,03	0,83	0,93	0,14	1,84	3,62	2,73	1,26	1,55	1,90	1,73	0,25	0,1
[Zn] (mg/Kg)	0,51	0,78	0,64	0,19	0,54	0,31	0,43	0,16	0,24	1,43	0,84	0,84	0,33	0,25	0,29	0,06	0,1

blank or "nd" = not detected

	BOT c-A / N															Detection limit	
	0 days				21 days				42 days				91 days				
	1	2	mean value	standard deviation	1	2	mean value	standard deviation	1	2	mean value	standard deviation	1	2	mean value		standard deviation
pH	4,24	3,08	3,66	0,82	11,20	10,70	10,95	0,35	10,07	10,70	10,39	0,45	11,79	11,23	11,51	0,40	
Conductivity (µS/cm)	390	450	420	42	470	317	394	108	405	385	395	14	654	452	553	143	
[Cl ⁻] (mg/Kg)	130,16	92,56	111,36	26,59	23,95	10,51	17,23	9,50	11,86	9,19	10,53	1,89	7,22	7,93	7,58	0,50	5
[F ⁻] (mg/Kg)	7,23	0,00	3,62	5,11	7,08	14,08	10,58	4,95	3,03	6,90	4,97	2,74	2,14	4,93	3,54	1,97	5
[SO4 ⁼] (mg/Kg)	289,42	182,05	235,74	75,92	50,00	7,94	28,97	29,74	32,37	19,26	25,82	9,27	16,66	13,69	15,18	2,10	5
[As] (mg/Kg)	0,01	0,01	0,01	0,00													0,02
[Ba] (mg/Kg)	1,72	1,70	1,71	0,01	0,50	9,19	4,85	6,14	7,33	9,20	8,27	1,32	9,54	7,17	8,36	1,68	0,2
[Cd] (mg/Kg)																	0,01
[Cr] (mg/Kg)	0,03	0,02	0,02	0,01					nd	0,14	0,07	0,10	0,17	nd	0,09	0,12	0,1
[Cu] (mg/Kg)	0,09	0,08	0,08	0,01	nd	0,16	0,08	0,11	0,20	0,20	0,20	0,00	0,32	nd	0,16	0,23	0,1
[Hg] (mg/Kg)																	0,01
[Mo] (mg/Kg)	0,21	0,13	0,17	0,06	nd	0,19	0,10	0,13	0,16	0,15	0,16	0,01	0,13	0,11	0,12	0,01	0,02
[Ni] (mg/Kg)									0,68	nd	0,34	0,48					0,2
[Pb] (mg/Kg)	0,03	0,02	0,03	0,01	0,01	0,05	0,03	0,03	0,06	0,03	0,05	0,02	0,10	0,01	0,06	0,06	0,01
[Sb] (mg/Kg)	0,01	0,01	0,01	0,00													0,02
[Se] (mg/Kg)	0,03	0,02	0,03	0,01													0,5
[V] (mg/Kg)	0,19	0,18	0,18	0,00	nd	1,24	0,62	0,88	1,13	1,31	1,22	0,13	1,46	0,11	0,79	0,95	0,1
[Zn] (mg/Kg)	0,31	0,09	0,20	0,16	0,17	0,56	0,37	0,28	0,65	0,64	0,65	0,01	0,67	0,12	0,40	0,39	0,1

blank or "nd" = not detected

ANNEX II

Grain Size Distribution

ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 0d	Fecha de lavado:	01/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	03/04/08

Masa seca total M_1 [g] = 4.219,2

Masa seca tras lavado M_2 [g] = 4.162,4

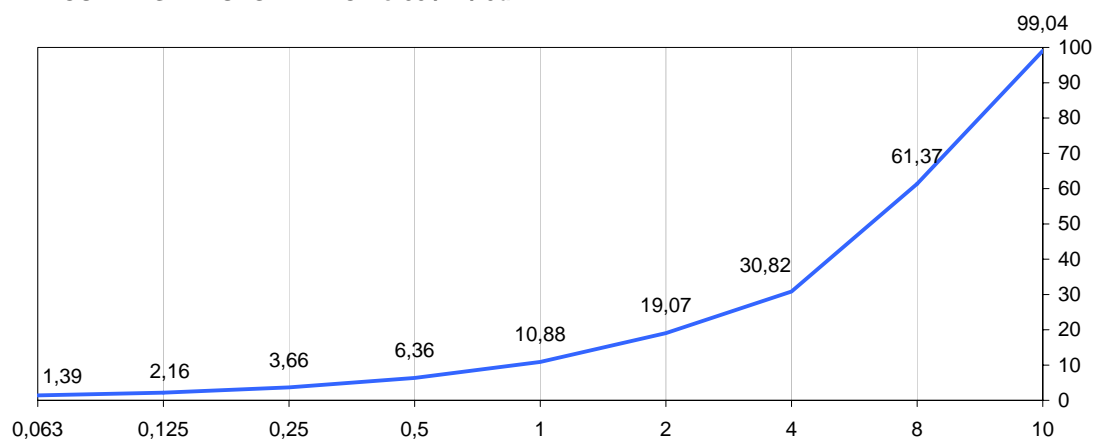
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 56,8$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasa ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	40,7	0,96	0,96	99,04	99,04
8	R_2	1.589,3	37,67	38,63	62,33	61,37
4	R_3	1.288,8	30,55	69,18	69,45	30,82
2	R_4	496,0	11,76	80,93	88,24	19,07
1	R_5	345,4	8,19	89,12	91,81	10,88
0,5	R_6	190,7	4,52	93,64	95,48	6,36
0,25	R_7	113,8	2,70	96,34	97,30	3,66
0,125	R_8	63,2	1,50	97,84	98,50	2,16
0,063	R_9	32,7	0,78	98,61	99,22	1,39
Material en la bandeja del fondo	P	0,3				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	1,35
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$\Sigma R_i + P =$	4160,9	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,04	<1%

CURVA GRANULOMETRICA c-55 / N / 0d



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 21d / c1	Fecha de lavado:	21/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	22/04/08

Masa seca total M_1 [g] = 2.950,3

Masa seca tras lavado M_2 [g] = 2.852,0

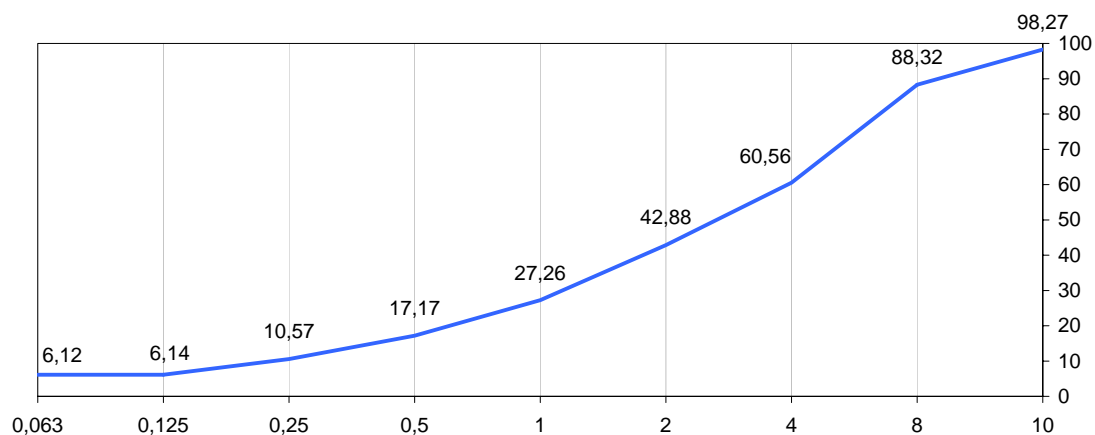
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 98,3$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	50,9	1,73	1,73	98,27	98,27
8	R_2	293,7	9,95	11,68	90,05	88,32
4	R_3	819,1	27,76	39,44	72,24	60,56
2	R_4	521,6	17,68	57,12	82,32	42,88
1	R_5	460,8	15,62	72,74	84,38	27,26
0,5	R_6	297,6	10,09	82,83	89,91	17,17
0,25	R_7	194,7	6,60	89,43	93,40	10,57
0,125	R_8	130,8	4,43	93,86	95,57	6,14
0,063	R_9	0,6	0,02	93,88	99,98	6,12
Material en la bandeja del fondo	P	0,0				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	3,33
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$\Sigma R_i + P =$	2769,8	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	2,88	<1%

CURVA GRANULOMETRICA c-55 / N / 21d / c1



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 21d / c2	Fecha de lavado:	21/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	22/04/08

Masa seca total M_1 [g] = 1.953,6

Masa seca tras lavado M_2 [g] = 1.899,0

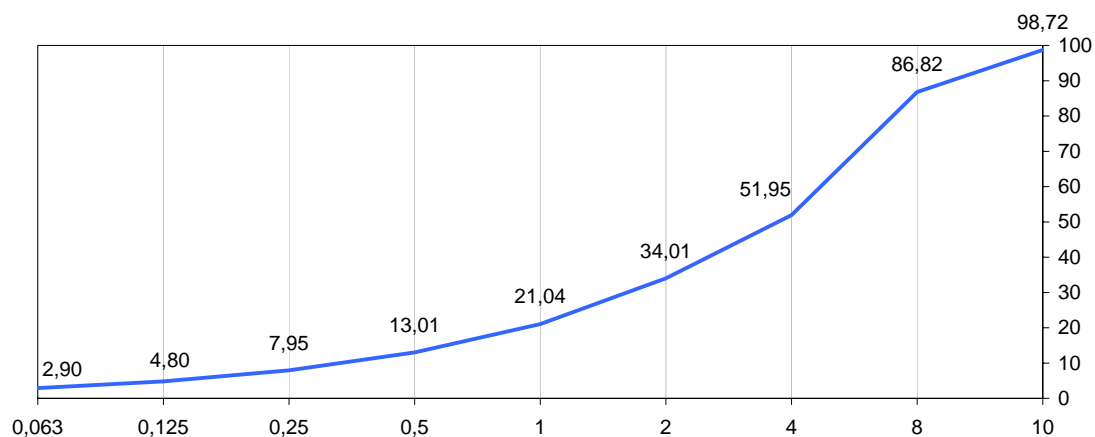
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 54,6$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	25,1	1,28	1,28	98,72	98,72
8	R_2	232,4	11,90	13,18	88,10	86,82
4	R_3	681,3	34,87	48,05	65,13	51,95
2	R_4	350,4	17,94	65,99	82,06	34,01
1	R_5	253,3	12,97	78,96	87,03	21,04
0,5	R_6	157,0	8,04	86,99	91,96	13,01
0,25	R_7	98,7	5,05	92,05	94,95	7,95
0,125	R_8	61,6	3,15	95,20	96,85	4,80
0,063	R_9	37,1	1,90	97,10	98,10	2,90
Material en la bandeja del fondo	P	0,6				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,83
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$\Sigma R_i + P =$	1897,5	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,08	<1%

CURVA GRANULOMETRICA c-55 / N / 21d / c2



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 42d / c1	Fecha de lavado:	08/05/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	14/05/08

Masa seca total M_1 [g] = 1.454,5

Masa seca tras lavado M_2 [g] = 1.421,7

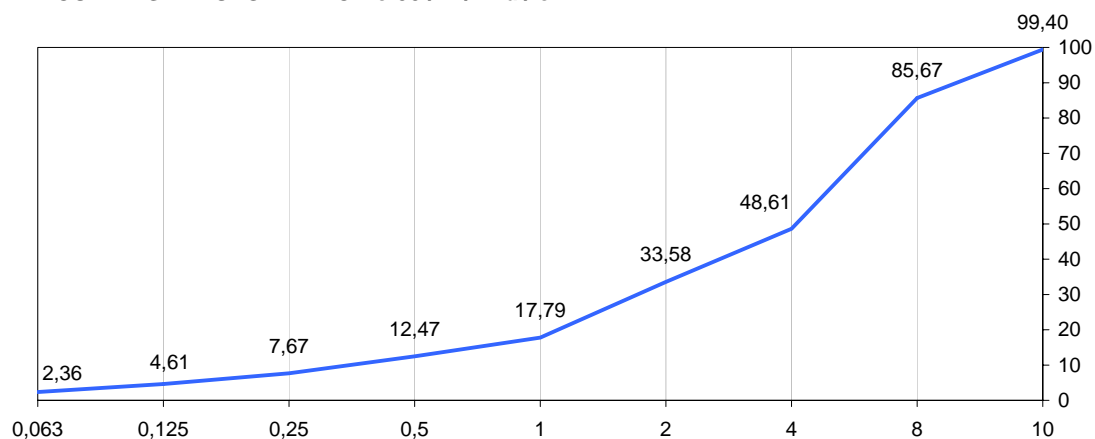
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 32,8$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]	Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	8,7	0,60	0,60	99,40
8	R_2	199,8	13,74	14,33	86,26
4	R_3	538,9	37,05	51,39	62,95
2	R_4	218,7	15,04	66,42	84,96
1	R_5	229,6	15,79	82,21	84,21
0,5	R_6	77,4	5,32	87,53	94,68
0,25	R_7	69,8	4,80	92,33	95,20
0,125	R_8	44,6	3,07	95,39	96,93
0,063	R_9	32,7	2,25	97,64	97,75
Material en la bandeja del fondo	P	0,7			

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,30
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$\Sigma R_i + P =$	1420,9
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,06 < 1%

CURVA GRANULOMETRICA c-55 / N / 42d / c1



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 42d / c2	Fecha de lavado:	08/05/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	14/05/08

Masa seca total M_1 [g] = 2.277,5

Masa seca tras lavado M_2 [g] = 2.220,9

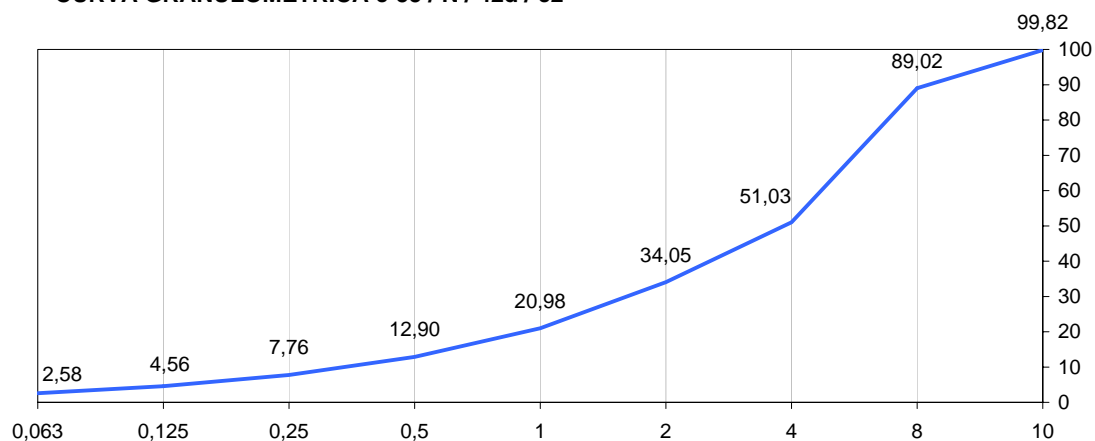
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 56,6$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]	Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	4,1	0,18	99,82	99,82
8	R_2	246,0	10,80	89,20	89,02
4	R_3	865,3	37,99	62,01	51,03
2	R_4	386,6	16,97	83,03	34,05
1	R_5	297,6	13,07	86,93	20,98
0,5	R_6	184,2	8,09	91,91	12,90
0,25	R_7	117,0	5,14	94,86	7,76
0,125	R_8	72,8	3,20	96,80	4,56
0,063	R_9	45,1	1,98	98,02	2,58
Material en la bandeja del fondo	P	1,7			

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,56
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$\Sigma R_i + P =$	2220,4
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,02 <1%

CURVA GRANULOMETRICA c-55 / N / 42d / c2



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 91d / c1	Fecha de lavado:	08/05/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	14/05/08

Masa seca total M_1 [g] = 1.495,0

Masa seca tras lavado M_2 [g] = 1.460,2

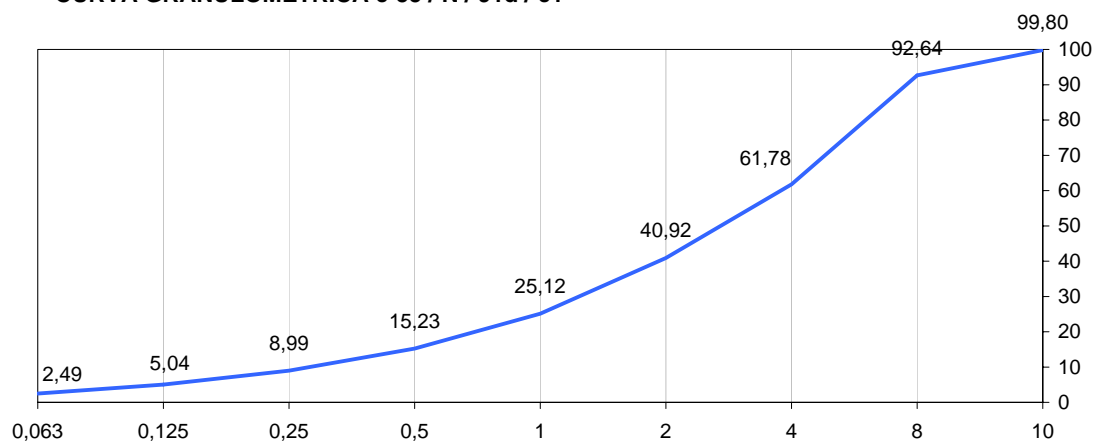
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 34,8$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	3,0	0,20	0,20	99,80	99,80
8	R_2	107,1	7,16	7,36	92,84	92,64
4	R_3	461,3	30,86	38,22	69,14	61,78
2	R_4	311,8	20,86	59,08	79,14	40,92
1	R_5	236,3	15,81	74,88	84,19	25,12
0,5	R_6	147,8	9,89	84,77	90,11	15,23
0,25	R_7	93,3	6,24	91,01	93,76	8,99
0,125	R_8	59,1	3,95	94,96	96,05	5,04
0,063	R_9	38,1	2,55	97,51	97,45	2,49
Material en la bandeja del fondo	P	1,8				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,45
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$\Sigma R_i + P =$	1459,6	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,04	<1%

CURVA GRANULOMETRICA c-55 / N / 91d / c1



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-55 / N / 91d / c2	Fecha de lavado:	08/05/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	14/05/08

Masa seca total M_1 [g] = 1.470,4

Masa seca tras lavado M_2 [g] = 1.435,3

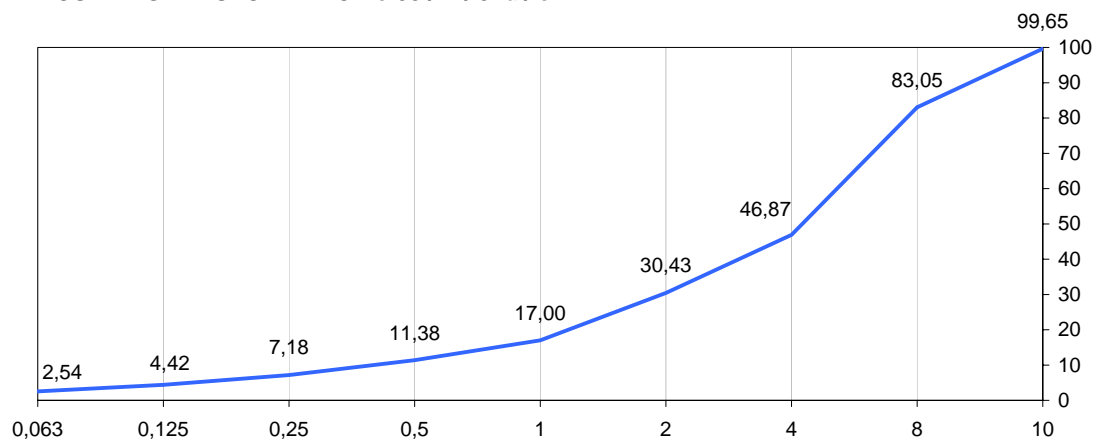
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 35,1$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	5,2	0,35	0,35	99,65	99,65
8	R_2	244,0	16,59	16,95	83,41	83,05
4	R_3	532,0	36,18	53,13	63,82	46,87
2	R_4	241,7	16,44	69,57	83,56	30,43
1	R_5	197,6	13,44	83,00	86,56	17,00
0,5	R_6	82,5	5,61	88,62	94,39	11,38
0,25	R_7	61,8	4,20	92,82	95,80	7,18
0,125	R_8	40,6	2,76	95,58	97,24	4,42
0,063	R_9	27,6	1,88	97,46	98,12	2,54
Material en la bandeja del fondo	P	0,9				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,45
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$\Sigma R_i + P =$	1433,9	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,10	<1%

CURVA GRANULOMETRICA c-55 / N / 91d / c2



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 0d	Fecha de lavado:	18/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	21/04/08

Masa seca total M_1 [g] = 3.699,1

Masa seca tras lavado M_2 [g] = 3.613,4

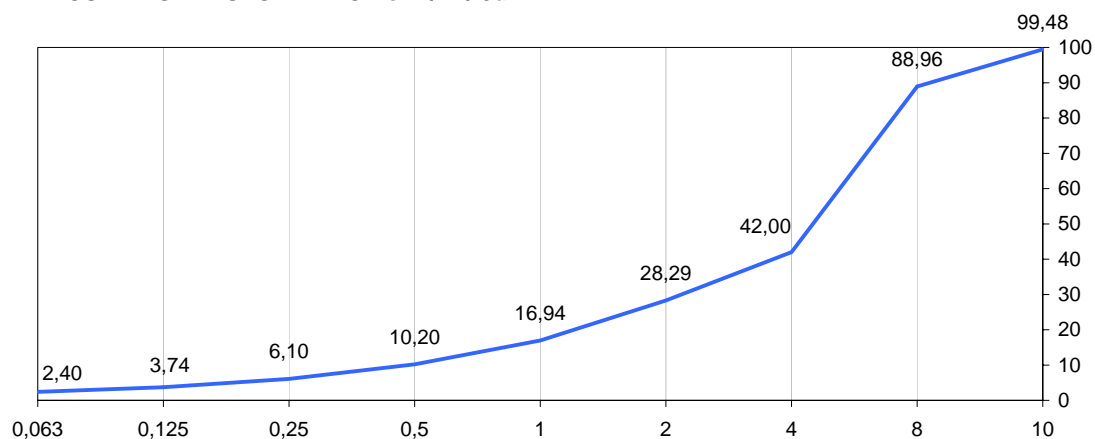
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 85,7$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]	Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	19,4	0,52	99,48	99,48
8	R_2	389,1	10,52	89,48	88,96
4	R_3	1.737,0	46,96	53,04	42,00
2	R_4	507,2	13,71	86,29	28,29
1	R_5	419,7	11,35	88,65	16,94
0,5	R_6	249,4	6,74	93,26	10,20
0,25	R_7	151,8	4,10	95,90	6,10
0,125	R_8	87,2	2,36	97,64	3,74
0,063	R_9	49,7	1,34	98,66	2,40
Material en la bandeja del fondo	P	0,9			

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,34
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$\Sigma R_i + P =$	3611,4	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,06	<1%

CURVA GRANULOMETRICA c-A / N / 0d



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 21d / c1	Fecha de lavado:	01/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	03/04/08

Masa seca total M_1 [g] = 2.662,8

Masa seca tras lavado M_2 [g] = 2.589,7

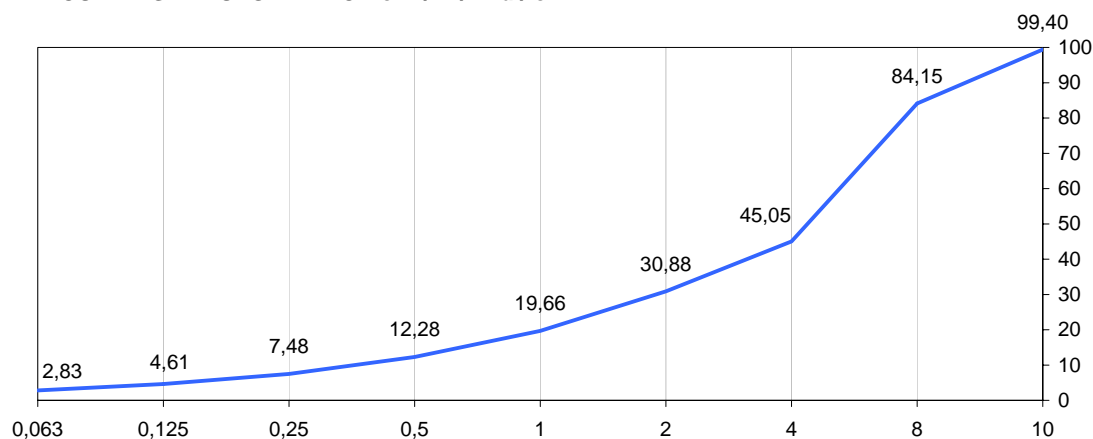
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 73,1$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	16,1	0,60	0,60	99,40	99,40
8	R_2	406,0	15,25	15,85	84,75	84,15
4	R_3	1.041,1	39,10	54,95	60,90	45,05
2	R_4	377,4	14,17	69,12	85,83	30,88
1	R_5	298,6	11,21	80,34	88,79	19,66
0,5	R_6	196,7	7,39	87,72	92,61	12,28
0,25	R_7	127,8	4,80	92,52	95,20	7,48
0,125	R_8	76,3	2,87	95,39	97,13	4,61
0,063	R_9	47,5	1,78	97,17	98,22	2,83
Material en la bandeja del fondo	P	1,4				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,80
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$\Sigma R_i + P =$	2588,9	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,03	<1%

CURVA GRANULOMETRICA c-A / N / 21d / c1



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 21d / c2	Fecha de lavado:	01/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	03/04/08

Masa seca total M_1 [g] = 2.738,2

Masa seca tras lavado M_2 [g] = 2.665,1

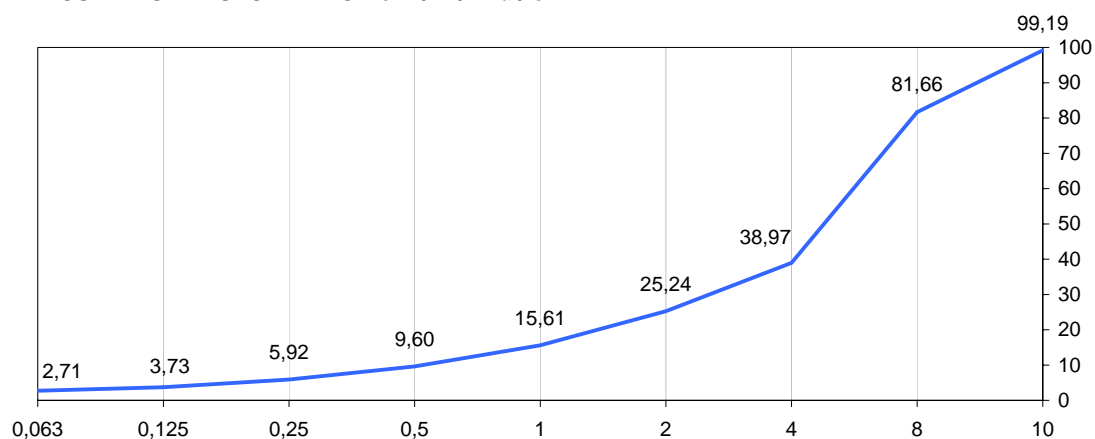
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 73,1$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	22,1	0,81	0,81	99,19	99,19
8	R_2	480,0	17,53	18,34	82,47	81,66
4	R_3	1.168,9	42,69	61,03	57,31	38,97
2	R_4	376,0	13,73	74,76	86,27	25,24
1	R_5	263,7	9,63	84,39	90,37	15,61
0,5	R_6	164,7	6,01	90,40	93,99	9,60
0,25	R_7	100,8	3,68	94,08	96,32	5,92
0,125	R_8	60,0	2,19	96,27	97,81	3,73
0,063	R_9	27,9	1,02	97,29	98,98	2,71
Material en la bandeja del fondo	P	0,0				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,67
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$\Sigma R_i + P =$	2664,1
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,04 <1%

CURVA GRANULOMETRICA c-A / N / 21d / c2



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 42d / c1	Fecha de lavado:	21/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	24/04/08

Masa seca total M_1 [g] = 2.358,7

Masa seca tras lavado M_2 [g] = 2.272,9

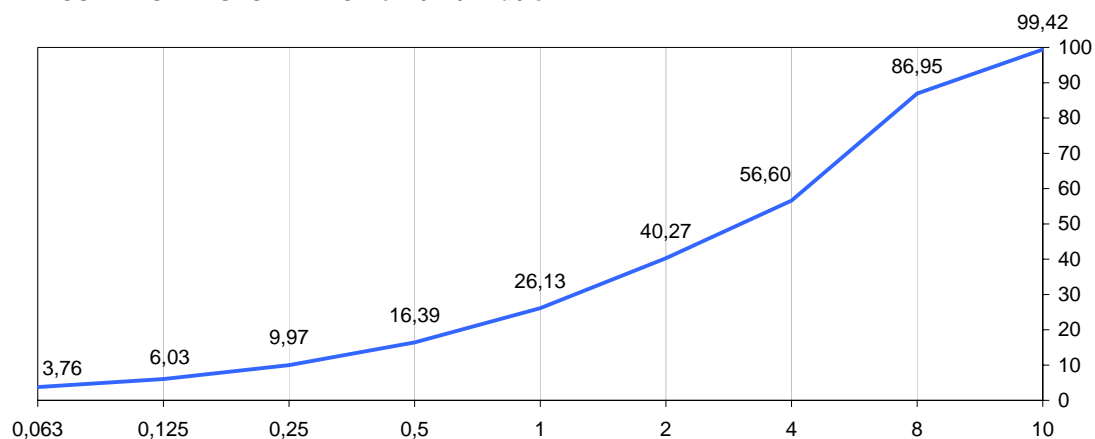
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 85,8$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	13,6	0,58	0,58	99,42	99,42
8	R_2	294,3	12,48	13,05	87,52	86,95
4	R_3	715,7	30,34	43,40	69,66	56,60
2	R_4	385,3	16,34	59,73	83,66	40,27
1	R_5	333,4	14,13	73,87	85,87	26,13
0,5	R_6	229,7	9,74	83,61	90,26	16,39
0,25	R_7	151,5	6,42	90,03	93,58	9,97
0,125	R_8	93,0	3,94	93,97	96,06	6,03
0,063	R_9	53,4	2,26	96,24	97,74	3,76
Material en la bandeja del fondo	P	0,6				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	3,66
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$\Sigma R_i + P =$	2270,5
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,11 <1%

CURVA GRANULOMETRICA c-A / N / 42d / c1



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 42d / c2	Fecha de lavado:	18/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	21/04/08

Masa seca total M_1 [g] = 2.971,7

Masa seca tras lavado M_2 [g] = 2.925,2

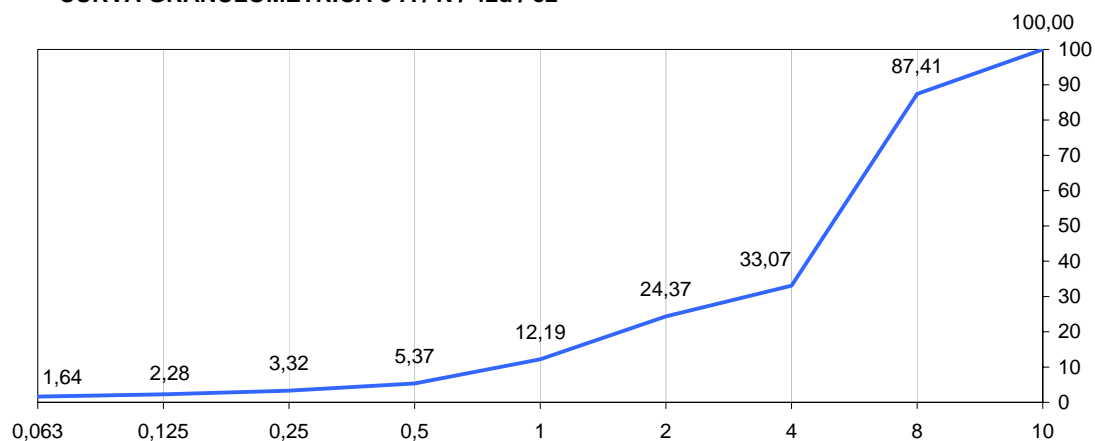
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 46,5$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]	Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	0,0	0,00	100,00	100,00
8	R_2	374,2	12,59	87,41	87,41
4	R_3	1.614,9	54,34	45,66	33,07
2	R_4	258,3	8,69	75,63	24,37
1	R_5	362,0	12,18	87,81	12,19
0,5	R_6	202,8	6,82	94,63	5,37
0,25	R_7	60,7	2,04	96,68	3,32
0,125	R_8	30,9	1,04	97,72	2,28
0,063	R_9	19,1	0,64	98,36	1,64
Material en la bandeja del fondo	P	0,6			

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	1,58
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$\Sigma R_i + P =$	2923,5
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,06 <1%

CURVA GRANULOMETRICA c-A / N / 42d / c2



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 91d / c1	Fecha de lavado:	06/05/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	08/05/08

Masa seca total M_1 [g] = 2.896,1

Masa seca tras lavado M_2 [g] = 2.808,7

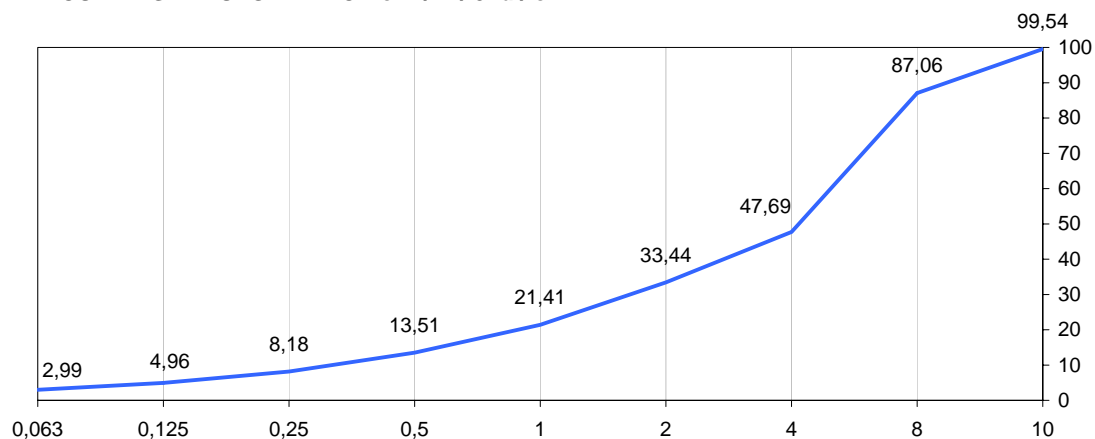
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 87,4$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]		Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	13,4	0,46	0,46	99,54	99,54
8	R_2	361,4	12,48	12,94	87,52	87,06
4	R_3	1.140,2	39,37	52,31	60,63	47,69
2	R_4	412,7	14,25	66,56	85,75	33,44
1	R_5	348,4	12,03	78,59	87,97	21,41
0,5	R_6	228,8	7,90	86,49	92,10	13,51
0,25	R_7	154,4	5,33	91,82	94,67	8,18
0,125	R_8	93,1	3,21	95,04	96,79	4,96
0,063	R_9	57,1	1,97	97,01	98,03	2,99
Material en la bandeja del fondo	P	1,3				

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	3,06
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$\Sigma R_i + P =$	2810,8	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	-0,07	<1%

CURVA GRANULOMETRICA c-A / N / 91d / c1



ANNEX II: Grain Size Distribution

DETERMINACIÓN DE LA GRANULOMETRÍA DE LAS PARTÍCULAS - MÉTODO DEL TAMIZADO EN 933-1			
Identificación de la muestra:	c-A / N / 91d / c2	Fecha de lavado:	18/04/08
Método utilizado: lavado y tamizado / tamizado por vía seca		Fecha de tamizado:	21/04/08

Masa seca total M_1 [g] = 3.085,6

Masa seca tras lavado M_2 [g] = 3.004,1

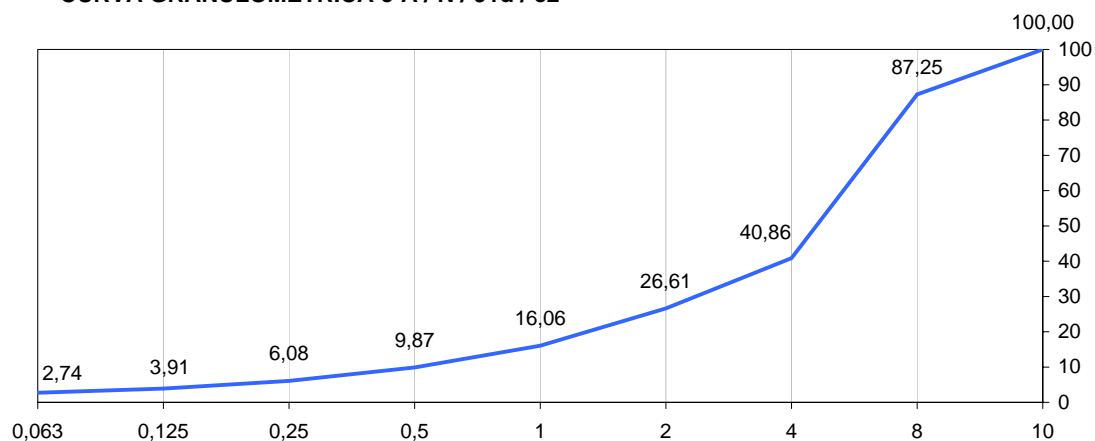
Masa seca de los finos eliminados mediante lavado $M_1 - M_2 = 81,5$

Tamaño de abertura del tamiz [mm]	Masa de material retenido (R_i) [g]	Material retenido ($R_i/M_1 \times 100$) [%]	Material retenido acumulado [%]	Material que pasan ($100 - R_i/M_1 \times 100$) [%]	Material que pasa acumulado [%]
10	R_1	0,0	0,00	100,00	100,00
8	R_2	393,5	12,75	87,25	87,25
4	R_3	1.431,2	46,38	53,62	40,86
2	R_4	439,8	14,25	73,39	26,61
1	R_5	325,6	10,55	83,94	16,06
0,5	R_6	190,9	6,19	90,13	9,87
0,25	R_7	117,1	3,80	93,92	6,08
0,125	R_8	66,7	2,16	96,09	3,91
0,063	R_9	36,4	1,18	97,26	2,74
Material en la bandeja del fondo	P	0,8			

Porcentaje de finos (f) que pasan por el tamiz de 0,063mm =	$\frac{(M_1 - M_2) + P}{M_1} \times 100 =$	2,67
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$\Sigma R_i + P =$	3002	
$\frac{M_2 - (\Sigma R_i + P)}{M_2} \times 100 =$	0,07	<1%

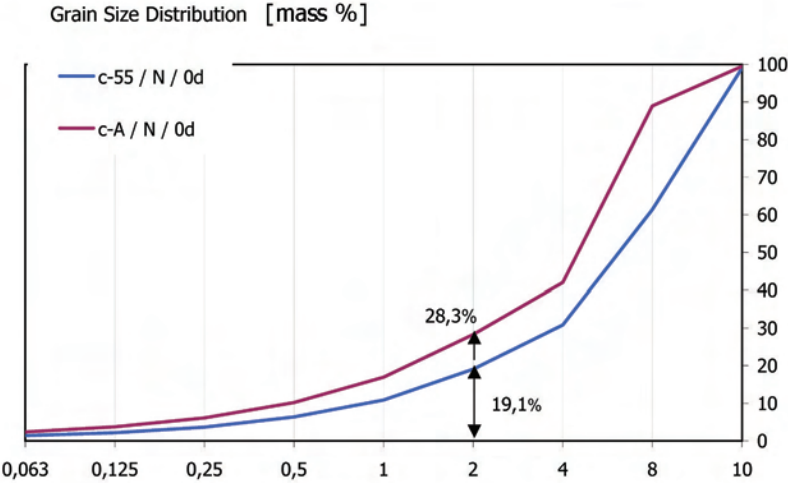
CURVA GRANULOMETRICA c-A / N / 91d / c2



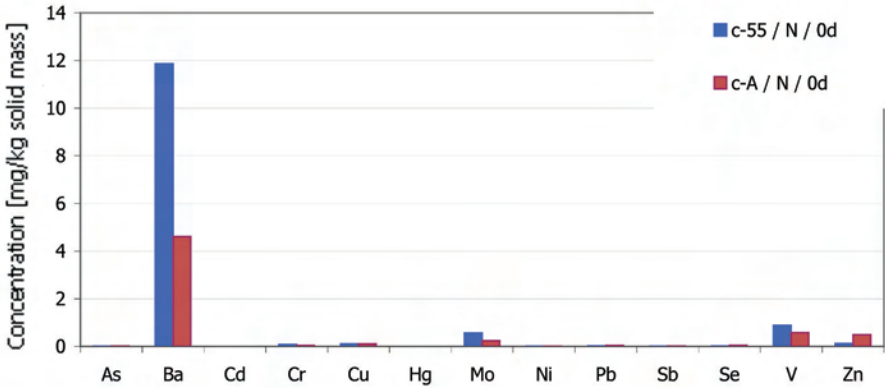
ANNEX III

Influence of Grain Size Distribution on the Release Behaviour

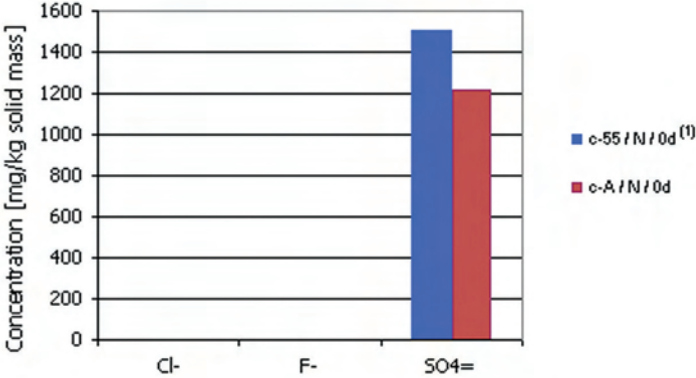
COMPARISON "0 days"



Cation Release

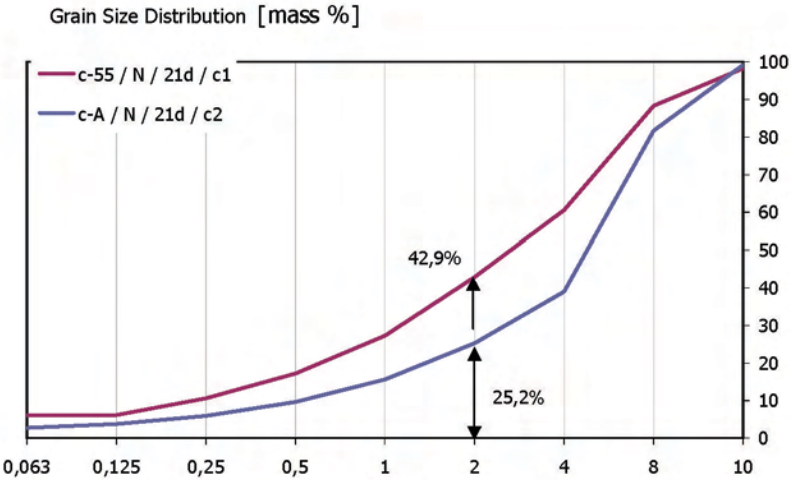


Anion Release

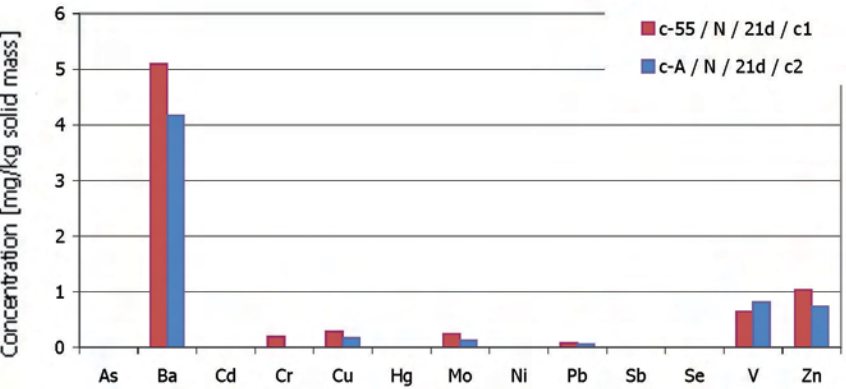


(1) mean value of three duplicates - c-55 / N / 0d - 1, 2 and 3; the duplicates number 4, 5 and 6 are not considered due to lack of plausibility

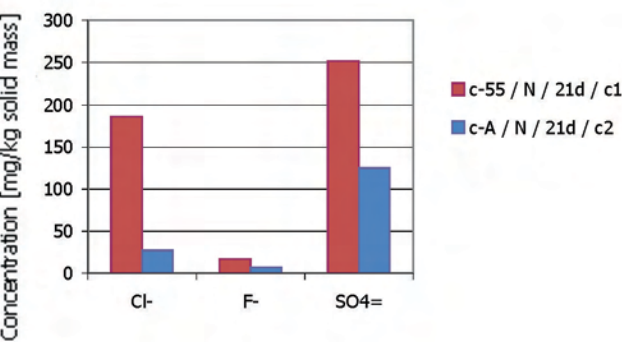
COMPARISON "21 days"



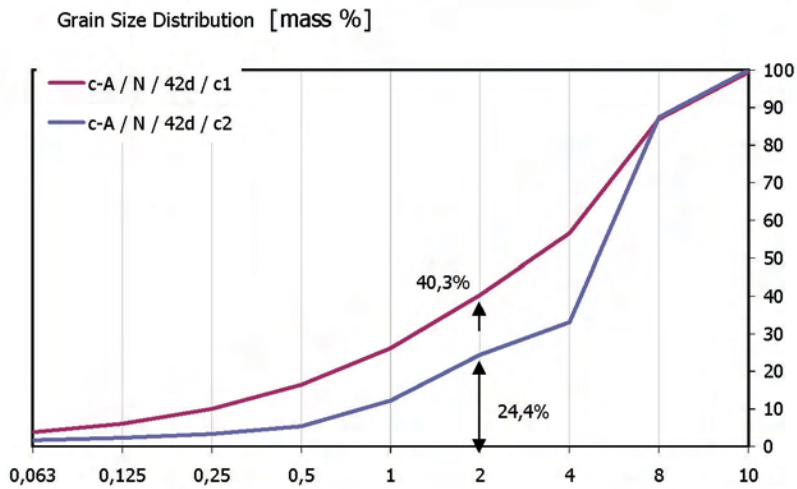
Cation Release



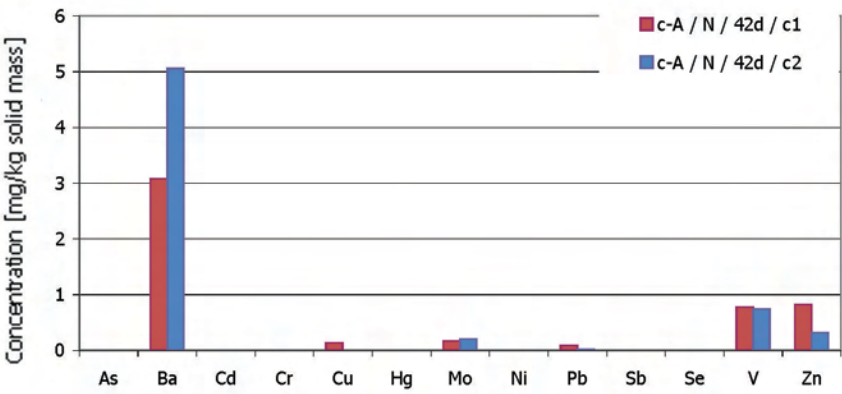
Anion Release



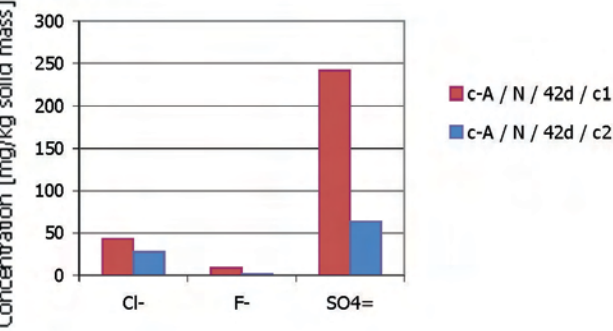
COMPARISON "42 days"



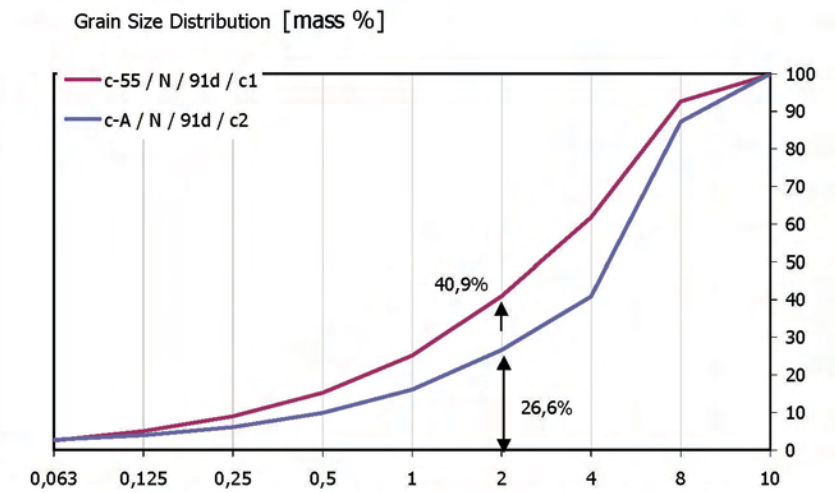
Cation Release



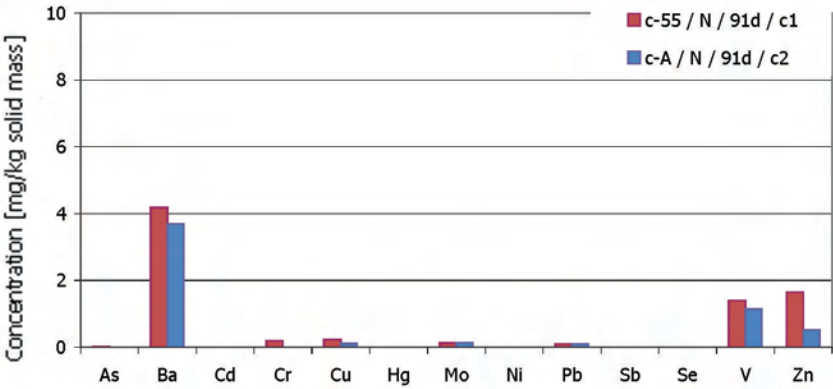
Anion Release



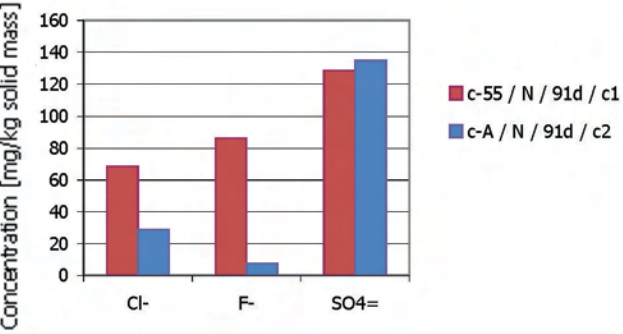
COMPARISON "91 days"



Cation Releas



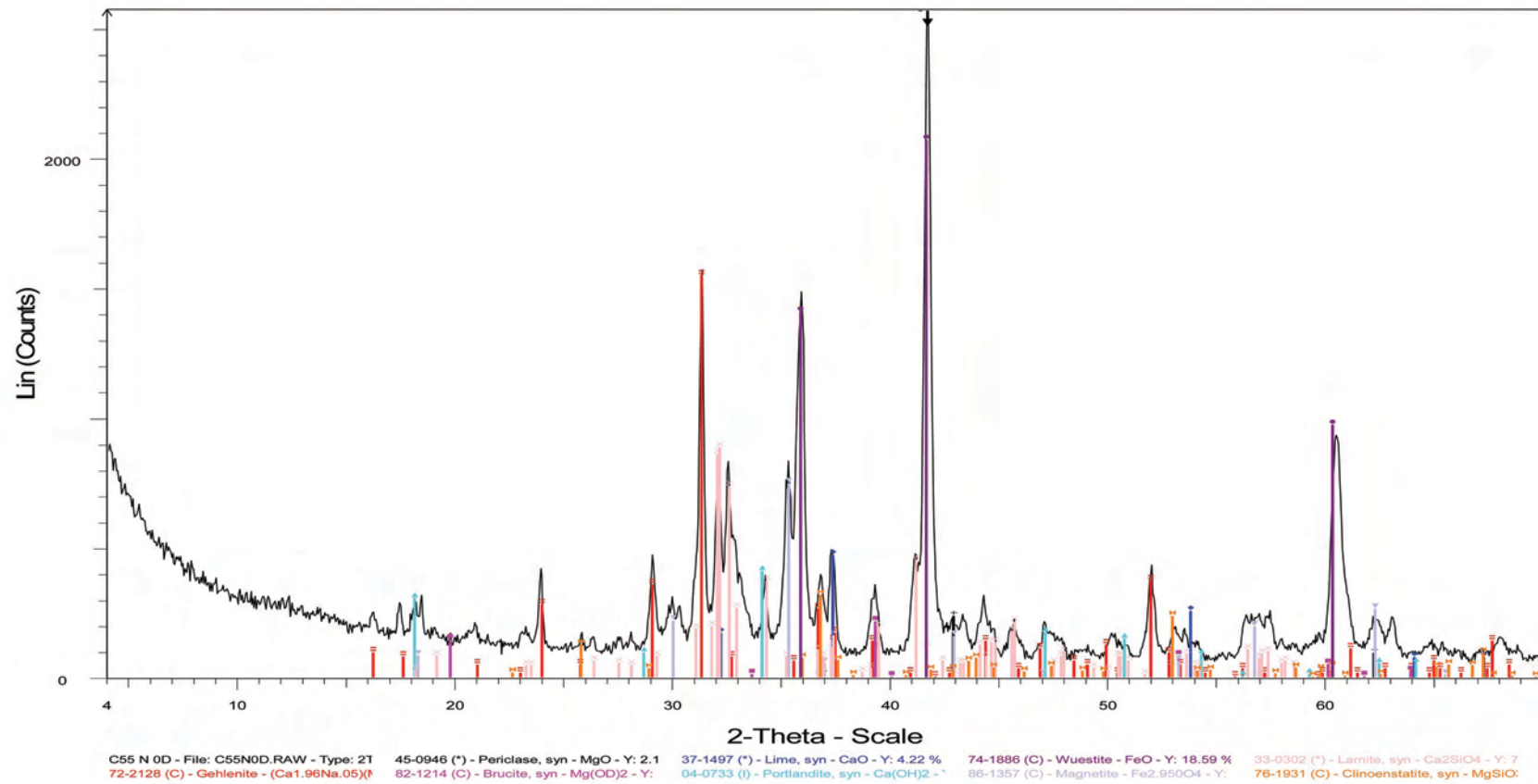
Anion Release



ANNEX IV
Diffraction Analysis

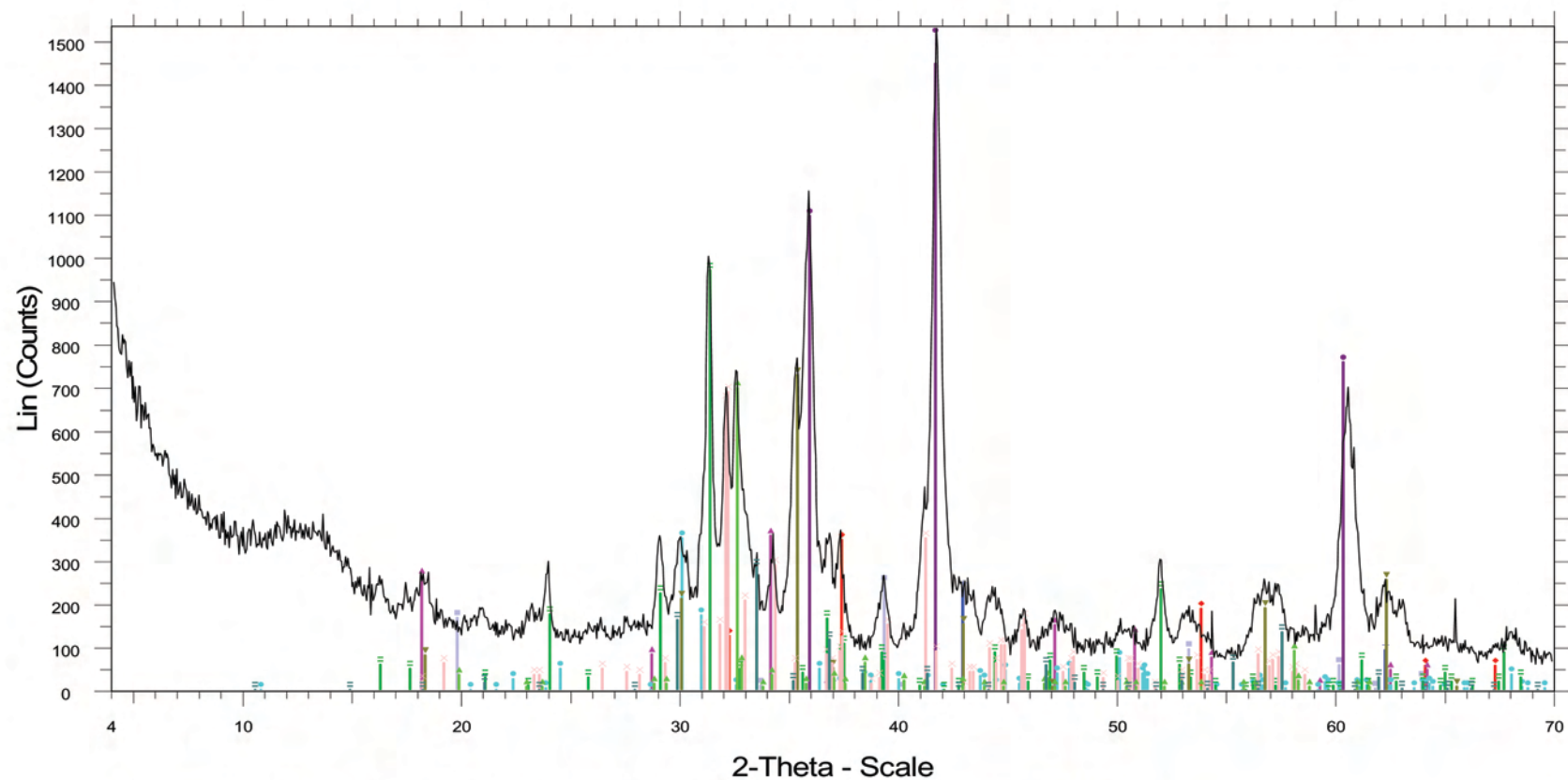
ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 0d



ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 21d / c1

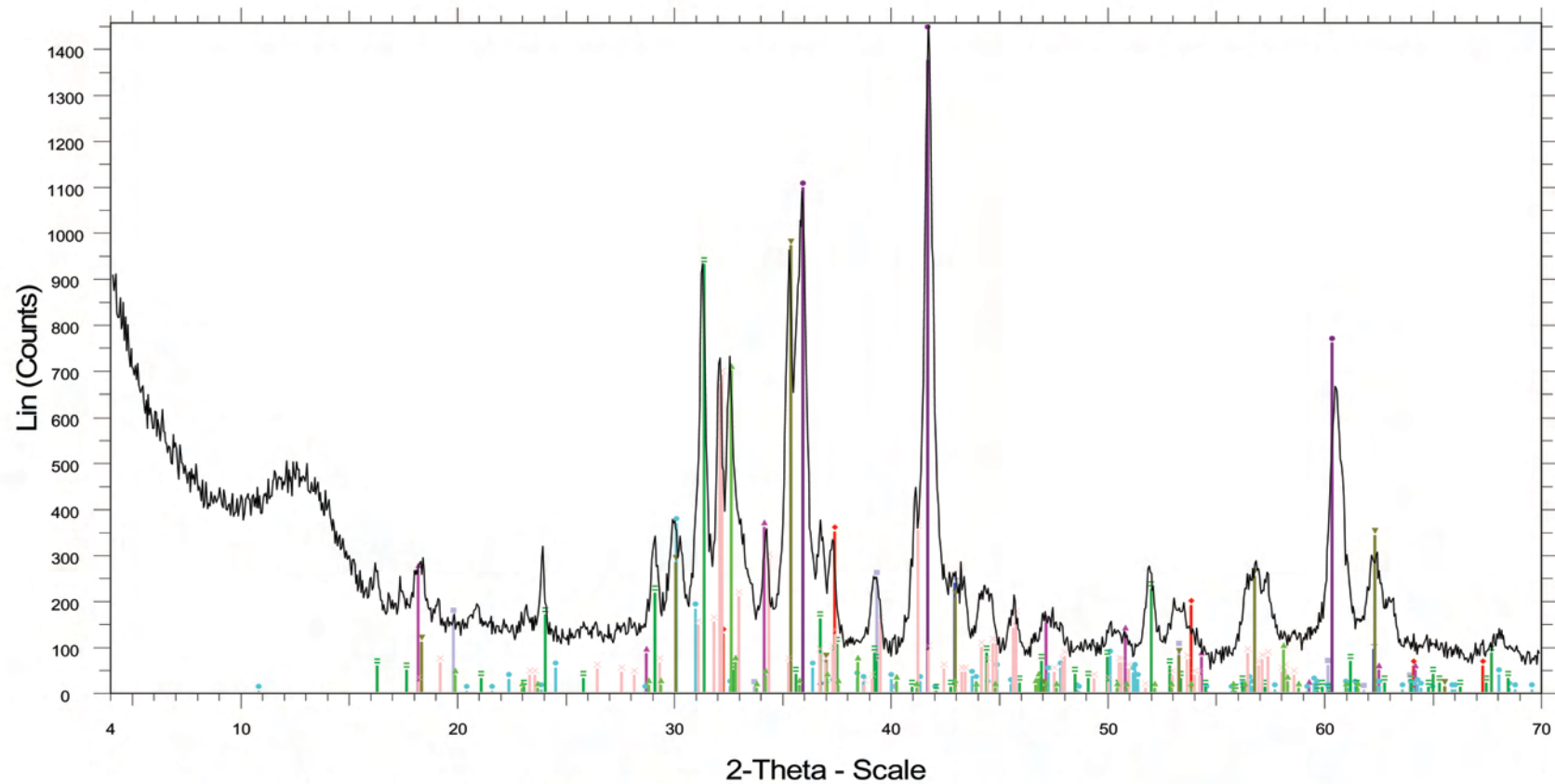


RC55N21DC1 - File: R4.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: (

45-0946 (*) - Periclase, syn - MgO	86-1357 (C) - Magnetite - Fe ₂ 950O ₄
82-1214 (C) - Brucite, syn - Mg(OD) ₂	33-0302 (*) - Larnite, syn - Ca ₂ SiO ₄
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K ₂ MgSiO ₄
04-0733 (I) - Portlandite, syn - Ca(OH) ₂	85-1370 (C) - Andradite aluminian - Ca ₃ Al _{1.84} Fe _{1.16} Si ₃ O ₁₂
87-1863 (C) - Calcite - Ca(CO ₃)	
72-2128 (C) - Gehlenite - (Ca _{1.96} Na _{0.05})(Mg _{0.24} Al _{0.64} Fe _{0.12})(Si _{1.39} Al _{0.61} O ₇)	
74-1886 (C) - Wuestite - FeO	

ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 21d / c2

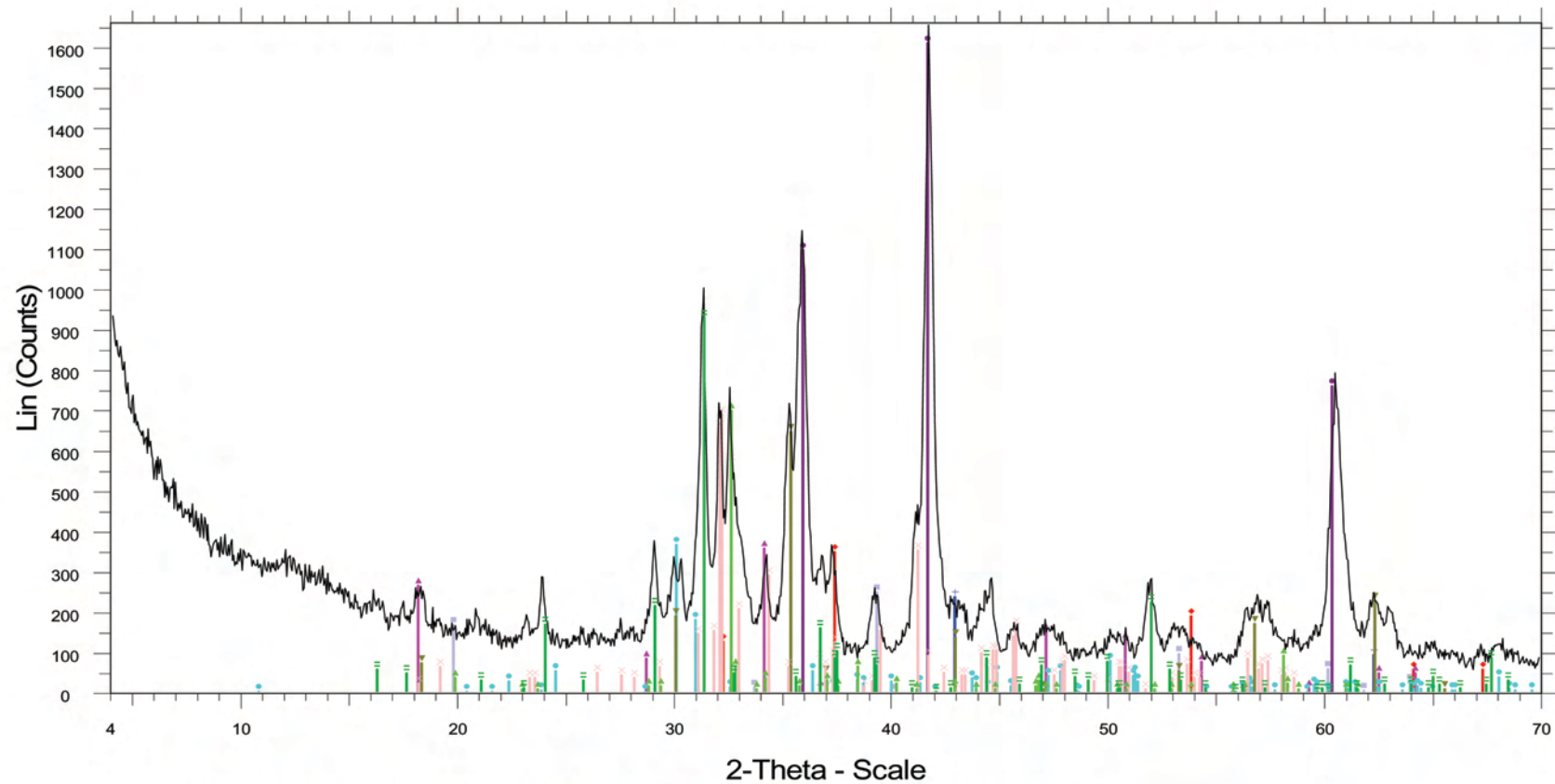


RC55N21DC2 - File: R5.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: (

45-0946 (*) - Periclase, syn - MgO	86-1357 (C) - Magnetite - Fe ₂ .950O ₄
82-1214 (C) - Brucite, syn - Mg(OD) ₂	33-0302 (*) - Larnite, syn - Ca ₂ SiO ₄
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K ₂ MgSiO ₄
04-0733 (I) - Portlandite, syn - Ca(OH) ₂	
87-1863 (C) - Calcite - Ca(CO ₃)	
72-2128 (C) - Gehlenite - (Ca _{1.96} Na _{0.05})(Mg _{0.24} Al _{0.64} Fe _{0.12})(Si _{1.39} Al _{0.61} O ₇)	
74-1886 (C) - Wuestite - FeO	

ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 42d / c1

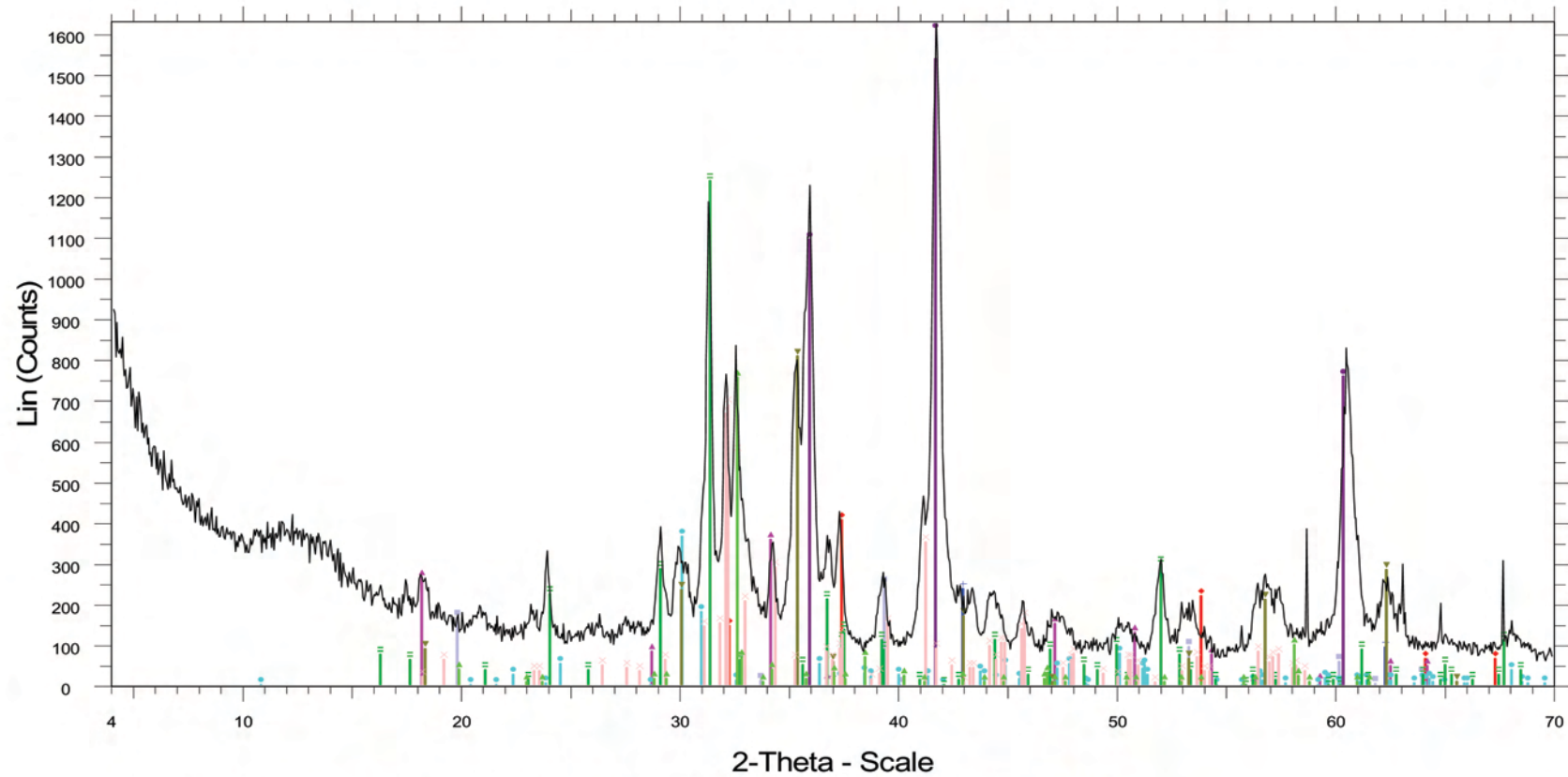


RC55N42DC1 - File: R6.raw - Type: 2Th/Th locked - Start: 3.976 °- End: 69.976 °- Step: (

45-0946 (*) - Periclase, syn - MgO	86-1357 (C) - Magnetite - Fe ₂ 950O ₄
82-1214 (C) - Brucite, syn - Mg(OD) ₂	33-0302 (*) - Larnite, syn - Ca ₂ SiO ₄
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K ₂ MgSiO ₄
04-0733 (I) - Portlandite, syn - Ca(OH) ₂	
87-1863 (C) - Calcite - Ca(CO ₃)	
72-2128 (C) - Gehlenite - (Ca _{1.96} Na _{0.05})(Mg _{0.24} Al _{0.64} Fe _{0.12})(Si _{1.39} Al _{0.61} O ₇)	
74-1886 (C) - Wuestite - FeO	

ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 42d / c2



RC55N42DC2 - File: R7.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: (

45-0946 (*) - Periclase, syn - MgO

82-1214 (C) - Brucite, syn - Mg(OH)₂

37-1497 (*) - Lime, syn - CaO

04-0733 (I) - Portlandite, syn - Ca(OH)₂

87-1863 (C) - Calcite - Ca(CO₃)

72-2128 (C) - Gehlenite - (Ca_{1.96}Na_{0.05})(Mg_{0.24}Al_{0.64}Fe_{0.12})(Si_{1.39}Al_{0.61}O₇)

74-1886 (C) - Wuestite - FeO

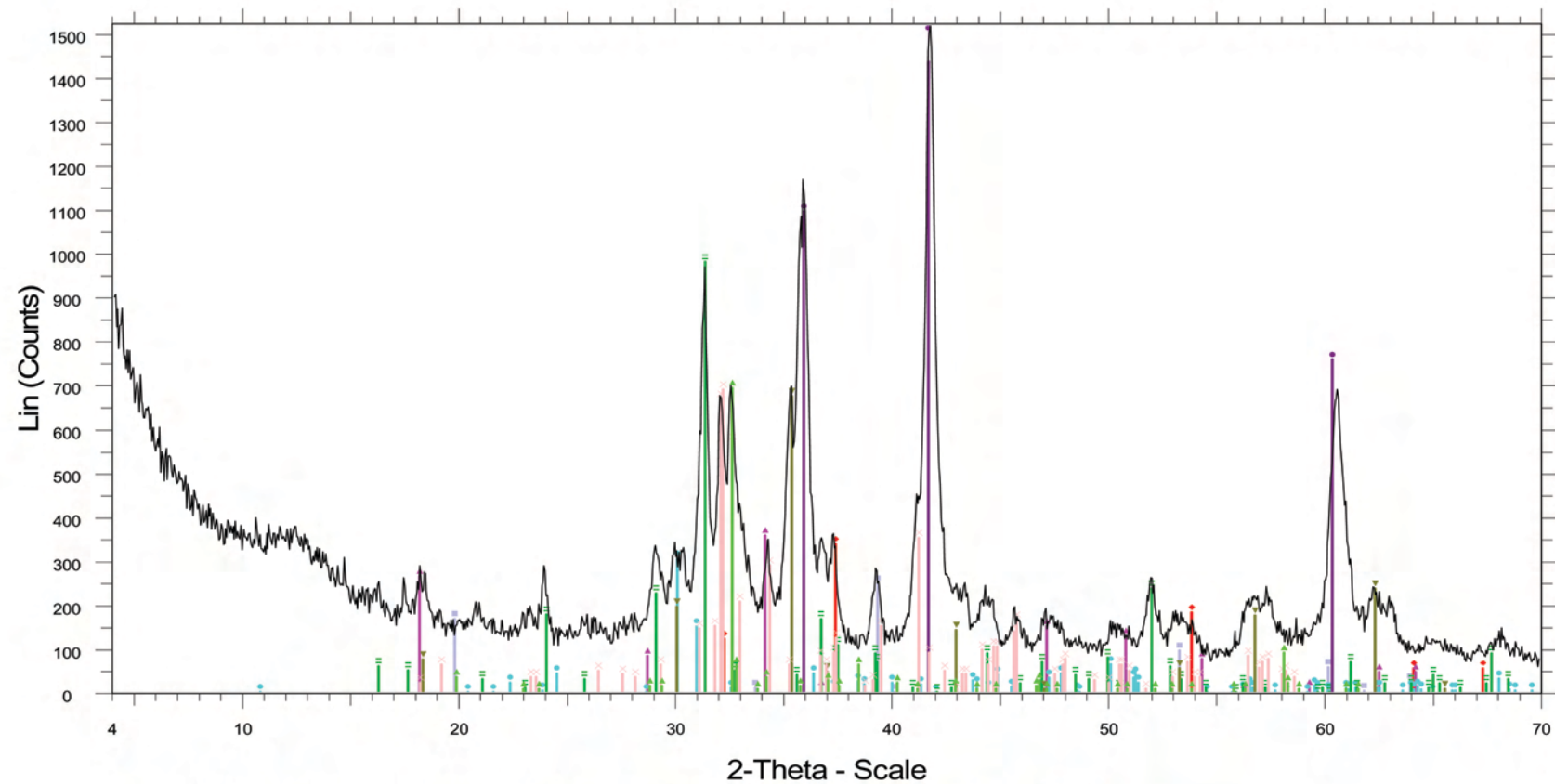
86-1357 (C) - Magnetite - Fe₂.950O₄

33-0302 (*) - Larnite, syn - Ca₂SiO₄

48-0900 (I) - Potassium Magnesium Silicate - K₂MgSiO₄

ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 91d / c1

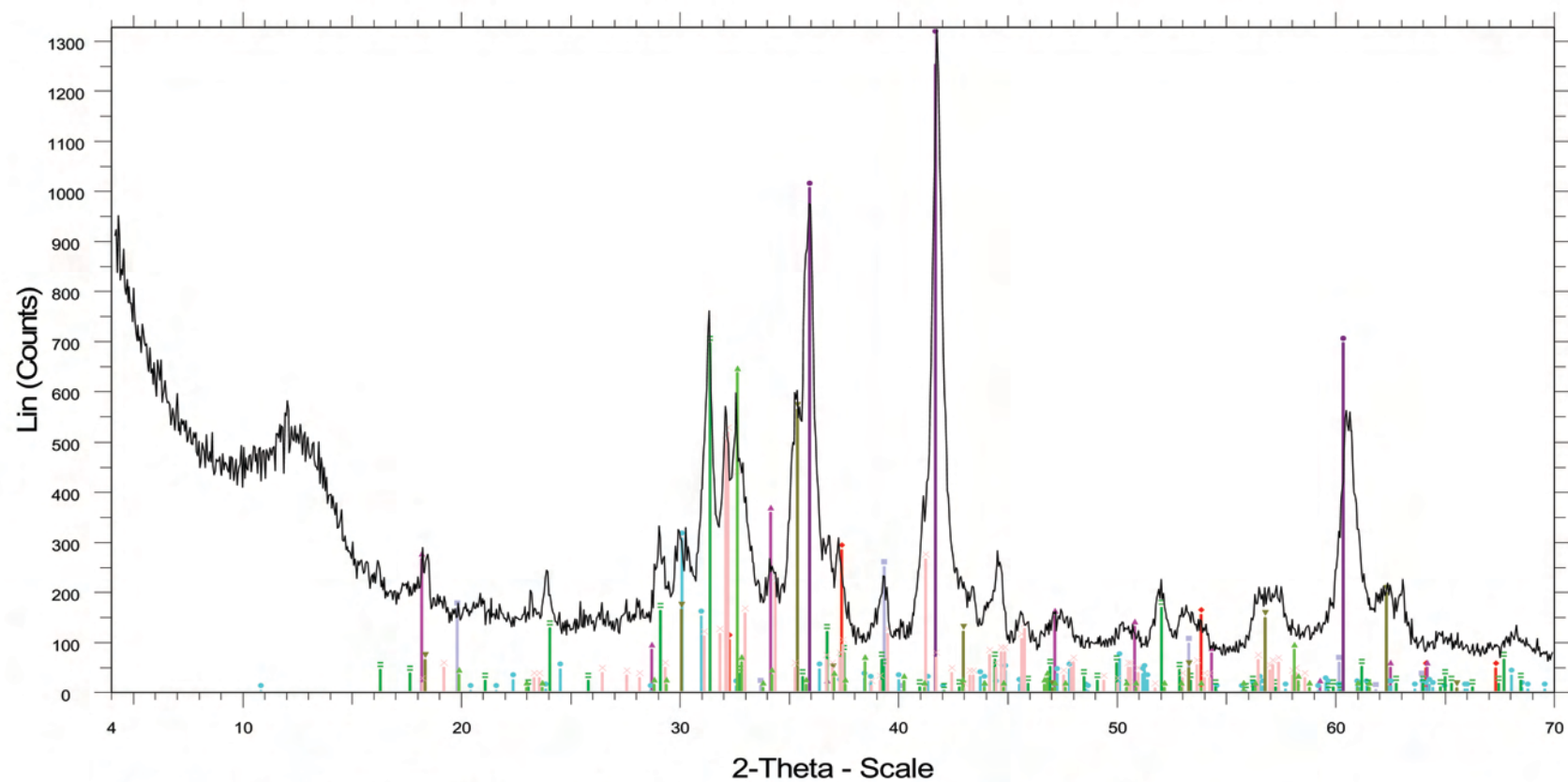


RC55N91DC1 - File: R8.raw - Type: 2Th/Th locked - Start: 3.976 °- End: 69.976 °- Step: (

82-1214 (C) - Brucite, syn - Mg(OD)2	33-0302 (*) - Larnite, syn - Ca2SiO4
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K2MgSiO4
04-0733 (I) - Portlandite, syn - Ca(OH)2	
87-1863 (C) - Calcite - Ca(CO3)	
72-2128 (C) - Gehlenite - (Ca1.96Na.05)(Mg.24Al.64Fe.12)(Si1.39Al.61O7)	
74-1886 (C) - Wuestite - FeO	
86-1357 (C) - Magnetite - Fe2.95O4	

ANNEX IV: DIFFRACTION ANALYSIS

c55 / N / 91d / c2

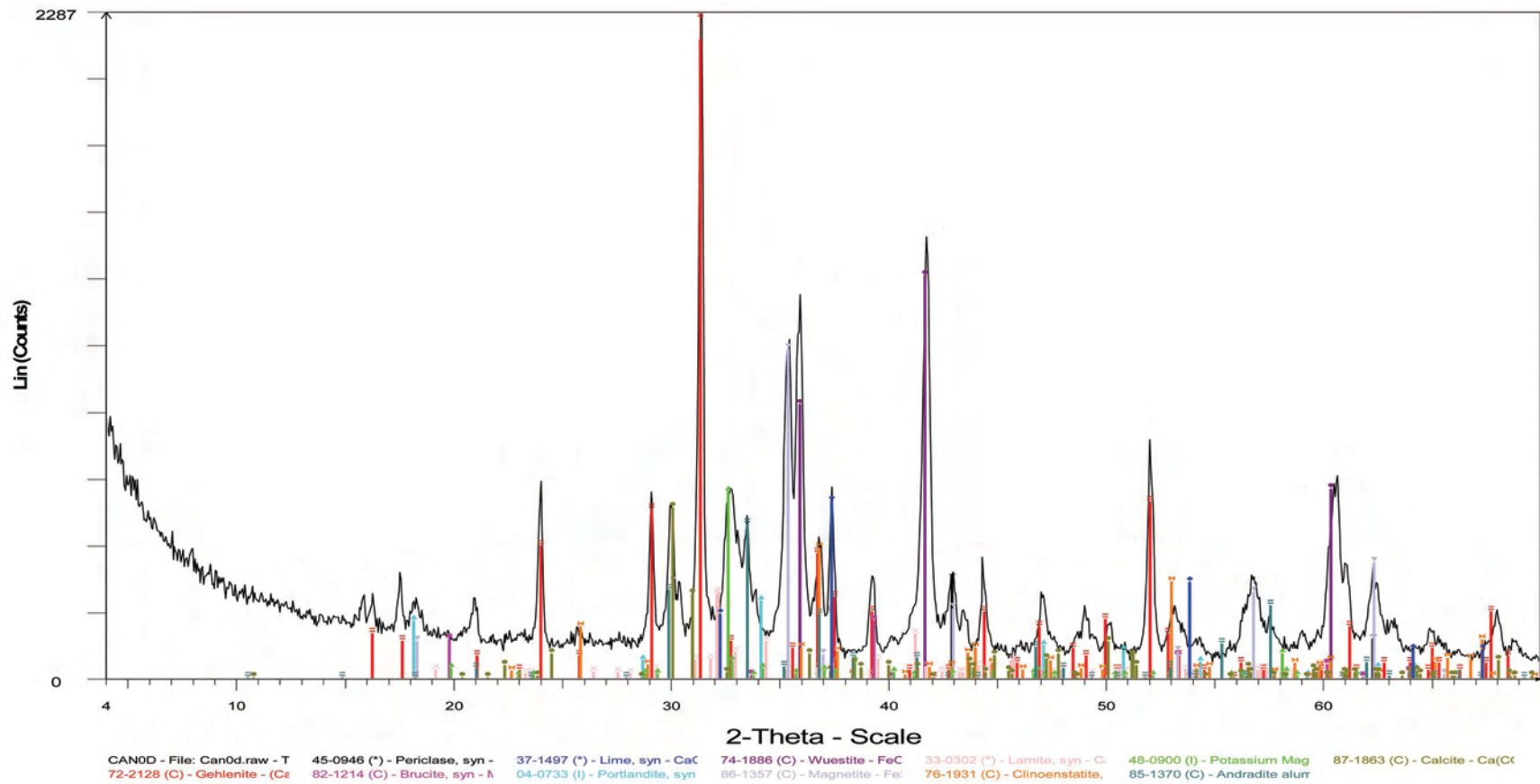


RC55N91DC2 - File: R9.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: (

82-1214 (C) - Brucite, syn - $Mg(OD)_2$	33-0302 (*) - Larnite, syn - Ca_2SiO_4
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K_2MgSiO_4
04-0733 (I) - Portlandite, syn - $Ca(OH)_2$	
87-1863 (C) - Calcite - $Ca(CO_3)$	
72-2128 (C) - Gehlenite - $(Ca_{1.96}Na_{0.05})(Mg_{0.24}Al_{0.64}Fe_{0.12})(Si_{1.39}Al_{0.61}O_7)$	
74-1886 (C) - Wuestite - FeO	
86-1357 (C) - Magnetite - $Fe_2.95O_4$	

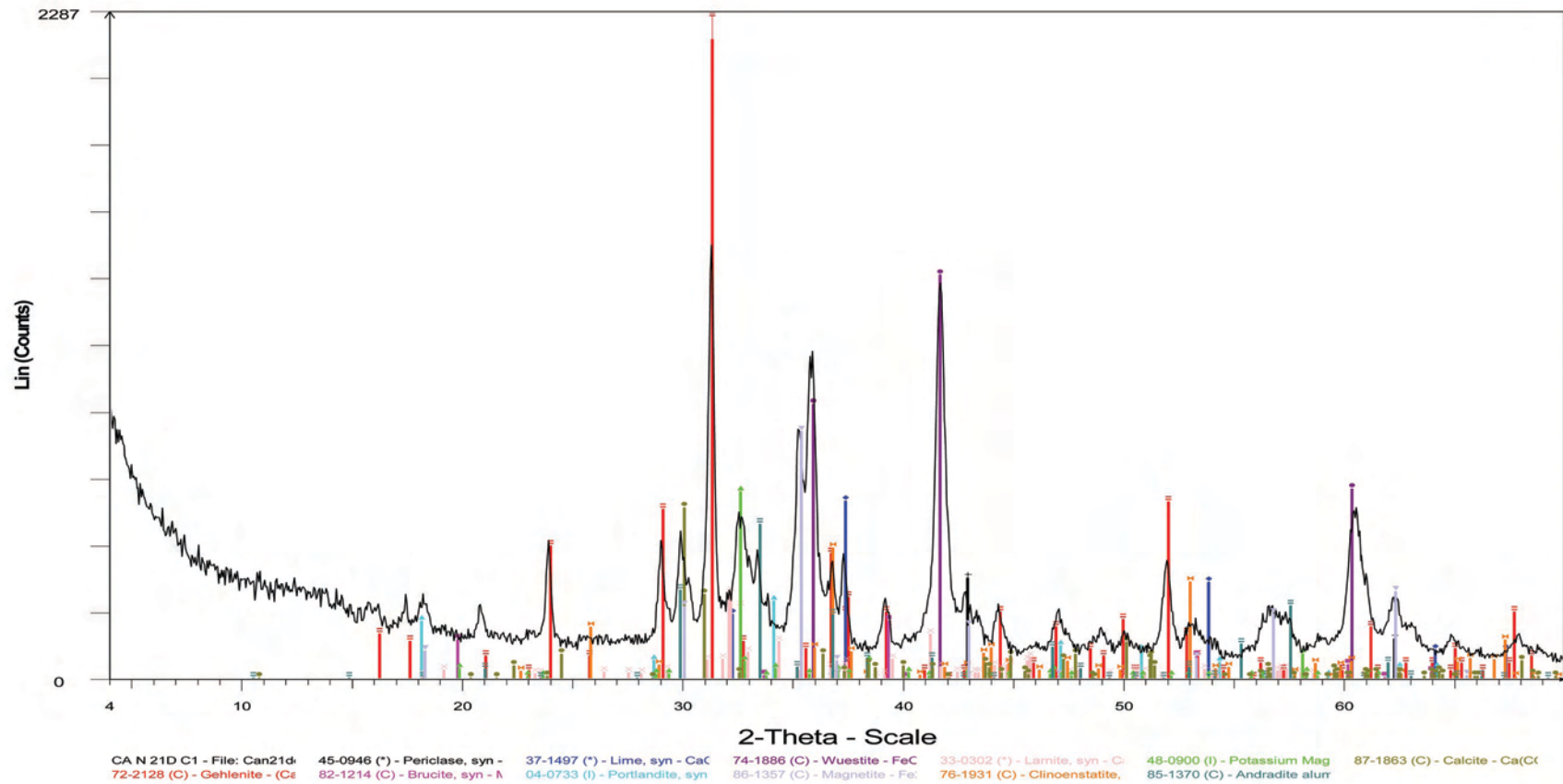
ANNEX IV: DIFFRACTION ANALYSIS

cA / N / 0d



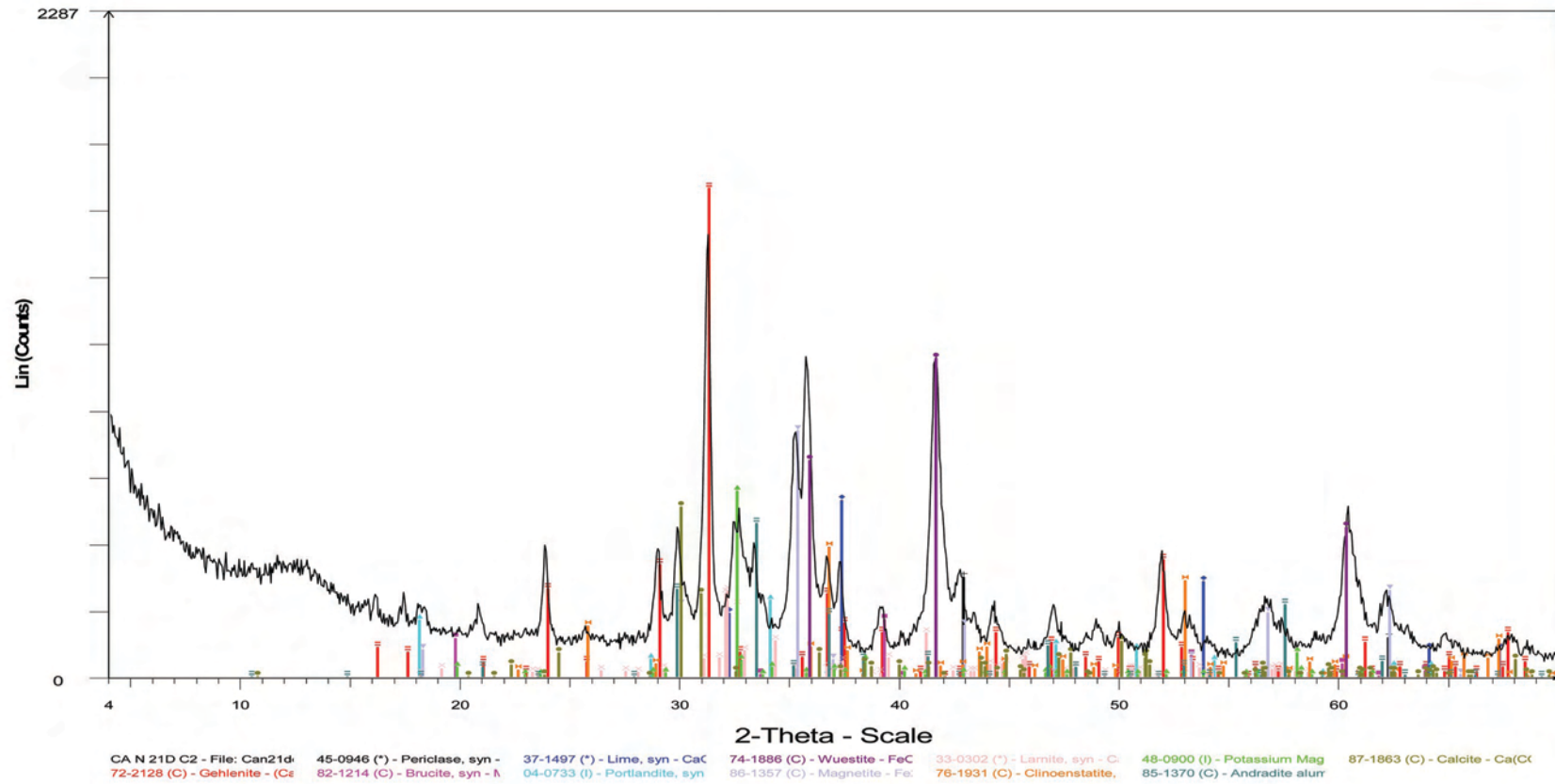
ANNEX IV: DIFFRACTION ANALYSIS

cA / N / 21d / c1



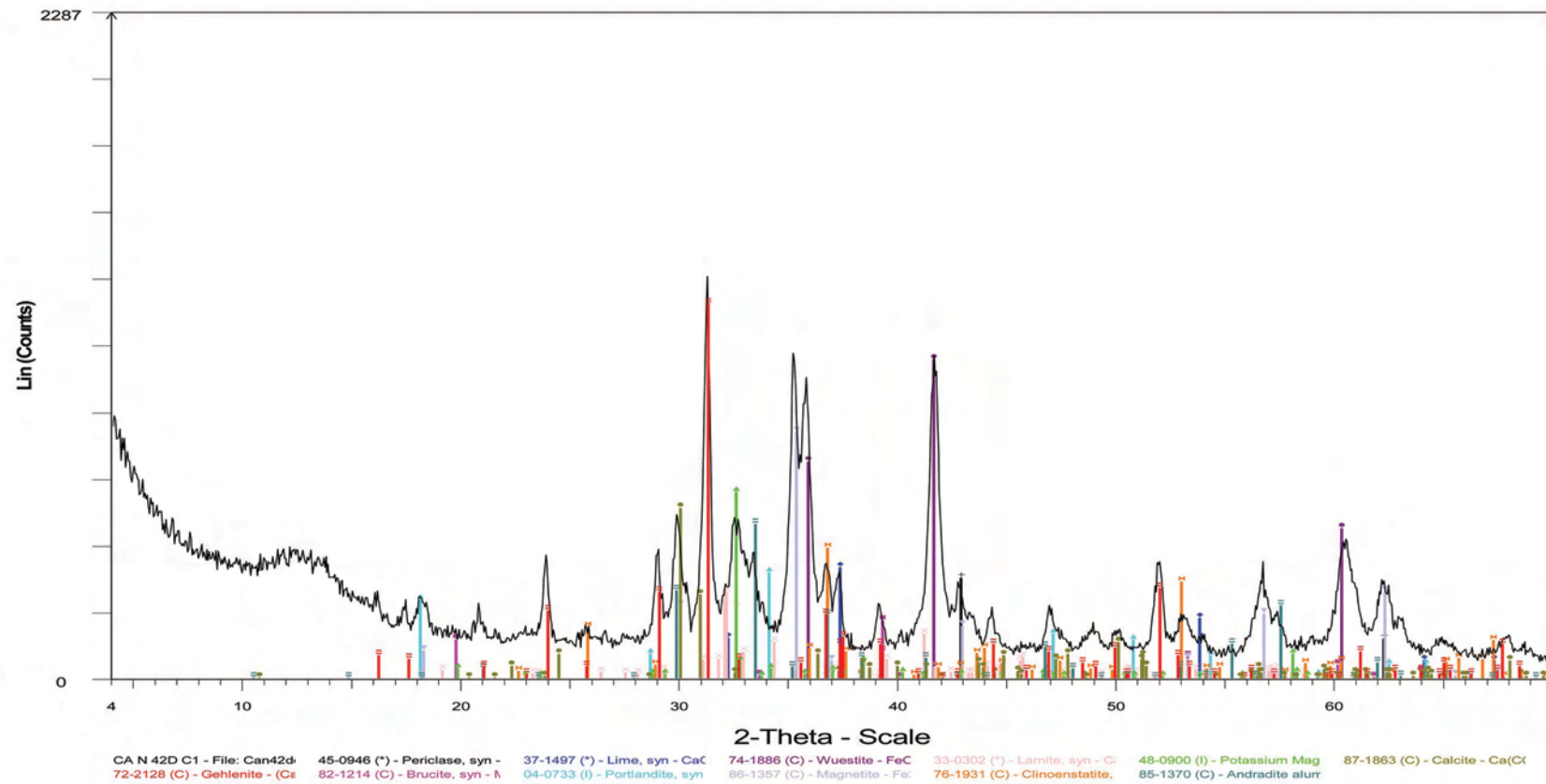
ANNEX IV: DIFFRACTION ANALYSIS

cA / N / 21d / c2



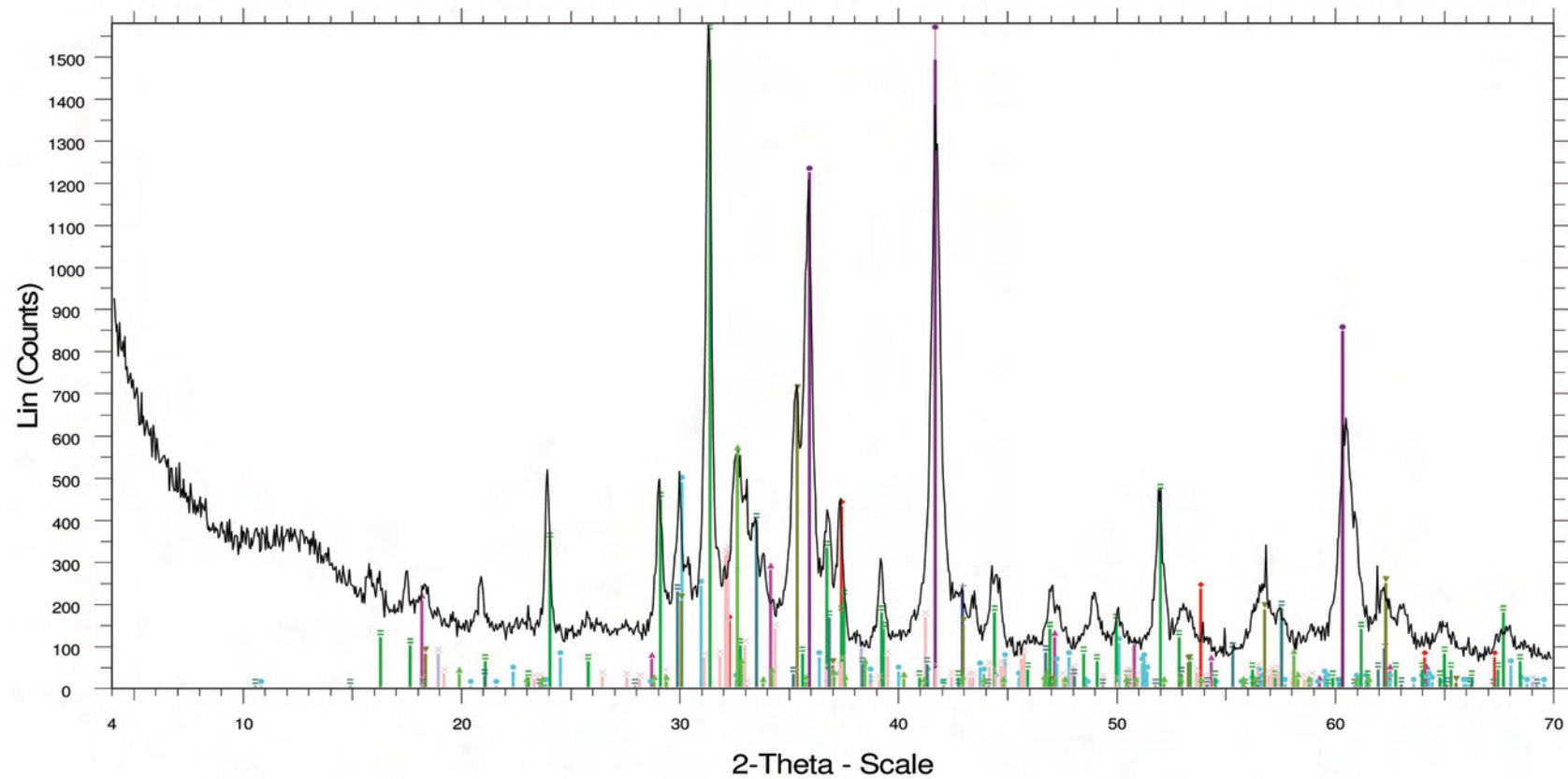
ANNEX IV: DIFFRACTION ANALYSIS

cA / N / 42d / c1



ANNEX IV: DIFFRACTION ANALYSIS

cA / N / 42d / c2

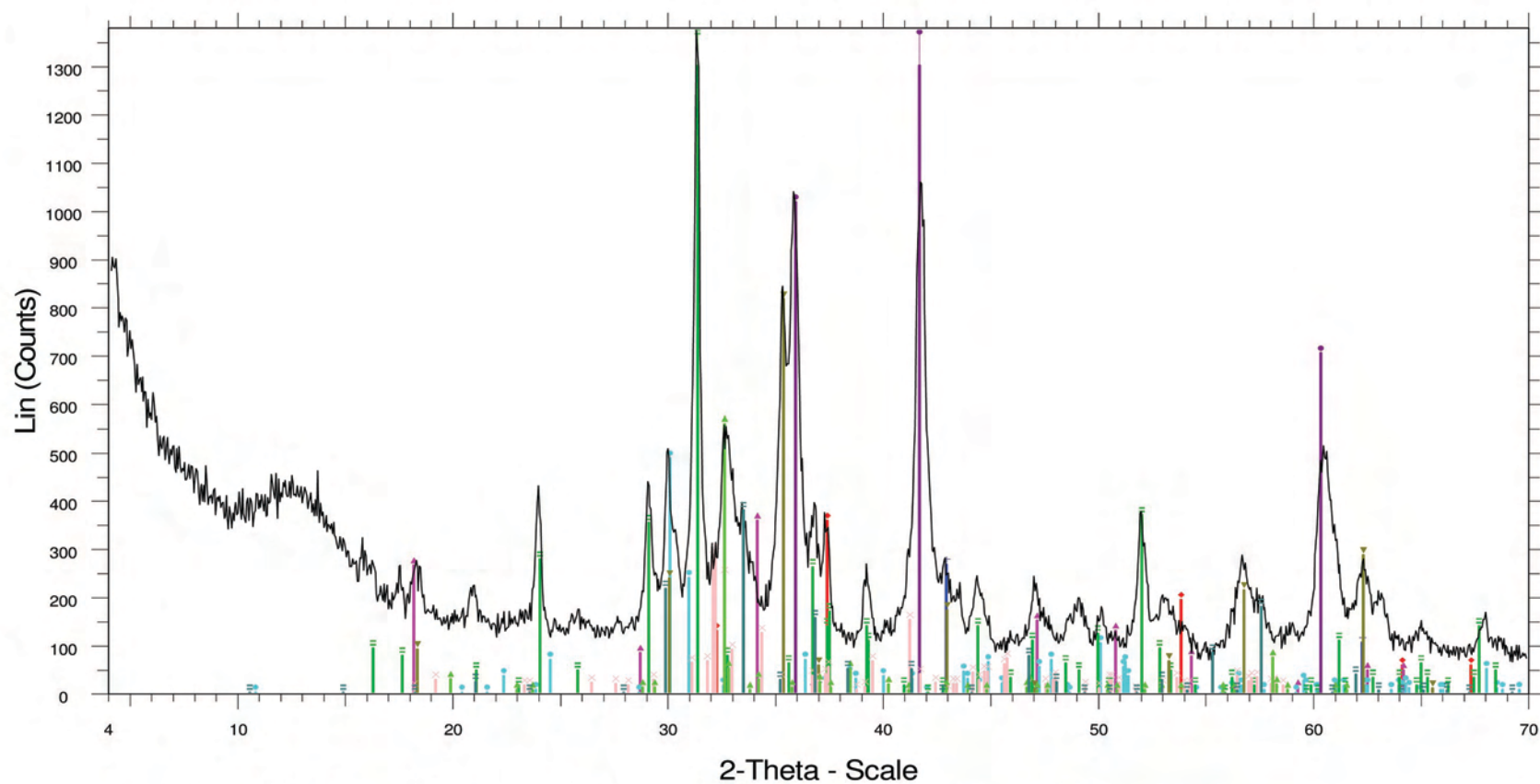


RCAN42DC2 - File: R1.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: (

45-0946 (*) - Periclase, syn - MgO	86-1357 (C) - Magnetite - Fe ₂ .950O ₄
86-0441 (C) - Brucite - Mg(OH) ₂	33-0302 (*) - Larnite, syn - Ca ₂ SiO ₄
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K ₂ MgSiO ₄
04-0733 (I) - Portlandite, syn - Ca(OH) ₂	85-1370 (C) - Andradite aluminian - Ca ₃ Al _{1.84} Fe _{1.16} Si ₃ O ₁₂
87-1863 (C) - Calcite - Ca(CO ₃)	
72-2128 (C) - Gehlenite - (Ca _{1.96} Na _{0.05})(Mg _{0.24} Al _{0.64} Fe _{0.12})(Si _{1.39} Al _{0.61} O ₇)	
74-1886 (C) - Wuestite - FeO	

ANNEX IV: DIFFRACTION ANALYSIS

cA / N / 91d / c1

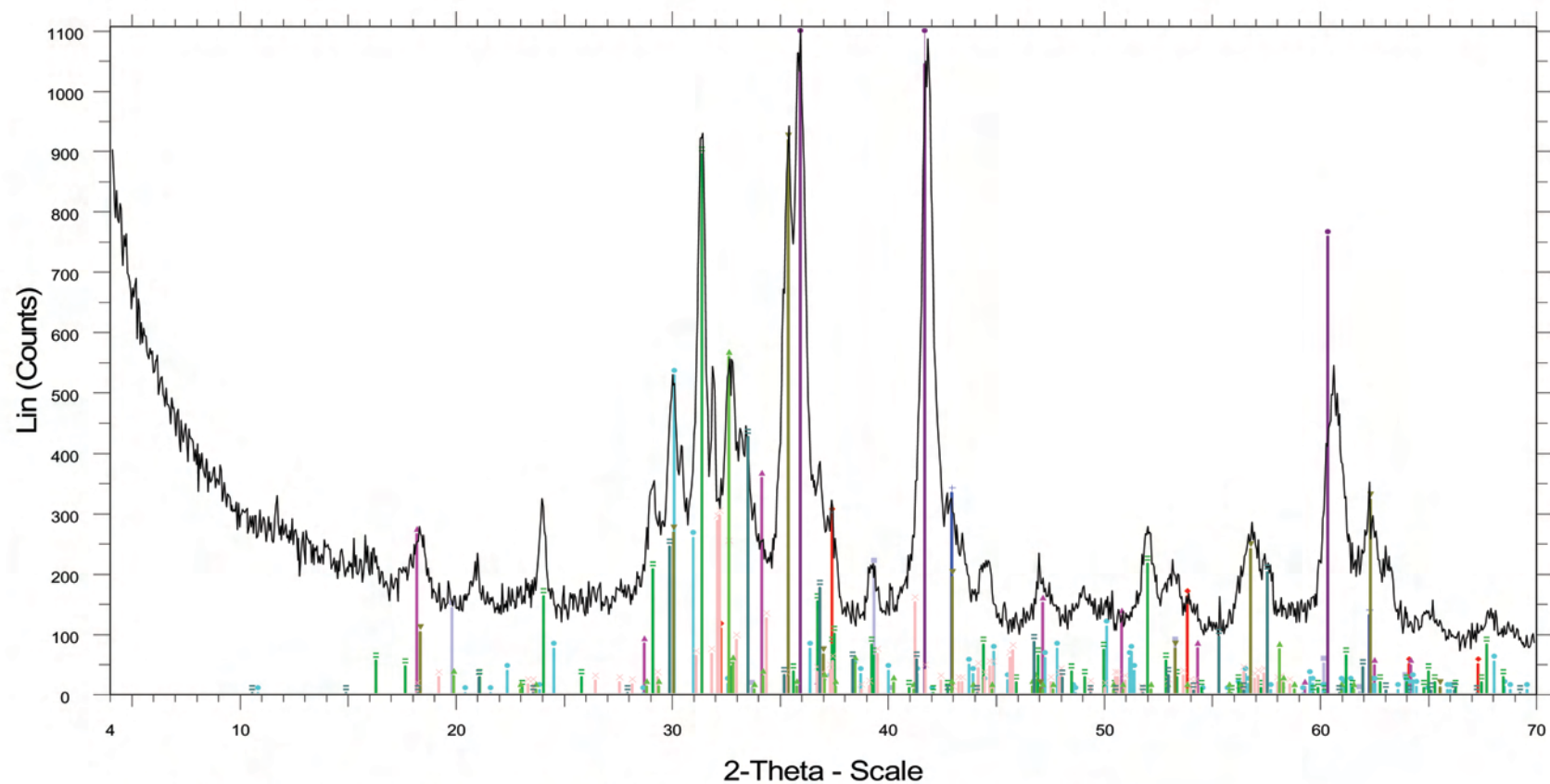


RCAN91DC1 - File: R2.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: 0.02 °

45-0946 (*) - Periclase, syn - MgO	33-0302 (*) - Larnite, syn - Ca ₂ SiO ₄
37-1497 (*) - Lime, syn - CaO	48-0900 (I) - Potassium Magnesium Silicate - K ₂ MgSiO ₄
04-0733 (I) - Portlandite, syn - Ca(OH) ₂	85-1370 (C) - Andradite aluminian - Ca ₃ Al _{1.84} Fe _{1.16} Si ₃ O ₁₂
87-1863 (C) - Calcite - CaCO ₃	
72-2128 (C) - Gehlenite - (Ca _{1.96} Na _{0.05})(Mg _{0.24} Al _{0.64} Fe _{0.12})(Si _{1.39} Al _{0.61} O ₇)	
74-1886 (C) - Wuestite - FeO	
86-1357 (C) - Magnetite - Fe _{2.95} O ₄	

ANNEX IV: DIFFRACTION ANALYSIS

c-A / N / 91d / c2



RCAN91DC2 - File: R3.raw - Type: 2Th/Th locked - Start: 3.976 ° - End: 69.976 ° - Step: 0.

45-0946 (*) - Periclase, syn - MgO

82-1214 (C) - Brucite, syn - Mg(OH)₂

37-1497 (*) - Lime, syn - CaO

04-0733 (I) - Portlandite, syn - Ca(OH)₂

87-1863 (C) - Calcite - Ca(CO₃)

72-2128 (C) - Gehlenite - (Ca_{1.96}Na_{0.05})(Mg_{0.24}Al_{0.64}Fe_{0.12})(Si_{1.39}Al_{0.61}O₇)

74-1886 (C) - Wuestite - FeO

86-1357 (C) - Magnetite - Fe_{2.950}O₄

33-0302 (*) - Larnite, syn - Ca₂SiO₄

48-0900 (I) - Potassium Magnesium Silicate - K₂MgSiO₄

85-1370 (C) - Andradite aluminian - Ca₃Al_{0.84}Fe_{1.16}Si₃O₁₂

